

RC1

We would like to thank the reviewer for their constructive and detailed feedback. We will adjust the manuscript based on the feedback as proposed below, and in addition correct all typographical errors identified by the reviewer.

[reviewer comments in blue font, replies in black font]

Supplement S.2: It is not stated what the three series in Fig. S.2 are. I infer that “Normalised Rubie et al. (2011)” is Rubie’s published output re-normalised to PlanetBuilder’s convention, and that “PlanetBuilder baseline” is a model run using HET-2 conditions and Rubie’s exchange coefficients, but neither is stated; the alternative reading, that the green curve is itself a PlanetBuilder run, would leave no independent benchmark. The published Rubie series is also visibly quantised in Fig. S.2q (Co, core), sitting flat at exactly 2300 ppm before stepping to 2200 and 2400, which indicates two-significant-figure values from which a mole-level renormalisation should not be possible. It would be helpful to state which series are model output and which are reprocessed literature data, how the renormalisation was performed and from what source, and that the baseline run sets all $\gamma = 1$. The last is nowhere stated.

We will provide all the requested clarification in Sect. 3 of the revised manuscript, making it clear that we did perform validation tests against the literature study models of Rubie et al. (2011).

Sect. 2.1 (Eqs. 7–11): The manuscript defines K_D^M (Eq. 7), K_A^M (Eq. 8) and K_M^{App} (Eq. 9) and fits K_M^{App} in Eq. (10), whereas Rubie et al. (2011) parameterise $\log K_D$ directly, assuming ideal metal activity. The authors have chosen the more physically realistic of the two, K^{App} . It carries the non-ideal activity coefficients of the metal, whereas Rubie’s K_D absorbs them into the fitted constants. The label “apparent” therefore implies the opposite of what the quantity is. I recommend renaming it (e.g. metal-activity-corrected equilibrium constant), stating at Eq. (10) that the two coincide only for $\gamma = 1$, and adding a symbol table distinguishing D_M , K_D^M , K_A^M and K_M^{App} .

We agree with the reviewer and propose to use the word ‘corrected’ instead of ‘apparent.’ We will also add a symbol table and rename the labels as suggested.

Table 1: Following from the above, the caption states that a, b and c are fits to $\log K^{App}$. If any of the source regressions (Fischer et al., 2015; Mann et al., 2009; Cottrell et al., 2009, 2010) were performed on uncorrected exchange coefficients, or already absorb the metal non-ideality of the experimental charges, then applying Eq. (9) on counts the effect twice. And, the size of that effect is the headline result of the paper. Please state for each source which quantity was fitted and if no double-counting occurs.

We would like to thank the reviewer for pointing this out, it has made us realise there was a mistake in Eq. 11. This was done correctly in the code (so our results remain identical) and effects of non-ideality are only incorporated once. We will adjust the error in Eq. 10 in the paper and add further clarification in the main text.

Standard states are unspecified, yet an equilibrium constant is not defined without them. Eq. (48) introduces γ_i^0 as the infinite-dilution coefficient in liquid Fe (Henrian) while γ_{Fe} and γ_{FeO} are evidently Raoultian. Mixing reference states is legitimate but must be declared, and the reader needs to know which convention each γ in Eqs. (8), (9) and (11) follows.

We are confused by this statement. The reference state of activity coefficient calculations for metals, including Fe, is clearly stated at the introduction of Eq. 49, and there are no reference state terms in Eq. 8-9-11. So, we are unsure how we could specifically address this point in a revision.

Thermodynamic terminology could be improved. Line 346 calls x_{FeO} and γ_{FeO} “the concentration and activity of FeO”; γ is the activity coefficient and x a mole fraction. See also “molar fraction” (line 148) against “mole fraction” elsewhere, and “the activity ... describes the effective concentrations” (line 164). The partition coefficient is defined by weight in the Introduction (line 42) but in mole fractions in Eq. (2), and D_M is then never used again. It is recommended to either use it or remove it. Related, please state which of Eqs. (4) and (5) the model reports as f_{O_2} , and whether it uses the nonideal γ values when activity corrections are on; Rubie et al. compute ΔIW from magnesiowüstite assuming ideality, which is neither.

We will adjust Eq. 5 and 7 to show the relevance of Eq. 2 and D_M . With regards to the f_{O_2} : Eq. 4 is a general expression for oxygen fugacity, whereas Eq. 5 is the extended version of it and the one used in the program. We aim to make this clearer by adding the connection between Eq. 2 and Eq. 5. When the activity corrections are enabled, the x_{FeO} of the mantle is automatically corrected for non-ideality, and used to calculate x_{FeOMW} and the subsequent f_{O_2} values.

Sect. 2.4 and 3.2: The paper’s central claim rests entirely on the metal activity module, yet the only validation offered is against a model that assumed ideality, so this branch appears unbenchmarked. An independent check could be performed to reproduce published γ values (Wade and Wood, 2005; Rubie et al., 2015) at 1873 K for a stated metal composition, or tabulating γ_{Fe} , γ_{Si} , γ_{Ni} and γ_{O} for one accretion step. This would considerably strengthen the paper.

We validated our coding for the metal activity module by directly comparing the outcomes of PlanetBuilder and the code used in both Wade and Wood (2015) and the online metal activity calculator by Norris. This code was kindly provided to us by Prof. Wade. As far as we are aware, Rubie et al. (2015) does not use any γ values that differ from 1 to compare our work with (they assume ideality). We will add this information to Sect. 3.

Lines 432–436 and Fig. S.2d: Normalisation accounts for the offsets in Fe and Si in the core, SiO_2 , NiO, Ni, Cr, W and Nb, but not for oxygen. The normalised and published Rubie curves are indistinguishable in panel d. PlanetBuilder gives roughly 0.34 wt% O against the HET-2 value of 0.48 wt% (Rubie et al., 2011, Table 2), rising to a factor of three to four between 20% and 40% accretion. This is the largest discrepancy in the comparison, in a headline

quantity, and belongs in the main text. The main text also attributes it to “a more accurate MIDACO solver” while the supplement attributes it to a different thermodynamic expression; these should be reconciled.

The offset of oxygen in Fig. S.2d is accounted for, even though it is difficult to distinguish due to the relatively low concentrations and large y-axis range of oxygen values presented. As for the differences in the oxygen concentration between the published HET-2 values and PlanetBuilder baseline, we agree that these two parts of the explanation should have been clarified better and we will adjust this in the Sect. 3 and Supplementary Material S.2 as suggested by the reviewer.

Supplement Eqs. (S.1) and (S.2): Eq. (S.2) is not an arbitrary “adjustment” by Rubie et al. For a strict Fe-FeO binary, the framework in which Frost et al.’s Margules parameters were fitted, $x_{\text{FeO}} = x_{\text{O}}$ and $x_{\text{Fe}} = 1 - x_{\text{FeO}}$, and (S.1) becomes (S.2) identically. The real difference is that PlanetBuilder applies the binary expression to a quaternary Fe–Ni–Si–O metal in which $x_{\text{Fe}} \approx 0.79$ but $x_{\text{FeO}} < 1e-4$, so the prefactor is ≈ 1 rather than ≈ 0.05 , some 20x in $RT \ln \gamma_{\text{FeO}}$? This needs justifying rather than presenting as a correction, particularly as $x_{\text{FeO}} < 0.01\%$ lies far outside the calibration range of W. Benchmarking against Rubie et al. (2015), which the authors state uses (S.1), would settle it.

We use the same composition as Rubie et al. (2011) and can fully reproduce their results when using the exact equations they used. Eq. S.1, calculating the γ_{FeO} in metal, is used to calculate the chemical potential (Eq. 43). That equation also uses the x_{FeO} in metal itself, introducing additional non-linear dependencies that need to be solved. Eq. S.2 uses the x_{Fe} and x_{O} in metal instead of the x_{FeO} in metal. While we agree that using a variable x_{Fe} and x_{O} in metal would be an improvement over using only the x_{FeO} in metal, Rubie et al. (2011) use fixed x_{Fe} and x_{O} values. Not allowing these values to vary makes Eq. S2 constant. The chemical potential (Eq. 46) can then be derived using only one occurrence of x_{FeO} metal. This can be solved using an incremental approach with step-halving to enforce positive values, while using fixed x_{Fe} and x_{O} comes at the cost of accuracy. We will make the corresponding changes in Sect. 3 and Supplementary Material S.2 to improve our explanation of this as well.

Lines 510–514 and Fig. 3b: The text states that core oxygen “stabilises at approximately 9.6 wt%”, but Fig. 3b shows O never exceeding about 7000 ppm (0.7 wt%) in any model, including “Combined”, if I am not mistaken. If 9.6 wt% refers to a different quantity, say so; if it is a genuine output it lies well outside published estimates and warrants discussion.

We apologise for this mistake in the text. The correct value should be approximately 7000 ppm. We will correct the text to match the observed results in Fig 3b.

Line 507: Eq. (3) is used as the operational criterion for declaring an impactor core too oxidised. Since it is unbalanced as printed, please confirm which O/Fe ratio the code applies, as this cutoff determines when the impactor core is reassigned to the mantle and thus the behaviour discussed throughout Sect. 3.3.

We apologise for the error in Eq. 3 and will adjust it. It was used correctly in the program and does not affect any of the results.

Eq. (12) is merely the sum of Eqs. (13)–(15), does not encode the oxygen balance (SiO_2 enters with a coefficient of 1 rather than 2), and sums moles of chemically distinct species. It has no counterpart in Rubie's Eqs. S7–S10; I would drop it and present (13)–(16) as the mass balance.

We will remove Eq. 12 from the revised manuscript.

Code availability and lines 240–242 contradict each other: the availability statement says MIDACO “is not included”, while Sect. 2.3 says the published code includes a limited version licensed.

Response: Our code incorporates a limited version of MIDACO, with the exception of the MIDACO library file (midacopy.dll) to avoid licensing issues. The link in the code availability section refers to the official MIDACO website where the library file can be found. All other files necessary to use MIDACO in PlanetBuilder are included in our program, and descriptions on how to add the library file can be found in the README file of PlanetBuilder.

Supplement Fig. S.2p (Co, mantle): the normalised Rubie curve departs from both other series, reaching about 135 ppm against about 107 ppm and lying some 60% high at 55% accretion. For every other element normalisation moves the Rubie curve towards PlanetBuilder; here it moves away, which may suggest a calculation error in that series, which is worth investigating.

This was indeed a calculation error, we thank the reviewer for pointing it out. We re-did all normalisation calculations to ensure there were no further errors.