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Key Points:

- We show that a layer at the top of the outer core, E', can only be produced by preferentially exchanging light elements for one another
- This rules out barodiffusion and simple sedimentation of a light phase for the formation of the E' layer
- The formation of E' layer is consistent with a reaction at the core-mantle boundary with an FeO-rich basal magma ocean

Supporting Information:

- Supporting Information S1

Correspondence to:
J. Brodholt,
j.brodholt@ucl.ac.uk

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Composition of the low seismic velocity E' layer at the top of Earth's core

John Brodholt[1] and James Badro[2,3]

[1]Department of Earth Sciences, University College London, London, UK, [2]Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Paris, France, [3]École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Abstract Using ab initio simulations on Fe-Ni-S-C-O-Si liquids, we constrain the origin and composition of the low-velocity layer E' at the top of Earth's outer core. We find that increasing the concentration of any light element always increases velocity and so a low-velocity and low-density layer (for stability) cannot be made by simply increasing light element concentration. This rules out barodiffusion or simple sedimentation of a light phase for its origin. However, exchanging elements can—depending on the elements exchanged—produce such a layer. We evaluate three possibilities. First, crystalization of a phase from a core may make such a layer, but only if the core contains more than one light element and only if crystalizing phase is very Fe rich. Second, the E' layer may result from incomplete mixing of an early Earth core with a late impactor, depending on the light element compositions of the impactor and Earth's core. Third, using thermodynamic models for metal-silicate partitioning, we show that a reaction between the core and an FeO-rich basal magma ocean can result in a light and slow layer.

Plain Language Summary The Earth's outer core is mostly made of liquid iron at extremely high temperatures (up to ~6000 K) together with a small amount of other elements such as oxygen or silicon. The high temperatures generate vigorous convection and so the core is generally considered to be well mixed. Nevertheless, evidence from seismology as far back as the 1980s show that there is a layer at the top of the Earth's core of a hundred kilometers or so thick. We call this the E' layer. There are a number of ideas of what this layer is made of and how it formed, but the data on the properties of iron and its light elements has not been available to test these ideas. In this paper we use recent ab initio data to rule out many ideas for its formation. We also show that the properties of the E' layer can be explained as (a) reaction between the liquid iron core and the rocky mantle above it, (b) the incomplete mixing of an early Earth core with a late impactor, or (c) the residue from crystallisation of a very Fe-rich phase at the top of the core.

1. Introduction

It has long been recognized that the Earth's outer core may have layers at both its top [*Garnero et al*., 1993] and bottom [*Souriau and Poupinet*, 1991]. Evidence for a layer at the top of the outer core has been available since the '90s [e.g., *Garnero et al*., 1993; *Tanaka and Hamaguchi*, 1993; *Tanaka*, 2007; *Helffrich and Kaneshima*, 2010; *Kaneshima and Helffrich*, 2013; *Kaneshima and Matsuzawa*, 2015] and while different studies suggest slightly different velocity contrasts and thicknesses, the common observation is that the layer has lower velocities than the bulk outer core. Although there are no direct measurements on the density of this layer, stability requires it to be less dense than the bulk outer core.

However, a layer with both reduced velocities and densities is problematic. This is because the simplest way of producing a light layer is to increase the concentration of a light element by some mechanism, whether by barodiffusion [*Gubbins and Davies*, 2013] or dissolving light element from the mantle [*Buffett and Seagle*, 2010]. The problem with this is that it is generally expected that the concentration of light elements affects the density more than the bulk modulus and so the layer should have increased velocities, not lower as observed. Similarly, light element depletion would reduce velocities as is seismically observed, but it would increase density and so destabilize the layer. *Helffrich* [2012] proposed a solution and suggested that nonideality in the mixing properties of the Fe-S system could result in lower velocities and lower densities, as observed seismologically. However, ab initio simulations on Fe-S-O-Si-C binary liquids under core conditions [*Badro et al*., 2014; *Umemoto et al*., 2014] show no strong deviation from ideality for any of the binaries and that higher concentrations of light elements always result in increased velocities. Simply increasing the

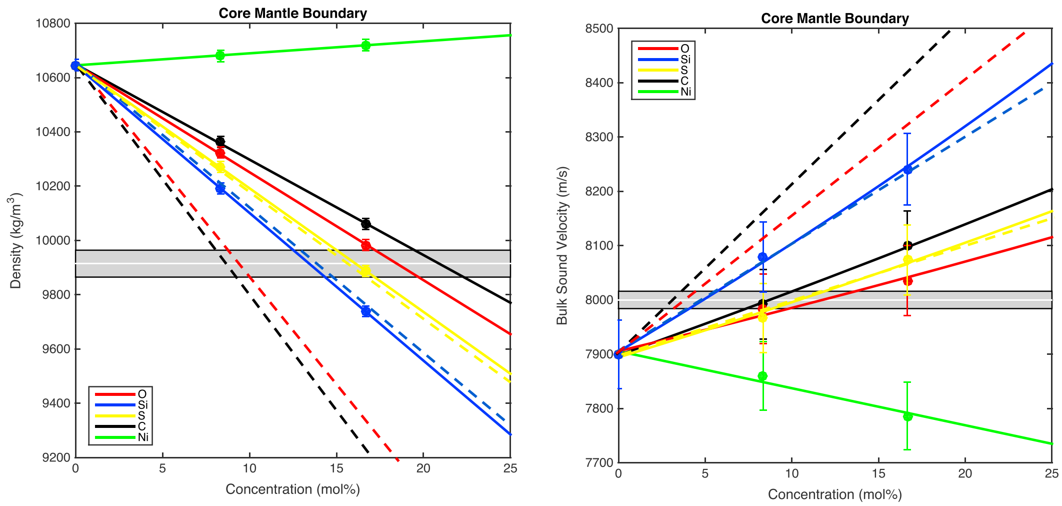

Figure 1. Density and V_Φ as a function of Si, O, S, C, and Ni concentration at CMB conditions. Solid lines are obtained from the AIMD simulations in *Badro et al.* [2014]. Dashed lines show the expected density and velocity if the light element has no effect on the molar volume and its effect on density is just due to its mass. The strong agreement between the two lines for S and Si show that they both substitute for Fe with little change in volume. O and C have a less pronounced effect on density and velocity than expected. This is the result of a strong decrease in the molar volume of these binaries. The gray horizontal band is density and V_Φ from PREM.

concentration of light elements in the core does not produce slower velocities, and so an alternative method for making the E' layer is required.

2. Methods

In order to estimate the composition of the layer at the top of the outer core, we use densities and bulk sound velocities of Fe–(Ni, C, O, Si, S) binaries from the ab initio molecular dynamics (AIMD) simulations in *Badro et al.* [2014]. The simulations were performed for liquid Fe and for two concentrations of each (Ni, C, O, Si, S) element (8.3 and 16.7 mol %). Simulations on binaries of 108 atoms were run for 13 to 15 ps with a time step of 1 fs to obtain adequate statistics on pressures. Calculations were performed at 136 GPa and a range of temperatures. These were fit to an equation of state to obtain V_Φ and density at temperatures between 3800 and 4700 K. Full details are given in *Badro et al.* [2014]. The results are plotted in Figure 1. The results shown here for the bulk sound velocity (V_Φ) are slightly different from those shown in *Badro et al.* [2014]. This is because we fit the bulk modulus (K_S) linearly with concentration, whereas in *Badro et al.* [2014], K_S was fit with a polynomial. This had the effect of producing unrealistically high negative curvature to V_Φ for some binaries at very high concentrations. Nevertheless, these results and the results shown in *Badro et al.* [2014] show that increasing light element concentration always decreases density and increases velocities.

In Figure 1 we also show the effect of light elements on ρ and V_Φ assuming that light elements do not change the molar volume of the alloy, but only its mass. To do this we use the volumes of pure iron and simply change the mass appropriate to the concentration of C, O, Si, or S. These are shown by dashed lines in Figure 1, alongside the solid lines corresponding to the full ab initio calculation. It is noteworthy that for S and Si the agreement between the two calculations is remarkable. This is because Si and S have almost the same partial molar volume as Fe in the alloy, and so the density of the alloy can be estimated from that of pure iron by simply changing the atomic mass. On the other hand, both O and C substantially decrease the volume of the binary alloy and so produce significantly higher densities and lower velocities than expected.

3. Results and Discussion

Figure 1 demonstrates that increasing the concentration of any light element in iron always increases V_Φ and decreases density. This is true for all light elements and does not support the suggestion that increasing the concentration of sulfur can lower velocities [*Helffrich and Kaneshima*, 2010; *Helffrich*, 2012]. Our results show, therefore, that a low-velocity stratified layer at the top of the core cannot simply be due to an accumulation of light elements. On the other hand, the slopes of density and bulk sound velocity with respect to composition vary strongly from one light element to the other (see supporting information) and so it is possible to swap, for example, Si for O to create a layer that is lighter and slower at the same time.

We have, therefore, searched systematically for all combinations of elements (at this point just solutions containing two light elements), whereby a bulk core composition can be modified to produce a lighter layer with a lower velocity. The resulting velocity and density changes are plotted in Figure 2. The velocities and densities at any composition are obtained using an equation of state fit to the ab initio results in *Badro et al*. [2014], assuming an ideal mixing model for the ternaries. As shown in *Badro et al*. [2014], this provides a satisfactory fit to the available ternary experimental data.

Figures 2a–2c show that reducing the concentration of Si and adding any of C, O, or S can produce a light and slow layer. This is because the effect of Si on velocity for a given density change is the largest among the four common light elements. As long as enough of the other light element is added to overcome the density increase caused by removing the Si, the resulting velocity will be lower than the bulk core. Along the same line of argument, carbon can be replaced with S or O to produce a light and slow layer (Figures 2d and 2e). Sulfur can also be replaced by oxygen (Figure 2f) to produce a slow and light layer, although the difference in velocity is so marginal it is unlikely to be seismically visible and so is unviable. Finally, oxygen cannot be replaced with any of the other three elements to make a light and slow layer.

The first direct consequence concerns the composition of the outer core as a whole, and in particular, oxygen and sulfur. Oxygen is often considered as a candidate for the light-element [e.g., *Jeanloz and Ahrens*, 1980; *Alfe et al*., 2002; *Rubie et al*., 2004; *Badro et al*., 2007; *Corgne et al*., 2009; *Fischer et al*., 2011; *Badro et al*., 2015], and indeed, *Badro et al*. [2014] show that oxygen can match the seismic properties of the core even as the sole element. However, Figure 2 shows that you cannot have a light and slow layer above a core containing just oxygen by swapping with another element (at least of those considered here). A similar argument can be made for sulfur. S can only be replaced by O (Figure 2f); however, it would produce a velocity contrast of less than 0.1% and so likely invisible to seismology. In other words, assuming the E' layer exists and that the properties of the core can be modeled from the binaries, neither O nor S cannot be the sole light element in the core. Moreover, the two of them together cannot be the main elements in the core; if O and/or S are present in the core, some silicon and/or carbon is also required.

A second direct consequence is that we can use our results to consider and, in some case, rule out, a number of mechanisms proposed for the formation of core layers. These are (1) barodiffusion, (2) solid sedimentation from the core, (3) incorporation of core material from the Moon-forming impactor, and (4) chemical reaction with the lowermost mantle at the core-mantle boundary. We consider each of these in turn.

1. Barodiffusion, where light elements tend to migrate down a pressure gradient, has been suggested as a mechanism for making a light layer at the top of the core [*Gubbins and Davies*, 2013]. Using diffusion coefficients for light elements in Fe, they show that a concentration gradient can be set up, extending as much as 400 km into the core from the CMB. However, this mechanism always enriches the layer in light elements, which our results show should increase the velocity in the layer, rather than decrease it as observed. Since barodiffusion cannot preferentially decrease concentrations of one element while increasing that of another, it alone cannot be the origin of the E' layer.

2. Another scenario is via sedimentation of a light phase such as FeSi [*Buffett et al*., 2000], MgO [*Badro et al*., 2016], or SiO_2 [*Hirose et al*., 2017] crystalizing from the core. Considering MgO and SiO_2 first, crystalizing either of these phases at the CMB would deplete the top of the core in light elements, increasing its density and making it unstable. Crystalizing MgO or SiO_2 from the bulk core and redissolving them into the E' layer will simply increase the concentrations of these elements in the layer. This will make a lighter layer, but also a faster layer. And finally, MgO or SiO_2 crystalizing in the bulk core and floating up to sediment on the CMB could result in a residual light layer enriched in MgO or SiO_2, but it too would have fast velocities incompatible with the seismic observations.

   Removing FeSi from a core with just Si as a light element would have the same effect as for MgO and SiO_2 described above; it simply changes its concentration and does not exchange elements as required. If, on the other hand, the core contains both Si and O as the light-elements then crystalizing FeSi can increase the concentration of O by removal of Fe, while at the same time decreasing the concentration of Si. Figure 2b shows that this may produce a light and slow layer. However, Figure 2b also shows that the

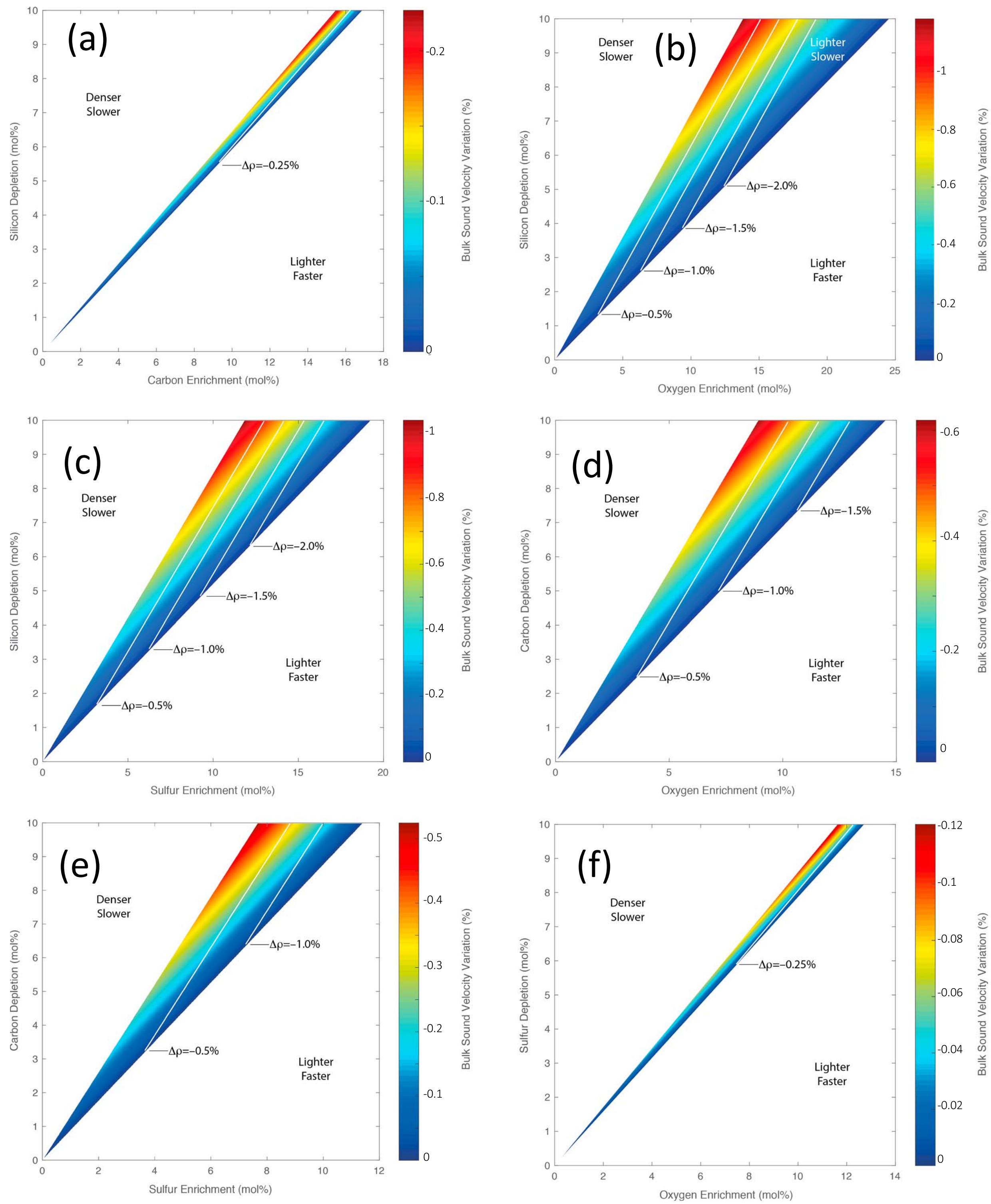

Figure 2. (a–f) Figure showing how the concentration of one element can be increased and another decreased to produce a light and slow layer. Changes to the composition which fall outside the colored wedges result in a layer which is either faster or denser and does not satisfy seismological constraints. For example, increasing the concentration of C by 10 mol % and decreasing Si concentration by 2 mol % would produce a layer that is lighter, but faster. Similarly, increasing the C concentration by 4 mol % and decreasing Si by 5 mol % produces a layer which is slower, but in this case denser. Also shown are contours of the change in density and velocity for compositional changes which produce a light and slow *E*′ layer. Note different scale bars.

enrichment in O must exceed the depletion in Si by a factor of about 1.5 to 2.5 to be within the lighter and slower region. This requires the crystalizing phase to be very enriched in Fe; crystalizing FeSi would only enrich the core in O by a very small amount and produce a layer that would fall well into the dense and slow region of Figure 2b. A core of say 10% Si and 5% O would require the crystalizing phase to have a composition between Fe_5Si and Fe_9Si in order to leave a layer in the light and slow regime. The range of compositions of the crystalizing phase depends on the core composition, but it always needs to be very Fe rich to increase the O content enough and yet have a higher Si/Fe ratio than the core. While such an Fe-rich phase may be possible, it has not yet been found. Moreover, both the core composition and the Fe-Si phase diagram must be consistent with this very Fe-rich phase crystalizing on the Si side of a eutectic. Alternatively, if there is a solid solution, then the melting temperature must increase toward the Si side. Either way, no evidence exists to support the sedimentation of such a phase and it seems unlikely that all the required conditions could be met. Nevertheless, we cannot rule it out entirely.

Although the previous paragraph concentrated on removing FeSi from a core with Si and O as the light elements, the same argument can be applied to any of the pairs of light elements shown in Figure 2 and the crystalizing phase must be strongly Fe-rich. In the case of carbon, a possible phase is Fe_3C; however, assuming a core with 3 wt % O and 2 wt % C [e.g.. *Badro et al*., 2014], then even Fe_3C is not sufficient and the composition of the crystalizing phase would have to have a composition of about Fe_4C. And similar arguments about the phase diagram and core composition would have to be met as for sedimentation of an Fe-Si phase.

It is, therefore, not possible to totally exclude sedimentation of a crystalizing phase as a method for producing a light and slow layer in the outer core, but there is currently no evidence for the crystalization of appropriate Fe-rich phases.

3. It has recently been suggested that layers in the core may have been formed from incomplete mixing of an early Earth core with the core of a late impactor [e.g., *Landeau et al*., 2016], and we can use our results to evaluate specific scenarios. For instance, if the core of the impactor is S rich [*Lee et al*., 2007*; Savage et al*., 2015; *Wade and Wood*, 2016], then such an impactor could make an E' layer only if Earth's core is Si rich (Figure 2c). Our results also rule out an impactor that has Si as the sole light element since this cannot make a light and slow layer regardless of the composition of the bulk core. However, Figure 2 shows there are many other combinations of core and impactor composition which would make a light and slow layer, and so our results cannot rule out this mechanism for forming E'.

4. A further set of scenarios for producing the E' layer involve a reaction between the core and the mantle at the CMB. Of the four light elements considered here, only O and Si may exist in both the mantle and the core as major elements, and so we consider them first.

   Using metal-silicate partitioning experiments and thermodynamic modeling we can calculate the equilibrium concentrations of O and Si in the core in contact with the mantle at the CMB. The results are shown in Figure 3. We test a number of mantle composition ranging from a pyrolitic mantle *[McDonough and Sun*, 1995*; Lyubetskaya and Korenaga*, 2007*]* to a silicate-depleted iron-enriched ferropericlase composition [e.g., *Wicks et al*., 2010; *Muir and Brodholt*, 2015a] consistent with ULVZs. The equilibrium concentrations are calculated from the metal-silicate thermodynamic data in *Badro et al*. [2015] and *Siebert et al*. [2013]. These metal-silicate partition coefficients are for liquid-liquid equilibria and are therefore valid only for a reaction with a deep magma ocean at the base of the mantle [*Labrosse et al*., 2007], possibly the final state of the mantle before full solidification. They may also be used as a rough guide if the reaction with the core involves solid mantle phases; however, as is discussed below, a core–mantle reaction involving solid mantle phases is strongly limited by diffusion and so is unlikely to affect the composition of a core layer, and the favored scenario is a reaction with a deep magma ocean lying atop the core.

   Figure 3 shows that a core in equilibrium with a pyrolitic mantle would have a composition ranging from about 12 mol % Si and 10 mol % O at 4000 K to about 15 mol % Si and 18 mol % O at 4300 K. Any core with a light element composition different from these would evolve toward these equilibrium compositions via a reaction with the mantle. Depending on how much exchange occurs, this reaction could produce a layer in the core somewhere between its initial concentration and that of the equilibrium concentration. The question then is whether the reaction leads to a light and slow layer consistent with seismology?

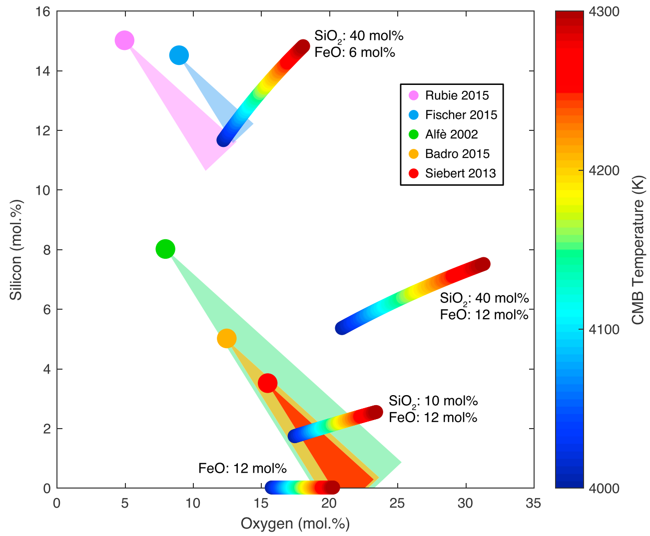

Figure 3. Results of thermodynamic modeling showing core compositions in equilibrium with a pyrolitic lower mantle, a lower mantle enriched in ferropericlase and depleted in SiO_2, and two intermediate compositions (thick colored lines, with colored gradient scale on the right indicating CMB temperature). Compositions at higher and lower temperatures can be inferred by extrapolation. Solid colored circles correspond to core compositions found in the literature [*Rubie et al.*, 2015, *Fischer et al.*, 2015, *Alfe et al.*, 2002, *Badro et al.*, 2015, *Siebert et al.*, 2013]. The fans leading from those compositions come from Figure 2 and show changes to the Si and O content which would result in a slower and lighter layer. If the core contains a relatively high concentration of Si (i.e., *Rubie et al.* [2015] or *Fischer et al.* [2015]), then a reaction between a cool core ($T < 4000$ K) and a pyrolitic mantle can produce a light and slow layer, as shown by the fans spreading from those compositions. Core compositions with less silicon [i.e., *Badro et al.*, 2014; *Alfe et al.*, 2002; *Siebert et al.*, 2013] cannot produce an E' layer from a reaction with a pyrolitic mantle. However, these compositions can evolve toward a light and slow layer if they react with an FeO-enriched lower mantle.

To test whether a core mantle reaction can produce an E' layer, we plot some recent Si-O core compositions from the literature (Figure 3). We also show a fan leading away from each one showing the compositions which will be lighter and slower (as in Figure 2). Finally, the equilibrium core compositions are plotted for various mantle compositions ranging from pyrolite (40 mol % SiO_2 and 6 mol % FeO) to iron-rich ferropericlase (12 mol % FeO), for CMB temperatures ranging between 4000 and 4300 K. If, for a given bulk core composition, the fan heads toward an equilibrium core composition, then a reaction between the core and the mantle can produce the observed E' layer. Alternatively, if the fan leads away from the equilibrium core composition, then a reaction between the core and the mantle will only produce a heavier or a faster layer. We can see from Figure 3 that only a core with a relatively high Si content [i.e., *Rubie et al.*, 2015; *Fischer et al.*, 2015] can evolve toward a light and slow core via a reaction with a pyrolitic mantle, and only for a low CMB temperature (~4000 K). In contrast, a core with less Si [i.e., *Alfe et al.*, 2002; *Siebert et al.*, 2013; *Badro et al.*, 2014] reacting with a mantle would produce a layer richer in Si. This will not produce a light and slow layer.

If, on the other hand, the mantle at the core-mantle boundary is enriched in ferropericlase as an outcome of the freezing of a FeO-rich dense basal magma ocean [*Labrosse et al.*, 2007] or due to the accumulation of a Fe-rich component at the CMB [*Dobson and Brodholt*, 2005; *Wicks et al.*, 2010; *Muir and Brodholt*, 2015a, 2015b], then the core becomes less rich in Si and more enriched in O. In this case Figure 3 shows that a core with lower Si contents can evolve via a reaction with the mantle to even lower Si contents and high O contents, and thus also produce an E' layer consistent with seismology.

Other reactions can also be considered. However, S and C only exist in trace concentrations in the mantle (200 ppm and 100 ppm, respectively), and so any reaction involving those components can only remove S and C from the core and not enrich it from the mantle. In both cases, Figure 2 shows that a core layer produced by S and C depletion requires O to be the element that is increased. So any core–mantle reaction involving S and or C in the core must involve O dissolving into the core at the same time.

Whether a reaction between the core and the mantle can produce an E' layer of ~100 km thick depends on diffusion rates in the core and mantle. Even using diffusion rates calculated along the fastest direction in postperovkite [*Ammann et al.*, 2010], Fe and Si can only diffuse on the order of 20 m over the age of the Earth. It seems unlikely, therefore, that a reaction between the core and a solid mantle can produce a significant change in the composition of a core layer of ~100 km thick. On the other hand, diffusion rates in melts are 6 to 10 orders of magnitude faster than crystalline phases, and so diffusion profiles in a partially molten mantle of tens or hundreds of kilometers are possible. Moreover, if the lowermost mantle is convecting, this will allow it to replenish itself with unreacted mantle, further increasing the amount of silicate which can react with the core. Whether such a reaction occurred during the early magma ocean stage and the E' layer remained stable ever since, or whether it requires a partially molten mantle for much longer, will be considered in future work.

One may also consider how a hotter core might affect the results. As can be seen in Figure 3, a core hotter than 4300 K (as expected earlier in Earth's history) would require the core to be very Si rich ($>$20 mol %) if the layer is to be formed via a reaction with a pyrolitic mantle. Alternatively, the layer can always be produced from a hotter core if the reaction involves an FeO-rich and SiO_2-poor lowermost mantle. If this scenario were to be confirmed, it would add support to the basal magma ocean hypothesis.

4. Conclusions

Using the results from AIMD simulations we show that

1. a light and slow layer at the top of the outer core (E' layer) cannot be produced by simply increasing the concentration of light elements. This rules out mechanisms such as barodiffusion for the formation of the layer.
2. sedimentation of crystalizing phases cannot produce a light and slow layer unless the crystalizing phase is very Fe rich—i.e., Fe_5Si or Fe_4C. However, these phases have never been observed or shown to crystalize at CMB conditions.
3. incomplete mixing of the early Earth's core with an impactor may be able to explain the light and slow layer depending on the relative compositions of the two bodies.
4. a reaction with a pyrolitic mantle or with an FeO-enriched lowermost mantle, such as that expected from a residual magma ocean or from the accumulation of FeO rich cumulates at the CMB, can also produce the characteristics of the E' layer. However, diffusion requires the reaction to be with a mantle melt and not a fully solid lowermost mantle.

The latter three options (sedimentation of a very Fe-rich phase, incomplete impactor core mixing, and core–mantle chemical exchange) are the only scenarios that can produce such a layer consistent with seismology. However, they are all problematic. It remains to be seen if a primordial layer dating back to the Moon-forming impact could survive to this day, and if a postimpact stratified outer core is consistent with thermodynamic constraints on the core [*Nakajima and Stevenson*, 2015] and geomagnetic constraints *Buffett* [2010], such as MAC waves [*Buffett et al*., 2016]. Sedimentation requires the Earth's core to be saturated in a currently undiscovered Fe-rich crystalline phase. Perhaps the most plausible scenario is a chemical interaction with an FeO-rich partially molten mantle at the core-mantle boundary. This requires the E' layer to have either been formed early in Earth's history through exchange with a basal magma ocean, or for the lowermost mantle to have remained partially molten for a significant amount of time (i.e., ULVZs). Although all scenarios considered here have their complications, our results show that they can produce a dynamically stable E' layer that is slower than the bulk core as shown by seismology. They offer a variety of possibilities as to its origin, and together with more seismological properties of the E' layer (density, thickness) may in time constrain its origin with more certainty.

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