The oxidation state and mass of the Moon-forming impactor

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ABSTRACT

Physical simulations of the origin of the Moon have, until recently, centred on impact, about 100 M.yr after the origin of the solar system, of a Mars-like body (10–20% Earth mass) on a near fully-accreted protoEarth. Although this model provides an explanation of the distribution of mass and moment of inertia of the Earth–Moon system it has recently been found that modification of the initial conditions greatly expands the range of permissible impactor masses. Here we take an alternative approach and consider how the oxidation state and mass of the impactor affect the chemical compositions of the product Earth and Moon. We apply the constraints that silicate Moon is richer in FeO than silicate Earth (9–13% as opposed to 8.05%), that their Hf/W ratios are both ∼25 and that they are virtually identical in isotopes of O, Ti, Si, Ni, Cr and W. We then grow protoEarth using a standard accretionary model which yields the correct mantle abundances of Ni, Co, W, Mo, Nb, V and Cr, and add to this body different masses of impactor. The impactor is assumed to be either highly oxidised (∼18% FeO), highly reduced (∼0.3% FeO) or undifferentiated and chondritic. In order to satisfy the isotopic constraints silicate Moon is assumed to be derived principally from silicate protoEarth.

We find that an oxidised or chondritic impactor of ∼ 0.15 M_E can satisfy the isotopic constraints (most importantly ε^{182}W), FeO contents and Nb/Ta of Earth and Moon, but leads to implausibly low Hf/W of ∼12–16 in silicate Earth and ∼4–6 in silicate Moon. This is because the Moon requires more impactor mantle, with low Hf/W, than Earth to reach its higher FeO content. In contrast, impact of a similar mass (10–20% M_E) of highly reduced, Mercury-like impactor on an oxidised protoEarth (∼10.7% FeO in mantle) satisfies the isotopic constraints, FeO contents, Nb/Ta and Hf/W of silicate Earth and Moon given a small amount of post-impact re-equilibration of terrestrial mantle with impactor core. The presence of a small S-rich lunar core is consistent with this reduced impactor scenario. We conclude that the geochemical properties of Earth and Moon strongly favour a reduced impactor of 10–20% M_E.

1. Introduction

Models of the conditions of terrestrial accretion and differentiation (e.g. Rubie et al., 2011; Wade and Wood, 2005) rely on the composition of bulk silicate Earth (BSE) (Allègre et al., 1995; McDonough and Sun, 1995), experimental measurements of the partitioning of elements between liquid silicate and segregating liquid metal core and the assumption that refractory elements are in CI chondritic proportions in the bulk Earth. Although models differ in detail, there is general agreement that pressures of core segregation became high (30–50 GPa) and some argue for increasing oxidation state during accretion, as expressed by an increasing FeO content of BSE (O'Neill, 1991a, 1991b; Rubie et al., 2011, 2015; Wade and Wood, 2005). The Moon-forming impact is

generally equated with addition of ∼15% of an oxidised, volatile-rich impactor to Earth (O'Neill, 1991b) a model which is consistent with the abundances of moderately volatile elements in BSE and with the isotopes of moderately volatile Ag. In the latter case the ^{107}Ag/^{109}Ag ratio depends on the short-lived ^{107}Pd–^{107}Ag isotopic system ($t_{1/2} = 6.5$ M.yr) and Schönbächler et al. (2010) showed that silicate Earth is CI chondritic in Ag isotope ratio. This result is only consistent with the accretionary timescale derived from the short-lived ^{182}Hf–^{182}W system if moderately volatile Ag was added very late in accretion, plausibly with about 15% of a CI-chondrite-like impactor (Schönbächler et al., 2010).

As the chemical similarities between Earth and Moon became clear during the 1970's and 1980's, geochemical models of lunar origin called for the Moon to be made, in the aftermath of a giant impact, of material dominantly from protoEarth (Ringwood, 1986; Wänke and Dreibus, 1983). When hydrodynamic simulations of the impact were made, however (Canup, 2004; Canup and Asphaug, 2001) the mass distribution and angular momentum of the

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Table 1
"Target" composition values.

	Body			Reference
	Chondrite	Earth	Moon	
Hf/W	1.11			McDonough and Sun (1995)
	1.18			Palme and O'Neill (2003)
		25.8		König et al. (2011)
			24.9	Münker (2010)
		$26 + 2/-3$		Kleine et al. (2009)
FeO		8.05%	9–13%	McDonough and Sun (1995)
				Wänke et al. (1977)
				Jones and Palme (2000)
Nb/Ta	19.9 ± 0.6	14.0 ± 0.3	17.0 ± 0.8	Münker et al. (2003)
	17.65			McDonough and Sun (1995)
ε^{182}W	0^a	1.9	1.9	Kleine et al. (2009)
		2.03 ± 0.04 (Isua)		Willbold et al. (2011)
		1.89 ± 0.01 (post-archaen)		
			$\varepsilon_{Earth} + 0.27 \pm 4$	Kruijer et al. (2015)
Δ^{17}O			Earth $+12 \pm 3$ ppm	Herwartz et al. (2014)
			Earth -1 ± 5 ppm	Young et al. (2016)
$\varepsilon^{50,48,46}$Ti	0	0	0	Leya et al. (2003)
Mn, V Cr		Terrestrial Mantle = Lunar Mantle		O'Neill (1991a, 1991b)
V (ppm)		82	~Earth	Drake et al. (1989)
Cr (ppm)		3010	~Earth	Ringwood et al. (1987)
Mn (ppm)		1020	~Earth	
V (ppm)		82		McDonough and Sun (1995)
Cr (ppm)		2625		
Mn (ppm)		1045		
Ni (ppm)		1960	~0.3 Earth	Walter et al. (2000)
Co (ppm)		105	~Earth	McDonough and Sun (1995)
W (ppm)		12	~Earth	König et al. (2011)

[a] ε^{182}W of Earth and Moon relative to Chondrite which is assigned a value of 0.

Earth–Moon system was generated with impactors of 10–20% of Earth mass and it was found that the Moon was produced from an accretion disc dominated by impactor rather than terrestrial material. The latter result is broadly consistent with the significant differences in composition of silicate Earth and silicate Moon. The BSE has an FeO content of 8% (McDonough and Sun, 1995) and an Nb/Ta of 14 (Münker et al., 2003) whereas silicate moon has values of 9–13% (Table 1) and 17 respectively (Münker et al., 2003). More recent trace element and isotopic data have shown, however that BSE and the Moon are essentially identical in Hf/W (Kleine et al., 2004; König et al., 2011) (Table 1) and in isotopes of O, Cr, Ti, Ni and W (Herwartz et al., 2014; Kleine et al., 2004; Regelous et al., 2008; Trinquier et al., 2008). These latter observations are extremely difficult to reconcile with models of the Moon being dominated by material from the impactor (e.g. Canup and Asphaug, 2001) implying, in agreement with the earlier hypotheses, that Earth and Moon were both made substantially of the same precursor materials. Although vapour-phase oxygen isotopic re-equilibration between Earth and Moon in the aftermath of the giant impact has been suggested (Pahlevan and Stevenson, 2007; Pahlevan et al., 2011) similar isotopic re-equilibration of involatile elements such as Ti, Ni and W is difficult to envisage. The implication, if the impactor was 10–50% of Earth Mass is that the moon was made from a similar mixture of protoEarth and impactor as the Earth itself (Young et al., 2016). This is a line of inquiry which we will pursue here. By making the assumption that there are similar proportions of impactor and protoEarth in both bodies we implicitly address most of the isotopic similarities between Earth and Moon. One similarity which, as will be shown, is difficult to reproduce, is that of ε^{182}W. We will show that this provides strong constraints on the amounts of protoEarth and impactor in the 2 bodies as well as on the requirement for post-impact core equilibration with Earth's mantle.

Recent simulations of the Moon-forming impact have expanded the possible range of impactor mass consistent with the physical properties of the Earth–Moon system into two end member scenarios. The first of these involves a small impactor ($\sim$2 to 5% of Earth Mass, Cuk and Stewart, 2012), colliding with a rapidly spinning proto-Earth while the second is a collision between two bodies of similar size (Canup, 2012). Either end-member can, under certain circumstances reproduce the physical properties of the Earth–Moon system and generate a Moon-forming disc predominantly from the proto-Earth's mantle. As we will show below, however, neither end-member is consistent with all the chemical properties of Earth and Moon and the most plausible impactor size, from the standpoint of chemical properties, remains close to the "canonical" value of $0.15M_E$. In this work our aim was to make chemical models of the proto-Earth (pre-impact) and of the impactor, which lead to the observed chemical and isotopic characteristics of the silicate Earth and Moon after the impact. We aimed to do this by constructing each body from different proportions of protoEarth and impactor without resorting to the hypothesis of vapour-phase re-equilibration of the Earth–Moon system in the aftermath of the Giant Impact.

2. Accretion of the protoEarth

Before the giant impact the protoEarth had, based on the models discussed above, grown to between 50 and 95% of its current mass. Although the timescale of accretion to this point is constrained by the ^{182}Hf–^{182}W system to be greater than $\sim$30 Ma after CAI formation (Kleine et al., 2004) there are considerable uncertainties attached to this figure. These uncertainties depend on the degree of metal–silicate equilibration before and after the impact and the size of the impactor. Siderophile ^{182}W was generated during radioactive decay of short-lived lithophile ^{182}Hf ($t_{1/2} = 9$ M.yr)

Table 2
Core–mantle partitioning (Di) on Earth.

Element	McDonough and Sun (1995), McDonough (2003)	König et al. (2011)	Allègre et al. (1995)	Palme and O'Neill (2003)	Likely range
Si	0.29		0.34		0.1–0.35[a]
V	1.83		–		1.5–2.2
Mn	0.29		5		0.2–2.0[a]
Fe	13.66		13.65		13.65
Co	23.8		24.7		23–26
Ni	26.5		24.4		24–27
W		40	–		
Mo	90			140	

[a] Range reflects uncertainty in constraining bulk Earth content due to element volatility.

and the difference between the ratio of ^{182}W to non-radiogenic ^{183}W in silicate Earth, which has Hf/W of 25.8 (König et al., 2011) and that of chondrites, with Hf/W of 1.1, provides a timescale of accretion provided the degree of metal–silicate equilibration is known. If each increment of metal added to silicate Earth completely equilibrated before being sequestered in the core the time of growth is 30–40 M.yr (Kleine et al., 2004). Partial disequilibrium lengthens the timescale while late addition of a chondritic or oxidised impactor shortens the calculated timescale of the earlier accretionary events.

We followed our earlier work (Wade and Wood, 2005; Wood et al., 2006) by assuming that, during accretion before the giant impact, each increment of metal added to the growing Earth equilibrated with the whole mantle before being sequestered in the core (Rubie et al., 2011). It transpires that this assumption is not critical to the results, but it provides a convenient and familiar starting point for discussion of events surrounding the giant impact. During growth of the Earth before the giant impact we assumed that all refractory elements (including W, Mo and Ni) were added in chondritic ratio one to another. This follows from the observation (McDonough and Sun, 1995) that refractory lithophile elements are in chondritic ratio in bulk silicate Earth and enables us to calculate "target" core–mantle partition coefficients for those refractory elements which are known to enter Fe-rich metal (Table 2). Fe was added in proportions constrained by the current mass of the core and mantle and assuming the metal is 85% Fe and the mantle 8.05% FeO (McDonough and Sun, 1995). The partition coefficients are based on the depletions of these refractory siderophile elements in bulk silicate Earth relative to their abundances in chondrites. We have previously shown that, if we assume continuous core segregation and equilibration of each increment of metal with the bulk mantle during growth of the Earth, the mantle abundances of Ni and Co are consistent with equilibration at about 30–40% of the pressure to the core–mantle boundary. This yields a maximum pressure of ∼40 GPa when the Earth is close to its present mass. Because the depth of a magma ocean is defined by the temperature and pressure of melting of the mantle, we fixed the temperature at that of the mantle liquidus and allowed it to increase with increasing pressure in a manner consistent with experimental data (Wade and Wood, 2005). Although the significant depletions of weakly siderophile V, Cr and Nb in silicate Earth may be due to dissolution of oxygen in the metal at high pressure (Corgne et al., 2009) they are most readily explained by their sequestration in the core during an extended period of accretion under reducing conditions, corresponding to low FeO content of the mantle (Ringwood, 1966; Wood et al., 2008). This part of our model is consistent with many-body simulations of inner planet accretion which call for the initially-added bodies to be reduced and volatile-depleted (Rubie et al., 2015). To take account of these observations we began accreting earth with an FeO content of the silicate of 2.6% and al-

lowed FeO to rise at rates depending on the mass and nature of the impactor until mantle FeO contents close to those observed today (Table 1) were reached. Note that, in all cases, we took explicit account of FeO dissolution into the metallic core of Earth (supplementary information).

The accretionary calculations and input data are described in the supplementary information.

3. Impactor compositions

To explore the consequences of impactor composition on the resultant bodies, we used two 'end-member' compositions: a Mars-like oxidised body, and a reduced, Mercury-like body, both with chondritic ratios of refractory elements, as shown schematically in Fig. 1. Note that we use the terms "oxidised" and "reduced" to refer to bodies with high and low FeO/Fe ratios respectively. We also considered the possibility of an undifferentiated chondritic impactor, but find that this case is equivalent to an oxidised impactor in which core and mantle completely re-equilibrate with the silicate fraction of the protoEarth. This case is discussed below. The impactors were assumed to have masses of 10–50% Earth mass with peak core formation pressures at the end of their growth of about 20 GPa, broadly consistent with the core–mantle boundary pressures of Mars (Bertka and Fei, 1998). The differentiated bodies were assumed to have accreted under one of two end-member oxygen fugacity (fO_2) regimes either oxidised, Mars-like with 18 wt% FeO in the mantle, or reduced, Mercury-like with a mantle containing 0.3 wt% FeO. These equate to approximate oxygen fugacities of 1 log unit and 5 log units below the iron-wüstite buffer respectively. In all scenarios sulphur was added in the final stages of accretion (Schönbächler et al., 2010) as a component of the impactor. This is consistent with the late addition of moderately volatile elements such as S which is implied by the chondritic Ag isotope ratio of silicate Earth (Schönbächler et al., 2010). In the latter case we are equating the timing of S and Ag accretion since these elements are of similar volatility in the solar nebula (Lodders, 2003). Note that the timing of S addition has only minor effects on the models and only in those cases where there is significant re-equilibration of impactor core with Earth's mantle.

Given the model of protoEarth accretion described above (see Supplementary Information for more details) and the two end-member impactor compositions discussed in this section, we use 4 principal chemical constraints to derive the most probable nature and mass of the moon-forming impactor. These are, respectively, the FeO contents of terrestrial and lunar mantles, their Nb/Ta and Hf/W ratios and their W isotopic compositions. Other isotopic similarities between Earth and Moon are, as discussed below, weaker constraints than that provided by ^{182}W. We added the requirement that the final concentrations of moderately siderophile elements in silicate Earth match those observed, as given in Table 1.
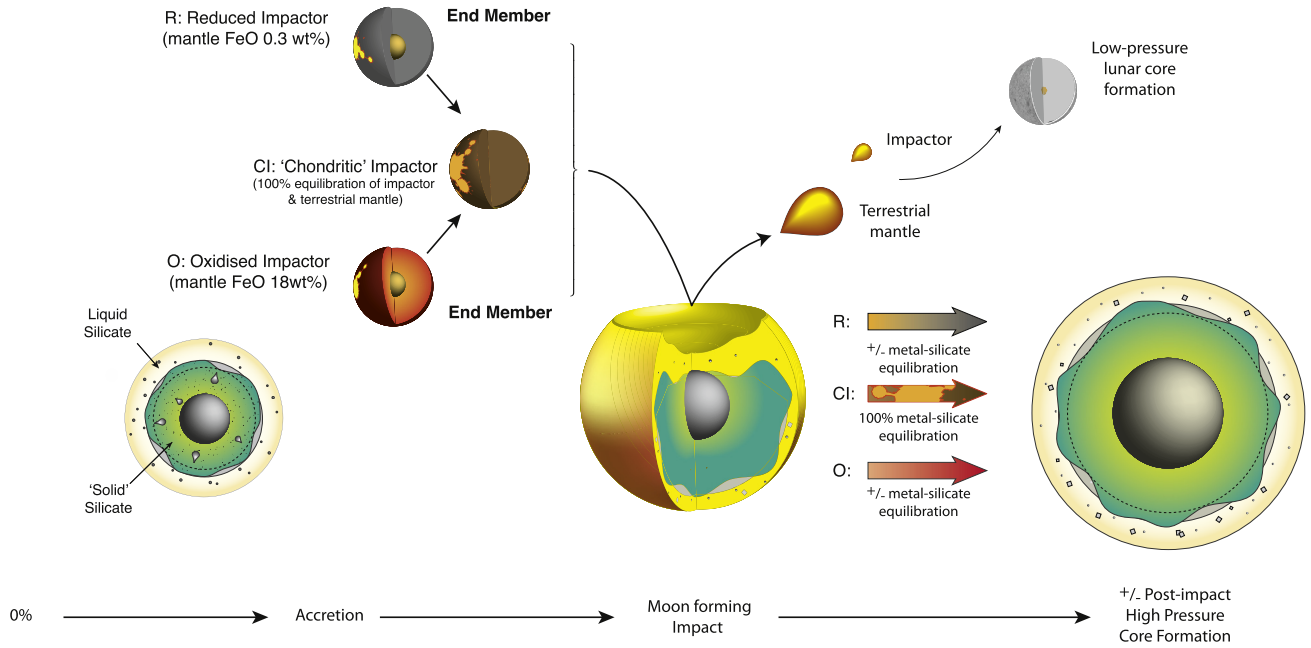
Fig. 1. Cartoon showing the scenarios we have investigated. Earth accretes with continuous core segregation up to the time of the Giant Impact. Three potential end-member impactors, R (reduced), CI (chondritic) and O (oxidised) are considered. After impact part of protoEarth's mantle and impactor mantle combine to form silicate moon. The remainder of the impactor is left in the Earth the mantle of which undergoes varying degrees of equilibration with the impactor core at high pressure (40 GPa).

4. Scenario 1 – reduced protoEarth, oxidised impactor

We assumed that, in its initial stages of accretion, protoEarth was reduced with a mantle FeO content of 2.6%. This starting value is not critical to the overall partitioning results. If we were to raise or lower it slightly, we could adjust the accretionary path to compensate for the changes in metal–silicate partitioning. The important point is that the protoEarth is assumed to be reduced. The mantle FeO content was allowed to increase to the appropriate level at the time Earth was struck by the oxidised impactor. We applied the constraint that the final FeO content of Earth's mantle must be the observed 8.05% (Table 1) and assumed a Mars-like impactor with 18% FeO in its mantle (Dreibus and Wänke, 1985) consistent with a number of recent accretionary models of Earth (Rubie et al., 2015). This means that the FeO content of protoEarth's mantle must be less than 8.05% and that it decreases with increasing mass of the impactor. In order to produce a silicate Moon which is more FeO-rich than silicate Earth, greater amounts of impactor are added to the Moon than to Earth. So, for example if we add 10% impactor to earth, the Moon must be about 30% impactor and 70% protoEarth (Fig. 2, Table 3) in order to arrive at a silicate Moon with about 10.5% FeO. In this case, we can readily show that protoEarth's mantle had an FeO content of ∼7.3%. This decreases to about 3.4% if the impactor is 30% of the mass of the Earth. We grew protoEarth and oxidised impactor along paths which yielded the final mantle concentrations of moderately siderophile elements (Table 1) using the accretionary model described in supplementary information.

One important variable is the degree to which the impactor core would re-equilibrate with Earth's mantle after impact. Since this is not known, we investigated all extents between 0 and 100%. With an oxidised impactor, addition of its silicate mantle to silicate Earth without further core–mantle equilibration (0% on Fig. 2b) leads to Hf/W of between 7 and 12, well below the expected value of 25.8. Increasing the degree of equilibration of BSE with impactor core increases Hf/W due to dissolution of W into the core such that values of 16–21 can be reached with full equilibration and impactors of 20–30% M_E. Furthermore, high pressure dissolution of

FeO into metal during high pressure metal–silicate re-equilibration on Earth would enable the difference in the amounts of impactor in Earth and Moon to decline from about 30% (0% re-equilibration line in Fig. 2c) to ∼15% (100% line in Fig. 2c). Irrespective of impactor size and degree of equilibration, silicate Earth and silicate Moon would, in this scenario differ slightly in Nb/Ta, with Earth ∼15 and Moon ∼17 close to the observed values (Table 1).

Turning to the isotopic properties of Earth and Moon, the negligible differences in O, Ni, Cr and Ti isotopic compositions of BSE and silicate (Table 1) are easily reconcilable with any model in which the amounts of impactor mantle in both bodies is similar (Young et al., 2016). Furthermore, current experimental data indicate almost no isotopic fractionation between metal and silicate for Cr (Bonnand et al., 2016) and Ni (Lazar et al., 2012), indicating that the extent of post-impact mantle–impactor core re-equilibration will not change this conclusion. Our analysis indicates that it is the W isotopic system which is most sensitive to the composition of the impactor and to the extent of post-impact metal–silicate equilibration. We accrete the protoEarth using the exponential model:

$$F_t = 1 - e^{-\frac{\Delta t}{\tau}} \tag{1}$$

where F_t is the cumulative fractional mass of Earth relative to present day at time t, Δt is $(t_0 - t)$ where t_0 is the age of the solar system and τ is the mean time of accretion. Tungsten is partitioned into the core during growth of protoEarth and impactor which means that the mantle becomes more radiogenic and core less radiogenic than chondrite. By adjusting τ for protoEarth, we then attempt to match $\varepsilon^{182}W$ for BSE and silicate Moon at +1.9 relative to chondrite (Fig. 2).

The Moon is required to have more of the silicate part of the oxidised FeO-rich impactor than Earth in order to give silicate Moon a higher FeO content (Table 3). Since the oxidised impactor has Hf/W close to chondritic, its $\varepsilon^{182}W$ is also closer to chondrite than silicate protoEarth. Therefore silicate Moon must have lower $\varepsilon^{182}W$ than silicate Earth unless there is substantial re-equilibration of Earth's mantle with the impactor core having $\varepsilon^{182}W$ below chondrite. This is depicted in Fig. 2a. A small im-
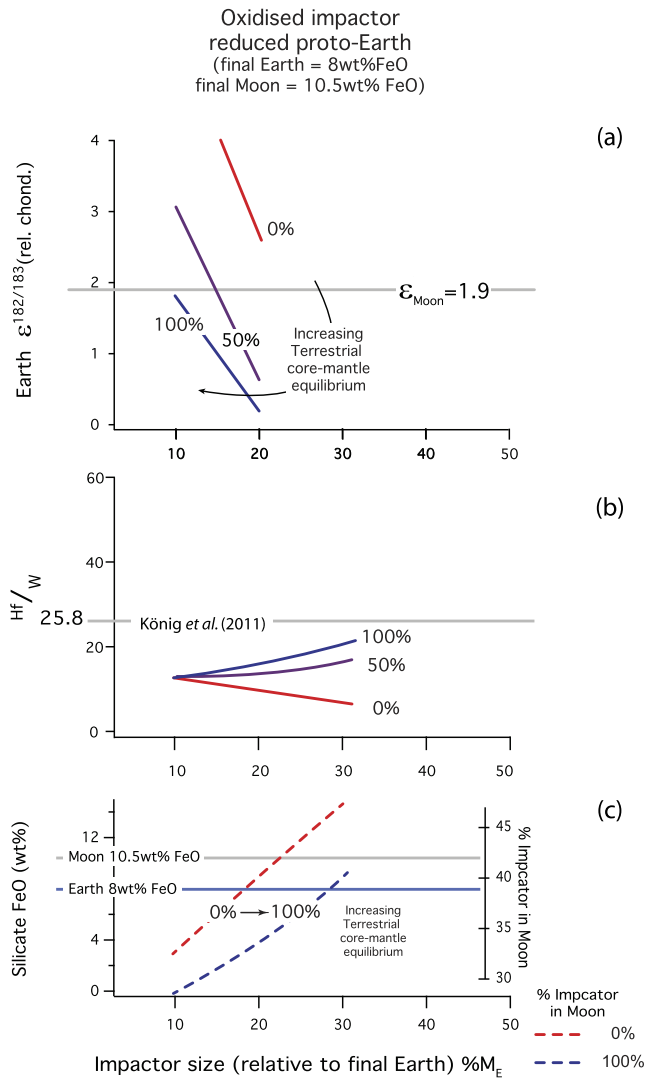
Fig. 2. Results of scenario 1 in which an oxidised impactor (18% FeO in mantle) strikes a reduced protoEarth. (a) We adjust mean time of accretion τ, mass of the impactor and degree of impactor core-terrestrial mantle equilibration in an attempt to match ε^{182}W in Earth and Moon to +1.9 relative to chondrite. The "0%" line ends where τ approaches zero. Extensive re-equilibration (~50%) is required to match terrestrial and lunar W isotopes. (b) Hf/W for silicate Earth given impactors of different mass and differing degrees of impactor core-terrestrial mantle re-equilibration. (c) Plot of % impactor in Moon vs% in Earth for 0% and 100% mantle–impactor core equilibration in Earth. For high pressure metal–silicate equilibration we can put more oxidised impactor in Earth because excess FeO dissolves in the metal.
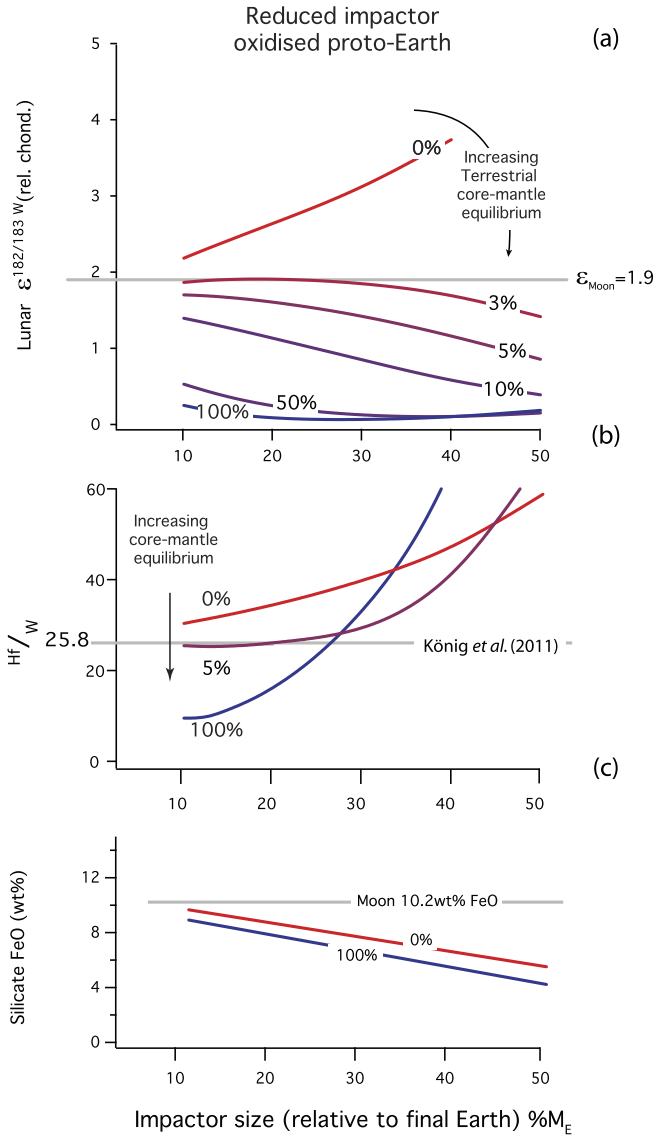
pactor 10–15% M_E with substantial re-equilibration (>50%) of core with silicate Earth is required to bring ε^{182}W for Moon and Earth into agreement at +1.9 relative to chondrite. Fig. 2b and supplementary Table 4 show, however, that Hf/W for the silicate Earth would be ~12–16 under these circumstances, probably unrealistically low given the observed value of 25.8 (König et al., 2011). The situation for the Moon is even more difficult to rationalise. Silicate Moon, containing more of the impactor than silicate Earth, is calculated to have Hf/W of ~4–6 if ε^{182}W is +1.9 relative to chondrite. This compares with an estimated silicate Moon Hf/W value of 25 ± 9 (Münker, 2010).

We conclude that in this scenario, the closest fit to observed properties of Earth and Moon (Table 1) would arise from an impactor of ~15% M_E whose core substantially re-equilibrated with Earth's mantle after impact (Fig. 2). However, the scenario of reduced protoEarth and oxidised impactor is only possible to reconcile with the compositions of BSE and silicate Moon if the Hf/W ratios of both bodies are substantially smaller than implied by all geochemical estimates made to date.

A final note on this scenario is that we have also considered the possibility of an undifferentiated chondritic impactor striking a reduced protoEarth. This is equivalent to taking a differentiated impactor and completely mixing all of it (core and mantle) into Earth's mantle prior to segregating the metal part to Earth's core. The chondritic impactor therefore gives the same results as 100% re-equilibration of impactor's core with Earth's mantle, as shown (100% lines) in Fig. 2 and supplementary Table 4. This would be difficult to reconcile with Hf/W and the W isotopic compositions of Earth and Moon (Fig. 2) for the reasons discussed above.

5. Scenario 2 – oxidised protoEarth, reduced impactor

Given a reduced impactor with low mantle FeO concentration, the silicate Moon, assuming it has an FeO content of ~10–11%, must come principally from an oxidised protoEarth. Earth, with its lower FeO content must contain a higher proportion of reduced impactor than the Moon. We assumed that, as it accreted, protoEarth grew from a reduced body with 2.6% FeO in the mantle to an oxidised body with 10.7% FeO (supplementary information) and considered a highly reduced impactor with 0.3% FeO in its mantle. Assuming, as before, that the Moon contains small amounts of impactor (~5%) the final lunar mantle would have ~10.2% FeO as shown in Fig. 3 and Table 4. Fig. 3c shows that, in this scenario, silicate Earth will have about 8% FeO if we add an impactor of 15–20% M_E. The degree of post-impact core–mantle re-equilibration has little effect on this result.

Table 3
Proto-Earth with variable mantle FeO at impact + an oxidised impactor. Earth contains 8 wt% FeO after accretion.

Impactor (% M_E)	10%			20%			30%		
Impactor core equilibration with Earth's mantle	0%	50%	100%	0%	50%	100%	0%	50%	100%
FeO (Earth)					8.05				
FeO (Moon)					10.05				
Nb/Ta (Earth)	15.9	15.6	15.3	15.5	15.1	14.8	14.7	14.5	14.2
Nb/Ta (Moon)	17.1	15.9	16.0	17.0	17.0	17.0	16.6	16.8	16.9
Hf/W (Earth)	12.6	12.3	12.1	8.7	13.6	15.8	7.0	16.6	20.6
Hf/W (Moon)	4.1	4.2	4.6	4.8	5.2	5.6	5.0	4.2	6.0
ε (Earth)	5.65	3.05	1.76	2.64	0.63	0.19	–	–	–
ε (Moon)					1.90		–	–	–
$\tau (\times 10^7$ yrs)	0.43	0.49	0.6	1.22	1.43	1.62	–	–	–
% Impactor in Moon	32	31	28	40	36.5	33	47	44	39

Fig. 3. Results of scenario 2 in which a reduced impactor (0.3% FeO in mantle) strikes an oxidised protoEarth. (a) We adjust mean time of accretion τ, mass of the impactor and degree of impactor core-terrestrial mantle equilibration in an attempt to match ε^{182}W in Earth and Moon to +1.9 relative to chondrite. We obtain a good fit with ∼3% equilibration and impactor of 0.1–0.25 M_E. (b) Hf/W for silicate Earth given impactors of different mass and differing degrees of impactor core-terrestrial mantle re-equilibration. Impactors of 0.1–0.2 M_E with <5% equilibration match the observed Hf/W. (c) FeO content of silicate Earth declines with increasing mass of the impactor and degree of post-impact re-equilibration, but impactors of 0.1–0.2 M_E can easily match the observed composition of silicate Earth.

The Nb/Ta ratio of silicate Earth, assuming 15–20% M_E impactor should be between 13.5 and 16, consistent with the observed value (Table 1) and slightly lower than that of the Moon (∼15.7). Hf/W of silicate Earth must be higher than that of the Moon if there is no post-impact re-equilibration of impactor core with terrestrial mantle and the extent of the difference increases with the amount of impactor in Earth, because the impactor has very high Hf/W. Even small amounts (3–5%) of impactor core re-equilibration is sufficient however, to reduce Hf/W of silicate Earth because Earth, being more oxidised than the impactor, acts to partition W *out* of the accreting metal (Fig. 3b, Table 4). Thus, we can achieve Hf/W of silicate Earth (∼26) with a few per cent of post-impact core re-equilibration and the Moon retains a value of ∼29 principally inherited from protoEarth. Similarly, complete core-merging (0% core–mantle re-equilibration) leads to silicate Earth being more radiogenic in ^{182}W than the Moon (Fig. 3a) because of the radiogenic W inherited from the impactor with very high Hf/W. A small amount (∼3%) of impactor core re-equilibration, however, partitions non-radiogenic W into the Earth's mantle and reduces ε^{182}W of Earth to essentially the same value as that of the Moon.

We conclude that scenario 2, with oxidised protoEarth and reduced impactor can reproduce all of the properties of Earth and Moon which we have identified as providing constraints on the impact. The "best-fit" impactor mass would be 10–20% M_E (Fig. 3). This scenario generates a value of Hf/W of 25–30 in both bodies, a slightly lower Nb/Ta in silicate Earth than in the Moon and the same ε^{182}W in both bodies. It also allows the silicate Moon to be slightly richer in FeO than BSE. This, it seems is the solution which requires no process other than mixing of impactor and protoEarth silicates with a small amount of core–mantle re-equilibration in the aftermath of the impact.

6. Chondritic impactors

As discussed above, each of the scenarios we have discussed can be converted into one in which the impactor is chondritic and either undifferentiated or completely mixed with protoEarth during the impact. This scenario corresponds to the case of 100% re-equilibration of impactor core with the mixed impactor–protoEarth mantle which is shown and detailed in each of the figures and tables. In neither of the cases considered does a chondritic impactor satisfy all of the constraints we have applied, although that of a moderately reduced protoEarth (scenario 1) comes closest in that it can reproduce ε^{182}W for both bodies, albeit with unreasonably low values of Hf/W of ∼12–15 for Earth and ∼5 for the Moon. Note that the latter value arises from the fact that the Moon contains more oxidised impactor than the Earth in this scenario.

Table 4
Proto-Earth with mantle containing 10.7 wt% FeO at impact + a reduced impactor (0.3 wt% FeO).

| Impactor (% M_E) | 10% | | 15% | | 17.5% | | | 20% | | 30% | | 40% | | 50% | |
Impactor core equilibration with Earth's mantle	0%	100%	0%	100%	0%	3%	100%	0%	100%	0%	100%	0%	100%	0%	100%
FeO (Earth)	9.64	8.97	9.12	8.31	8.86	8.84	7.99	8.60	7.67	7.56	6.46	6.53	5.33	5.49	4.29
FeO (Moon)								10.2							
Nb/Ta (Earth)	14.95	15.83	14.06	15.60	13.61	13.68	15.93	13.17	15.33	11.38	14.69	9.58	13.94	7.76	13.06
Nb/Ta (Moon)	15.78		15.70		15.66			15.62		15.40		15.09		14.65	
Hf/W (Earth)	30.36	9.49	32.29	11.42	33.35	28.07	13.58	34.48	16.31	39.91	33.56	47.46	65.78	58.80	123.69
Hf/W (Moon)	28.77		28.89		28.96			29.03		29.41		29.98		30.95	
ε (Earth)	2.18	0.25	2.41	0.14	2.53	1.91	0.11	2.64	0.09	3.12	0.07	3.74	0.10	–	0.19
ε (Moon)								1.90							
τ (×10^7 yrs)	2.04		2.37		2.62			2.73		3.53		4.55		5.94	

7. Implications of presence of a Lunar core

Thus far we have concentrated most of our analysis on the composition of silicate Earth, which is much better-constrained than that of silicate Moon and have assumed that the Moon is a mixture of the mantles of protoEarth and the impactor. Recent analysis of data from the Lunar passive seismic experiment has shown, however, that the Moon possesses a partially molten core which constitutes about 1.5% of its mass (Weber et al., 2011). The presence of even such a small core has implications for the abundances of moderately siderophile elements, notably Ni, in the lunar mantle and, potentially for its W isotopic composition.

In scenario 1, reduced protoEarth and oxidised impactor, the presence of 1.5% lunar core can be modelled by assuming that the Moon combines protoEarth mantle with a chondritic impactor containing sufficient metal to yield the observed amount of lunar core. The small core and the total mantle are then equilibrated. Core segregation reduces the Ni and Co contents of the lunar mantle (Table 1) and also reduces ε^{182}W for the Moon because of the admixture of chondritic W. In order to compensate for the latter effect we can reduce the mean accretion time τ of protoEarth to about 10^6 yrs but this means we have to increase the extent of impactor core–Earth Mantle equilibration to ∼75% in order to obtain ε^{182}W of 1.9 for the Earth. The Hf/W ratios of Earth and Moon are little changed from those of Table 3, ∼12 and ∼5 respectively. This scenario still does not, therefore, match the observed Hf/W ratios of terrestrial and lunar mantles.

In scenario 2, where the impactor is highly reduced (0.3% FeO) the effects of adding ∼1.5% of a lunar core are slightly more significant than those discussed above, provided this core re-equilibrates with the lunar mantle. If the lunar core were not to have reacted with its mantle, the results of Fig. 3 and Table 4 would be unaltered by its presence. In the case of lunar core reaction, we add ∼5% of chondritic material containing 33% metal to the Moon and allow the metal to equilibrate with the total mass of silicate. This lowers the Hf/W of silicate Moon from ∼29 (Table 4) to ∼13 as chondritic Hf/W is added. Back-partitioning of W into the small core increases Hf/W to ∼13–18 (lower values corresponding to higher S in the core) while the partitioning of Ni and Co into this core lowers their concentrations in the lunar mantle to values below those of Earth, in reasonable agreement with observations (Table 1). Addition of chondritic W to the Moon decreases ε^{182}W of the lunar mantle. As before, we compensate for this by decreasing τ for the protoEarth to about 3×10^6 yrs. This has the effect of increasing ε^{182}W for Earth unless we increase the degree of earth's mantle equilibration with the impactor core metal, which has negative ε^{182}W. We can therefore match ε^{182}W for Earth and Moon at +1.9 relative to chondrite, but we require ∼20% re-equilibration of the impactor core with Earth's mantle, a process which reduces Hf/W of silicate Earth to ∼20 and that of the Moon to ∼13–18 (Table 4). This scenario generates, as before, results which are closest to the observations of Table 1, but the lunar core, if reacted with the mantle, results in Hf/W ratios of the silicate parts of both Earth and Moon which are lower than those observed. We have some flexibility to increase the Hf/W ratio of protoEarth by changing the early stages of the accretionary process so that W is more siderophile (Supplementary information). But at the point of impact, in this scenario, the Earth is so oxidised (10.7% FeO) that W is only weakly siderophile and it is difficult to achieve values of Hf/W of 25–30 in Earth and Moon.

One final possibility is that the highly reduced impactor (0.3% FeO) has a Si-rich metallic core, consistent with formation under highly reducing conditions. Under these conditions the S in the body is strongly partitioned into the silicate rather than into the metal (Kilburn and Wood, 1997; Wood and Kiseeva, 2015) akin to what is observed on Mercury (Nittler et al., 2011). In this scenario

accretion of impactor silicate to pre-existing protoEarth and Moon would deliver S to the silicate parts of these bodies. The latter are oxidised and FeO-rich, which means that there would be formation of a secondary FeS-rich metallic liquid (the "Hadean Matte"). There would be some partitioning of Ni and Co into this sulphide liquid, but W is essentially lithophile in S-rich liquids under oxidising conditions (Wood et al., 2014) so that Hf/W in the Moon would be unchanged from the values of Table 4 (Fig. 3). Thus, we can match the properties of BSE and silicate moon essentially as shown in Fig. 3 by production of an endogenous secondary core on the Moon. The fact that this would be an S-rich core is consistent with observations that the Moon's core is still at least partially liquid (Weber et al., 2011).

8. Conclusions

We have performed a detailed analysis of the consequences of different scenarios for formation of the Earth–Moon system in terms of the chemical properties of protoEarth and impactor and the proportions of the 2 bodies added to final Earth and Moon. Our initial assumption was that the similarities of silicate Earth and Moon in the isotopes of O, Cr, Ti, Ni and W implied that they contain similar proportions of the precursor materials. We then grew protoEarth along accretionary paths which yielded different values of the FeO content of its mantle prior to impact, these values reflecting either oxidised or reduced protoEarth. One major aim of the accretionary modelling was to obtain a final Earth with appropriate partitioning of moderately siderophile elements between core and mantle. The hypothetical mantle of protoEarth was then mixed with impactors of different mass and composition to yield final Earth and final moon compositions. These calculated compositions were then tested against observed compositional properties of the 2 bodies.

We find that, although a model with moderately reduced protoEarth and oxidised Mars-like impactor (∼0.15 M_E) can yield the correct FeO contents, Nb/Ta and ε^{182}W of both bodies, calculated Hf/W for Earth (12–16) and Moon (∼5) are substantially below those observed. In the case of the Moon this is because large amounts of oxidised impactor are required to bring the FeO content of its mantle up to >10.5% and the silicate part of the impactor has Hf/W close to that of chondrite because W is only weakly siderophile in the oxidised impactor. For the Earth, the substantial amount of post-impact re-equilibration (∼50%) with the impactor core required to give the correct ε^{182}W of Earth's mantle, does not raise BSE's Hf/W substantially. It remains approximately half the observed value. These conclusions are not significantly affected by considering the effects of a small lunar core.

Our most successful model is one in which protoEarth is relatively oxidised (∼10.7% FeO in the mantle) and the impactor highly-reduced and Mercury-like with ∼0.3% FeO in its mantle. Mixing more (10–20% M_E) reduced impactor into Earth than into the Moon generates a terrestrial mantle which is lower in FeO (8%) than the lunar mantle (∼10.7%). The two bodies have the same ε^{182}W (+1.9 relative to chondrite) if there is a few % re-equilibration of impactor core with terrestrial mantle. Similarly, Nb/Ta and Hf/W of both bodies closely approximate those observed (Table 1). In this case, adding the effects of a small, fully equilibrated, lunar core are significant because, in order to match the observed ε^{182}W values of BSE and the Moon we need to lower the mean time of terrestrial accretion and increase the degree of post-impact re-equilibration of Earth's mantle with impactor core from ∼3% to ∼20%. This decreases Hf/W of silicate Earth to ∼20 and of the Moon to 13–18 in both cases by the addition of W from the added metal. Although we can raise these to some extent by changing the accretionary path of protoEarth, an intriguing possibility that

obviates the necessity of doing this is that the lunar core is endogenous.

One of the implications of the impactor being Mercury-like, is that the sulphur it delivers should be dominantly present in the mantle rather than in the reduced, Si-bearing core. Addition of S to the mantle of the oxidised Moon would have created a "Hadean matte" of FeS-rich metal which would partition the chalcophile elements significantly but leave Hf/W and ε^{182}W of the lunar mantle unchanged. In such a case, the presence of the FeS-rich core would have minimal effects on the results presented, without lunar core involvement, in Table 4. We conclude that the best match to the observed properties of Earth and Moon are provided by an oxidised (~10.7% FeO) protoEarth struck by a reduced impactor of mass ~10–20% M$_E$. This runs counter to the commonly-accepted model of an oxidised Moon-forming impactor (e.g. O'Neill, 1991a, 1991b).

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.02.053.

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