Zirconium isotope constraints on the composition of Theia and current Moon-forming theories

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A B S T R A C T

The giant impact theory is the most widely recognized formation scenario of the Earth's Moon. Giant impact models based on dynamical simulations predict that the Moon acquired a significant amount of impactor (Theia) material, which is challenging to reconcile with geochemical data for O, Si, Cr, Ti and W isotopes in the Earth and Moon. Three new giant impact scenarios have been proposed to account for this discrepancy – hit-and-run impact, impact with a fast-spinning protoEarth and massive impactors – each one reducing the proportion of the impactor in the Moon compared to the original canonical giant impact model. The validity of each theory and their different dynamical varieties are evaluated here using an integrated approach that considers new high-precision Zr isotope measurements of lunar rocks, and quantitative geochemical modelling of the isotopic composition of the impactor Theia. All analysed lunar samples (whole-rock, ilmenite and pyroxene separates) display identical Zr isotope compositions to that of the Earth within the uncertainty of 13 ppm for $^{96}Zr/^{90}Zr$ (2σ weighted average). This 13 ppm upper limit is used to infer the most extreme isotopic composition that Theia could have possessed, relative to the Earth, for each of the proposed giant impact theories. The calculated Theian composition is compared with the Zr isotope compositions of different solar system materials in order to constrain the source region of the impactor. As a first order approximation, we show that all considered models (including the canonical) are plausible, alleviating the initial requirement for the new giant impact models. Albeit, the canonical and hit-and-run models are the most restrictive, suggesting that the impactor originated from a region close to the Earth. The fast-spinning protoEarth and massive impactor models are more relaxed and increase the allowed impactor distance from the Earth. Similar calculations carried out for O, Cr, Ti and Si isotope data support these conclusions but exclude a CI- and enstatite chondrite-like composition for Theia. Thus, the impactor Theia most likely had a Zr isotope composition close to that of the Earth, and this suggests that a large part of the inner solar system (or accretion region of the Earth, Theia and enstatite chondrites) had a uniform Zr isotope composition.

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1. Introduction

The giant impact theory – a collision between a late-accretion stage planet (protoEarth) and a smaller Mars-sized impactor (Theia) approximately 4.5 billion years ago – is the leading theory to explain the origin of the Moon (Hartmann and Davis, 1975; Cameron and Ward, 1976; Benz et al., 1986). Underlying models reveal that the energy released during this impact is sufficient to vaporize and eject material (>1 Moon mass) into Earth's or-

bit, which later re-accretes to form the Moon. This theory successfully reproduces key dynamical and geochemical constraints unique to the Earth–Moon system, including the relatively high specific angular momentum of the system and the small iron core of the Moon. The *canonical* subset of giant impact model simulations (Canup and Asphaug, 2001; Canup, 2004) further predict that the majority ($\leq$70%) of the Moon's mass originates from the impactor Theia. However, the similar isotopic compositions of the Moon and bulk silicate Earth (BSE) reported for several elements – O ($\Delta^{17}O$ – Wiechert et al., 2001; Spicuzza et al., 2007; Hallis et al., 2010; Young et al., 2016), Si (Georg et al., 2007; Fitoussi and Bourdon, 2012), Cr (Lugmair and Shukolyukov, 1998), Ti (Zhang et al., 2012), Zr (Schönbächler et al., 2005a, 2005b) and W (Touboul et al., 2007, 2015; Kruijer et al., 2015) – sug-

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gests that the dominant fraction of the Moon derived from the protoEarth. Five potential solutions to this irregularity can be proposed: taking the giant impact model at face value, (1) the isotopic composition of Theia was comparable to that of the Earth (Ringwood, 1979; Wiechert et al., 2001; Meier et al., 2014; Dauphas et al., 2014) or (2) chemical equilibrium between the vapour phases of the protoEarth atmosphere and the lunar forming disk occurred by post-impact processes (Pahlevan and Stevenson, 2007). Alternatively, by increasing the collisional angular momentum, the simulation parameter space (e.g., impact velocity and collisional mass) can be extended to include further variants of the giant impact models. These new models significantly lower the predicted amounts of impactor material ending up in the Moon. These models are: (3) hit-and-run impact (Reufer et al., 2012), (4) impact with a fast-spinning protoEarth (Ćuk and Stewart, 2012) and (5) a collision between two roughly equal-sized massive impactors (Canup, 2012). The excess angular momentum is removed from the system by invoking different post-impact mechanisms, such as mass loss to space (Reufer et al., 2012) or evection resonance between the Earth, Moon and Sun (Ćuk and Stewart, 2012).

The first solution (case (1) above – identical building materials for the protoEarth and the impactor) is difficult to test due to the absence of direct isotopic measurements of Theia, while in case (2), the large uncertainties on the thermodynamic quantities (e.g. temperature) and formulations (e.g. equation of state), which are necessary for the thermal equilibration calculations, hinder the validation. Semi-empirical arguments against the first two cases can be raised and are discussed elsewhere (e.g. see Pahlevan and Stevenson, 2007; Ćuk and Stewart, 2012). In the present study, we focus on determining the isotopic compositions of Theia to verify case (1), examine the significance of case (2) and evaluate the newly proposed giant impact scenarios (cases (3)–(5)) in the context of new (Zr) and existing isotopic data from various elements (O, Cr, Ti, Si, W). Each element has its own advantages and disadvantages, which are discussed in the following section.

Oxygen. Herwartz et al. (2014) identified small (up to 15 ppm, 95% confidence level) differences in the O isotope compositions ($\Delta^{17}O$) of the BSE and Moon. These results are contested by Young et al. (2016) who report identical terrestrial and lunar O isotope compositions within analytical uncertainties, as with other previous works (e.g., Wiechert et al., 2001). Young et al. (2016) argue for isotopic homogenisation through violent post-impact mixing (cf. Pahlevan and Stevenson, 2007), while Wiechert et al. (2001) attribute the homogeneous O isotope composition of the Earth–Moon system to Theia forming at a similar heliocentric distance as the protoEarth. This debate about possible O isotope differences between Earth and the Moon as well as the unique O isotope composition observed for each planetary body except for the Earth–Moon system raises the important question of whether isotopic differences between the Earth and Moon may exist for other elements, but have been concealed within the analytical uncertainties. Such compositional differences would provide crucial constraints for the evaluation of different giant impact theories. The identification of such small differences (≈ 10 ppm level), however, requires a careful consideration of the isotopic data.

Tungsten. In the case of the W isotope similarity, the effect of the short-lived ^{182}Hf–^{182}W decay system is considered. New studies show that W isotopes display an actual difference of 20–30 ppm ($\varepsilon^{182}W$) between the BSE and the bulk silicate Moon (Touboul et al., 2015; Kruijer et al., 2015). This difference was attributed to the late veneer, which affected the Moon and the Earth differently. In light of these new findings, it is not possible to unambiguously exclude the possibility that the BSE and the Moon had slightly different W isotope compositions.

Silicon. The similarity in Si isotopes refers to isotopic effects that are induced by chemical mass-dependent isotope fractionation (e.g. see Young et al., 2002). The complication here is that this type of isotope fractionation can occur during various geological processes such as core formation or magmatic differentiation that take place on rocky planets during or after its accretion.

Chromium, Titanium, Zirconium. Nucleosynthetic isotope variations (non-mass-dependent effects), instead, are robust indicators of the source materials from which a planet or small rocky body formed. These intrinsic anomalies reflect incomplete mixing of presolar components and are inherited from the building materials of a planetary body. They are characteristic for each planetary body and, most importantly are not affected by subsequent geological processing. High-precision nucleosynthetic data are available for Cr, Ti and Zr isotopes. Unfortunately, the Cr and Ti isotope compositions can be modified by the long lasting cosmic ray irradiation on the lunar surface (Zhang et al., 2012; Qin et al., 2010). Zhang et al. (2012) provide evidence that the difference between lunar and terrestrial samples of up to 23 ppm in $\varepsilon^{50}Ti$ is due to cosmic ray irradiation of the lunar surface, while Herwartz et al. (2014) argued for a true difference between BSE and the Moon. This illustrates the need for an element that shows nucleosynthetic effects, but is not significantly affected by the cosmic rays. A very promising element to fill this gap and address all the above-mentioned complications is Zr.

The element Zr is naturally suited to search for nucleosynthetic isotope differences between the Earth and Moon. Zirconium is an ultra-refractory element (half-mass condensation temperature of 1736 K; Lodders, 2003), and therefore very unlikely to be equilibrated isotopically between the Earth and Moon in the aftermath of the giant impact (cf. O, Si, Cr). Its isotopes receive minimal contributions from (i) galactic cosmic rays (Leya et al., 2003; Schönbächler et al., 2003; cf. Ti), (ii) radioactive decay (cf. Cr, W), and (iii) as a lithophile element it is very abundant in the silicate fraction of a planet and thus not significantly affected by the late veneer (cf. W), all of which point to Zr as an ideal system for this study. The five naturally occurring Zr isotopes are predominantly synthesized by slow – ($^{90,91,92,94}Zr$) and rapid – (^{96}Zr) neutron-capture processes. The s-process largely occurs during the thermally pulsating phases of asymptotic giant branch stars, while the r-process may occur in core-collapse supernovae. Charged particle reactions (fusion of light charged nuclei), principally occurring in core-collapse supernovae environments, also contribute to the synthesis of Zr isotopes (e.g. Farouqi et al., 2010; Akram et al., 2013). Nucleosynthetic Zr isotope variations are reported for different bulk solar system materials: (i) $^{96}Zr/^{90}Zr$ enrichments in carbonaceous chondrites relative to the Earth, which scale with the abundance of ^{96}Zr enriched Calcium–Aluminium-rich inclusions (CAIs; Schönbächler et al., 2003; Akram et al., 2013, 2015) and potential correlated $^{96}Zr/^{90}Zr$–$^{91}Zr/^{90}Zr$ variations in primitive and differentiated meteorites, which arise from the addition/removal of different s-process phases relative to the Earth (Akram and Schönbächler, 2013; Akram et al., 2015). Due to this nucleosynthetic Zr isotope heterogeneity between different solar system materials, it is likely that Theia and the protoEarth exhibited distinct Zr isotope compositions. Since the Earth and the Moon reflect different mixtures of these two bodies, isotopic differences in the precursor material should lead to distinct mass-independent isotope compositions for the Earth and the Moon.

Previous work (Schönbächler et al., 2005a) did not identify such differences. Therefore, the aim of this study is to determine the Zr isotope composition of lunar rocks and minerals to a higher precision (< 13 ppm for $^{96}Zr/^{90}Zr$, using 2σ weighted average uncertainties; Section 2.1). These data are utilised to assess the plausibility of each of the giant impact models from a mass-balance

approach. To achieve this, the allowed range of isotopic compositions of Theia is calculated for each giant impact scenario (Section 2.2), using (i) the measured isotopic compositions (including their uncertainties) of the Earth and Moon (Section 3.1) and (ii) the different quantities of lunar material originating from Theia (Section 3.2), as predicted by each model. The resulting Theian compositions are compared with the isotopic compositions of different solar system materials to determine the likely origin of Theia (Sections 3.3, 3.4), following the approach of Akram and Schönbächler (2014). Furthermore, models that predict extreme Theian isotope compositions – relative to the known isotopic compositions of solar system materials – can be excluded. The findings are complemented by similar calculations carried out on O, Si, Cr and Ti isotope data from previous studies.

2. Methods

2.1. Analytical procedure

The lunar samples analysed encompass the lunar whole-rocks 15555 (olivine-norm mare basalt) and 71566 (high-Ti-mare basalt), a pyroxene separate from 77516 (high-Ti-mare basalt) and ilmenite separates from 77516 and 70035 (high-Ti-mare basalts) (Table 1). The samples were provided by NASA's curation and analysis planning team for extraterrestrial materials (CAPTEM) and were previously analysed by Schönbächler et al. (2005a, 2005b), who reported lower precision Zr isotope data. Terrestrial Zr isotope data from the same study for USGS rock standards BHVO-2 (basalt), SCo-1 (Cody Shale, marine shale) and AGV-2 (andesite), and two Archean zircons (zircon (50) Jack Hills Australia, 4.01 Ga and zircon (41) Jack Hills, Australia, 3.4 Ga; Amelin et al., 1999; Schönbächler et al., 2004) are presented in Akram et al. (2015).

The analytical procedure is documented in previous publications (Schönbächler et al., 2004; Akram et al., 2013, 2015). A summary is given here. Powdered rock samples (up to 300 mg) of the terrestrial and lunar rocks and mineral separates were digested in a Parr® bomb digestion vessel using a mixture of concentrated HF–HNO$_3$ (3 ml: 0.1 ml) (170 °C, 108 hrs; Schönbächler et al., 2004; Akram et al., 2013). The samples were subsequently evaporated and re-dissolved in 5 ml 6M HCl – trace HF on a hotplate (120 °C, 48 hrs). A two-stage ion exchange procedure using AG1-X8 anion exchange resin (200–400 mesh, Cl⁻ form) was employed to chemically separate Zr from the matrix elements (Schönbächler et al., 2004). The chemistry yields were between 70–100% and the total procedural blank (chemistry and sample dissolution) was below 150 pg (Schönbächler et al., 2004).

The isotope compositions of the Zr fractions were determined on a Nu Plasma multiple collector – inductively coupled plasma mass spectrometer (MC–ICPMS) coupled with an Aridus II nebulizer sample introduction system (University of Manchester). The intensities of interfering isobars (^{94,96}Mo, ^{96}Ru) and argides (^{50}Ti^{40}Ar, ^{51}V^{40}Ar, ^{52}Cr^{40}Ar, ^{54}Fe^{40}Ar) were always within the acceptable limits (Mo/Zr ≤ 0.001, Ru/Zr ≤ 0.01, Ti/Zr ≤ 1, V/Zr ≤ 0.3, Cr/Zr ≤ 0.3, Fe/Zr ≤0.9; Schönbächler et al., 2004). All five Zr isotope (^{90,91,92,94,96}Zr) signal intensities were measured simultaneously on five different Faraday collectors: L4 (^{90}Zr), L3 (^{91}Zr), L2 (^{92}Zr), H2 (^{94}Zr), and H5 (^{96}Zr). The measured intensities (^{i}Zr$_m$, $i = 90, 91, 92, 94, 96$) were normalized to ^{90}Zr$_m$, and corrected for natural and instrumental mass fractionation relative to ^{94}Zr/^{90}Zr = 0.3381 (Minster and Richard, 1981) using the exponential law (Equation (1a)) to obtain the mass fractionation corrected compositions,

$$R^i\text{Zr} \equiv (^i\text{Zr}/^{90}\text{Zr})_{MF\_corr} = \left(\frac{^i\text{Zr}_m}{^{90}\text{Zr}_m}\right)\left[\frac{m_i}{m_{90}}\right]^{\beta(^{94}\text{Zr}/^{90}\text{Zr})} \quad (1a)$$

with the exponential fractionation factor, β, (Equation (1b)), where m_{90}, m_{94} denote the masses of ^{90}Zr and ^{94}Zr.

$$\beta(^{94}\text{Zr}/^{90}\text{Zr}) = \frac{\log[(^{94}\text{Zr}_m/^{90}\text{Zr}_m)/0.3381]}{\log[\frac{m_{94}}{m_{90}}]} \quad (1b)$$

Isotopes of Mo (^{95}Mo) and Ru (^{99}Ru) were also measured to correct for isobaric interferences on ^{92}Zr (Mo), ^{94}Zr (Mo) and ^{96}Zr (Mo, Ru), using two cycles (cycle 1: masses 90–96, cycle 2: masses 97–103). A sample measurement consisted of 5 s integrations, repeated 60 times. Electronic baselines were measured for 15 s before every analysis. Samples were bracketed with a synthetic Zr Alfa Aesar (#63-061671G) Specpure® standard solution, with signal intensities matching within 20%. Approximately 200–400 ng Zr was consumed per measurement, depending on the sensitivity of each measurement session, which translates to total Zr ion beam intensities in the range 2.5×10^{-10} A and 3.5×10^{-10} A (using $10^{11}\Omega$ amplifiers). The mass fractionation corrected Zr isotope ratios (R^iZr, $i = 91, 92, 96$) of the samples (R^iZr$_{sam}$) are expressed as a deviation from the Alfa Aesar standard solution #63-061671G (R^iZr$_{std}$) in parts per ten thousand, ε: ε^{91}Zr, ε^{92}Zr and ε^{96}Zr, (Equation (2))

$$\varepsilon^i\text{Zr} = \left[\left(\frac{R^i\text{Zr}_{sam}}{R^i\text{Zr}_{std}}\right) - 1\right] \times 10^4. \quad (2)$$

2.2. Calculation of the isotopic composition of Theia

The isotopic composition of Theia is calculated using mass-balance equations based on two-component mixing for a system with pre-impact (protoEarth, Theia) and post-impact (Earth, Moon, escaping mass) components, assuming a negligible escaping mass. Equations (3a) and (3b) give the mixing relations for the isotopic composition of the Earth (ε_E) and Moon (ε_M) as a function of the isotopic compositions of Theia (ε_T) and the protoEarth (ε_{pE}), in epsilon,

$$\varepsilon_M = \varphi_M \cdot \varepsilon_T + (1 - \varphi_M)\varepsilon_{pE} \quad (3a)$$

$$\varepsilon_E = \varphi_E \cdot \varepsilon_T + (1 - \varphi_E)\varepsilon_{pE} \quad (3b)$$

The coefficients φ_E and φ_M denote the amount of Zr in the present day Earth and Moon that originates from Theia, respectively. These quantities are defined in terms of the Zr mass fractions of the Earth (g) and Moon (f) derived from Theia, and the bulk Zr concentrations of Theia (C_T^{Zr}) and the protoEarth (C_{pE}^{Zr}),

$$\varphi_M = \frac{f \cdot C_T^{Zr}}{f \cdot C_T^{Zr} + (1 - f) \cdot C_{pE}^{Zr}} \quad (4a)$$

$$\varphi_E = \frac{g \cdot C_T^{Zr}}{g \cdot C_T^{Zr} + (1 - g) \cdot C_{pE}^{Zr}}. \quad (4b)$$

The unknown quantity (ε_{pE}) is eliminated from the equations by rearranging Equation (3b) for (ε_T) and substituting this value into (3a). After simplifying, Equation (3a) yields

$$\varepsilon_T = \frac{(1 - \varphi_E)\varepsilon_M - (1 - \varphi_M)\varepsilon_E}{(\varphi_M - \varphi_E)}. \quad (5)$$

Thus, ε_T is a function of C_{pE}^{Zr}, C_T^{Zr}, f, g, ε_E and ε_M. As a first order approximation the Earth and protoEarth are ascribed identical Zr concentrations ($C_{pE}^{Zr} = C_E^{Zr}$) equal to the BSE ($C_{BSE}^{Zr} \sim 10.5$ ppm; McDonough, 2003). For the special case $C_T^{Zr} = C_{pE}^{Zr}$, which is primarily used in this study, Equations (4a) and (4b) simplify to give $\varphi_M = f$ and $\varphi_E = g$, such that Equation (5) reduces to

$$\varepsilon_T = \frac{(1 - g)\varepsilon_M - (1 - f)\varepsilon_E}{(f - g)}. \quad (6)$$

Table 1
Zirconium isotope compositions of synthetic standards, terrestrial and lunar rock samples.

Sample	Type	$\varepsilon^{91}Zr$	$\varepsilon^{92}Zr$	$\varepsilon^{96}Zr$	N
Synthetic standards:					
Alfa Aesar # 71-070882	Synthetic	0.13 ± 0.14	0.05 ± 0.10	-0.13 ± 0.21	6
VWR	Synthetic	0.03 ± 0.14	0.01 ± 0.10	-0.12 ± 0.21	6
NIST SRM 3169	Synthetic	-0.14 ± 0.11	-0.06 ± 0.09	0.20 ± 0.19	9
Terrestrial samples:					
Zircon 50[a]	Zircon	0.09 ± 0.12	0.05 ± 0.15	-0.02 ± 0.34	3
Zircon 41[a]	Zircon	-0.02 ± 0.11	0.08 ± 0.11	0.11 ± 0.41	2
BHVO-2[a]	Basalt	-0.12 ± 0.04	-0.08 ± 0.03	0.19 ± 0.08	14
SCo-1[a]	Shale	-0.06 ± 0.02	-0.06 ± 0.02	0.02 ± 0.04	52
AGV-2[a]	Andesite	-0.01 ± 0.11	-0.09 ± 0.10	0.22 ± 0.30	2
Terrestrial mean		$\mathbf{-0.07 \pm 0.02}$	$\mathbf{-0.06 \pm 0.02}$	$\mathbf{0.06 \pm 0.04}$	
Lunar samples:					
15555	Whole-rock	-0.06 ± 0.07	-0.01 ± 0.04	-0.06 ± 0.15	7
71566	Whole-rock	-0.09 ± 0.05	-0.01 ± 0.04	0.16 ± 0.11	8
70035	Ilmenite	-0.05 ± 0.10	-0.14 ± 0.07	0.02 ± 0.34	4
77516	Ilmenite	-0.09 ± 0.09	-0.01 ± 0.07	0.17 ± 0.14	3
77516	Pyroxene	-0.08 ± 0.05	-0.06 ± 0.04	0.05 ± 0.12	6
Lunar mean		$\mathbf{-0.08 \pm 0.03}$	$\mathbf{-0.04 \pm 0.02}$	$\mathbf{0.09 \pm 0.06}$	

The weighted mean ($\bar{x}_w = \sum_{i=1}^{n}(x_i \cdot w_i)/\sum_{i=1}^{n} w_i$; with weights w_i) and its associated uncertainty ($1/\sqrt{\sum_{i=1}^{n} w_i}$, 2σ) are given (see Supplementary Table S1 for more information). Samples are bracketed relative to an Alfa Aesar ($\sharp$63-061671G) synthetic Zr solution, normalised to $^{94}Zr/^{90}Zr = 0.3381$ (Minster and Richard, 1981) and expressed in ε-notation (see Section 2.1). The *t*-values obtained between (i) all 73 terrestrial and (ii) all 28 lunar measurements are 1.16 ($\varepsilon^{91}Zr$), 0.84 ($\varepsilon^{92}Zr$) and 0.12 ($\varepsilon^{96}Zr$), which are all less than the required 95% confidence level critical t-values (one-tail: 1.66; two-tail: 1.99) for two distinct populations. This indicates that there are no discernable differences in the Zr isotope compositions between either group of terrestrial or lunar rock samples analysed.

[a] Data from Akram et al. (2015).

Only values of *f* and *g* that correspond to the successful Moon-forming scenarios are considered here. These are defined by the respective authors of the different giant impact models (Canup and Asphaug, 2001; Reufer et al., 2012; Ćuk and Stewart, 2012; Canup, 2012), or identified in this study based on the criteria that they yield sufficient amounts of iron in the Moon-forming disk (to match the present day iron content of the Moon) together with a sufficient orbiting mass to produce a lunar-mass Moon.

3. Results and discussion

3.1. The Zr isotope compositions of Earth and the Moon

The Zr isotope compositions of the terrestrial and lunar samples are identical within the analytical uncertainties (2σ weighted averages, Table 1; Fig. 1). This conclusion is based on a solid data set that includes 28 analyses of 5 lunar samples (whole rocks and mineral separates) and 73 analyses of 5 terrestrial samples (zircons and whole rocks; Akram et al., 2015) (Table 1; Supplementary Table S1). A t-test analysis (95% confidence level analysis) yields no resolvable difference between the terrestrial and lunar samples, nor does it indicate inter-lunar sample variations (Table 1). The weighted average of the lunar composition ($\varepsilon^{91}Zr = -0.08 \pm 0.03$, $\varepsilon^{92}Zr = -0.04 \pm 0.02$ and $\varepsilon^{96}Zr = 0.09 \pm 0.06$, Table 1) agrees well with previous work ($\varepsilon^{91}Zr = 0.00 \pm 0.29$, $\varepsilon^{92}Zr = -0.03 \pm 0.17$, $\varepsilon^{96}Zr = -0.06 \pm 0.81$, Schönbächler et al., 2005a), but is of considerably higher precision because more measurements of sample aliquots were acquired. The overlap of the low and high precision data documents the accuracy of the analytical method. For the terrestrial whole rocks and zircons, the weighted average uncertainties (based on data from 11 individual digests; Akram et al., 2015) are ± 2 ppm ($\varepsilon^{91}Zr$), ± 2 ppm ($\varepsilon^{92}Zr$) and ± 4 ppm ($\varepsilon^{96}Zr$) (Table 1), while the standard deviations (2σ) – representing the scatter of the population – are ± 15 ppm ($\varepsilon^{91}Zr$), ± 15 ppm ($\varepsilon^{92}Zr$) and ± 25 ppm ($\varepsilon^{96}Zr$). Interestingly, the *weighted averages* reveal small negative $\varepsilon^{91}Zr$ and $\varepsilon^{92}Zr$ values relative to the synthetic Alfa Aesar ($\sharp$63-061671G) Zr standard solution, for both the terrestrial (E) and lunar (M) samples ($\varepsilon^{91}Zr$ E: -0.07 ± 0.02, M: -0.08 ± 0.03,
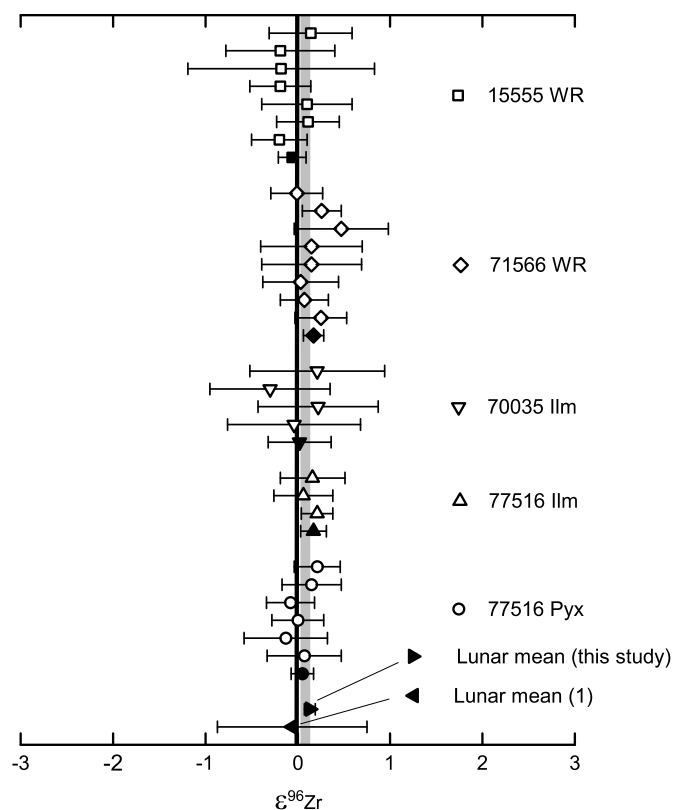

Fig. 1. Zirconium isotope composition ($\varepsilon^{96}Zr$) of lunar samples. Individual measurements are displayed as open symbols. The uncertainties are the internal error (error of the mean, 2σ) of the sample propagated with the external uncertainties (standard deviation, 2σ) of the bracketing standards. Closed symbols reflect the weighted averages of the samples with the associated weighted uncertainty (2σ). (1): Data from Schönbächler et al. (2005a, 2005b). The grey band indicates the average terrestrial isotope composition from Akram et al. (2015).

and $\varepsilon^{92}Zr$: E: -0.06 ± 0.02, M: -0.04 ± 0.02). They are associated with small positive values in $\varepsilon^{96}Zr$ (E: 0.06 ± 0.04, M: 0.09 ± 0.06). In contrast, when single element Zr solutions (NIST, VWR and
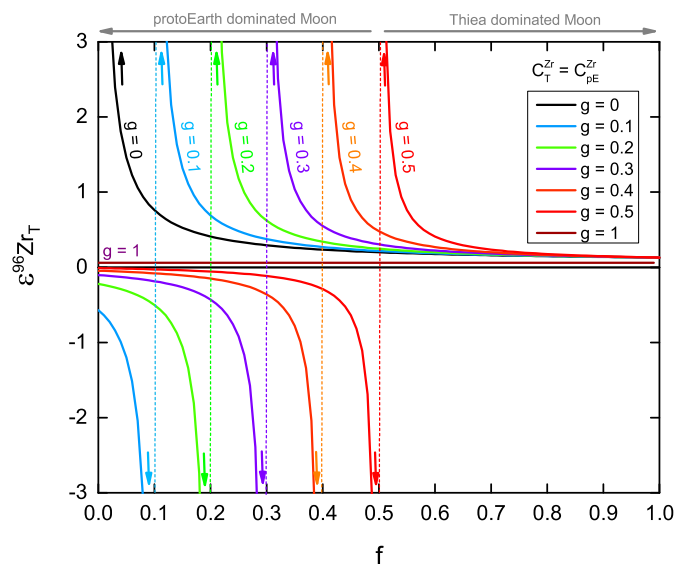
Fig. 2a. The calculated Zr isotope compositions of Theia ($\varepsilon^{96}Zr_T$) as a function of the mass fractions derived from the Earth (g) and Moon (f). The mixing equations are evaluated using the measured Zr isotope compositions of the Earth and Moon (Table 1). The maximum difference of 13 ppm for $\varepsilon^{96}Zr$ is assigned between the Earth and Moon, and identical Zr concentrations for protoEarth and Theia are assumed. At $f = g$, the equations yield $\varepsilon^{96}Zr_E = \varepsilon^{96}Zr_M$, which leads to a discontinuity at this point (i.e. the isotopic composition of Theia tends to infinity).

Fig. 2b. Dependence of $\varepsilon^{96}Zr_T$ on Zr concentration of Theia. The calculations are the same as for Fig. 2a for the case of $g = 0$ and three different Zr concentrations of Theia.

two Alfa Aesar synthetic standards, Table 1) are compared to each other, $\varepsilon^{91}Zr$, $\varepsilon^{92}Zr$ and $\varepsilon^{96}Zr$ overlap using the weighted average and it's associated uncertainty. The small offset between rock samples and synthetic solutions is discussed in Supplementary Text S2. However, it is not a concern for this study as long as geological samples are compared with each other because both the Zr isotope compositions of lunar and terrestrial rocks overlap one another with a similar offset from the single element standard solution. Overall, the new high-precision data provide strong evidence for an identical Zr isotope composition of the Earth and Moon within 13 ppm for $\varepsilon^{96}Zr$, when the upper (0.02) and lower (0.15) boundary defined by the terrestrial and lunar data is considered (Table 1).

3.2. Factors that influence the isotopic composition of Theia

The isotopic composition of Theia is determined using the mixing and mass balance formulation derived in Equations (3)–(6). These equations yield solutions only if the Earth and Moon possess distinct isotopic compositions, i.e. $\varepsilon^{96}Zr_E \neq \varepsilon^{96}Zr_M$. Our data, however, show that the Earth and the Moon display identical Zr isotope compositions within the analytical uncertainty. Using the upper (max) and lower (min) limits of the weighted average compositions ($\varepsilon^{96}Zr_E$, $\varepsilon^{96}Zr_M$; Fig. 1, Table 1), yields the maximum difference between $\varepsilon^{96}Zr_E$ and $\varepsilon^{96}Zr_M$. Two extreme cases can be specified, depending on whether (i) $\varepsilon^{96}Zr_E < \varepsilon^{96}Zr_M$ or (ii) $\varepsilon^{96}Zr_E > \varepsilon^{96}Zr_M$, corresponding to ($\varepsilon^{96}Zr_E$, $\varepsilon^{96}Zr_M$) = ($\varepsilon^{96}Zr_{E,min}$, $\varepsilon^{96}Zr_{M,max}$) or ($\varepsilon^{96}Zr_E$, $\varepsilon^{96}Zr_M$) = ($\varepsilon^{96}Zr_{E,max}$, $\varepsilon^{96}Zr_{M,min}$), which yield differences of 13 ppm and 7 ppm, respectively. Utilizing these maximum differences, Equation (6) is used to place limits on the most extreme isotopic composition and the *range* of isotopic compositions that Theia could have possessed. In the following section, the dependence of Theia's isotopic composition on (1) the proportion of mass that the Moon (f) and the Earth (g) inherited from Theia, and (2) the Zr concentration of Theia is discussed.

Dependence of $\varepsilon^{96}Zr_T$ on f and g. Two scenarios are considered to emphasize the significance of f and g in determining $\varepsilon^{96}Zr_T$. **Case (1):** $f \neq 0$, $g = 0$: If the dominant source of lunar material originates from Theia (i.e., $f \gg 0$), while the protoEarth does not
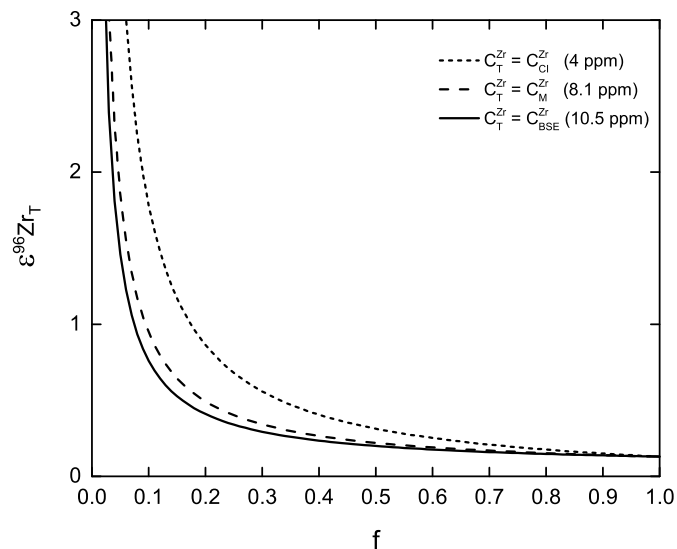
receive any ($g = 0$), the Theian isotopic composition dominates todays lunar composition. In order to reproduce the close isotopic composition of the Earth and Moon (to within 13 ppm), the Theian composition must have been very similar to that of the Earth, i.e. $\varepsilon^{96}Zr_T \approx \varepsilon^{96}Zr_E$ (Fig. 2a; case $g = 0$). As the fraction of Theia in the Moon diminishes (f tends to lower values), more of the Moon forms from protoEarth material, and naturally moves closer to having a terrestrial composition. Decreasing f leads to a dilution of the Theian material present in the Moon with protoEarth material, which allows Theia to assume relatively extreme isotopic compositions, whilst preserving the similar isotopic composition of the Earth and Moon. **Case (2):** $g \neq 0$, $f \neq 0$. In more realistic scenarios, the Earth also receives a contribution of material from Theia and with this, the original isotopic composition of the protoEarth also shifts towards the Theian composition. Hence, the final composition of the Earth also deviates from the starting protoEarth composition – but to a lesser extent than that of the Moon, because the protoEarth possessed a higher initial mass. Similar quantitative behaviour as in case (1) above is observed as f varies from low to high values, but with Theia being able to take more extreme isotope compositions (Fig. 2a; cases $g \neq 0$). The isotopic composition of Theia becomes unimportant in the unlikely case where the Earth and the Moon received exactly the same relative proportion of Theian material ($f = g$, the denominator of Equation (6) goes to $0 \rightarrow$ no solution). When the proportions are nearly identical ($f \approx g$) (indicated with arrows in Fig. 2a), Theia can take very extreme isotopic compositions. The $\varepsilon^{96}Zr_T$ value also moves towards more extreme values as g increases for a fixed value of f (Fig. 2a; cases $g \neq 0$). Thus, the determination of $\varepsilon^{96}Zr_T$ is very sensitive to the delicate interplay between f and g – the respective fractions of lunar material from the Moon and Earth.

Dependence of $\varepsilon^{96}Zr_T$ on C_T^{Zr}. The two cases considered above assume identical Zr concentrations, $C_T^{Zr} = C_{pE}^{Zr}$ ($= C_{BSE}^{Zr}$), as a first order approximation. The Zr concentration of Theia is unknown, but in all likelihood will be confined to the observed range of Zr concentrations of different solar system materials: 4 ppm Zr (CI chondrites; Schönbächler et al., 2005b) to 10.5 ppm Zr (BSE; McDonough, 2003). The current assumptions adopt the upper limit (10.5 ppm) for C_T^{Zr}. For lower Zr concentrations ($C_T^{Zr} < C_{BSE}^{Zr}$), similar quantitative trends (as those described for case (1) and (2)) are obtained for $\varepsilon^{96}Zr_T$ as a function of f and g (Fig. 2b), but with systematically higher $\varepsilon^{96}Zr_T$. This is because the Theian ma-
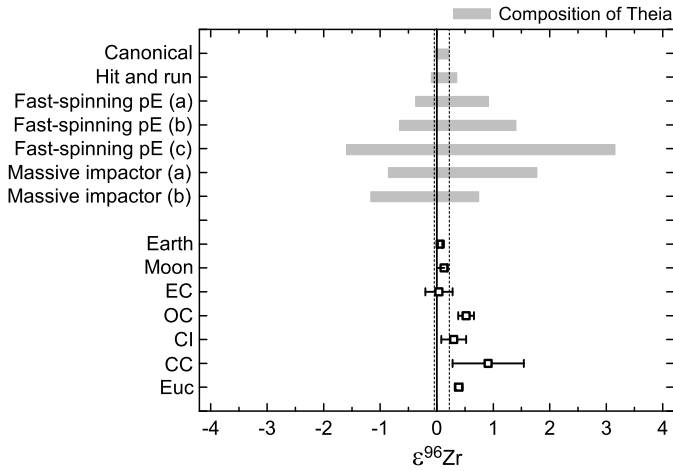
Fig. 3. Predicted range of $\varepsilon^{96}Zr_T$ for different giant impact scenarios. The grey bands show the allowed Theian compositions for the canonical (Canup, 2004), hit-and-run (Reufer et al., 2012), fast-spinning protoEarth – (a) $f = 0.176$, (b) $f = 0.130$, (c) $f = 0.084$; $g = 0.04$ (Ćuk and Stewart, 2012) and the massive impactor (= two colliding half-mass protoEarths) – (a) $f = 0.5$, $g = 0.46$, (b) $f = 0.5$, $g = 0.55$ (Canup, 2012) models. The measured Zr isotope compositions (2σ weighted average uncertainties) for different solar system materials from Akram et al. (2015) are indicated by the open symbols. Black dashed lines indicate the boundaries of the Theian compositions for the canonical model. EC = enstatite chondrites, OC = ordinary chondrites, CI = CI chondrite, CC = carbonaceous chondrites excluding CI chondrites, Euc = eucrites.

terial affects the overall lunar and terrestrial material less if it has a lower Zr concentration. As a result, the allowed values of $\varepsilon^{96}Zr_T$ slightly increase (see Fig. 2b) when $C_T^{Zr} < C_{BSE}^{Zr}$, relative to cases with ($C_T^{Zr} = C_{BSE}^{Zr}$), for any scenario characterized by particular values of f and g.

3.3. Isotopic composition of Theia ($\varepsilon^{96}Zr_T$) for different giant impact models

This section evaluates the calculated isotopic compositions of Theia for the different giant impact models and explores the consequences with respect to Moon-forming theories. Each of the giant impact models is characterized by a different set of values for f and g, which leads to unique values for $\varepsilon^{96}Zr_T$. For simplicity, the assumption $C_T^{Zr} = C_{pE}^{Zr}$ ($= C_{BSE}^{Zr}$) is retained from hereon. The calculated Theian isotopic composition is then compared to measured values of various solar system materials to trace the origin of Theia. A simplified summary of likely solar system matches is given in Supplementary Table 3.

Canonical ($f = 0.7$, $g = 0.1$; Canup and Asphaug, 2001; Canup, 2004). In the original canonical model (Canup, 2004), the majority of the Moon ($\sim$70%) originates from the impactor with the remaining material (30%) coming from the protoEarth. Only a small fraction of the Earth ($\sim$10%) is formed from Theian material. This restricts the Zr isotope composition of Theia to the range $-0.01 \leq \varepsilon^{96}Zr_T \leq 0.22$ (Fig. 3), which overlaps with the terrestrial ($\varepsilon^{96}Zr_E = 0.06 \pm 0.04$), enstatite chondrite ($\varepsilon^{96}Zr_{EC} = 0.04 \pm 0.24$) and CI chondrite composition ($\varepsilon^{96}Zr_{CI} = 0.30 \pm 0.22$) (Fig. 3). Taken at face value, this model predicts that Theia likely originated from a region close to, or within the accretional region of the Earth, i.e. from the inner solar system. The CI chondrites, which also overlap with the predicted $\varepsilon^{96}Zr_T$, are an exception, because they originate from further out in the solar system. A discussion as to why CI chondrites can be excluded as impactor material is given in Section 3.4. The Zr isotope uniformity observed for the Earth, Moon, enstatite chondrites and Theia (in the context of the canonical giant impact model) suggests that the innermost solar system in general displayed very similar or identical Zr isotope compositions.

Hit-and-run ($f = 0.45$, $g = 0.1$; Reufer et al., 2012). Reufer et al. (2012) considered 62 hit-and-run impact scenarios, with different impactor compositions (chondritic, iron-rich and icy impactors). The iron-rich impactors deliver too much iron (5%–70% Moon mass, M_M) to the Moon-forming disk, whereas the icy impactors produce disks with little ($\approx$1% M_M) or no iron, which renders these two classes of impactors unsuccessful. Interestingly, the most successful icy impactor simulation requires most of the Moon (75%) to form from the impactor. This is not very realistic because these impactors will contain little silicate materials or Zr. We therefore limit our analyses to the successful variants of the chondritic impactors. In these scenarios, the amount of impactor material in the Moon is reduced by $\sim$25% compared with the canonical model (Canup, 2004), but the same amount of impactor material ($\sim$10%) ends up in the Earth. The result yields a similarly restricted range of isotopic compositions for Theia $-0.08 \leq \varepsilon^{96}Zr_T \leq 0.35$, which is consistent with the composition of the Earth, enstatite chondrites, CI chondrites, and eucrites ($\varepsilon^{96}Zr_{Euc} = 0.39 \pm 0.07$). As in the canonical case, this points towards the inner solar system as the likely source for Theia.

Fast-spinning protoEarth ($0.08 \leq f \leq 0.18$, $g = 0.04$; Ćuk and Stewart, 2012). A range of f values are accommodated by the successful Moon-forming scenarios in this model, which includes the lowest fraction of impactor-derived material in the Moon (8%) considered in this study. In all of these cases, the range of compositions of Theia matches all measured solar system materials to date (Earth, enstatite, ordinary and carbonaceous chondrites, and eucrites, Fig. 3). However, as f decreases from 18% to 8% (Fig. 3), the corresponding *average* $\varepsilon^{96}Zr_T$ values increase (from $\sim$0.3 to $\sim$0.8). Therefore, models with lower f values produce increasingly more positive $\varepsilon^{96}Zr_T$ (including the uncertainties), which are outside the observed limits of the Zr isotope compositions reported for bulk solar system materials. Consequently, the Zr isotope data favour those variants of a fast-spinning protoEarth model with high f values, because they yield $\varepsilon^{96}Zr_T$ in the range of the known values for solar system materials. The models preferred by Zr isotopes (high f) generally require a higher collisional angular momentum ($\sim$3 L_{EM}), than the low f variants ($\sim$2 L_{EM}). The exclusion of the low f scenarios is also in good agreement with dynamic considerations, because the low f cases correspond to some extent with fast-spinning protoEarth's possessing very fast spin periods ($T \sim 2.3$ hrs). These spin–periods are close to the limit at which the resulting centrifugal forces would tear apart the body. A conclusion can also be drawn regarding the Zr concentration of Theia. Lowering the Zr concentration of Theia to CI chondrite concentrations ($C_T^{Zr} \sim 4$ ppm) results in elevated $\varepsilon^{96}Zr_T$ compositions, which exceeds the maximum $\varepsilon^{96}Zr$ value measured ($\sim +1.2$, Allende, Akram et al., 2015). Thus, in the context of the fast-spinning protoEarth model, Theia likely possessed a Zr concentration similar to BSE (i.e., $C_T^{Zr} \sim 10.5$ ppm).

Massive impactor ($f \sim 0.5$, $0.46 \leq g \leq 0.55$; Canup, 2012). This model examines the case where Theia and the protoEarth originally possessed similar masses. In this scenario, approximately the same fraction of the impactor material ends up in the Moon as in the hit-and-run model. However, the amount of impactor derived material in the Earth is increased substantially, from $\sim$10% to $\sim$50%. As a result the initial isotopic composition of the protoEarth is substantially altered upon impact and strongly shifts towards a Theia-like composition, as is the case for the Moon. Both the Earth and Moon therefore naturally develop similar isotopic compositions (Fig. 3). This allows Theia to carry a more extreme isotopic composition (relative to the Earth) than the hit-and-run scenario and still respect the close Zr isotope compositions of Earth and Moon today. In cases where the Earth receives more impactor material than the Moon (i.e. $g > f$), the range of Theian compositions takes on negative $\varepsilon^{96}Zr_T$. To date, negative $\varepsilon^{96}Zr$ values are

not reported for solar system materials (Schönbächler et al., 2003; Akram et al., 2015, this work). This renders massive impactor scenarios with $g > f$ unlikely. From a dynamical viewpoint the case $g > f$ will leave behind too much protoEarth material, after subtracting the amount of material ending up in the Moon, which violates our assumption that mass escape is negligible. Thus, both isotopic and dynamical arguments are consistent with one another, and disfavour impacts between two large bodies under the conditions $g > f$. The successful case $f > g$ permits Theia to assume the Zr isotope composition of all measured solar system bodies, as with the fast-spinning protoEarth model.

3.4. The origin of Theia and implications for Moon-forming theories

Evaluation of the giant impact models. An important observation is that the calculated Zr isotope compositions of Theia based on the evaluated giant impact models mainly remain within the observed range of Zr isotope compositions of different solar system materials. This demonstrates that all investigated giant impact models (hit-and-run, fast-spinning protoEarth and massive impactor) are equally plausible as the canonical model (Canup and Asphaug, 2001; Canup, 2004) based on evidence from Zr isotopes. Albeit, the canonical model is favoured by the geochemical data, if the impactor was restricted to a very narrow range of isotopic compositions close to the Earth's composition (Fig. 3). Thus, the original need to reduce the amount of impactor material in the Moon, which led to the development of the new dynamic models in order to resolve the isotopic uniformity reported for several elements, is relieved in light of our mass balance calculations. Nevertheless, our study is able to exclude some variants of the fast-spinning proto-Earth and massive impactor models.

Origin of the impactor. The canonical and hit-and-run models are the most restrictive, suggesting that Theia could have borne an Earth-like, enstatite- or CI-chondrite like Zr isotope composition. These bodies likely originate from the inner solar system, and therefore Theia most probably accreted quite close to Earth's orbital region. The fast-spinning protoEarth and massive impactor models are more relaxed and increase the impactor distance to include the source region of the carbonaceous chondrites. A universal result is that all models reproduce the similar Zr isotope compositions of the Earth and Moon if Theia possessed either (i) an Earth-like, (ii) enstatite chondrite or (iii) CI chondrite Zr isotope composition. The plausibility of each of these three cases is assessed in the following section by considering other isotope systems.

Similar calculations as for Zr isotopes were performed with isotopic data for the more abundant elements O (Clayton and Mayeda, 1996; Wiechert et al., 2001; Herwartz et al., 2014; Young et al., 2016), Si (Georg et al., 2007; Armytage et al., 2011; Fitoussi and Bourdon, 2012), Cr (Trinquier et al., 2007; Qin et al., 2010) and Ti (Leya et al., 2008; Trinquier et al., 2009; Zhang et al., 2012; Williams et al., 2012). The most recent terrestrial and lunar O isotope data ($\Delta^{17}O$, using 2sd uncertainties, sd: standard deviation) of Young et al. (2016) further exclude Theia possessing a CI, ordinary chondrite and eucrite composition for the canonical and hit-and-run model (Supplementary Fig. S2). The debated O isotope data of Herwartz et al. (2014), if taken at face value, are even more constraining and in addition exclude the Earth as the sole source material for Theia (Supplementary Fig. S3). Nevertheless, the O isotope data of (Herwartz et al., 2014) also point to the inner solar system as the origin of Theia, despite the apparent isotopic heterogeneity between the Earth, Moon and enstatite chondrites in $\Delta^{17}O$. The Cr isotope data (Supplementary Fig. S4) confirm the conclusion drawn from Zr and O, and are also in good agreement with recent Si isotope data. The data reveal non-terrestrial mass-dependent Si isotope variations ($\delta^{30}Si$) for enstatite chondrites
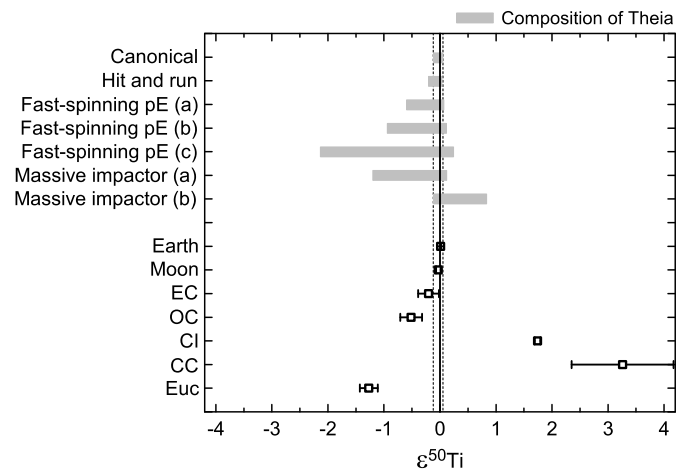

Fig. 4. Predicted range of $\varepsilon^{50}Ti_T$ values for different giant impact scenarios. Grey bands and black dashed lines are the same as Fig. 3. The Ti isotope data are from Leya et al. (2008), Trinquier et al. (2009), Zhang et al. (2012) and Williams et al. (2012), with 2σ error of the mean uncertainties ($2sd/\sqrt{N}$; N = number of measurements). EC = enstatite chondrites, OC = ordinary chondrites, CI = CI chondrite, CC = carbonaceous chondrites excluding CI chondrites, Euc = eucrites.

(Fitoussi and Bourdon, 2012) and CI chondrites (Georg et al., 2007; Armytage et al., 2011). Consequently, these data do not permit an enstatite chondrite or CI chondrite-like Si isotope composition for Theia in either the canonical or hit-and-run models (see Supplementary Fig. S5). This conclusion needs to be considered with caution because it is based on the assumption that geological processes were not accompanied by stable isotope fractionation that altered the isotopic composition of the planetary reservoirs. The relatively high Rb/Sr ratios, the low FeO contents and the refractory element abundance patterns of enstatite chondrites, relative to the BSE, also provide evidence against an impactor with an enstatite chondrite composition (Jacobsen et al., 2012). Comparable results, as for Zr, are also obtained for Ti isotopes (Fig. 4) with one major difference. The Ti isotope data (Trinquier et al., 2009; Zhang et al., 2012; Williams et al., 2012) clearly exclude a Theia with a CI-like or a carbonaceous chondrite composition in general for all giant impact models (Fig. 4). A similar conclusion was also obtained by Zhang et al. (2012) and is independent of potential cosmic ray effects in lunar samples.

The exclusion of a carbonaceous chondrite impactor for the Moon-forming giant impact may even be extended to volatile-rich bodies in general. This conclusion is well constrained if all volatile-rich materials from the outer solar system possess positive $\varepsilon^{50}Ti$. The relevant Ti data are not available yet. However, the overall observed trend in Ti isotopes points toward such a composition, because carbonaceous chondrites, thought to have formed furthest away from the Sun out of all the material available for high precision Ti isotope analyses, display positive $\varepsilon^{50}Ti$, while the remaining available materials show negative $\varepsilon^{50}Ti$ relative to the Earth.

In summary, Zr, O, Si, Cr and Ti isotope data are consistent with a volatile element depleted composition for Theia. This volatile-poor nature of Theia suggests that it may have formed close to the sun.

Implications for planet formation. The omission of a volatile-rich impactor has important implications for planet formation models. Overall, the Zr, O, Si, Cr and Ti isotope data collectively support a Theia with an isotopic composition very similar to the Earth today. Previous work (e.g., Morbidelli et al., 2000; O'Brien et al., 2006) opted for an accretion model characterised by the accumulation of volatile-rich material towards the end of Earth's accretionary period. Similarly, Schönbächler et al. (2010) proposed, based on modelling of radioactive decay systems, a ter-

restrial accretion scenario that consists of the initial accretion of volatile-depleted material, followed by the addition (≤ 0.3 Earth masses) of volatile-rich material similar to carbonaceous chondrites towards the end. The source and delivery mechanism of this late volatile addition may have involved Theia through the giant impact (Schönbächler et al., 2010). This idea, however, rests upon an impactor with a volatile-rich, carbonaceous chondrite-like composition, which is excluded here for Theia, based on the Ti isotope data (Fig. 4). Hence, the volatile-rich material that was delivered towards the end of the Earth's accretion (while core formation was on-going; Schönbächler et al., 2010; O'Brien et al., 2006; Rubie et al., 2015) unlikely involves the Moon-forming giant impact. As a result, the bulk of the volatile-rich material must have been delivered (i) before the final giant impact, which added the final ~10% of the Earth's mass and (ii) after the accretion of volatile-depleted material (>0.7 Earth masses, Schönbächler et al., 2010). Thus the addition of the volatile-rich material is estimated to have occurred whilst the Earth was accreting 70%–90% of its mass, possibly through multiple impacts.

Implications for accretion in the inner solar system. As discussed previously, the material that accreted to form Theia most likely originated within the inner solar system, close to the sun and the Earth. Furthermore, this material must have had similar or even identical isotopic compositions to the Earth and enstatite chondrites. This conclusion was also reached by a similar study (Meier et al., 2014) based on the isotopic similarity of Earth and Moon. The overall Zr isotope uniformity of the Earth, Moon, enstatite chondrites (and possibly Theia) indicate that the inner solar system as a whole had a uniform Zr isotope composition. This agrees with recent Ca isotope data for enstatite chondrites and aubrites (Dauphas et al., 2014), which suggests that the inner protoplanetary disk had a uniform isotopic composition for another refractory element. However, it is also important to note that there is a sampling bias when probing the inner solar system. It is unclear whether material is available in our meteorite collections that built up the planets of the inner solar system and we do not have unmistakable samples from Venus or Mercury (e.g., Righter et al., 2006).

4. Conclusions

New high-precision Zr isotope data are reported for lunar rock samples and are compared to those of terrestrial rocks. The measurements provide the best evidence to date for identical Zr isotope compositions of the BSE and Moon, within 13 ppm for ^{96}Zr/^{90}Zr (2σ weighted average uncertainties). In the context of the giant impact models and neglecting secondary processes (e.g. post-impact chemical equilibration), this places an upper limit on how much the Zr isotope composition of the impactor, Theia, can deviate from that of the Earth. The calculated Theian compositions are compared to the measured range of values for known solar system objects to identify a match for Theia. As a first order approximation, all considered giant impact models (hit-and-run, fast-spinning protoEarth and massive impactor) produce solutions that match known solar system materials, rendering all models viable. Conversely, since the different Moon-forming scenarios are characterised by distinct (non-zero) fractions of f and g, a wide range of impactor derived mass-fractions in the Moon can be tolerated, providing that a corresponding amount of impactor material ends up in the Earth. Thus, the original need to reduce the amount of impactor material in the Moon, which led to the development of the new dynamic models in order to resolve the isotopic uniformity reported for several elements, is relieved in light of our mass balance calculations.

Albeit, the canonical and the hit-and-run models remain the most restrictive and constrain Theia to an Earth-like composition.

The cases of the fast-spinning protoEarth and massive impactor are valid only when the proportion of impactor material in the Moon (f) is low, and $f > g$, respectively. Analyses of Ti and Zr isotope data for the Earth and Moon eliminate a carbonaceous chondrite like composition for Theia. Thus Theia most likely was depleted in volatile elements and could not have been the source of volatile-rich material that is proposed to have accreted towards the end of Earth's accretion period (Schönbächler et al., 2010; Rubie et al., 2015). In general, all models agree with a Theian composition that is very similar to the Earth and provide evidence that both Theia and the protoEarth originated from within the inner solar system. The Zr isotope uniformity of the Earth, Moon, enstatite chondrites (and possibly Theia) reveal that a large part of the inner solar system exhibits a uniform Zr isotope composition.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.05.022.

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