Chemically defining the building blocks of the Earth

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Abstract

Chondrites are undifferentiated sediments of material left over from the earliest solar system and are widely considered as representatives of the unprocessed building blocks of the terrestrial planets. The chondrites, along with processed igneous meteorites, have been divided into two broad categories based upon their isotopic signatures; these have been termed the CC and NC groups and have been interpreted as reflecting their distinctive birth places within the solar system. The isotopic distinctiveness of NC and CC meteorites document limited radial-mixing in the accretionary disk. The enstatite and ordinary chondrites are NC-type and likely represent samples from inner solar system (likely <4 AU). Measurement and modeling of ratios of refractory lithophile elements (RLE) in enstatite chondrites establish these meteorites as the closest starting materials for the bulk of the silicate Earth and the core. Comparing chondritic and terrestrial RLE ratios demonstrate that the Bulk Silicate Earth, not the core, host the Earth’s inventory of Ti, Zr, Nb, and Ta, but not the full complement of V.

Keywords: chondrites, building blocks of Earth, early solar system, refractory lithophile elements, Nb/Ta

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Highlights

- Relative abundance of refractory lithophile elements (RLE) show up to ~10% variation among chondrite classes.
- Enstatite chondrites and the bulk silicate Earth have similar ratios of RLE.
- Building blocks of the Earth were chemically and isotopically similar, but not identical to, enstatite chondrites.

1 Introduction

Compositional models of the Earth assume refractory lithophile elements (RLE) are in chondritic proportions (constant RLE ratio rule) in the silicate fraction of the planet. For the Earth this means the Bulk Silicate Earth (BSE). There is, however, considerable discussion about the behavior of Nb and Ta during core-mantle differentiation, with some authors suggesting that Nb and Ta are exclusively lithophile (Sun and McDonough, 1989; McDonough, 1991; Rudnick et al., 2000), whereas, others have suggested that Nb and less so Ta behaved as a chalcophile (Münker et al., 2017) and/or siderophile (Wade and Wood, 2001; Münker et al., 2003; Corgne et al., 2008; Cartier et al., 2014) element and has been partially sequestered into the core. These latter models have based their conclusions on an assumed ”chondritic” ratio for Nb/Ta in the BSE.

Chondritic meteorites, undifferentiated solar system materials that are widely considered the building blocks of the terrestrial planets, have been divided into two broad categories based upon their isotopic signatures and interpreted as reflecting their distinctive birth places within the solar system (Warren, 2011). The specific chondritic building blocks for the Earth are unknown, but the Earth and enstatite chondrites (EC) share many isotopic ratios, which sets them apart from the other groups of chondrites (Javoy et al., 2010; Boyet et al., 2018).

Recent analyses of chondrites can now be used to define better the values for constant RLE ratios. Bulk data for the CI carbonaceous chondrites (CC), those with closest compositional match to the solar photosphere, have been reported (Barrat et al., 2012; Braukmüller et al., 2018). Stracke et al. (2012) reported a series of experiments to evaluate the mass of sample needed to obtain a representative bulk rock composition in Allende. Barrat et al. (2014) reported bulk compositional data for EC. Focused studies on elements and their ratios in groups of chondrites have been reported (e.g., (REE) (Pourmand et al., 2012; Dauphas and Pourmand, 2015), Y/Ho (Pack et al., 2007), Zr/Hf (Patzer et al., 2010), Nb/Ta (Münker et al., 2003)). Here we report major and trace element data on bulk rock, chondrules, and sulfides from EC, chondrules from an ordinary chondrite (OC), and refractory inclusions (Ca,Al-rich inclusions (CAIs) and amoeboid olivine aggregates (AOAs)) from CV carbonaceous chondrites. Using these and published data, we examine the compositional variability in some chondritic ratios, the behavior of elements in the protoplanetary disk and during core-mantle differentiation, and the chondritic reference frame for the BSE.
2 Background and historical perspective

The cosmochemical classification of elements is based on the partitioning behavior during condensation into a silicate (lithophile), metal (siderophile) or sulfide (chalcophile) phase, with an assumed reference frame of half-mass condensation temperatures from a solar nebula at 10 Pa density condition (Lodders, 2003). The refractory elements (e.g., Zr, Re, Os, Ca, Al) are those with nebular half-mass condensation temperatures >1360 K. Importantly, the abundant elements, Mg, Si, Fe and Ni (along with O), which make up the mass of terrestrial planets, have nebular half-mass condensation temperatures of 1360–1290 K. Moderately volatile (e.g., K, S, Zn) and volatile elements (e.g., H, C, N, often considered as ices or atmophile elements) have lower condensation temperatures. Abundances of the moderately volatile elements in chondritic meteorites can show enrichments (in EC) or depletions (in CC) relative to the refractory elements when normalized to CI abundances (Wasson and Kallemeyn, 1988).

There are some 36 refractory elements, and for the Earth most of them are generally considered to be lithophile (e.g., Be, Al, Ca, Ti, Sc, Sr, Y, Zr, Nb, Ba, REE, Hf, Ta, Th and U), while V, Mo, and W are moderately siderophile/chalcophile, and Ru, Rh, Re, Os, Ir, and Pt are highly siderophile. The constant RLE ratio rule asserts that the RLE are in chondritic proportions and not fractionated by core segregation processes. An important question to be addressed, particularly in the light of greatly improved analytical precision, is what are our working definitions of ”constant” ratios for element pairs. Here we provide additional perspective.

The REE are the archetypal example of the rule. The flat, unfractionated Masuda-Coryell plot of the REE (chondrite-normalized plot of the REE; e.g., Masuda, 1957) is a poignant visual of the rule of the constant RLE ratio rule, demonstrating that the relative abundances of the REE are invariant between chondrite classes and that this principle should be reflected in the BSE. The limited Sm/Nd variation (<1%) and even narrower variation in $^{143}\text{Nd}/^{144}\text{Nd}$ values in chondrites (e.g., Bouvier et al., 2008) reinforce the rule.

In the 1960s, Gast (1960) and Wasserburg et al. (1964) established that the Earth did not have chondritic proportions of the alkali metals, which are moderately volatile elements, and did so with respect to the RLE. In the 1970s and 1980s, with the advent of Nd (DePaolo and Wasserburg, 1976) and Hf (Patchett and Tatsumoto, 1980) isotope systems, we further refined the constant RLE ratio rule demonstrating that the BSE has chondritic Nd and Hf isotopic compositions and also chondritic Lu/Hf. Using correlations of Hf and Nd isotope systems with $^{87}\text{Sr}/^{86}\text{Sr}$ for mantle derived rocks (noting that Sr is a RLE) provided a constraint on the present day $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio of the BSE (e.g., 0.704–0.706) and from that its Rb/Sr value (0.032 ± 0.007, with uncertainty representing the spread in Sr isotope ratios) (McDonough et al., 1992).

The concept of ”constant” RLE ratios came into question recently (2005–2015), with the measurement of variable $^{142}\text{Nd}/^{144}\text{Nd}$ in chondrites, which emboldened some to assert that the BSE did not possess chondritic proportions of Sm/Nd (e.g., Boyet and Carlson, 2005). Solutions to this
conundrum included: (1) a sequestered, isolated reservoir in the silicate Earth that was created in
the first few hundreds of million years, which re-balanced the Earth’s Sm/Nd back to “chondritic”,
(2) the Earth experienced mass loss of differentiated early Hadean crust by collisional erosion
processes, and/or (3) fractionation of Sm/Nd between the core and primitive mantle (Caro, 2011
and references therein). However, by 2016 these debates were silenced by the observations of coupled
$^{142}\text{Nd}$, $^{145}\text{Nd}$, $^{148}\text{Nd}$, $^{150}\text{Nd}$ and $^{144}\text{Sm}$ nucleosynthetic isotopic anomalies between groups
of chondrites, implying preserved isotopic heterogeneities in the protoplanetary accretion disk (e.g.,
Bouvier and Boyet, 2016; Burkhardt et al., 2016; Fukai and Yokoyama, 2017). Consequently, the
rule remains intact, albeit with the recognition that there are isotopic differences between the chon-
drites. Thus, the constant RLE ratio rule has limits on the level of what is meant as constant and,
for the ratio of the REE, this concept of being constant does not extend down to the ppm level
of precision.

Concurrently, Warren (2011) defined two isotopically distinct compositional meteoritic do-
 mains (carbonaceous (CC) and non-carbonaceous (NC)) for chondritic and non-chondritic mete-
orites and in doing so established the Warren Gap. To date there are more than 10 isotopic systems
(e.g., O, Ca, Ti, Cr, Ni, Mo, Ru, Nd, W, Os) that reveal measurable differences between CC
and NC groups, with some isotope systems showing gross compositional distinctions. The dynamical
implications for radial transport across the protoplanetary accretion disk is significant (e.g., Krui-
jer et al., 2017). Importantly, the Urey-Craig diagram, established in the 1950s (Urey and Craig,
1953), documents a redox gradient in meteorite groups and further elucidates that the Warren Gap
shows the CC-group are definitively more oxidized than the NC-group (Figure 1).

Understanding the partitioning behavior of elements and their ultimate residence in the silicate
shell or metallic core requires knowledge of the redox conditions in the protoplanetary accretion
disk and/or during planetary core formation. The integration of these two environments determines
whether an element is wholly or partially lithophile, with the latter state indicating that an ele-
ment’s chemistry has been partially dictated by the extraction of a siderophile (Fe-affinity) and/or
chalcophile (S-affinity) phase into a planetary core.

3 Samples and methods

Primitive EC, OC and CC from Antarctica were studied. Analyses were conducted on bulk
samples, chondrules, and sulfides from Alan Hills (ALH) A77295 (EH3), ALH 84170 (EH3), ALH
84206 (EH3), ALH 85119 (EL3) and MacAlpine Hills 88136 (EL3) and chondrules from Queen
Alexandra Range 97008 (L3.05). We also studied two CAIs (3529-63-RR1 and 3529-61-RR1)
from Allende (CV3) and a CAI (R7C-01) and 6 AOAs from Roberts Massiff 04143 (CV3). All
samples were chosen for the lack of or limited terrestrial weathering. To obtain representative bulk
chondrite composition, large sample aliquots ($\sim$1 g) were used in this study. Extensive details of
the petrography of the studied samples are reported as supplementary information.
Petrology, mineralogy and major element chemistry of polished sections of samples were analyzed using scanning electron microscopes (SEM) and electron microprobes at Tohoku University and University of Maryland, College Park (UMd). Trace RLE compositions of chondrules from EC (mostly porphyritic pyroxene chondrules; Tables E.2 and E.3) and OC, sulfides from EC (e.g., troilite, oldhamite; Tables E.5 and E.6), and refractory inclusions from CC (Table E.7) were determined using a New Wave frequency-quintupled Nd:YAG laser system coupled to the Element2 ICP-MS at UMd. National Bureau of Standards (NIST) 610 glass (for EC chondrules and CC refractory inclusions), United States Geological Survey (USGS) reference glass BCR-2g and NIST 612 glass (for OC chondrules) were used as external standard materials. Internal standards were $^{29}$Si for chondrules and $^{29}$Si, $^{43}$Ca or $^{47}$Ti for refractory inclusions, which were determined as a polymineralic bulk composition using EPMA. For sulfides, the group IIA iron meteorite Filomena (for siderophile elements) and the NIST 610 glass (for lithophile elements) were used as reference materials. Count rates were normalized using $^{57}$Fe (for Filomena) and $^{63}$Cu (for NIST 610) as internal standards, which were determined using electron microprobe or energy-dispersive spectrometers equipped with the SEM.

Details of sample preparation and analytical technique are also provided in supplementary files. In short, about 25 mg of powder was weighed in Teflon vessels from ~1 g of homogenized powder. Two aliquots of each sample were prepared. The powder was mixed with $^{91}$Zr-$^{179}$Hf and $^{113}$In-$^{203}$Tl spikes for isotope dilution-internal standardization mass spectrometry of HFSE and REE (Lu et al., 2007; Yokoyama et al., 2017), and Al solution to avoid precipitation of HFSE as fluoride compounds (Tanaka et al., 2003). The sample was then digested by a combination of HCl, HNO$_3$, HF and a solution for HFSE measurement was isolated. The mother solution was then attacked with HClO$_4$ and HNO$_3$ and a split for REE analysis was separated. The HFSE and REE solutions were further divided into two aliquots for measurements at University of Maryland (UMd) (using Thermo Finnigan Element2 single-collector, sector field inductively coupled plasma mass spectrometer (ICP-MS)) and Tokyo Institute of Technology (Thermo Scientific X Series Q-pole ICP-MS) (Table E.1). A standard basaltic rock JB-3 (Geological Survey of Japan) was also digested and used as a reference material.

4 RLE in chondrites and their components

Most of the RLE are transition elements and some of these can have non-lithophile behavior in some systems (e.g., V). Here, we report on the relative abundances of the triad Sc-Ti-V and the higher Z element members of each IUPAC group in the Periodic Table (i.e., Y, REE – Zr, Hf – Nb, Ta). Each of these element pairs are often considered as rarely fractionated, geochemical twins (i.e., Y/Ho, Zr/Hf and Nb/Ta). Bulk compositional data for primitive EC are presented, along with a literature compilation for bulk unequilibrated chondrites showing the mean values for several RLE ratios (e.g., Ti/Sc, Nb/Ta and Nb/La) (Figure 2 and Table 1). Ratios of Nb/Ta and
Differences in refractory transition element ratios in different chondrite groups could reflect (1) volatility-driven fractionation of these elements in the protoplanetary disk and/or (2) non-lithophile behavior of one of these elements in the nebular disk or parent body in which metal-silicate fractionation occurred (e.g., Kuebler et al., 1999; Wurm et al., 2013). What remains as an unknown is whether an element that behaved as non-lithophile in the disk keeps (or not) its non-lithophile character in the differentiating planet. Previously-reported variation in ratios of geochemical twins Y/Ho and Zr/Hf among chondrite groups (Pack et al., 2007; Patzer et al., 2010) become less clear but still observable when considering only unmetamorphosed samples (Table 1 and Figure S.1), indicating that modification of these ratios occurred in the nebular environment.

A comparison of ratios of RLE in individual chondrules from EC, OC and CC provides evidence for compositional heterogeneity in the early solar system (Figure 3). Although there is considerable compositional scatter in each group of chondrules, their means and standard errors provide a measure of distinction between classes of chondrites. There is no clear relationship between RLE ratios in chondrules and their petrological type. The Nb/Ta, Zr/Hf, Ti/Sc and possibly Sm/Nd ratios of EC chondrules appear to have the strongest offsets. Scatter in Sm/Nd for EC chondrules is larger than that in bulk rock samples (Figure S.1); low Sm/Nd values in chondrules are comparable with that seen in bulk rock data. EC chondrules show a weakly increasing trending in Sm/Nd with higher metamorphic grade. Cl- and Y-normalized abundance of most RLE in chondrules ranges within CI ± 20%, whereas most non-refractory lithophile elements show depletion with a larger variation (Figure 4). When compared to CC chondrules, EC chondrules have lower Nb and Ta abundances and lower Nb/Ta values, whereas OC chondrules are enriched in Nb and Ta (Figure 4).

Refractory inclusions from CC show highly fractionated REE abundances, as well as for other RLE compositions (Figure S.3 and Table E.7), which reflect volatility-driven fractionation of RLE during condensation of these inclusions (e.g., Boynton, 1975). Ca,Al-rich inclusions (CAIs) show clearly lower Nb/Ta value (3–9) than all bulk CC and CAI-free AOAs, and most CC chondrules (Table E.7)).

Troilites from primitive EC are enriched in Ti, Nb and Zr (normally lithophile elements) along with typical enrichment of chalcophile and siderophile elements (Figure 5). Thus, under highly reducing conditions, as observed in EC (∼IW−5; Wadhwa, 2008), these nominally lithophile elements become chalcophile. On the other hand, Ta and Hf, which are generally considered to be geochemical twins of Nb and Zr, respectively, were not detected in troilites from EC, reflecting their strictly lithophile properties. There is no relationship between RLE abundance in these troilites and their 50% condensation temperatures (Lodders, 2003) as observed in the refractory inclusions (e.g., Boynton, 1975). Therefore, the chondrite-normalized abundances of Ti, Nb and Zr in these troilites reflects their relative chalcophilic behavior under reducing condition, making Ti
more chalcophile-like than Nb and much more so than Zr. Additionally, no detectable amounts of RLE were found in Fe-Ni metal grains from an unequilibrated EH3 chondrite (Alan Hills A77295), indicating the weakly siderophilic behavior of these elements.

5 Discussion

5.1 Nebular versus planetary fractionation of RLE ratios

Chondrules, silicate droplets formed in the nebular disk, are one of the major RLE carriers in chondritic meteorites. Most chondrules are depleted in metals and from that it follows that metal/silicate fractionation occurred before/during chondrule formation (e.g., Grossman [1982]). Moreover, it is well established that chondrule formation occurred locally (e.g., oxygen isotopic distinction between chondrules in different chondrite groups) with rare mixing of chondrules between distinct chondritic reservoirs before parent body formation (e.g., Clayton [2003]; Hezel and Parteli [2018]). Although there is considerable scatter, on average, CC and EC chondrules have lower Nb/Ta values and lower Nb and Ta abundances than bulk CI chondrites (Figures 3 and 4). In contrast, chondrules from OC show mean Nb/Ta ratios higher than the CI value. EC chondrules have distinctly lower mean values for Zr/Hf, Ti/Sc and Sm/Nd as compared to OC and CC chondrules.

Since removal of Ti-bearing, Ta-free sulfide (Figure 5) from CI-like reservoir cannot produce the RLE pattern observed in EC chondrules, there should have been another mechanism that caused RLE fractionation in EC chondrules. We propose less refractory behavior of Nb and Ta under reducing conditions, with higher volatility of Nb than Ta. Although condensation chemistry of RLE at low $f_{O_2}$ is still poorly constrained, Lodders and Fegley Jr [1993] showed that relative volatility of REE can be different under high and low C/O conditions. Further thermodynamic calculations are needed to understand fully changes of refractory behavior of RLE.

Compositional variations in chondrules from different chondrite groups reveal chemical fractionation prior to and/or during chondrule formation in the nebular disk. Combination of chemical (e.g., volatility, redox-dependent siderophility and chalcophility) and physical fractionation processes (e.g., sorting by density, size, magnetism, and/or thermal conductivity) of metal and silicates in the disk (e.g., Kuebler et al. [1999]; Wurm et al. [2013]) likely caused the observed variation in RLE ratios between chondrite groups. Chondrule populations, which likely accreted at different radial distances from the Sun, record the heterogeneous spatial distribution of chondrule source material with fractionated Nb/Ta ratio and/or localized fractionation of Nb and Ta. Thus, Nb/Ta variations among chondrite groups point to RLE fractionation before the accretion of chondrite parent bodies.

CV chondrites, recognized as having low bulk Nb/Ta values compared to other (mostly) CC (Münker et al. [2003]; Stracke et al. [2012]), are unique among the CC in that they host abundant
CAIs (mean $\sim$3 vol%; Hezel et al., 2008), which formed as some of the earliest solids in solar system by high-temperature processes in a nebular gas. Small differences in condensation temperatures for Nb and Ta (1559 K and 1573 K, respectively, at 10 Pa; Lodders, 2003) could produce volatility-driven fractionation of these elements, resulting in the low Nb/Ta ratios in CAIs (Table E.7; Stracke et al., 2012). Thus, low Nb/Ta values in bulk CV chondrites document fractionation processes controlled by the nebular temperature.

Positive Tm/Tm* anomalies (deviations of measured Tm from expected Tm abundance derived from the interpolation between Er and Yb using a CI abundance), which is also caused by incorporation of CAIs, are detected in CC (e.g., Dauphas and Pourmand, 2015). In contrast, the Earth, Mars, EC and OC, and several achondrites all share a slight ($\sim$3%) negative Tm/Tm* anomalies (e.g., Dauphas and Pourmand, 2015). Thus, volatility-dependent fractionation may be the origin for the observed variation in Nb/Ta and Nb/La ratios among the NC-group chondrites and the BSE.

There is $\sim$10% variation in Nb/RLE values in bulk chondrites, even without considering CV chondrites. These findings place limits on the use of the constant RLE ratio rule when estimating planetary composition, but enables us to constrain the building materials of a planet based on its RLE composition. Among the three major chondrite classes, EC have the closest compositional match for Nb/RLE ratios to the terrestrial values, whereas those in CC are distinctly different from the Earth’s, indicating a close genetic link between Earth and EC, as suggested by many isotope systems (e.g., Dauphas, 2017).

Ratios of other geochemical twins, like Y/Ho and Zr/Hf, are also not constant between chondrites classes (Pack et al., 2007; Patzer et al., 2010), which demonstrates the limits to the application of the constant RLE ratio rule. It might be argued that there is no meteorite group which is chemically identical in RLE ratios as that of the Earth. Further investigations of RLE in meteoritic and terrestrial samples, including determination of Nb/Ta ratio of unequilibrated OC, can provide new insights into the origin of these heterogeneities in the protoplanetary disk. In turn these studies can be used as a new guide to constraining the composition of planetary building materials.

These above studies begin to document that variations in ratios of RLE can be linked with isotopic systematics that establish the Warren Gap and document compositional heterogeneities in the early solar system. Moreover, to understand the details of terrestrial geochemistry we endorse the idea (Dauphas and Pourmand, 2015) that CC in general and CI chondrite specifically are not appropriate for normalizing refractory element abundances.

Thus, the inner (e.g., Earth and NC-group meteorites) and outer solar system materials (CC-group meteorites) are likely to be distinctive, not only in isotopic composition (Warren, 2011) and redox state (Figure 1), but also in RLE composition. The higher Nb/Ta ratio of the bulk silicate Mars ($20.1 \pm 0.9$; Münker et al., 2003) indicates that Mars incorporated less EC-like material than Earth, which is consistent with multiple isotopic systematics (e.g., Dauphas, 2017). Primitive EC and the Moon have a similar Nb/Ta ratio ($17.6 \pm 0.6$ and $17.0 \pm 0.8$, respectively; this study; Münker).
et al., 2003), in harmony with the isotopic constraints that predict such an EC-like composition for the giant impactor that formed the Moon (e.g., Dauphas, 2017).

Sulfide-silicate separation under highly reduced conditions, as in some regions of the nebular disk, may fractionate RLE in the early solar system. Sub-solar Fe/Si values seen in most chondrite groups, except for CI and EH chondrites (Figure 1), document metal-silicate fractionation processes in the nebular disk. Likewise, it has been postulated that most chondritic asteroids preferentially sample the silicate-rich portion of nebular materials (e.g., Wurm et al., 2013). Some amount of RLE fractionation (Figures 2 and 3) may have been caused by separation of RLE-bearing sulfides from the solar-like reservoir in the nebular disk. Since only sulfides formed under highly reduced conditions can contain significant amounts of RLE (e.g., this study; Schrader et al., 2018), the bulk OC and CC composition is not affected by this process. Finally, given accretion of different chondrite groups took place in distinct time and/or space settings in the protoplanetary disk, we predict there to have been spatial and/or temporal variation in RLE ratios in the chondrite forming regions.

5.2 Chemical composition of the Earth

Compositional modeling of the bulk Earth requires identifying which elements are hosted in BSE versus the core, which is done by comparing the chemical composition of the accessible parts of the Earth (crust and mantle) and undifferentiated chondritic meteorites. However, it is recognized that elements show different behaviors (siderophile, chalcophile, lithophile) in the solar nebula and during differentiation of a planet. Thus, combined geochemical and isotopic studies of chondritic and non-chondritic meteorites coupled with similar such studies of mantle samples and mantle-derived melts, are required to determine the composition of the BSE, which remains the best avenue for establishing the bulk Earth’s composition.

A comparison of chondritic ratios with that observed in primitive samples of the Earth’s mantle and its melts is given in Figure 6. We highlight the composition of sample 49J, an Al-undepleted Barberton komatiite, which is a least altered, Paleoarchean mantle-derived melt having an exceptionally primitive composition (Sossi et al., 2016) that samples a primitive mantle-like composition (e.g., Sun and Nesbitt, 1978). The coincidence of Al/Ti, Ti/Sc, and Nb/Ta in 49J and the values for EC is notable. The offset between 49J and EC for Nb/La may reflect differences in the relative incompatibility of these elements, source depletion due to continental crust extraction, and/or differences between the Earth and EC. The data for komatiites and peridotites straddle the chondritic values for Ti/Sc and Al/Ti, reflecting melt-residue differentiation processes.

It has been proposed that Nb and less so Ta have been depleted in the BSE due to their siderophile behavior under reducing conditions of core formation (Wade and Wood, 2001; Corgne et al., 2008; Cartier et al., 2014). Evidence against partitioning of Nb into the Earth’s core due to its...
siderophile behavior comes from the composition of metals in meteorites and in experimental studies. In the reduced meteorites, Nb concentrations in metal (mostly <0.1 ppm) are much lower than that in coexisting sulfides (typically >0.4 ppm) (this study; Humayun and Campbell, 2003; Kamber et al., 2003; van Acken et al., 2012; Münker et al., 2017), indicating that Nb is chalcophile rather than siderophile under reducing conditions. Partitioning experiments under low $f_{O_2}$ show that Ti, Nb, Ta and Ce can become more chalcophile than siderophile (Wood and Kiseeva, 2015; Münker et al., 2017); similarly, these studies find that these elements are strongly partitioned into the sulfide relative to the co-existing metal phase. Therefore, if Nb is partitioned into a sulfide-bearing core (1.5–2 wt% S is in the Earth’s core; McDonough and Sun, 1995; Dreibus and Palme, 1996) under reducing conditions, then a range of transition metals would have been sequestered into the sulfide portion of the core forming liquid. Finally, the common sulfide in reduced chondrites are Ti- and Cr-troilites (this study; van Acken et al., 2012; Weyrauch et al., 2018 and references therein), and as we have found, these sulfides also contains Nb and lesser amounts of other transition elements (Figure 5).

Cartier et al. (2014) observed that there is no pressure dependence on the siderophile behavior of Nb and Ta, which, if extrapolated to formation pressures of meteorites, would again argue for the chalcophile and not siderophile behavior for these elements. Moreover, a comparison of the experimental studies (e.g., Wade and Wood, 2001; Corgne et al., 2008; Cartier et al., 2014) shows that they have conflicting relative D-values for critical elements (e.g., Ni, Ga, Mn). This conflict is important as noted by Corgne et al. (2008) who points out that it is possible to fit the data using an increasing $f_{O_2}$ during core separation, but that there is a delicate balance to get right the mass fraction, redox conditions and D-values to match the Earth’s observed composition. There are diminishing probabilities of this highly deterministic model when factoring in all of these findings.

In addition, the BSE has been proposed to be Nb-depleted due to its chalcophile behavior of Nb under reducing conditions (Münker et al., 2017), a conclusion based on the bulk Earth having a CC-like RLE composition. However, if Nb partitioning into the core was controlled by its chalcophile behavior, then combined Nb- and Ti-enrichments in EC troilites (Figure 5) document that Nb-depletion in the BSE should be accompanied by an even stronger Ti-depletion. In contrast, the coincidence of chondritic values for Ti/Sc and Al/Ti in the BSE and EC (Figure 6) indicate that the BSE hosts the Earth’s inventory of both Nb and Ti, which is inconsistent with sequestering of Nb into the core via a sulfide.

The nature of an early Earth sulfide component and its migration to the core is poorly understood. Many proposals have been put forth for a wide range of elements (e.g., K, U, REE, RLE) partitioning into a sulfide phase and entering into the Earth’s core during its formation (e.g., Murthy et al., 2003; Münker et al., 2017; Wohlers and Wood, 2017). However, evidence is lacking for the role of a sulfide in controlling the inventory of these elements in the Earth (Corgne et al., 2007; Bouvier and Boyet, 2016; Burkhardt et al., 2016; Wipperfurth et al., 2018).

The above models envisage extraction of Nb and perhaps Ta into the core based on a reference
frame that assumes a CC model for the Earth’s Nb/Ta value. A far simpler observation, and one consistent with supporting stable and radiogenic isotopic data (Warren 2011), is that the Earth has a Nb/Ta value comparable to that in EC. Thus, the BSE is not depleted in Nb compared to EC and the Earth’s Nb inventory is not hosted in the metallic core. We conclude that the BSE and the bulk Earth have a shared Nb/Ta values of ∼17.

Our findings allow us to characterize the chemical behavior of the left half of the transition metals in the periodic table (groups 3–7, using IUPAC nomenclature). Elements in each group oftentimes have the same electron configurations in their valence shells. However, during core-mantle differentiation these elements displayed markedly different geo-/cosmochemical (lithophile versus siderophile/chalcophile) behavior. The relative differences in their chemical behavior reflects their sensitivity to the oxidation state of their environment, which means changes in their electron configurations within a group. Figure 7 is color coded in terms of mass fraction of the planet’s budget of these elements in the BSE (blue) or core (red). In the Earth, 50% of the planet’s inventory of V is in the core and 50% in the BSE (McDonough 2014). Elements in groups 3 and 4 and Nb and Ta (from group 5) all seem to have been lithophile during core-mantle differentiation and remained in the BSE. Also, the latter Period 4 (first row) transition metals have marked differences in their behavior (V, Cr, and Mn show variable affinities for the core), compared to those in Periods 5 and 6. For example, Mo is known to be more chalcophile than W, which is relatively more siderophile, and Re (and Tc?) is highly siderophile, meaning that is ∼99% of the planet’s budget is in the core (McDonough 2014).

Resolvable chemical and isotopic distinctions between chondrites (including EC) and Earth indicate that the building blocks of the Earth are not in our meteorite collection (e.g., McDonough and Sun 1995, Drake and Righter 2002). Chondrites are residual solar system materials that originate from primitive asteroids that escaped any melting and differentiation processes. Their parent bodies formed some ≥2 Myr after solar formation (e.g., Hopp et al. 2016, Blackburn et al. 2017), when radiogenic heating from 26Al was waning. In addition, meteorites collected on the Earth are, except in rare instances, providing a restricted sampling of the asteroidal belt (2.0–3.5 AU) over the last <100 Myr (Heck et al. 2017). Not only are these meteorites sampling a region of the nebula far from the Earth, they are likely further biased because of 4.5 billion years of harvesting of the asteroid belt by orbital resonances with Jupiter (DeMeo and Carry 2014). Therefore, we are faced with considerable challenges when asserting the representativeness of materials present in the earliest stage of solar system formation. It is likely that the Earth accreted from inner solar system materials that were chemically and isotopically similar, but not identical to, EC, given chemical and isotopic heterogeneities and fractionation processes in the protoplanetary disk.
6 Conclusions

We have found that Nb/Ta values differ between different groups of chondrites, likely due to redox conditions in the protoplanetary disk. We revealed that the BSE’s Nb/Ta value (∼17) matches that seen in enstatite chondrites (∼17). The Bulk Silicate Earth, not the core, host the Earth’s inventory of Ti, Zr, Nb, and Ta, but not the full complement of V.

These findings provide insight into what are the limits of the “constant” RLE ratio rule. We conclude that different ratios of RLE have greater variability than others (e.g., ratios involving only the REE show less variation than ratios involving Nb and/or Ta relative to other RLE). Thus, the chondritic record documents both chemical and isotopic variability in the nebular disk that can be used to inform dynamical model of stirring in the disk.

Similar to the findings of Münker et al. (2017), we find that sulfides in reduced meteorites host Nb, but importantly we also observed that these phases contain great amounts of Ti, which, if subtracted into the core, would have produced non-chondritic Al/Ti, Ti/Sc, and Ti/Zr values in the BSE and these are not observed. What remains as an unknown is whether an element that behaved as non-lithophile in the disk maintains (or not) its non-lithophile character during core separation.

Further studies of RLE ratios in chondrites are warranted, particularly those that focus on identifying chemical differences and similarities between groups of chondrites. A challenge which remains is understanding what are the causes for the differences in RLE ratios found between the Earth and chondrites. Are they due to nebular disk conditions, including phase separation, or to core-mantle differentiation processes?

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Author contributions

WFM proposed and conceived the study with input from TaY. TaY conducted nearly all of sample preparation and measurements, with MDL performing some of the electron microprobe measurements, RDA and MDL conducting some of the LA-ICP-MS analyses and TeY performing some parts of sample digestion. Quantitative modeling was carried out by TaY in consultation with
WFM, TeY, RDA, and WFM provided laboratory facilities and training to TaY. The manuscript was written by TaY and WFM, and all the authors contributed to it.

**Competing financial interests**

The authors declare no competing financial interests.
Figure 1: The Urey-Craig diagram showing variation in oxidation state of iron relative to silicon among chondrite groups (after Urey and Craig, 1953). Metal-rich CB and CH chondrites are not included in the plot because their origin (condensation from a gas-melt plume formed by a planetary-scale collision; e.g., Krot et al., 2012) is distinct from that of major chondrite groups. Non-carbonaceous (NC: enstatite and ordinary) and carbonaceous (CC) group chondrites are colored in red and blue, respectively, based on their isotopic compositions (Warren, 2011 and references therein; Budde et al., 2018). The Earth’s composition is from McDonough (2014). As recognized in many isotope systems, NC- and CC-groups are also distinct in their redox status except for Rumuruti (R)-type chondrites. Based on the redox condition of the Kakangari (K)-type chondrites, we predict that it is a member of the NC-group, which is supported by their low refractory element abundance and limited number of isotopic data (Scott et al., 2018 and references therein).
Figure 2: Refractory lithophile element ratios of unmetamorphosed, bulk enstatite (green), ordinary (orange) and carbonaceous (blue) chondrites. Colored box and inside solid line represent mean \( \pm 2\sigma_m \) values for each chondrite groups. Gray box and inside solid line correspond mean \( \pm 2\sigma_m \) for the Orgueil CI chondrite (Barrat et al., 2012). For Al/Ti ratio, data for metamorphosed enstatite chondrites are also shown and used to calculate the mean \( \pm 2\sigma_m \) value, since the number of available data for type 3 enstatite chondrites are limited. Sources of literature data are available as supplementary information.
Figure 3: Refractory lithophile element ratios of bulk chondrules from each class of unequilibrated chondrite. Lines and boxes are as in Figure 2. Data for chondrules from metamorphosed samples are also shown for a comparison. Sources of literature data are available as supplementary information.
Figure 4: Mean abundance of lithophile elements in chondrules from each class of unequilibrated chondrite normalized to CI chondrite (Barrat et al., 2012) and Y. Elements are arranged in order of decreasing 50% condensation temperature (Lodders, 2003). Error bars represent $2\sigma$. Sources of literature data are available as supplementary information.
Figure 5: Ranges of mean transition element abundance in troilite from three EH3 (Alan Hills (ALH) A77295, ALH 84170 and ALH 84206) and two EL3 (ALH 85119 and MacAlpine Hills 88136) chondrites, normalized to CI chondrite composition (Barrat et al., 2012).
Figure 6: Comparison of refractory lithophile element ratio of the bulk silicate Earth (data from literature) and enstatite chondrites. Lines and boxes are as in Figure 2. Red stars shows composition of the least altered komatiite 49J from Barberton, South Africa (Sossi et al., 2016), which might be close to the primitive mantle composition (e.g., Sun and Nesbitt, 1978; Sossi et al., 2016).
Figure 7: Geochemical classification of transition elements. Areas of blue and red correspond fraction of planetary inventory in the silicate Earth and the core, respectively. Data for V, Cr, Mn, Mo, W and Re are taken from Table 6 of [McDonough](2014). We expect that most fractions of Tc were partitioned into the core if its short-lived isotopes had been present in the planetary building materials.
Table 1: Refractory lithophile element ratios of bulk unequilibrated chondrites and the bulk silicate Earth (BSE). Sources of literature data are available as supplementary information.

| Class        | Al/Ti | Ti/Zr | Ti/Sc | Ti/V | Sc/V | Sc/Yb | Nb/Ta | Nb/La | Zr/Hf | Zr/Nb | Y/Ho | Sm/Nd |
|--------------|-------|-------|-------|------|------|-------|-------|-------|-------|-------|------|-------|
| Enstatite    | Mean  | 21.9  | 18.8a | 113  | 63   | 7.5   | 0.12  | 35.1  | 17.6  | 1.11  | 33.0 | 13.4  | 26.8  | 0.324 |
|              | 2σ    | 13.0  | 10.4a | 12   | 21   | 1.3   | 0.03  | 12.2  | 2.0   | 0.27  | 2.3  | 2.5   | 5.0   | 0.015 |
|              | 2σm   | 4.3   | 1.8a  | 4    | 6    | 0.4   | 0.00  | 1.8   | 0.6   | 0.06  | 0.5  | 0.5   | 1.1   | 0.003 |
|              | n     | 9     | 33a   | 11   | 11   | 11    | 39    | 47    | 11    | 22    | 25   | 23    | 22    | 29    |
| Ordinary     | Mean  | 19.4  | 94    | 67   | 8.5  | 0.12  | 36.4  | NA    | NA    | 38.4  | NA   | 26.1  | 0.332 |
|              | 2σ    | 10.1  | 32    | 1    | 2.6  | 0.04  | 7.8   | NA    | NA    | 7.5   | 0.1  | 0.038 |
|              | 2σm   | 1.0   | 13    | 1    | 1.3  | 0.01  | 1.5   | 3.1   | 0.1   | 0.007 |
|              | n     | 103   | 6     | 2    | 4    | 39    | 28    | 6     | 3     | 30    |
| Carbonaceous | Mean  | 18.9  | 107   | 73   | 9.1  | 0.12  | 35.8  | 19.4b | 16.8c | 1.24  | 35.5 | 13.7  | 27.5  | 0.328 |
|              | 2σ    | 8.6   | 42    | 24   | 2.7  | 0.03  | 9.1   | 2.4b  | 1.2c  | 0.34  | 11.5 | 3.2   | 5.9   | 0.038 |
|              | 2σm   | 0.7   | 5     | 4    | 0.3  | 0.00  | 0.8   | 0.6b  | 0.3c  | 0.05  | 1.2  | 0.4   | 0.8   | 0.003 |
|              | n     | 172   | 71    | 33   | 82   | 121   | 145   | 17b   | 12c   | 47    | 95   | 80    | 56    | 146   |
| Komatiite 49J | Mean   | 18.9  | 109   | 72   | 11.1 | 0.15  | 32.3  | 16.8  | 0.88  | 38.3  | 16.5 | 28.1  | 0.326 |
| BSE         | Mean   | 19.5  | 115   | 74   | 14.7 | 0.20  | 36.8  | 17.8  | 1.01  | 37.1  | 16.0 | 28.9  | 0.325 |

NA–not available.
a) includes metamorphosed samples [Mason, 1966; von Michaelis et al., 1968; Wrick, 1969; Jarosewich, 1990; Yanai and Kojima, 1995].
b) except for CV chondrites [Jochum et al., 2000; Münker et al., 2003; Barrat et al., 2012; Göpel et al., 2015; Friend et al., 2018].
c) CV chondrites [Jochum et al., 2000; Münker et al., 2003; Lu et al., 2007; Barrat et al., 2012; Stracke et al., 2012].
d) from Sossi et al. [2016].
e) from McDonough and Sun [1995].
Appendix A  Supplementary materials

Supplementary materials associated with this article can be found in the online version.

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