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Feedstocks of the Terrestrial Planets

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Abstract The processes of planet formation in our Solar System resulted in a final product of a small number of discreet planets and planetesimals characterized by clear compositional distinctions. A key advance on this subject was provided when nucleosynthetic isotopic variability was discovered between different meteorite groups and the terrestrial planets. This information has now been coupled with theoretical models of planetesimal growth and giant planet migration to better understand the nature of the materials accumulated into the terrestrial planets. First order conclusions include that carbonaceous chondrites appear to contribute a much smaller mass fraction to the terrestrial planets than previously suspected,

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The Solar System's Evolution Before the Moon
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that gas-driven giant planet migration could have pushed volatile-rich material into the inner Solar System, and that planetesimal formation was occurring on a sufficiently rapid time scale that global melting of asteroid-sized objects was instigated by radioactive decay of ^{26}Al. The isotopic evidence highlights the important role of enstatite chondrites, or something with their mix of nucleosynthetic components, as feedstock for the terrestrial planets. A common degree of depletion of moderately volatile elements in the terrestrial planets points to a mechanism that can effectively separate volatile and refractory elements over a spatial scale the size of the whole inner Solar System. The large variability in iron to silicon ratios between both different meteorite groups and between the terrestrial planets suggests that mechanisms that can segregate iron metal from silicate should be given greater importance in future investigations. Such processes likely include both density separation of small grains in the nebula, but also preferential impact erosion of either the mantle or core from differentiated planets/planetesimals. The latter highlights the important role for giant impacts and collisional erosion during the late stages of planet formation.

1 Introduction

Our Solar System was assembled from a dense clump inside a molecular cloud consisting of dust and gas. Elements heavier than H and He were produced by nucleosynthetic processes in the deep interiors of stars that upon their deaths ejected their newly made elements into space over the circa 10 billion years between the Big-Bang and Solar System formation that began 4.567 billion years (Ga) ago. The terrestrial planets provide a clear example that the path from molecular cloud to planet involved both physical and chemical processes that resulted in a final product very different in composition than the average of the starting materials. The most obvious compositional difference is that the terrestrial planets are deficient in H and He by some 4 to 7 orders of magnitude compared to the Sun (Palme and Jones 2003; Palme and O'Neill 2014), which at 99.87% the mass of the Solar System, is the best representative of its average composition. Recent advances both in theoretical understanding of the process of planet formation and in the detection of nucleosynthetic isotopic variability in various Solar System materials can be used to investigate the earliest history of the assembly of the dispersed material from the Solar protoplanetary disk into discrete planetesimals and subsequently into planets. This paper explores the implications of these new data sets, and attempts to broaden our understanding of the mechanisms of terrestrial planet formation and the processes that dictated their ultimate composition.

2 Nucleosynthetic Variability as a Fingerprint of Planetary Feedstocks

The elements in our Solar System consist of a mixture of the hydrogen and helium left from the Big Bang along with heavier elements made by a variety of nucleosynthetic processes occurring in stellar interiors (e.g. Burbidge et al. 1957) or during more complex scenarios such as the coalescence of two neutron stars (e.g. Thielemann et al. 2017). The different paths of nucleosynthesis that depend on pressure, temperature, and density of the stellar interior leave distinct isotopic signatures in the material ultimately ejected into space by various types of stellar outflows. In the classical model of Solar System formation, collapse of the proto-Solar molecular cloud raises temperatures in at least the inner disk to the point

of evaporating any preexisting solids. Eventually, cooling of the nebula allowed the gases to condense to form the solids (e.g. Grossman 1972) that accumulated into meteorite parent bodies, and eventually into planets. Effective mixing of nebular material while in the gas phase was traditionally assumed to have averaged out any isotopic information that would track original compositional heterogeneity in the proto-Solar molecular cloud.

The expectation of an isotopically homogeneous Solar nebula began to unravel when large isotopic differences, particularly mass-independent effects, were found in the noble gases (Black and Pepin 1969) and then oxygen (Clayton 1976) between different types of meteorites and Earth. The cause(s) of the isotopic variability, particularly in oxygen, are not entirely clear. Likely explanations include both preserved nucleosynthetic variability (Clayton et al. 1973) and non-mass dependent photo-chemical reactions (e.g. Thiemens and Heidenreich 1983). The discovery of isotopic variability in heavier elements, such as Ti, Ba, and Nd (McCulloch and Wasserburg 1978; Niederer et al. 1980; Niemeyer and Lugmair 1981) in rare Ca and Al-rich refractory mineral inclusions called CAIs (MacPherson 2003) in some primitive meteorites, that can only reflect nucleosynthetically distinct materials, reopened the question of how well-mixed the protoplanetary disk was in the inner Solar System. The discovery of small mineral grains in meteorites that have isotopic anomalies so extreme that the grains must have originated in other stars (e.g. Zinner 1996; Clayton and Nittler 2004) made it clear that at least some material survived unmodified from the molecular cloud to make it into meteorite parent bodies. More recent, and higher precision, isotopic analyses have revealed that nucleosynthetic variability exists in many elements, even at the size scale of whole meteorites, planetesimals, and planets. The current focus of such work, and this portion of the paper, is on how this variability can be used to determine the degree to which compositional heterogeneity in the proto-Solar molecular cloud was preserved through the planet-forming process, and what this tells us about the physical and chemical processes involved in building planets.

2.1 Nucleosynthetic Isotope Anomalies in Bulk Meteorites

Nucleosynthetic isotope anomalies in meteorites arise from the heterogeneous distribution of stellar-derived dust at the planetesimal size scale. They serve as a powerful tool to investigate how well-mixed the Solar nebula was before the formation of asteroids and planetary bodies and to establish genetic ties between primitive meteorites and planetary materials. This is possible because the isotopic composition of meteorites reflects an inherent blend of presolar and nebular components incorporated into their parent bodies. Consequently, only materials with the same nucleosynthetic mix would display the same isotopic composition and could therefore derive from the same planetary body or nebular reservoir.

Isotopic variability unambiguously related to nucleosynthetic causes at the scale of meteorite parent bodies has now been seen in a wide range of elements including Ca (Chen et al. 2011; Dauphas et al. 2014b; Simon et al. 2009), Ti (Leya et al. 2008; Trinquier et al. 2009; Zhang et al. 2012), Cr (Qin et al. 2010; Trinquier et al. 2007), Ni (Regelous et al. 2008; Steele et al. 2011), Mo (Budde et al. 2016a; Burkhardt et al. 2011; Dauphas et al. 2002a; Poole et al. 2017; Render et al. 2017; Yin et al. 2002b), Ru (Chen et al. 2010; Fischer-Gödde et al. 2013, 2015; Fischer-Gödde and Kleine 2017), Zr (Akram et al. 2015; Schönbächler et al. 2003), Pd (Mayer et al. 2015), Ba, Nd, and Sm (Andreasen and Sharma 2006; Burkhardt et al. 2016; Carlson et al. 2007; Gannoun et al. 2011; Hidaka et al. 2003), and W (Kruijer et al. 2013, 2017; Qin et al. 2008; Wittig et al. 2013). A recent review of these anomalies and their likely cause is given in Qin and Carlson (2016). The magnitude of the anomalies may show some dependence on the mass of the element, which most likely reflects the different nature of the mineral carriers and the different nucleosynthetic sources for

Fig. 1 Isotopic differences in ^{48}Ca/^{44}Ca, ^{50}Ti/^{47}Ti, ^{54}Cr/^{52}Cr and ^{62}Ni/^{61}Ni in different meteorite groups relative to Earth. Epsilon reflects the parts in 10,000 difference between the measured ratios and that ratio in terrestrial materials. Figure from Qin and Carlson (2016)
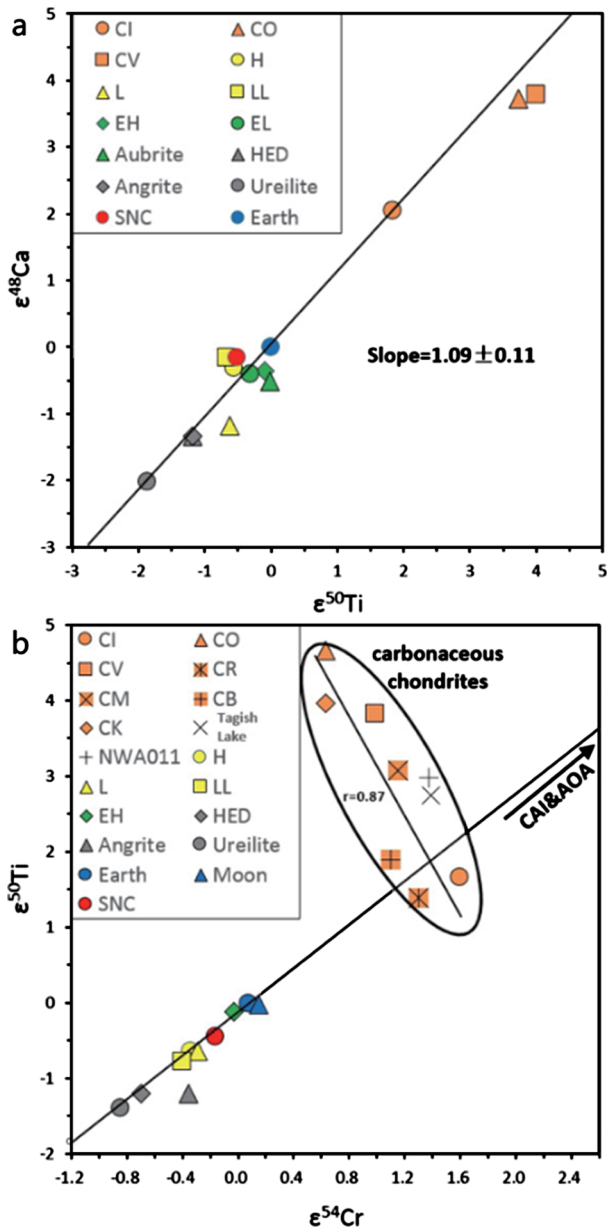
different elements (Brennecka et al. 2013). Isotopic anomalies likely exist in other elements, but are either waiting to be documented, or are too small to resolve with current techniques.

Collectively, the results of these studies show that carbonaceous chondrites in general display the most distinct isotopic signatures compared to other primitive meteorites and differentiated bodies (Figs. 1 and 2). These data therefore revealed a fundamental dichotomy between 'carbonaceous' and 'non-carbonaceous' meteorites (Budde et al. 2016a; Poole et al. 2017; Qin et al. 2010; Trinquier et al. 2009; Warren 2011). A similar dichotomy in at least
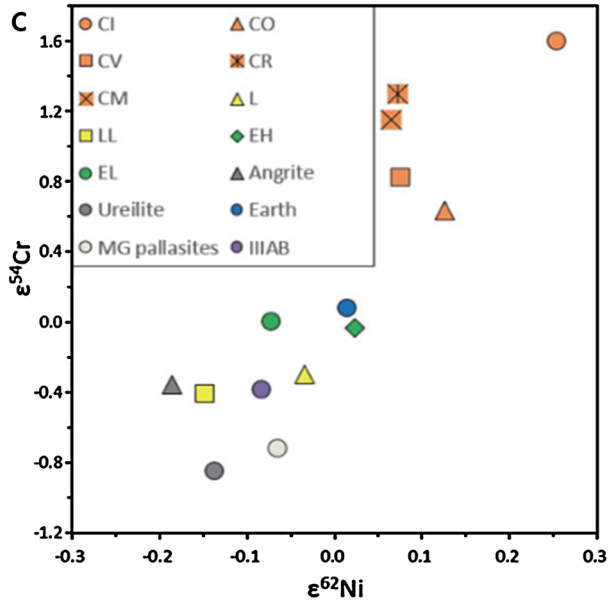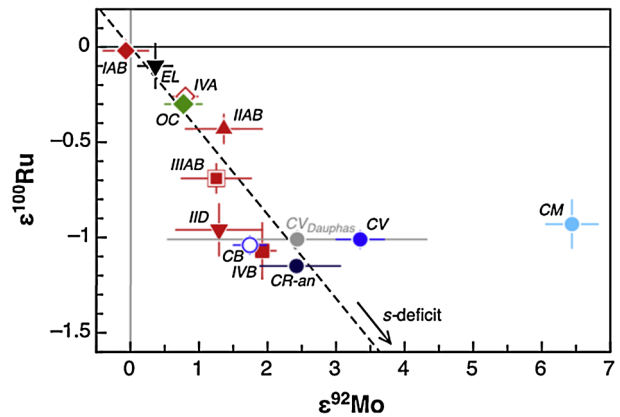
Fig. 1 (*Continued*)

Fig. 2 Correlation of Ru and Mo nucleosynthetic isotope variability for various meteorite groups. Figure from Fischer-Gödde et al. (2015)

the isotopic composition of Mo, and possibly W, is observed for different groups of iron meteorites (Kruijer et al. 2017). In the silicate meteorites, the differences are largest, and most systematic, in the iron-peak elements Ca, Cr, Ti, and Ni. For these elements, Earth lies intermediate between carbonaceous chondrites that show enrichment in the neutron-rich isotopes of these elements, and ordinary chondrites and various types of differentiated meteorites, all of which have deficits in the neutron-rich isotopes (Fig. 1). The meteorite group that plots closest to Earth in all of these isotope systems are the reduced, dry, enstatite chondrites. Enstatite chondrites are also the only meteorite group that have oxygen isotopic compositions similar to Earth (Clayton 2003). In contrast, Mars plots between ordinary and enstatite chondrites in terms of its isotopic composition for this group of elements (Fig. 1).

For Mo, Ru, and possibly Nd, Earth lies at one end of the nucleosynthetic spectrum displayed by meteorites (Fig. 2), but the lack of known samples from Venus and Mercury precludes examination of how this trend extrapolates through the terrestrial planet region.
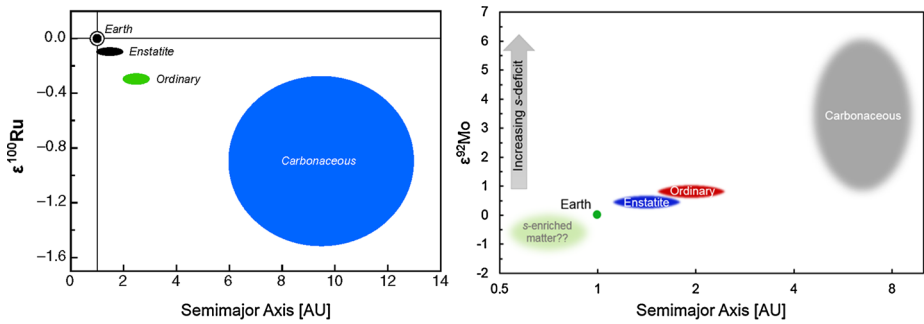
Fig. 3 The magnitude of ε^{100}Ru and ε^{92}Mo anomalies increases with increasing heliocentric distance (ε expresses the difference in ^{100}Ru/^{101}Ru and ^{92}Mo/^{96}Mo in parts per 10,000 compared to the terrestrial standard). Shown are mean values for enstatite, ordinary and carbonaceous chondrites and their presumed formation regions based on the Grand Tack model. Note that the source region for carbonaceous meteorites is likely to be even wider than shown in the figure panels (e.g. Raymond and Izidoro 2017a, 2017b). Figure for Ru from Fischer-Gödde and Kleine (2017) and for Mo slightly modified from Render et al. (2017)

For Mo, Ru, and Nd, Earth is enriched in nuclides produced by the s-process of stellar nucleosynthesis (Budde et al. 2016a; Burkhardt et al. 2016, 2011; Carlson et al. 2007; Dauphas et al. 2002a, 2002b; Fischer-Gödde et al. 2015; Fischer-Gödde and Kleine 2017; Poole et al. 2017; Render et al. 2017). In the case of Mo and Ru, the magnitude of the anomalies compared to Earth increases from enstatite to ordinary to carbonaceous chondrites indicating that meteorites formed at greater heliocentric distance contain larger anomalies and therefore greater deficiencies in the isotopes produced by s-process nucleosynthesis (Fig. 3). Hence, the Ru and Mo isotopic anomalies (and those of other elements) can be used as a tool to track the dispersion of materials originating from different heliocentric distances in numerical simulations of planetary growth (Brasser et al. 2018; Fischer et al. 2018). The width of the carbonaceous region of Fig. 3 could, in principle, be a lot wider: Raymond and Izidoro (2017b) found a minimum width of 5 AU for carbonaceous material implanted into the main asteroid belt during gas giant growth and a potential width of up to 10–20 AU when giant planet migration and the ice giants are accounted for.

2.2 Isotopic Constraints on the Feedstocks of the Terrestrial Planets

The isotopic distinctions between meteorite groups and the terrestrial planets have been used to generate mixing models to estimate which group of meteorites served as the potential dominant building blocks of the terrestrial planets (Brasser et al. 2018; Dauphas 2017; Fitoussi et al. 2016; Warren 2011). For example, Warren (2011) estimated that Earth was likely made up of at most 30% carbonaceous chondrite and Mars only 15%. The Monte Carlo mixing model of Fitoussi et al. (2016) additionally uses the chemical compositions of the various meteorite groups to suggest that Earth and Mars accumulated from a compositionally similar population, but one dominated by differentiated planetesimals—for example the parent body of the angrite meteorites—instead of primitive chondrites. Their results suggest that Earth and Mars are mixtures that consist of 50% or more of material compositionally similar to the angrite parent body, and of order 18–28% carbonaceous chondrite. These results, however, were based on their imposed constraint that enstatite chondrites could constitute no more than 15% of the terrestrial planets, which in turn was based on an observed difference in the Si isotopic composition of enstatite chondrites compared to Earth (Fitoussi

and Bourdon 2012). Relaxing that constraint on the grounds that the Si isotopic difference could reflect mass fractionation induced by planet differentiation, either by impact volatilization (Pringle et al. 2014) or through Si incorporation into the core (Fitoussi et al. 2009; Georg et al. 2007), allowed fits to the isotope data with Earth composed almost entirely of EH chondrite (Fitoussi et al. 2016). This result is in accord with previous models (Lodders 2000; Sanloup et al. 1999) that relied primarily on the oxygen isotope similarity of Earth and enstatite chondrites.

These models were further strengthened by the isotopic similarity between Earth and enstatite chondrites observed for many other elements including Ca, Ti, Nd, Cr, Ni (e.g. Dauphas et al. 2014a). Therefore, these data highlight the prevailing role of enstatite chondrites, or something with a similar mixture of nucleosynthetic components, as the main building blocks of Earth throughout its *entire* accretion history (Dauphas 2017; Brasser et al. 2018). Perhaps the most surprising result to derive from the isotopic distinctions of different meteorite groups is that owing to their clearly distinct signatures, carbonaceous chondrites always come out as a minor component of Earth and Mars, with ordinary chondrites constituting an intermediate amount. This is in contrast to decades worth of modeling of bulk-Earth composition (McDonough and Sun 1995; Palme and O'Neill 2014; Wänke and Dreibus 1988) that assumed carbonaceous chondrites were the predominant feedstock of Earth because this group of meteorites comes closest to matching the composition of the Sun, at least in elements that are not highly volatile. Terrestrial planet formation models predict that, like Earth, Venus is also compositionally similar to enstatite chondrites, (Brasser et al. 2017), with a low fraction of ordinary and carbonaceous chondrites. The same could be true for Mercury.

The concept that the isotopic composition of different elements in planetary mantles may track changes in the nature of materials being accumulated was expanded by Dauphas (2017) who noted that the isotopic composition of lithophile elements in Earth's mantle, for example, Ca, Ti, and Nd, reflect the average composition of everything that combined to create Earth. In contrast, elements in the mantle that have moderately siderophile tendencies, for example Cr and Mo, provide an isotopic composition biased towards the latter fraction of accumulating material as at least some portion of the Cr and Mo in earlier accreted material had been segregated into the core. Finally, the highly siderophile elements (HSEs) in the mantle track only the material that was added to the mantle after core formation was complete. Hence, the isotopic composition of elements with different geochemical affinities for metal can be used to examine how the material from which Earth accumulated may have changed over time (Fig. 4). This approach indicates that for the first 60% of Earth formation, the material accumulated was 51% enstatite chondrite, 9% CO and CV carbonaceous chondrite, and 40% ordinary chondrite (Dauphas 2017). The latter 40% of Earth growth appears to have been highly dominated by material with isotopic characteristics closest to enstatite chondrite (Dauphas 2017).

Render et al. (2017), however, showed that even enstatite chondrites display nucleosynthetic Mo isotope anomalies relative to Earth, as many also do for Nd (Gannoun et al. 2011), thus the predominant growth from enstatite chondrite-like bodies during the waning stages of Earth's main accretion remains valid only if the inherent s-deficit of enstatite chondrites was balanced by the accretion of materials with an s-process excess. Such material may have originated from a reservoir located within 1 AU (Fig. 3), where it was accreted by Venus and Mercury. Although the population of objects present in the asteroid belt today predominantly derive from past Earth's orbit, dynamical models for terrestrial planet formation predict that planetesimals originating from orbits inside 1 to 1.5 AU were also transported to the asteroid belt (Bottke et al. 2006; Raymond and
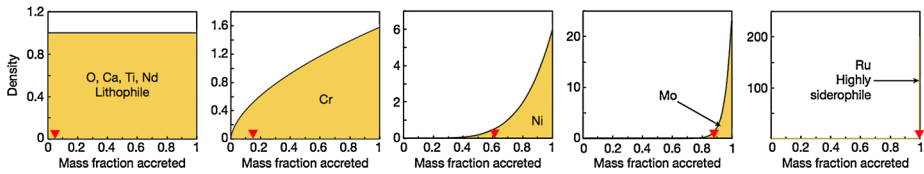
Fig. 4 Schematic examples of the period of Earth accretion monitored by elements in Earth's mantle that have different propensities for segregation into Earth's core from those that are insoluble in the core (O, Ca, Ti, Nd) to those that almost quantitatively dissolve in iron metal (e.g. Ru). Figure from Dauphas (2017)

Izidoro 2017a, 2017b). The current inventory of meteorites on Earth does not provide evidence for the existence of such material, but if found, would support the idea of a compositional gradient throughout the inner Solar System (Fischer-Gödde and Kleine 2017; Render et al. 2017). The possibility that our current collection of meteorites is a biased population compared to the feedstocks of the terrestrial planets from 4.5 Ga ago is suggested by recent work on the meteorite flux 460 Ma ago that is preserved in a sedimentary deposit in Sweden (Schmitz et al. 2016). The detection of nucleosynthetic isotope variability has thus become important input into the type of theoretical models of planet formation explored in the next section.

3 Dynamical Background and the Classical Model of Planet Formation

The feedstocks of the terrestrial planets can be quantified by knowing the distribution of primitive and differentiated material from which the terrestrial planets were assembled. This can be approached in two ways: from a study of isotopic heterogeneities at the planetary scale level when compared to the various known meteoritic classes and intra-planetary isotopic differences, as discussed above, or through N-body dynamics. In this section we focus on the latter.

3.1 The Classical Model

In an early study on the formation of the terrestrial planets, Wetherill (1980) showed that the terrestrial planets coagulated from planetesimals, and that the formation of the planets was linked with the evolution of the asteroid belt. Wetherill and Stewart (1989) elaborated that in a protoplanetary disk consisting of planetesimals, some would undergo rapid collisions with other planetesimals. The larger accretion cross section of the merged body would lead to a phase of runaway growth wherein the mass of the planet increases as $\frac{dM}{dt} \propto M^\alpha$, where α is a free parameter. During the earliest stages of planet formation $\alpha = 4/3$ due to effective gravitational focusing (Kokubo and Ida 1996). This phase of runaway growth traditionally results in the formation of a number of progressively-spaced planetary embryos (Kokubo and Ida 1998). These embryos would then subsequently collide to form the terrestrial planets (Chambers 2001; Chambers and Wetherill 1998). The above studies presuppose that terrestrial and giant planet formation can be treated separately.

In this simplified model of terrestrial planet formation, the so-called Classical model, the Sun is assumed to be surrounded by a protoplanetary disk of gas and planetesimals that are gravitationally interacting. Jupiter and Saturn are further assumed to have already formed and reside on their current orbits. In N-body simulations, the planetesimals are usually assumed to have the same size and mass, and a fairly steep radial surface density gradient (typically $\frac{dln(\Sigma)}{dln(r)} = \frac{-3}{2}$; (Weidenschilling 1977)). The planetesimals gravitationally stir each

other (Ida and Makino 1993), resulting in their eccentricities and inclinations being pumped up. Once the eccentricities reach orbit-crossing values, the planetesimals will collide with each other and, under the assumption of perfect mergers, the formation enters into a runaway growth in which the size-frequency distribution of the bodies in the disk becomes approximately bimodal. During this bimodal stage, the Sun is surrounded by a disk composed of approximately lunar to Mars-sized protoplanets (dubbed planetary embryos) spaced by about 10 mutual Hill radii, and a sea of planetesimals (Kokubo and Ida 1998). The Hill radius of a planet is given by $r_H = a(\frac{m_p}{3M_s})^{\frac{1}{3}}$ where a is the semi-major axis, m_p and M_s are the mass of the planet and the star. The embryos gravitationally perturb the planetesimals and each other, but due to the presence of the gas from the protoplanetary nebula their eccentricities and inclinations are kept low due to damping forces from the gas, and the system is dynamically quasi-stable. The planetary embryos all grow at roughly the same rate as they vie for space and for their ability to accrete planetesimals. During this so-called oligarchic growth stage approximately half of the solid mass within the disk is in the embryos, with the other half being in planetesimals (Kokubo and Ida 1998).

The gas density from the solar nebula decreases with time (Hartmann et al. 1998) so that the damping forces from the gas disk on the embryos weaken accordingly. There comes a point in time when gravitational stirring overcomes the tidal forces from the gas disk. By this time, the gravitational perturbations from the embryos and from Jupiter cause their eccentricities to rise to orbit-crossing values so that the whole chain eventually becomes dynamically unstable and the system subsequently evolves into a phase wherein planetary mergers through large impacts (or sometimes 'giant impacts' in the sense of Earth's Moon-forming event) are commonplace. Over tens of millions of years these protoplanetary collisions eventually lead to the observed terrestrial planet inventory (Chambers 2001; Chambers and Wetherill 1998; Raymond et al. 2009, 2006).

An example of the evolution of the Classical model of terrestrial planet formation, albeit with slightly different initial conditions (Chambers 2006), is shown in Fig. 5. In each pair of time steps, the left panel shows snapshots of the eccentricities of planetary embryos and planetesimals as a function of the semi-major axis. The right panel shows planetary masses versus semi-major axis. The sizes of the symbols are proportional to their radii. The horizontal error bars show their perihelion and aphelion distances respectively. The simulation is started during the oligarchic stage with planetary embryos and planetesimals side by side. Since there is no disk gas in this simulation, the embryos stir each other and rapidly collide to form more massive planets. The more massive planets form closer in because the orbital period is shorter, leading to more collisions per unit time, and the surface density is also higher. After 150 Ma of evolution, the simulation has produced a Venus, Earth, and Mars analogue as well as another small planet near 2 AU. This outcome is a decent proxy for the current inner Solar System.

Early simulations of terrestrial planet formation yielded estimates for the growth time scale of several tens of millions of years. Overall results indicated that the final terrestrial system would be assembled by 100 Ma (Chambers 2001; Raymond et al. 2009, 2006), in accordance with Hf-W chronology (Kleine et al. 2002, 2009; Yin et al. 2002a). Most of these early systems, however, were found to suffer from excess eccentricity and inclination of the final planets, but the inclusion of a large number of planetesimals, which take away angular momentum from the system when they are passed to Jupiter and subsequently ejected, alleviated this concern (O'Brien et al. 2006). Still, a chronic and fundamental shortcoming of the Classical model remained: the output systematically yielded a Mars analogue that was far too massive.
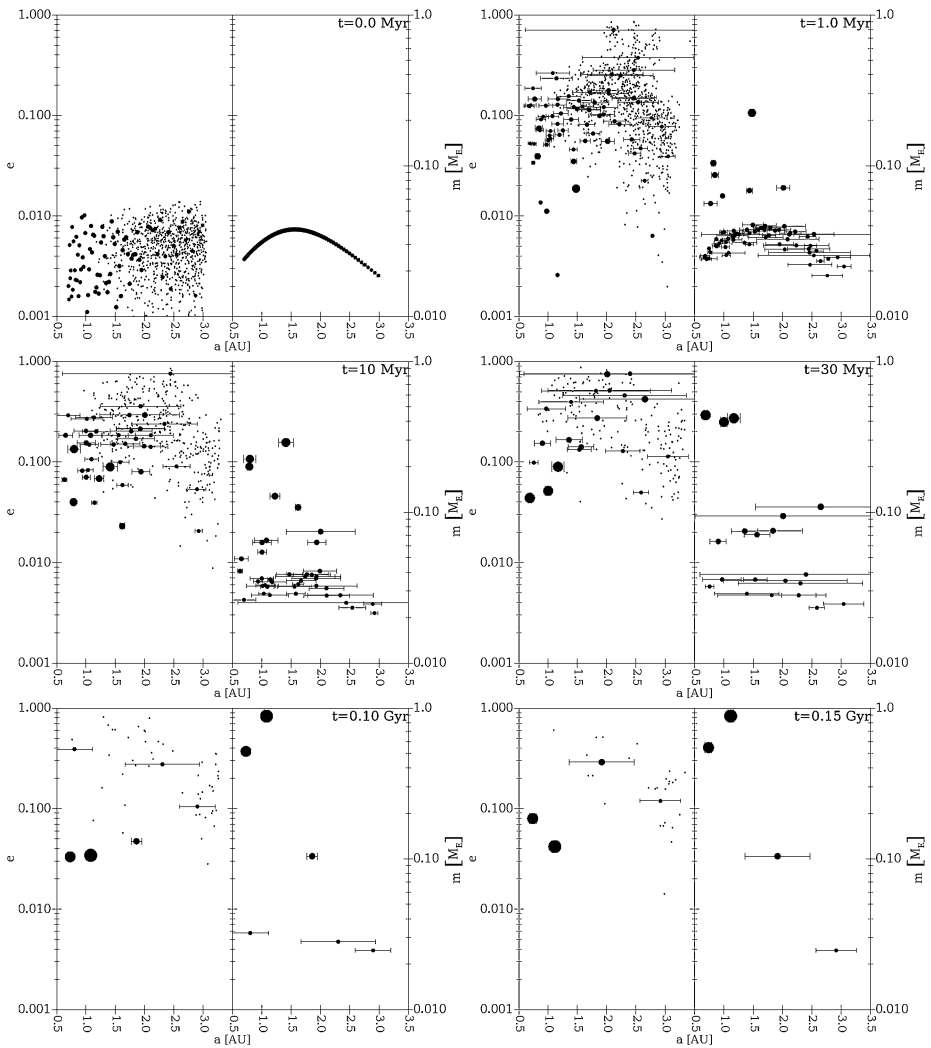
Fig. 5 Snapshots of the evolution of the Classical model simulation of terrestrial planet formation. In each pair, the columns on the left are eccentricity vs. semi-major axis. The columns on the right plot the mass vs. semi-major axis

3.2 The Grand Tack model

The problem of Mars' low mass appears to be solved by the popular Grand Tack model (Walsh et al. 2011). Briefly, Grand Tack relies on the early, gas-driven radial migration of Jupiter. After the gas giant formed it opened an annulus in the gas disk and continued migrating towards the Sun (Lin and Papaloizou 1986) because the torques acting on the planet from the protoplanetary disk are imbalanced. At the same time, beyond Jupiter, Saturn also accreted its gaseous envelope, albeit more slowly. Once Saturn reached a critical mass of about 50 Earth masses it rapidly migrated Sunward too, caught up with Jupiter and became

trapped in the 2:3[1] mean motion resonance (Masset and Snellgrove 2001). This particular and fortuitous configuration of orbital spacing and mass ratio between the gas giants reversed the total torque from the gas disk on both planets, thus reversing their migration; the planets 'tacked', a term from sailing reflecting a change of direction. Pierens et al. (2014) showed that outward migration is possible with Jupiter and Saturn in both 2:3 and 1:2 resonances (cf. Zhang and Zhou 2010), but that stable evolution with little migration may also happen. Thus, the inward-outward migration is a possible outcome, but is not guaranteed. To ensure that Mars did not grow beyond its current mass, the location of this 'tack' was set at 1.5 AU (Walsh et al. 2011). Apart from Mars' low mass compared to Earth, the Grand Tack scenario can further account for the mass-semi major axis distribution of the terrestrial planets and the stirred demography of the asteroid belt (DeMeo and Carry 2014).

The dynamical consequences of the Grand Tack model on the terrestrial planet region are two-fold. First, as Jupiter migrated towards the Sun, it strongly scattered all protoplanets and planetesimals in its path due to its high mass. This scattering places more than half of the mass of the disk from the inner Solar System to farther than 5 AU from the Sun. Second, Jupiter acted as a snow plow that pushed some protoplanets and planetesimals towards the Sun. This shepherding of material mostly occurred within the 2:1 mean motion resonance with the planet. When Jupiter reversed its migration at 1.5 AU it caused a pileup of solid material inside of 1 AU, which approximately corresponds to the location of the 2:1 resonance when Jupiter is at 1.5 AU. Thus, almost all protoplanets and planetesimals that originally formed beyond 1 AU were scattered outward by Jupiter, with a few pushed inside of 1 AU.

Figure 6 shows an example of the evolution of a Grand Tack simulation taken from Brasser et al. (2016a). The top-left panel depicts the initial conditions. Jupiter and Saturn are at 3.5 and 4.5 AU, respectively. The protoplanetary disk resides between 0.7 AU and 8 AU, interrupted by the gas giants. The disk contains planetary embryos of 0.05 Earth masses and two thousand planetesimals. Inside 1.5 AU the disk is assumed to consist of material mostly akin to enstatite chondrite (EC; green) (Brasser et al. 2018, 2017), while between 1.5 AU and Jupiter the material is assigned to ordinary chondrite (OC; orange). The blue dots are a proxy for the carbonaceous chondrites (CC). Symbol sizes are proportional to their radii. In this illustration, Jupiter and Saturn are made the same size and colored in black for clarity. As the gas giants migrate inwards (top-right panel) a significant fraction of OC and CC material gets ejected while some OC material is pushed closer to the Sun by Jupiter. After 5 Ma of simulation evolution, when the gas giants have reversed their migration and stalled close to their current positions (bottom-left), they leave behind a nearly empty asteroid belt region and a predominantly EC inner Solar System. By this time Earth and Venus have reached approximately half of their masses and the number of embryos has declined substantially. By 30 Ma (middle-right) the terrestrial planets are almost fully formed, as indicated by the lack of dynamical and size evolution in the next two panels at 60 Ma of simulation evolution (bottom-left) and 150 Ma (bottom-right). At the end of the simulation four terrestrial planets and a mostly-empty asteroid belt region remain.

The Classical model and the Grand Tack model predict different outcomes for the bulk compositions of the terrestrial planets. In the Classical model, the planets tend to accrete mostly locally. In contrast, in the Grand Tack model, all the accretion is confined to an annulus between approximately 0.5 AU and 1 AU, but this region also contains material that originated in the outer parts of the protoplanetary disk that was scattered inwards by the migration of Jupiter. Additional contamination of the inner Solar System with material from

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[1]We say 2:3 resonance here because the subject of the sentence is Saturn, not Jupiter. If Jupiter was the subject then we would have said 3:2.
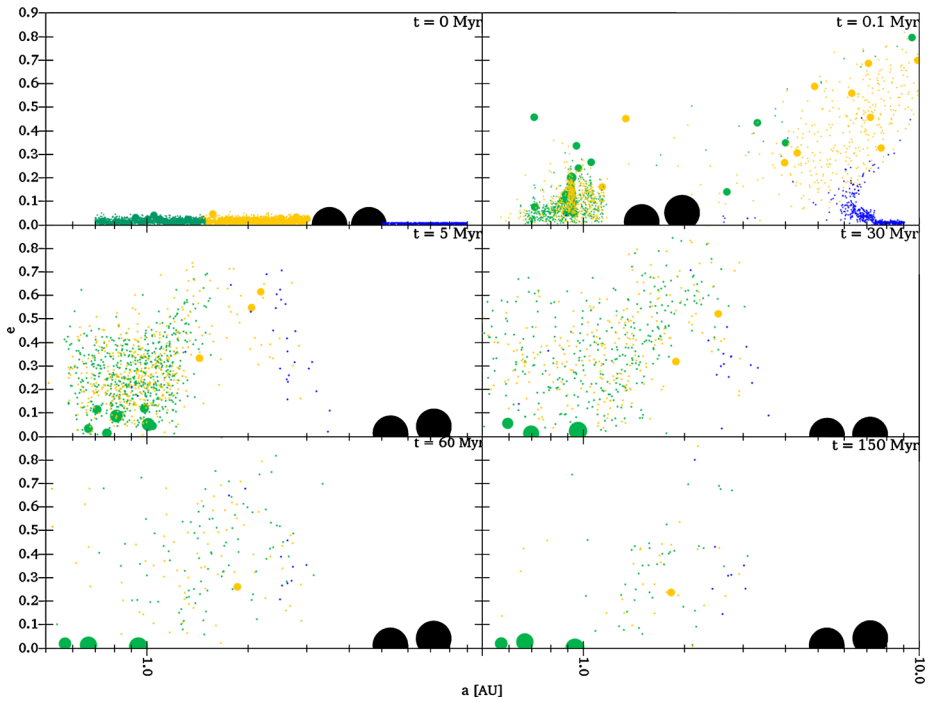
Fig. 6 Snapshots of the evolution of the coupled migrations of Jupiter and Saturn in the Grand Tack model (Walsh et al. 2011). The color coding indicates the composition of planetesimals in the protoplanetary disk: green for EC, orange for OC and blue for CC. The gas giants Jupiter and Saturn migrate inwards and reach 1.5 AU in 0.1 Ma. They subsequently change directions (tack) and terminate their migration at their current positions after 5 Ma. During their journey they remove >99% of the planetesimals and planetary embryos in the asteroid belt

the outer Solar System occurs during the growth of the gas giants (Raymond and Izidoro 2017b). But how much is the inner Solar System contaminated exactly, and what does this imply for the compositions of the terrestrial planets?

3.3 Other Models

We briefly mention several alternative models of terrestrial planet formation which have either not (yet) gained much traction or are too new to have been thoroughly explored, especially for their cosmochemical implications. The first is the depleted disk model (Izidoro et al. 2014, 2015; Raymond and Izidoro 2017a) wherein the mass of the asteroid belt is initially a few orders of magnitude lower than elsewhere in the protoplanetary disk, and is subsequently filled up by the outward scattering of material from the terrestrial planet formation zone and the inward scattering of material from the giant planet region during giant planet migration (Raymond and Izidoro 2017a). In this model Mars' small mass compared to Earth's is caused by the density drop around 1.5 AU and that the Mars analogue was unable to accrete much material.

A second model invokes a dynamical instability in the outer Solar System wherein the giant planets scatter each other and all material around them. There is ample evidence that such a dynamical instability has occurred (Thommes et al. 1999; Tsiganis et al. 2005;

Gomes et al. 2005; Morbidelli et al. 2005, 2010; Brasser et al. 2009; Levison et al. 2011; Nesvorny and Morbidelli 2012; Brasser and Lee 2015), but thus far it has been assumed that this instability happened after terrestrial planet formation to account for the late heavy bombardment purported to be recorded by the formation of the large lunar impact basins (Tera et al. 1974). In Clement et al. (2018) the authors assume that this dynamical instability occurred early, while the terrestrial planets were still forming. Mars' low mass is then a result of material in its vicinity being removed through perturbations by the migrating giant planets.

A third alternative explores the idea of drifting pebbles piling up in the terrestrial planet region that first form planetesimals and subsequently the terrestrial planets (Drazkowska et al. 2016). Last, there is the pebble accretion model (Ormel and Klahr 2010; Lambrechts and Johansen 2012) wherein sunward-drifting pebbles accrete onto large planetesimals or small planetary embryos which then rapidly grow into either the giant planets (Levison et al. 2015a) or the terrestrial planets (Levison et al. 2015b). The pebble accretion model is actively studied both in the Solar System and for exoplanets.

3.4 Feeding Zones and Expected Composition

One way to quantify the amount of material mixing in the disk, and thus the final expected compositions of the terrestrial planets, was introduced by Chambers (2001). His implementation was limited to planetary embryos. We shall employ a slightly revised definition, which is

$$S_{r,j} = \frac{\sum_i m_i \left| \frac{a_{init,j}}{a_{fin,j}} - 1 \right|}{\sum_i m_i}$$

where m_i are the masses of planetesimals and embryos that are accreted by planet j, $a_{init,j}$ are the original semi-major axes of embryos and planetesimals that wind up in planet j, and $a_{fin,j}$ is the final semi-major axis of planet j. In essence $S_{r,j}$ is a mass-weighted relative distance between where material originated in the disk and where it ends up. The original definition from Chambers (2001) summed over all the final planets and S_r was a measure that characterized the whole system. Here we perform the summation over planetesimals and embryos that are assembled into each planet in our simulations and evaluate this quantity for each planet at the end of the simulations and then calculate the average and standard deviation. This is similar, but not identical to, the method from Chambers (2001). The distribution of S_r for all the planets yields information about the feeding zones of the planets.

In the Classical model, the individual feeding zones ($S_{r,j}$) increase with time (Fischer et al. 2018; Raymond et al. 2006). The reason for this is simple: the orbital period increases with distance to the Sun, so that the time scale for collision must increase as well. Thus, material closer to the Sun will coagulate faster than material farther out (Kokubo and Ida 1996; Raymond et al. 2009, 2006), which implies that there is a delay in material from the outer edge of the disk being accreted into planets (Kobayashi et al. 2010). In addition, material from the outer portions of the disk will need a high eccentricity (e) to collide with planets near 1 AU, and the excitation to high values by scattering and secular interaction with Jupiter takes longer for higher values of e.

With this in mind, the mean of $S_{r,j}$ for all the planets at various epochs are plotted in Fig. 7. Two things are clear. First, the feeding zones of the planets are increasing with time in the Classical model (as has been stated elsewhere) while in Grand Tack it peaks and then reduces ever so slightly. This suggests that in the first half, the Grand Tack source region must lead to a greater difference in composition than the Classical model. Second,
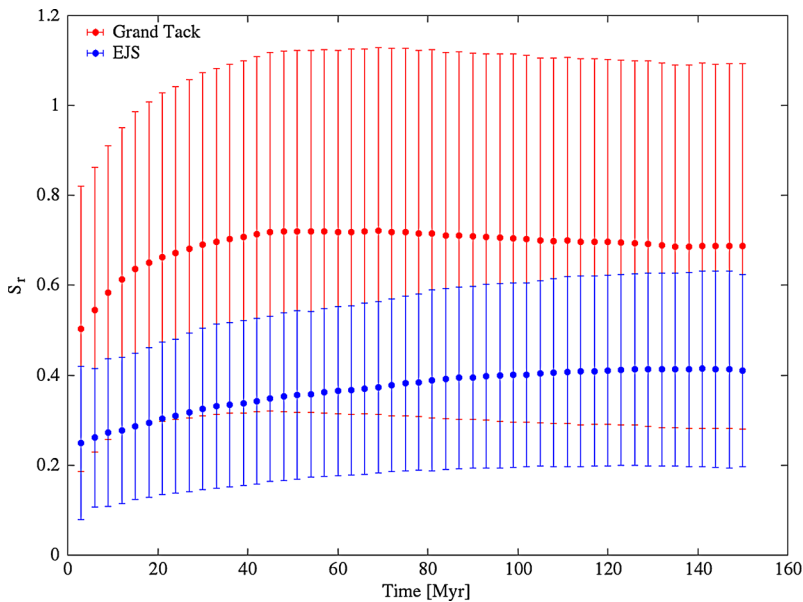
Fig. 7 Width of the terrestrial planets' feeding zones as a function of time. The red is for the Grand Tack model, the blue for the Classical model. The Grand Tack model mixes the disk much more than the Classical model. Simulation data from Brasser et al. (2016a) and Matsumura et al. (2016)

the Grand Tack planets sample a greater portion of the disk than those in the Classical model, in which the planets accrete more locally. The reason for the Grand Tack's greater feeding zones is because of Jupiter pushing some material to the inner Solar System, which skews the distribution. If additional contamination from giant planet growth were to be considered (Raymond and Izidoro 2017b) we expect $S_{r,j}$ to have a higher value for both models, albeit only slightly because the amount of mass deposited in the inner Solar System from the giant planet region is low (Raymond and Izidoro 2017b). The expected outcome, therefore, is that in the Classical model there is some compositional gradient amongst the terrestrial planets, but in the Grand Tack the prediction is that the disk is fully mixed and planetary compositions should be nearly identical (Fitoussi et al. 2016). However, is this truly the case?

3.5 Isotopic Composition as a Proxy for Bulk Composition

As discussed in Sect. 2, several recent studies have shown that when assuming the primitive meteorites are the building blocks of the terrestrial planets, Earth has a high ($\geq 80\%$) fraction of enstatite chondrite-like material (Brasser et al. 2018; Dauphas 2017; Dauphas et al. 2014b; Fitoussi et al. 2016; Javoy et al. 2010; Lodders 2000), even though enstatite chondrites have compositional characteristics that are difficult to reconcile with the bulk composition of (at least) Earth and Mars. Brasser et al. (2018) used a Monte Carlo model based on isotopic variations in various chondrites to determine that Earth's best-fit meteoritic mixture consists of $71\%^{+14}_{-12}$ EC + $24\%^{+10}_{-12}$ OC + $0\%^{+3}_{-0}$ CI + $5\%^{+1}_{-3}$ CC. The uncertainties are a result of the reported error values in the isotopic composition of the various meteorite classes, and are 2σ. A similar analysis for Mars results in $68\%^{+0}_{-39}$ EC + $32\%^{+35}_{-0}$ OC with up to 3% CC, consistent within uncertainties with the 45% EC
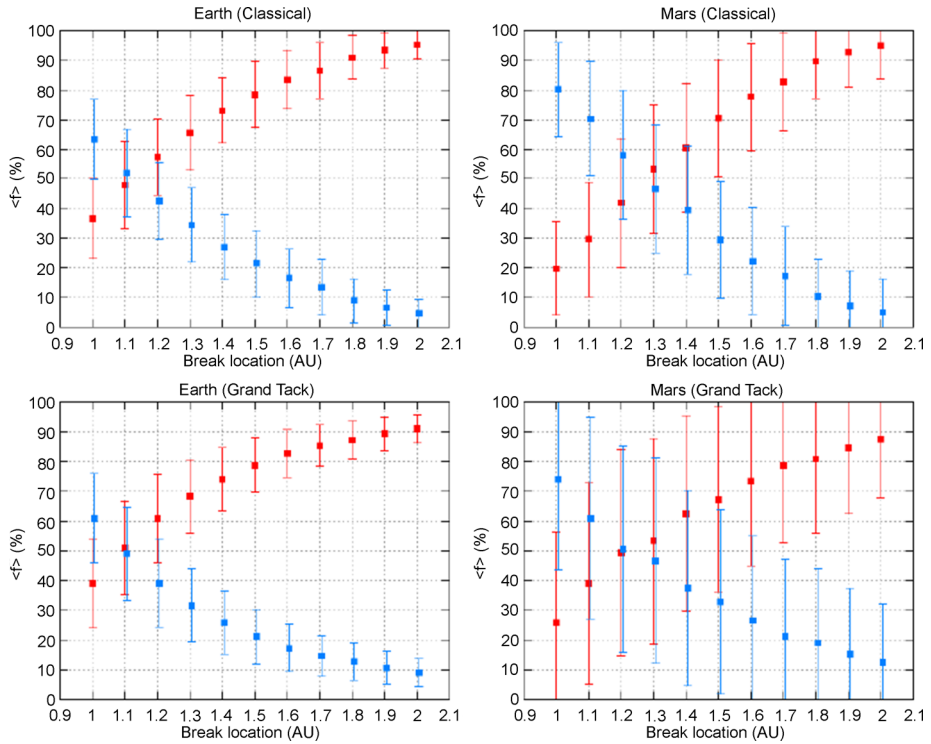
Fig. 8 Fraction of EC (red) and OC (blue) in Earth (left) and Mars (right) as a function of the distance at which the disk's composition changes from one to the other. Upper panels show the results for the Classical Model while the lower panels are for the Grand Tack Model. Simulations from Brasser et al. (2016a)

+ 55% OC reported by Sanloup et al. (1999) and Tang and Dauphas (2014). Mars' high fraction of OC led Brasser et al. (2017) to suggest that Earth and Mars formed at different locations, with Mars preferentially forming in the asteroid belt. The large uncertainties for Mars' composition are caused by the convolution of the uncertainties in the isotopic composition of the chondrites as well as of Mars.

The overall composition of the terrestrial planets can be predicted in two ways. First, we can use N-body simulations and assume that the composition of the disk has radial variations. The simplest way is to assume that the inner portion of the disk consists of E-chondrite and the outer part is composed of O-chondrite (Brasser et al. 2017; Fischer-Gödde and Kleine 2017; Morbidelli et al. 2012). In this model, the composition of the solids in the disk is purely EC inside of some transition radius, r_{break}, and purely OC outside of that. Nominally we set $r_{break} = 1.5$ AU, but this can also be left as a free parameter.

The result of these numerical experiments is displayed in Fig. 8, which depicts the fraction of EC (red) and OC (blue) in Earth (left) and Mars (right) as a function of r_{break}. A break between 1.2 to 1.4 AU can roughly reproduce the composition of Earth and Mars simultaneously (Woo et al. 2018). The isotopic compositional differences between Earth and Mars suggests that the two planets have different feeding zones, which is somewhat supported by Fig. 8.

The lower panels of Fig. 8 show the fraction of EC (orange) and OC (blue) in Earth and Mars for Grand Tack simulations as a function of r_{break}. Earth's and Mars' composition

is best reproduced simultaneously when the transition occurs near 1.3 AU. Alone, Mars' composition is best reproduced when r_{break} is near 1.3 AU, but the error bars are large enough that even setting r_{break} at 1.5 AU yields a consistent outcome (Brasser et al. 2017). With the changeover radius at 1.5 AU, the bulk composition of both planets from the Grand Tack model is predicted to be $87\%^{+9}_{-17}$ EC + $12\%^{+14}_{-10}$ OC for Earth, and Mars consists of $67\%^{+29}_{-66}$ EC + $32\%^{+65}_{-32}$ OC, with about 1% CC for each planet (Brasser et al. 2018).

Even though both models are capable of reproducing the bulk planetary compositions, these results can be improved upon by looking at the accretion through time and thereby make predictions about the surface and interior conditions when most of the accretion has ceased.

3.6 Accretion Through Time

As discussed in Sect. 2, the method proposed by Dauphas (2017) allows examination of how the composition of material accreted to Earth and Mars may have changed during the period of accretion. Dauphas (2017) divided the accretion into three stages corresponding to the first 60 wt.% of the Earth's mass (Stage I), the following 39.3 wt.% (II), and the final 0.7 wt.% (III). The best-fit mixture during stage I for Earth is $51\%^{+28}_{-20}$ EC + $40\%^{+15}_{-24}$ OC + $0\%^{+5}_{-0}$ CI + $9\%^{+2}_{-5}$ CO/CV by mass, while Stages II and III are dominated by EC ($100\%^{+0}_{-13}$ for stage II and $100\%^{+0}_{-6}$ for Stage III) (Brasser et al. 2018; Dauphas 2017). For Mars these values are $100\%^{+0}_{-89}$ EC + $0\%^{+85}_{-0}$ OC during Stage I. Stage II contains a higher proportion of OC: $20\%^{+50}_{-17}$ EC + $80\%^{+11}_{-52}$ OC, while for Stage III the fractions are $100\%^{+0}_{-95}$ EC + $0\%^{+90}_{-0}$ OC. All three stages contain up to 4% in both CI and CO/CV. The overall compositions are those listed above. The overall accretion of both planets is depicted in Fig. 9 (Brasser et al. 2018).

The existence of primitive material in the asteroid belt today, more than 4.5 Ga after the supposed turmoil caused by the migrating giant planets that cleared out more than 99% of the mass in the asteroid belt, may appear strange. Indeed, the mass of the asteroid belt is so low that explaining its depletion is a challenge in itself, and forms the basis for several new dynamical models of terrestrial planet formation and Solar System evolution (Raymond and Izidoro 2017a; Izidoro et al. 2014). At the same time, however, apart from a few specific locations, motion in the asteroid belt is stable. Primitive material that found its way into one of the stable niches of the asteroid belt can remain there for very long time scales. These materials can be delivered from the asteroid belt to Earth through the same mechanisms that bring the near-Earth asteroids; collisions in the asteroid belt break off small pieces from larger bodies that then drift to one of the unstable regions because of the Yarkovsky effect. The powerful mean-motion resonances with Jupiter, or the ν_6 secular resonance, then delivers them to Earth.

To summarize thus far, when using isotopic compositions as a proxy for bulk composition, modern N-body simulations can reproduce the terrestrial planets for the Classical and Grand Tack models. Future studies that merge these two disciplines should be able to decide which dynamical models are better than others. Though planetary accumulation models can reasonably match the observed nucleosynthetic stable isotopic variations of the terrestrial planets, there remains the important step of relating the isotope distinctions of planetary building blocks with their implications for the bulk composition of the planets. For example, while E-chondrites have similar stable isotopic compositions for many elements compared to Earth, a compositional model for Earth based on E-chondrites predicts a bulk composition for the mantle that does not match the composition of at least the upper portions of Earth's mantle (e.g. Palme and O'Neill 2014; Javoy et al. 2010).

Fig. 9 Proportions of each major chondrite component that goes into Earth and Mars at each stage of accretion. For both planets, the first stage involves a sizeable amount of OC and some CC. In Stages II and III, however, the OC and CC components are practically absent for Earth, while for Mars' the OC contribution varies
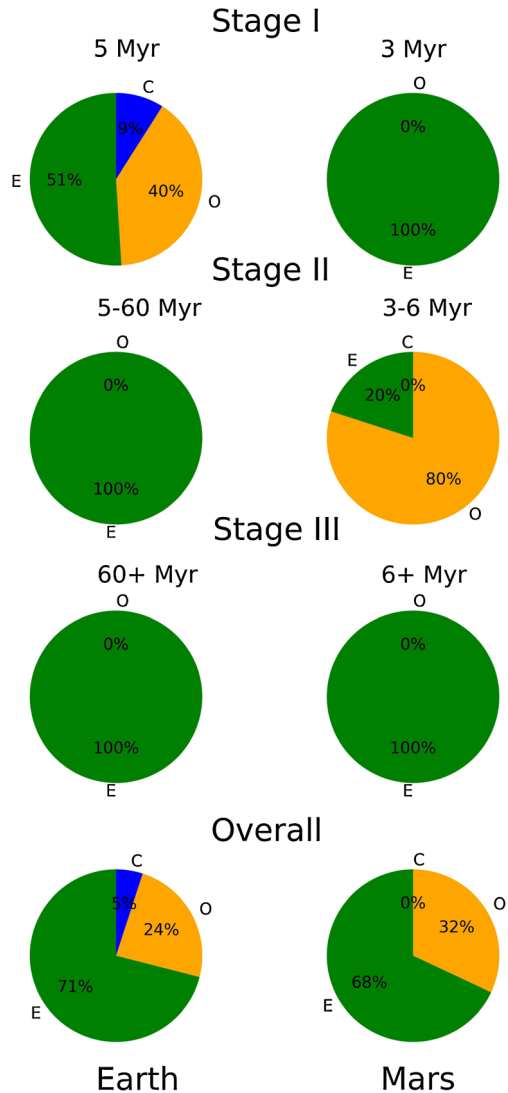
4 Processes Affecting Volatile and Metal Abundances During Planet Growth

## 4.1 Accretion and Loss of Volatile Elements

The isotopic distinctions between various meteorite groups and Earth/Mars have provided new insights into the materials from which the terrestrial planets accumulated, but translating very small nucleosynthetic isotope variability into the large-scale compositional distinctions between the planets is not straightforward; indeed, it is a topic of intense and continuing debate. While the range in refractory lithophile element abundances between different types of meteorites and the terrestrial planets is small, there are large differences in the relative abundances of Mg and Fe compared to Si (e.g. Jagoutz et al.

1979), and particularly in the abundance of moderately volatile elements between meteorite groups and between the meteorites and the terrestrial planets (McDonough and Sun 1995; Palme and O'Neill 2014). These differences might represent initial compositional variations in the protoplanetary disk, but also likely point to two processes acting in the Solar nebula during planet formation that can result in significant compositional changes: separation of metal from silicate, and volatile-loss.

All the terrestrial planets lack the type of dense atmospheres that characterize the giant gas planets. This first order distinction between the inner and outer planets of the Solar System has been interpreted to reflect the temperature-dictated boundary between where ices could, or could not, condense and accumulate together with more refractory materials. The detection of "hot jupiters", giant gaseous exoplanets that orbit close to their stars (Marcy and Butler 1998; Mayor and Queloz 1995), hints at the importance of gas-driven planetary migration in the evolution of planetary systems, but does not necessarily invalidate the concept of a "snow line" that separates regions where ice-rich and ice-poor planets can form. The compositional differences between the terrestrial planets and the Sun, however, are not restricted only to elements that would primarily condense at, or lower than, the temperature where water ice forms. Compared to the composition of the Sun, Earth clearly is relatively deficient even in elements that are only moderately volatile, e.g. those elements with condensation temperatures lower than about 1300 °C (McDonough and Sun 1995; Palme and O'Neill 2014; Wänke et al. 1984). Earth is not alone in its depletion in moderately volatile elements; orbital measurements of the K/Th ratio in both Mercury and Mars show values of around 5500 (Peplowski et al. 2011), higher than the value (3000) for Earth (McDonough and Sun 1995) (Fig. 10). These values are significantly lower than the CI chondrite ratio of 19,000 (Anders and Grevesse 1989). The Moon is even more strongly depleted in moderately volatile elements like K (Fig. 10). The similar degree of depletion of the moderately volatile element K compared to refractory Th across the planets of the inner Solar System points either to very efficient mixing of the planetary building blocks across the terrestrial planet-forming region, which was demonstrated in the previous section to be mostly true, or alternatively to removal of nebular gas when only about a third of the potassium had been condensed into solids that remained to be accumulated into the terrestrial planets. Perhaps not coincidentally, the condensation temperature that delineates the separation between refractory and moderately volatile elements is near the temperature that the major "rocky" phases, e.g. olivine, enstatite, and metal, condense from the nebula (Grossman 1972; Lodders 2003). Efficient segregation of the large amount of dust that would be formed by the condensation of these abundant phases may explain the common depletion of moderately volatile elements not only in the terrestrial planets, but also in most meteorite groups.

The key question is the nature of the process(es) that separate the volatile and refractory elements during the period of planet formation. Yin (2005) suggested that the depletion in moderately volatile elements displayed by most meteorite groups and all the terrestrial planets is an inherited characteristic from the interstellar medium where refractory elements are predominantly contained in dust grains, but the moderately volatile elements are in the gas phase. Separation of gas from dust during molecular cloud collapse could lead to at least an inner nebula that is generally deficient in the moderately volatile elements. If the refractory-volatile element separation instead occurred in the early Solar nebula, for the primitive meteorites, the most obvious process is mechanical separation of refractory (CAIs and chondrules) from volatile-rich (matrix) material. Chondrules show a range of chemical compositions that if segregated could explain at least the gross chemical differences between most chondrites and the volatile-rich CI chondrites. Several studies, however, have found either chemical (Bland et al. 2005;

Fig. 10 Comparison of the
abundance of the moderately
volatile element K against
refractory Th measured in surface
rocks from Mercury, Venus,
Earth, Mars and the Moon.
Figure from Peplowski et al.
(2011)
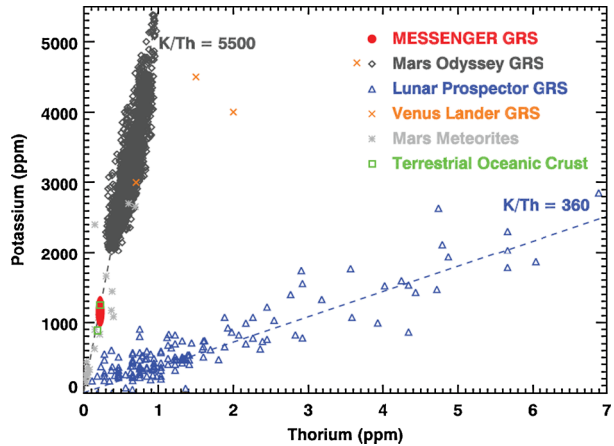
Hezel and Palme 2010) or isotopic (Budde et al. 2016b) complementarity between chondrules and the matrix of their host meteorites indicating that the refractory and volatile-rich components of these meteorites were not effectively separated from one another. Although this evidence is compelling for the particular meteorites examined in these studies, the results do not rule out the possibility that in other areas of the nebula, the separation of refractory and volatile-rich components was more efficient. Models that form chondrules via shock waves in the nebula require the simultaneous presence of gas and dust (Ciesla and Hood 2002), implying that chondrule formation occurred prior to complete condensation and the removal of nebular gas. Chondrule formation could have been a critical step in developing grain aggregates large enough to decouple from surrounding gas so that they could settle into the nebular mid-plane and accumulate into planetesimal size objects (Hewins and Herzberg 1996) while the moderately volatile elements remained in the gas.

The compositional variability seen in primitive meteorites most likely reflects processes occurring in the protoplanetary disk during the growth of the meteorite parent bodies. When considering the composition of planet-sized objects, however, another process that must be considered is the internal differentiation of planetesimals. Ages for the formation of various groups of magmatic iron meteorites are in the range of 0.5 to 3 Ma after CAI formation (Kruijer et al. 2013, 2012). As these meteorites likely reflect the cores of differentiated, and disrupted, planetesimals, thermal models of the formation times of their parent planetesimals suggest accumulation times of 0.1 to 0.6 Ma after CAI formation if the parent planetesimals were melted by heating from the decay of ^{26}Al (Kruijer et al. 2014). Support for such early melting on planetesimals is provided by ages only 3–4 Ma younger than CAIs for the older samples of igneous meteorites such as angrites and eucrites (e.g. Amelin 2008; Nyquist et al. 2009; Amelin et al. 2018).

The importance of this observation is two-fold. First, if differentiation at the planetesimal scale indeed was driven by ^{26}Al heating, the likelihood of a similar process occurring in exoplanetary systems depends both on the initial abundance of ^{26}Al in that area of the Galaxy, which is quite variable (Diehl 2006), and the time period required to accumulate planetesimals of sufficient size to retain enough heat to melt. In our Solar System, planetesimal formation was occurring on roughly the same time scale as the half-life of ^{26}Al, so heating by this mechanism was efficient. Second, production of a magma ocean on a planetesimal allows for the separation of core, mantle, and atmosphere. While losing the atmosphere from a planet the size of Earth is difficult, gravitational loss of an atmosphere

Fig. 11 Ratios of the moderately volatile (K, Rb) to refractory (U, Sr) lithophile element content. These data extend the results shown in Fig. 10 and illustrate the extreme depletion in moderately volatile elements of the differentiated parent bodies of the igneous HED and angrite (ADOR) meteorites. Figure from Halliday and Porcelli (2001)
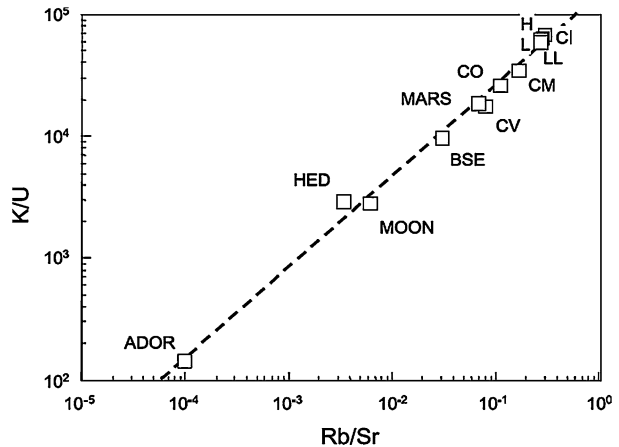
from an asteroidal-sized object is effective. This effect is well demonstrated by a comparison of moderately volatile to refractory element abundances in chondrites, differentiated meteorites, and the terrestrial planets (Fig. 11). The two meteorite parent bodies that experienced an early global melting event from which we have meteoritic samples, the parent body of the angrites, of which Angra dos Reis (ADOR) is an example, and that of the Howardite-Eucrite-Diogenite (HED) family of meteorites, are severely depleted in moderately volatile elements. The Moon is similarly depleted (Fig. 10), likely as a result of its formation in the aftermath of a highly energetic giant impact into Earth (e.g. Stevenson 1987).

The volatile depletion illustrated in Fig. 11 must have occurred during the first few million years of Solar System history (Carlson et al. 2015). Two recent studies point to aspects of Earth's volatile element depletion that appear to reflect evaporation from a magma rather than lack of condensation from nebular gas (Hin et al. 2017; Norris and Wood 2017). An important conclusion from the trend of depletion in moderately volatile elements displayed by all terrestrial planets is that it introduces the possibility that differentiated planetesimals constituted a significant mass fraction of their feedstocks. For example, to reach the K/U ratio of the terrestrial planets assuming a mixture of chondrites and volatile-depleted differentiated planetesimals would suggest that Earth and Mars consist of 87% HED + 13% OC and 72% HED + 28% OC, respectively. The implications of Earth forming not from primitive chondrites, but predominantly from differentiated planetesimals has been tentatively explored by Fitoussi et al. (2016), but much remains to be investigated regarding the compositional consequences of growing the terrestrial planets from already differentiated objects.

4.2 Adding Back Volatiles at the End of Planet Formation?

The importance of material accreted late in the history of planet formation is most clearly illustrated by the highly siderophile elements (HSEs); those elements whose solubility in iron metal is many orders of magnitude higher than in silicate melts (Kimura et al. 1974). When core formation occurs on a planet or planetesimal, almost all of the HSEs sink with the iron metal to the core, leaving vanishingly small abundances of these elements in the silicate mantle (Morgan 1986). On Earth, however, the abundances of the HSEs in the mantle are much higher than would be expected if the core were in chemical equilibrium with the mantle (Chou et al. 1983; Becker et al. 2006). This gave rise to the idea that the excess

abundance, and chondritic relative abundances, of the HSEs in Earth's mantle, and in other differentiated planets and planetesimals, were contributed by a small amount of late accreted chondritic material (Chou et al. 1983; Day et al. 2016; Walker 2009; Morbidelli and Wood 2015). For the Earth this late accretion is estimated at 0.5 wt% of Earth's mass and 0.8 wt% for Mars (Day et al. 2016). While often referred to as "late veneer", a better term would be "late accretion", as this is a natural outcome of terrestrial planet formation (Wetherill 1975). In the case of the HSEs, the late accreted material was added to Earth, Mars, and some larger bodies in the asteroid belt (Day et al. 2016), after chemical separation of core from mantle, so its inventory of HSEs was retained within the mantle.

A popular model to explain Earth's current volatile abundances relies on the material that brought the HSEs to have also been volatile-rich (e.g. Halliday 2013; Marty 2012). If late accreted material was volatile-rich carbonaceous chondrite, it would also add an amount of water roughly equivalent to the volume of Earth's oceans (Wang and Becker 2013; Wänke et al. 1984). More recent estimates that focus only on Earth's volatile inventory suggest that the late accreted material may have been as much as 2% to 4% of Earth's current mass (Albarede et al. 2013; Halliday 2013; Marty 2012). Although all chondrites have similar abundances of HSEs (Horan et al. 2003), only some carbonaceous chondrites have sufficient water abundances to add Earth's water in this small a mass of late accretion. The accretion histories inferred in Sect. 3 imply that volatile elements must have been added to the Earth during its early stages of accretion, lessening the need to add them as part of the late accreted material (Fischer-Gödde and Kleine 2017).

The models of accretion discussed in Sect. 3 show that the delivery of carbonaceous chondrite material to the terrestrial planets was shut off very early in the Solar System's history due to the formation of Jupiter (Brasser et al. 2018), therefore the volatile elements had to be delivered early. In accord with this conclusion, the nucleosynthetic differences, particularly in Ru, between carbonaceous chondrites and Earth as discussed in Sect. 2 also limit the amount of carbonaceous chondrite that could have been added to Earth post core formation (Dauphas 2017; Fischer-Gödde et al. 2013; Fischer-Gödde and Kleine 2017). The only meteorite group with Ru isotopic composition similar to the Ru in Earth's mantle is enstatite chondrite, but enstatite chondrites are essentially anhydrous, although some (e.g. EH chondrites) have higher abundances of the moderately volatile elements than do most other meteorite groups. These results suggest that the late accretionary component that supplied HSEs to the mantle is not the same material responsible for Earth's content of water and other highly volatile elements.

Accretion of secondary disk materials (silicate mantle) will not be able to account for the elevated HSE patterns seen in terrestrial and other dwarf planets' mantles, because planetary mantle materials are likely low in their HSE abundances as core formation on their own parent bodies would have already stripped off HSEs. Therefore, accreting secondary disk material resulting from hit-and-run collisions to a growing planet after core formation would not be able to account for their elevated HSE abundances. Orbit crossing of growing planets during the late giant impact stage, and damping the eccentricities and inclinations of these same planets are two competing and conflicting objectives. Schlichting et al. (2012) argued that primordial disk materials that primarily consist of small (10 m) planetesimals would provide both the needed dynamic friction to dampen the high eccentricities and inclinations of the terrestrial planets after giant impacts, and reproduce the HSE abundances for the post core formation mantle for the terrestrial planets. However, Schlichting et al. (2012) did not provide a mechanism for how primordial disk materials could be preserved in such small planetesimals throughout the planetary formation processes all the way to post giant impact stages. They simply assumed such material exists. On the other extreme, Bottke et al.

Fig. 12 Chondrite normalized abundances of the highly volatile elements in the bulk Earth. Many of these elements are present at approximately 0.02–0.03 times chondritic with the exception of significant depletions in Xe and N. Figure from Marty (2012)
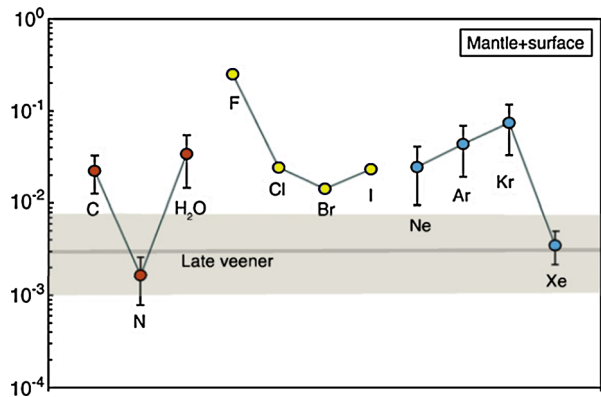
(2010) argued that most of the late accreted mass delivered to the terrestrial planets had a shallow cumulative size-frequency distribution, with most of the mass residing in its largest members. This led Brasser et al. (2016b) and Brasser and Mojzsis (2017) to conclude that most of the mass of late accretion delivered to Earth and Mars consisted of single events and were the result of a collision of a lunar/Ceres-sized body with the Earth/Mars.

The best isotopic match to Earth's H and N isotopic composition is CI and CM carbonaceous chondrites where 2–4 weight percent of the Earth composed of such material can account for the abundances of Earth's water and nitrogen (Alexander 2017; Halliday 2013). This amount of volatile-rich material also accounts for the observation that many of the more highly volatile elements are present in the bulk Earth at concentrations well below typical chondritic abundances, but are present in chondritic relative abundances (Fig. 12). For single stage depletion processes, such as core formation for the HSE or some volatile loss mechanism for the highly volatile elements, the chondrite-normalized abundances should correlate with the metal-silicate distribution coefficient of the element for HSEs, or with the condensation temperature for volatile elements. In this case, for example in Fig. 13, the normalized abundances of the volatile elements should continue along the trend shown by the dotted line. The fact that the chondrite-normalized volatile element abundances plateau at around 0.001 for elements with condensation temperatures less than 800°K is most easily explained by adding a small amount of material with chondritic abundances of these elements. This addition will most dramatically increase the relative concentration of only the most highly depleted elements, and instill in just those elements concentrations relative to one another similar to the elemental ratios seen in chondrites. In contrast, for the elements that were originally less depleted, the amount of these elements added by the small late accretion will increase their concentration by too little to overprint the initial elemental signature of the process that caused their depletion. In other words, these less depleted elements will not be present in chondritic relative proportions with respect to one another. The plateau in chondrite-normalized abundance of the elements that would be most depleted either by core formation or volatile loss (e.g. Fig. 13) gives rise to the idea that both the highly volatile and HSE were added back to the Earth after some processes, atmosphere loss for the volatile elements and core formation for the HSEs, severely reduced the abundance of these elements in Earth's outer layers.

Given the very high abundance ratios of volatile to refractory elements in comets, at the limits of comet contributions dictated by the H and N isotopic composition difference between comets and Earth, comets are unlikely to imprint a signature on other elements in the Earth (Marty et al. 2017). On the other hand, the Ru isotopic results for
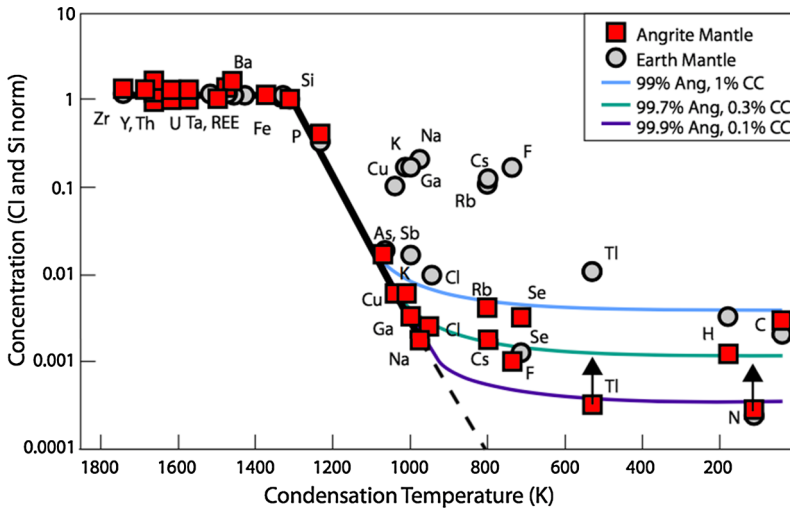
Fig. 13 Estimated elemental concentrations in the mantles of Earth and the angrite parent body. In a body completely devoid of the more highly volatile elements, the elemental abundance pattern would be expected to follow the dashed line. The colored lines show the enhancement in abundance of the most volatile elements through the addition of a small amount of carbonaceous chondrite. Figure from Sarafian et al. (2017)

Earth's mantle require that if Earth acquired its water through accretion of CI and CM chondrites, most of this material must have accreted before core formation was complete so that the Ru they provided was removed from the mantle by core formation processes. Volatile element analyses (Sarafian et al. 2017) in two of the oldest members of the angrite group of igneous meteorites that crystallized at 4563.37 ± 0.25 Ma (Amelin 2008; Brennecka and Wadhwa 2012) confirm the volatile-element depleted nature of the angrite parent body, but also show the more highly volatile element abundances to plateau at about 0.001 times CI values (Fig. 13). The interpretation provided for these results is that the angrite parent body accreted of order 0.1 to 1% by weight carbonaceous chondrite before the time when the angrite melts were produced (Sarafian et al. 2017).

   This result supports the idea that Earth's current volatile inventory largely reflects the mix of materials accreted to Earth throughout its formation, not just in the final stages, and that mix contained at least a few percent of volatile-rich material similar to carbonaceous chondrites (Brasser et al. 2018; Dauphas 2017). While the HSE abundances in Earth's mantle require addition of material after chemical communication between core and mantle ceased, there is no other time constraint on the late accretion. Evidence for addition of material with relative HSE abundances similar to chondritic to the mantles of Mars, the Moon, and even the parent body of the HED meteorites (Day et al. 2012) suggests that continued addition of material with chondritic HSE relative abundances may simply be an intrinsic part of the latter stages of planetary accretion (Wetherill 1975) when the rate of incoming material subsided to the point that the kinetic energy of collisions no longer caused global stirring of the mantle to the point of allowing effective chemical exchange with the core.

4.3 Collisional Erosion

Another major compositional distinction between the terrestrial planets and chondritic meteorites is their variability in the ratio of total iron to silicon. Some groups of chondrites clearly

Fig. 14 Ratio of atomic iron to silicon in different chondrites and terrestrial planets. The yellow line gives the Fe/Si ratio of the Sun (Palme and O'Neill 2014). Data from: chondrites (Wasson and Kallemeyn 1988), Earth (McDonough and Sun 1995), Mercury and Venus (Morgan and Anders 1980), Mars (Wänke and Dreibus 1988), and Moon (Dauphas et al. 2014a) assuming a core diameter of 300 km (Shimizu et al. 2012). The chondrites are arranged in arbitrary order from the inner to the outer edge of the asteroid belt
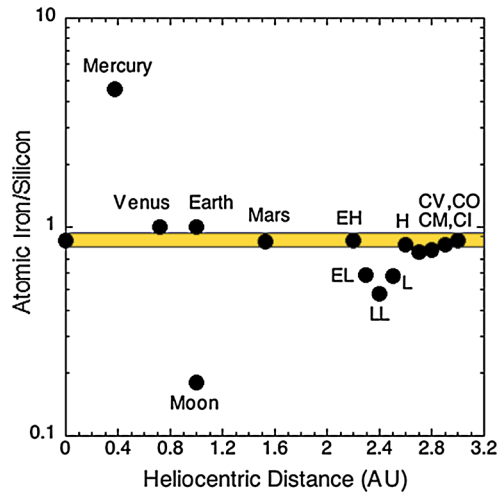
preserve a divergence from Solar composition in the ratio of Fe to Si that is not easily explained by volatility. While all the carbonaceous chondrites and the high-Fe ordinary and enstatite chondrites have Fe/Si ratios similar to the Solar value, the EL, L- and LL-chondrites show substantially sub-solar Fe/Si ratios (Fig. 14). Although the relative temperatures of iron-metal and forsterite/enstatite condensation can change depending on the assumed pressure during condensation in the Solar nebula (Grossman 1972), the similar bulk moderately volatile lithophile element contents of H and L chondrites does not support the possibility that the Fe/Si ratio difference between these two groups of ordinary chondrites reflects different ratios of refractory and volatile-rich components. Instead, the iron-silicate separation more likely reflects mechanical separation of metal from silicate within the region of the protoplanetary disk where the different groups of ordinary and enstatite chondrites formed.

Another mechanism to separate iron from silicon is core formation. While core formation will not change the Fe/Si ratio of the bulk planetesimal, it does effectively concentrate Fe in the core and reduce its abundance in the mantle. Collisions of sufficient energy to eject material at velocities exceeding the escape velocity of the planetesimal/planet potentially can be an effective process in modifying planet bulk composition if the impact selectively separates crust from mantle from core (Asphaug et al. 2006). The most obvious evidence for this process is seen in the iron to silicon ratios of the terrestrial planets and the Moon (Fig. 14). The low iron content of the Moon is a persuasive observation in support of the idea that the Moon formed predominantly from the mantle of Earth when a giant impactor hit Earth near the end of Earth's accretion (Stevenson 1987; Zhang et al. 2012). The high Fe/Si ratio of Mercury may reflect that Mercury is the remnant of a giant collision that stripped a good portion of its silicate mantle to leave behind a core-dominated planet (Benz et al. 2007, 1988). Because of the widely differing physical properties of iron metal and silicate, collisions between planetesimals of sufficient energy to push ejecta above escape velocities can be an effective way to separate silicate from metal (Bonsor et al. 2015).

Whether collisional erosion can be effective at changing the refractory lithophile element contents of planets by separating a differentiated crust from residual mantle is not as clear. This possibility was most recently considered (O'Neill and Palme 2008) to explain the elevated ^{142}Nd/^{144}Nd of Earth's mantle compared to most meteorites (Boyet and Carlson 2005). As ^{142}Nd is generated by the radioactive decay of 103 Ma half-life ^{146}Sm, one explanation for the elevated ^{142}Nd of Earth is that Earth formed with a Sm/Nd ratio higher

than chondritic (Boyet and Carlson 2006; Caro et al. 2008). As Sm and Nd are neighboring rare-earth elements that share similar geochemical properties as refractory lithophile elements, processes such as volatile-refractory element or metal-silicate separation would not obviously modify the Sm/Nd ratio. Sm and Nd can be fractionated by partial melting of a silicate mantle, however. As silicate partial melts tend to be less dense than their source materials, such melts often rise to form planetary crusts. The amount of Sm-Nd fractionation during this process, however, is quite small, so large masses of such crust would have to be removed to explain Earth's elevated ^{142}Nd/^{144}Nd through this mechanism. For example, the 18 ppm higher ^{142}Nd/^{144}Nd of Earth compared to ordinary chondrites would require loss of approximately a continental crust's mass (2.3×10^{22} kg) worth of material with the degree of REE enrichment typical of continental crust (e.g. Nd concentrations about 40 times higher than chondritic with Sm/Nd ratios about 40% lower than chondritic, Carlson and Boyet 2008). For planetesimal crusts that are characterized by lower Nd enrichment, for example eucrites that typically have Nd concentrations some 10–20 times higher than chondritic with Sm/Nd ratios only 2–3% lower than chondritic, correspondingly greater masses would have to have been lost from the materials that accumulated to form Earth. Collisional erosion would thus struggle to explain the degree of ^{142}Nd excess in Earth's mantle if due solely to ^{146}Sm decay. Another means to create variability in ^{142}Nd, however, notes that ^{142}Nd is produced mostly by the s-nucleosynthetic process whereas ^{144}Nd is produced by a combination of s- and r-process nucleosynthesis (Arlandini et al. 1999). Thus, changes in the ratio of r- to s-process components in the nebula would create variability in ^{142}Nd that is not related to ^{146}Sm decay. Such nucleosynthetic variability in Nd has now been clearly documented (Bouvier and Boyet 2016; Burkhardt et al. 2016; Carlson et al. 2007; Gannoun et al. 2011). Carbonaceous chondrites have the lowest ^{142}Nd/^{144}Nd followed by ordinary chondrites with only some enstatite chondrites extending the chondritic array to values of ^{142}Nd/^{144}Nd as high as seen in Earth's mantle. Neodymium thus joins Mo and Ru as one of the elements that display nucleosynthetic variability where Earth is one end member of the variability while carbonaceous chondrites are the other end member.

Whether or not atmospheres can survive the large impacts involved in planet growth is an interesting question without a firm answer at the present time. The high He/Ne ratio of the incompatible element depleted portion of Earth's mantle has been used to argue for multiple large impacts that each stripped significant portions of the atmosphere from the growing Earth (Tucker and Mukhopadhyay 2014). Models of impacts indicate that the efficiency of atmospheric stripping depends on impactor size (Schlichting et al. 2015). Even giant impacts are unlikely to remove more than 20% of the atmosphere (Genda and Abe 2003). The presence of an ocean on the planet surface can substantially enhance atmospheric loss during a giant impact (Genda and Abe 2005), but whether or not an atmosphere can be severely eroded in this manner remains to be investigated.

5 Conclusions

The understanding of the processes of planet formation is growing rapidly through a combination of theoretical models that are increasingly being coupled to observational information provided by chemical and isotopic studies of meteorites and the terrestrial planets. Some of the newer theoretical models such as pebble accretion (Ormel and Klahr 2010; Lambrechts and Johansen 2012; Johansen and Lambrechts 2017; Levison et al. 2015a, 2015b) have yet to be investigated for their potential to create the compositional diversity discussed in this paper. A major obstacle is that the pebbles predominantly form in the outer

Solar System supplying the terrestrial planets with too much volatile-rich material (Levison et al. 2015b). Observations of exoplanetary systems provide yet another new avenue to develop general models of the planet formation process that can explain not only our Solar System, but the diversity of other planetary systems now seen.

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