


# Geochemical models of core–mantle differentiation

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**Abstract** The core–mantle differentiation process is one of the most significant events in the Earth’s early history, which profoundly affects the Earth’s internal structure. According to the simple core–mantle differentiation mechanism, elements such as iron and nickel should be extracted from silicate to form an iron-rich proto-core, and the residual silicate materials form the proto-mantle. However, the composition of the lower mantle and the core remains controversial, which largely affects the partition of elements, thus the referred differentiation process of the Earth. In recent years, many experimental studies on the partition coefficient of siderophile elements between metal and silicate under high-temperature and high-pressure conditions have put forward new ideas on the issues around Earth’s core–mantle differentiation. Meanwhile, some researchers suggested that the redox state of the Earth’s mantle changes during its formation and evolution, and many isotope geochemistry studies support that some enstatite chondrites have a common nebular precursor as the Earth. These new studies bring dispute on the Earth’s building materials, which dominates the core–mantle

differentiation process and largely affects the partitioning behaviors of elements during the core–mantle differentiation. This chapter aims to review recent experimental studies on the siderophile element geochemistry and discussions on the Earth’s building blocks.

**Keywords** Proto-Earth · Siderophile element · Earth’s building block · High-temperature and high-pressure experiment · Enstatite chondrite

## 1 Introduction

In the classic models of terrestrial planet formation, planetary embryos that formed from larger planetesimals perturb each other, resulting in “giant impacts”, and eventually get stable orbits, becoming planets. The early history of the Earth is marked by its core–mantle differentiation, which determines the compositions of the Earth’s proto-mantle and proto-core. However, Earth’s core–mantle differentiation process is less understood due to the continuous differentiation and lack of samples. Compositional constraints on the early Earth thus rely on indirect methods, such as experimental and theoretical modeling the composition of the Earth’s lower mantle and its core or searching for the Earth’s possible building blocks.

In this chapter, we mainly focus on the siderophile element geochemistry and the Earth’s building blocks. We start with siderophile element geochemistry and discuss the progress in estimating the compositions of the bulk Earth (BE) and the bulk silicate Earth (BSE). Then we pay attention on the composition of proto-Earth and propose possible models of the Earth’s building blocks. This part covers similar ground to some earlier reviews. In a

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comprehensive study on highly siderophile elements in terrestrial planets by Walker (2009) and Righter et al. (2015), a great deal of information about the building block of the Earth can be found in Moynier and Fegley (2015), and some new studies (e.g. Yoshizaki and McDonough 2021; Alexander 2022), which explored the chondritic component model of the Earth with detailed analysis on its elemental and isotopic composition. Please refer to Lü and Liu (2022) in this volume for more information on the formation models of terrestrial planets and the composition of the Earth's core.

## 2 Siderophile element geochemistry

### 2.1 Siderophile element geochemistry

Siderophile (iron-loving) elements strongly partition into the metallic phase relative to the silicate phase during the cosmochemical and geochemical processes, also some siderophile elements are chalcophile and tend to enter sulfide melts and some sulfide minerals (Goldschmidt 1937). The partitioning of a siderophile element M between metal and silicate melt can be described by the following reaction if M exists in silicate melt as oxide:



where  $n$  is the valence state of the element M in the silicate melt. Its partition coefficient ( $D$  value) between metal and silicate melt is defined as:

$$D_M = \frac{X_M^{\text{metal}}}{X_{MO_{n/2}}^{\text{silicate}}} \quad (2)$$

where  $X_M^{\text{metal}}$  is the mole fraction of the element M in the metallic melt and  $X_{MO_{n/2}}^{\text{silicate}}$  is the mole fraction of the element's oxide in the silicate melt. If  $n$  is known, the effects of oxygen fugacity can be removed through the use of the exchange coefficient ( $K_D$ ), which is defined as:

$$K_D = \frac{D_M}{D_{Fe}^{n/2}} \quad (3)$$

where  $D_{Fe}$  is the partition coefficient of iron.

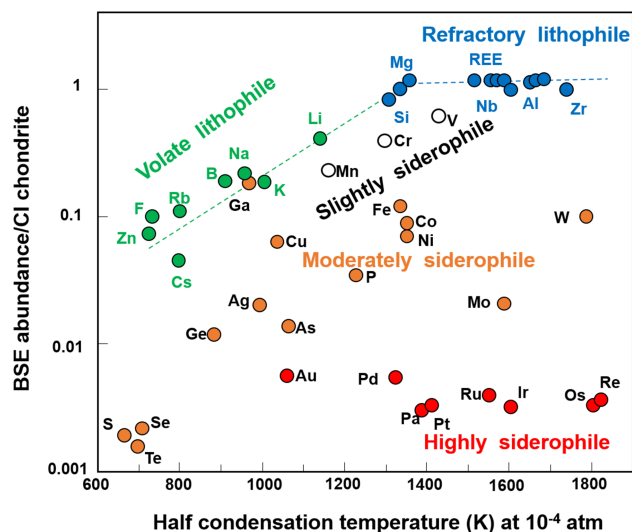
In the actual research, researchers usually parameterize the effects of pressure and temperature on the partitioning of element M using the relationship:

$$\log_{10}(K_D^M) = a_M + \frac{b_M}{T} + \frac{c_M P}{T} \quad (4)$$

with pressure in GPa and temperature in Kelvin. This equation includes no compositional dependences.

According to the strength of affinity (siderophilic tendency), siderophile elements are commonly divided into sub-groups based on experimental determined metal-silicate partitioning coefficients at one atmosphere condition (e.g. Borisov et al. 1994; Kimura et al. 1974) (Fig. 1): (1) highly siderophile elements (HSE; Re, Os, Ir, Ru, Pt, Rh, Au, Pd), are characterized by metal-silicate partition coefficient ( $D$  value) greater than 10,000; (2) moderately siderophile elements (MSE: including Mo, W, Fe, Co, Ni, P, Cu, Ga, Ge, As, Ag, Sb, Sn, Tl, Bi, S, Se, Te) are characterized by metal-silicate  $D$  value ranging from 10 to 1,000; and (3) slightly siderophile elements (SSE; Mn, Cr, V, Pb), whose metal-silicate  $D$  value is less than 10, but greater than 1 (Day 2020; Walker 2016). The unique affinity of siderophile elements makes them very vital tools to explore some crucial issues in Earth and planetary science, such as the origin and process of nucleosynthesis of the solar system, planetary differentiation process, the composition of early mantle reservoir, mantle geodynamics, the late veneer process, and so on (e.g., Dale et al. 2012; Day et al. 2016, 2017; Day 2020; Fischer et al. 2015; Siebert et al. 2011, 2013; Siebert and Shahar 2015; Walker 2016).

The primitive upper mantle (or bulk silicate Earth, BSE) has a refractory lithophile element ratio of  $\sim$  CI chondrite, implying that the Earth's refractory elements content is close to that of CI chondrites, and the depletion of siderophile elements in the mantle is due to their partitioning to the Earth's core (e.g., Allegre et al. 1995; McDonough and Sun 1995). However, as pointed out by Ringwood (1966) that the concentration of siderophile elements such as Ni and Co in the Earth's mantle seems too high to be

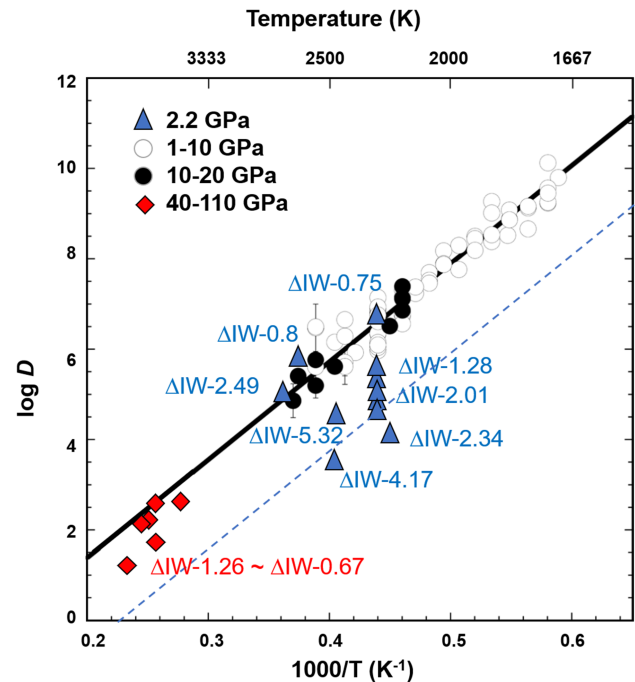


**Fig. 1** Element abundances of the bulk silicate Earth (BSE) normalized to CI chondrite, which is based on half condensation temperature. Modified from Siebert and Shahar (2015)

explained by the simple mass balance between the mantle and the core. Ever since then, many studies have tried to solve the “excessive siderophile elements” problem from different aspects: (1) siderophile elements becoming much less siderophile at high-pressure and high-temperature (high P–T) conditions (e.g. Fischer et al. 2015; Holzheid et al. 2000; Li and Agee 1996, 2001; Siebert et al. 2012; Wade and Wood 2005); (2) the composition of metals in the Earth’s core is impure (e.g. Cottrell and Walker 2006; Chabot et al. 2004; Walker 2009); (3) imperfect metal-silicate equilibration during core formation (e.g., Arculus and Delano 1981; Jones and Drake 1982; Jones and Drake 1986); and (4) accretion of a late veneer (e.g. Chou 1978; Li 2022; Walker 2009).

## 2.2 The shift of partitioning behavior of siderophile elements

As the planet grows, the huge internal pressure is likely to cause the element partitioning behavior to deviate strongly from the low-pressure partition experimental results because the affinity of some siderophile elements may be greatly weakened under high P–T conditions. For example, Cottrell and Walker (2006) carried out high-temperature (2273–2773 K) experiments to study the partitioning of platinum (Pt) between metal and silicate. Their results revealed that the partition coefficient of Pt ( $\log D_{(Pt)}$ ) decreases greatly with increasing temperature and shows dependence on oxygen fugacity ( $fO_2$ ) of the system (Fig. 2) (Cottrell and Walker 2006). The temperature effect on the partitioning behavior of Pt was further confirmed by many other experimental studies (e.g., Bennett et al. 2014; Mann et al. 2012). Recently, Suer et al. (2021) obtained metal-silicate partition coefficients of Pt ( $D_{(Pt)}$ ) at conditions close to the bottom of the Earth’s magma ocean by Laser-Heated Diamond Anvil Cell (LHDAC) experiments (43–111 GPa, 3600–4300 K), and demonstrated that  $D_{(Pt)}$  decreases to a much smaller value of 21.22 (111 GPa, 4300 K). Consequently, the mantle was likely enriched in Pt immediately following core-mantle differentiation and subsequent process such as iron exsolution or sulfide segregation is needed to remove excess platinum and to explain the mantle’s modern HSE signature (Suer et al. 2021). However, these experimental results also show another effect that should be evaluated on the partitioning behavior of siderophile elements, the oxygen fugacity of the system (Bennett et al. 2014). For example, Cottrell and Walker (2006) reported that a much lower  $\log D_{(Pt)}$  might owing to a much reduced ( $\Delta IW$ –4.17) experimental system than the experiments from other groups. And the experimental results from Suer et al. (2021) also indicated that a more reduced condition may result in a relatively smaller  $\log D_{(Pt)}$  as the smallest  $\log D_{(Pt)}$  (1.02) corresponds to a



**Fig. 2** Partitioning of Pt between metal and silicate. Metal-silicate partitioning coefficients of  $\log D_{(Pt)}$  vary as a function of temperature. The circles are from experiments between 1 and 20 GPa (compiled by Suer et al. 2021 from Bennett et al. 2014; Ertel et al. 2006; Mann et al. 2012 and Médard et al. 2015); the triangles are results from Cottrell and Walker (2006) at 2.2 GPa; and the red diamonds are from experiments higher than 40 GPa (Suer et al. 2021)

most reduced condition ( $\Delta IW$ –1.26) in their experimental results (Fig. 2). In addition, as mentioned by Suer et al. (2021), the metallic phase in their experiment contains 3.51 wt% Si, 4.34–6.86 wt% O, and 0.64–8.4 wt% S. The light elements in the core will also affect the partitioning behavior of siderophile elements between silicate and metal, which need to be rationalized when we take siderophile elements as powerful tools to discuss issues related to the formation and differentiation of the proto-Earth.

Like platinum, most siderophile elements show smaller  $D$  values with increasing pressure and temperature (Mann et al. 2012; Righter and Drake 1997). However, the “good” theories to explain the excess HSE in the Earth’s mantle need to be consistent with most of the HSE because the ratios of most HSE appear to be near-chondritic (Fig. 1). Righter et al. (2008) studied the partitioning of palladium (Pd) at high P–T and found that  $\log D_{(Pd)}$  decreases sharply with increasing temperature and suggested that the superchondritic Pd/Ir ratio in the Earth’s primitive upper mantle (Becker et al. 2006) can be explained by metal-silicate equilibrium at magma ocean pressure and temperature conditions. Furthermore, Mann et al. (2012) systematically investigated the partitioning of Ru, Rh, Pd, Re, Ir, and Pt between liquid metal and silicate at high P–T conditions

(3.5–18 GPa and 2423–2773 K) and showed that the partition coefficients of all platinum group elements (PGE) decrease with increasing pressure and to a greater extent with increasing temperature. However, the decrement in  $D$  values of PGE at a single P–T– $fO_2$  equilibration condition that prevailed during core–mantle differentiation of the Earth (e.g., 60 GPa, 3560 K) is insufficient to explain their abundances in the mantle. Therefore, an additional process, such as a late veneer composed of some type of chondritic materials, is still required to account for the excess HSE in the Earth's mantle. As mentioned by Mann et al. (2012), the light element carbon (C) or sulfur (S) in the metal will make HSE less siderophile. Laurenz et al. (2016) confirmed experimentally that the increasing sulfur content in the metallic phase has a similar effect on the metal–silicate partition coefficient of Ir, Pt, Pd, and Ru as increasing pressure and temperature. And Rubie et al. (2016) further suggested that sulfur was added throughout the planetary accretion process. Therefore, when using the partition coefficient of HSE to explain the abundance of these elements in the Earth's mantle and constrain the formation process of the Earth's core, we need to consider not only the effect of temperature and pressure, but also the light elements in the Earth's core, and the oxygen fugacity of the system.

If the final equilibrium occurs at the bottom of the magma ocean with a depth of 1200–1500 km, corresponding to an average P–T condition between 45–65 GPa and 3500–4000 K (Righter et al. 2015), then equilibrium between metal and silicate should also account for the current mantle ratio of the moderately siderophile elements, such as Ni and Co. Thibault and Walter (1995) found that the partitioning of Ni and Co between molten iron and silicate [ $D_{(Ni)}$  and  $D_{(Co)}$ ] decreases with increasing pressure and temperature and the pressure effect is more profound than temperature. Li and Agee (1996, 2001) showed that the partitioning of Ni and Co between S-bearing iron and silicate decreases largely with pressure and suggested that the observed Ni/Co ratio in the Earth's mantle can be explained by core segregation at the base of the magma ocean. Later, many experimental studies have approved that both Ni and Co become less siderophile with increasing pressure. Bouhifd and Jephcoat (2003, 2011) used LHDAC to further expand the experimental condition to  $\sim 52$  GPa and  $\sim 3500$  K. Their experimental results demonstrated that Ni and Co partitioning coefficients converge at a pressure of around 30 GPa (Fig. 4 in Bouhifd and Jephcoa 2011). However, Siebert et al. (2012) measured  $D_{(Ni)}$  and  $D_{(Co)}$  at super-liquidus conditions using LHDAC (35–74 GPa, 3100–4400 K), and found that both  $D_{(Ni)}$  and  $D_{(Co)}$  decrease with increasing pressure and reach the values that are required to yield present mantle concentrations of Ni and Co at  $\sim 50$  GPa. Another study about the

partitioning of Ni, Co, V, Cr, Si, and O between metal and silicate at high P–T conditions also confirmed the deeper magma ocean scenario (Fischer et al. 2015). But the later study proposed that the temperature effect on  $D_{(Ni)}$  and  $D_{(Co)}$  is profound from low pressure to 45 GPa (Fig. 3).

Based on Eq. 4, we use the least-squares regression method and obtain the following results for coefficients  $a$ ,  $b$  and  $c$ :

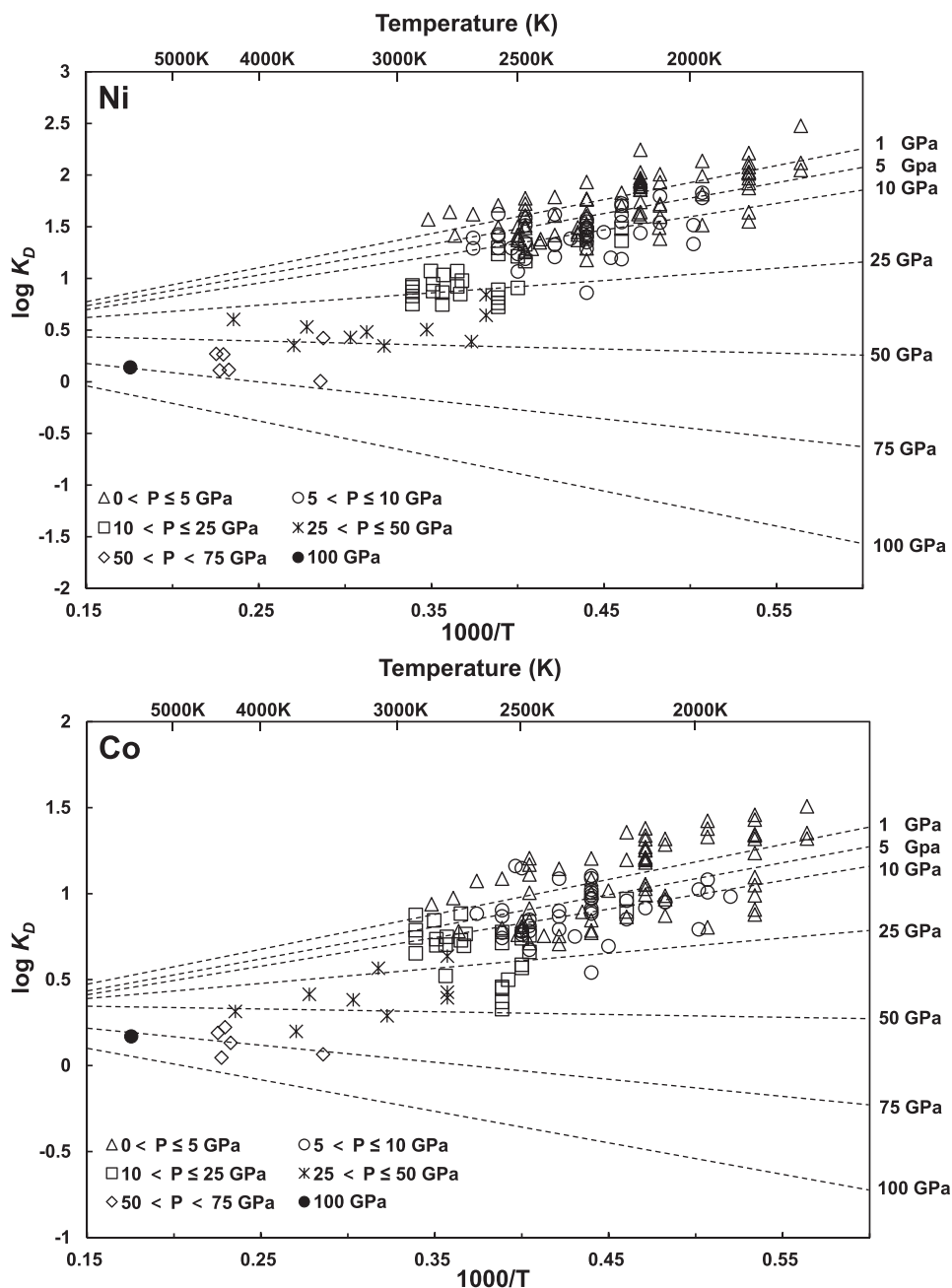
$$\log_{10}K(Ni) = 0.27(1) + \frac{3368(191)}{T} - \frac{75(1)P}{T} \quad (5)$$

$$\log_{10}K(Co) = 0.15(1) + \frac{2112(176)}{T} - \frac{44(5)P}{T} \quad (6)$$

The least-squares regression for Ni (174 data) and Co (155 data) shows a remarkable fit to Eqs. (5) and (6) with  $R^2 = 0.933$ . The regression equations are plotted in Fig. 3 as a function of reciprocal temperature (x-axis) and pressure (symbol shape).

Besides the high P–T conditions during core–mantle differentiation, the redox state of the proto-Earth also affects the partitioning of the siderophile elements between its mantle and core. Compared with chondrites, the cumulative effect on the partitioning of siderophile elements is reflected in the concentration of these elements in the present mantle. The concentration ratios of elements such as V/Sc and Zn/Fe show that the oxygen fugacity ( $fO_2$ ) of the mantle has not changed much in the past 3 billion years (Berry et al. 2008; Dauphas et al. 2009; Li and Lee 2004). However, the depletion of siderophile elements such as Cr and V in the mantle is not consistent with  $fO_2$  inferred from its FeO content (Frost et al. 2008), therefore, some studies suggest that the  $fO_2$  evolves over time during the Earth's accretion, from a more reduced condition increased with time to a more oxide condition as current value (e.g., Wood et al. 2006, 2008). The major shift in oxygen fugacity ( $fO_2$ ) of the terrestrial mantle from reduced to more oxidized may result from the disproportionation of ferrous iron into ferric iron plus metal, as occurs in bridgmanite at high pressure (Frost et al. 2004; Frost and McCammon 2008). According to the LHDAC partition experiments by Siebert et al. (2013), the highly reduced accretion model results in a high concentration of Si ( $> 10$  wt%) and low concentration of O ( $< 1$  wt%) in the core. But the Si content estimated by this model is incompatible with cosmochemical ( $\leq 8$  wt% Si) (Allègre et al. 1995; Javoy et al. 2010) and geophysical constraints (1–4 wt% Si) (Antonangeli et al. 2010; Badro et al. 2007). Instead, Siebert et al. (2013) supported the scenario that the Earth accreted from oxidized material, such as carbonaceous chondrites, ordinary chondrites, or a mixture (21% FeO in the mantle) of chondrites (Fitoussi et al. 2012), and then gradually reduced (through O solubility in the core)

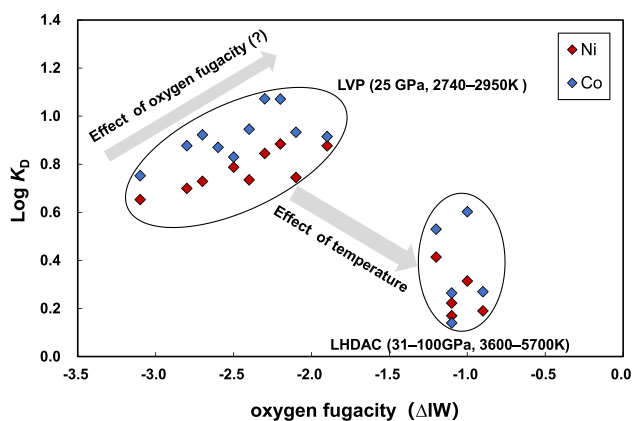
**Fig. 3** Exchange coefficients ( $K_D$ ) for Ni and Co plotted as a function of reciprocal temperature. Data are from Thibault and Walter (1995), Hillgren et al. (1996), Jana and Walker (1997), Geßmann and Rubie (1998), Bouhifd and Jephcoat (2003, 2011, 2013), Chabot et al. (2005), Corgne et al. (2008), Kegler et al. (2008), Richter et al. (2010), Siebert et al. (2011, 2012, 2013), Bouhifd et al. (2013), and Fischer et al. (2015). The dashed lines correspond to least-squares regressions Eqs. 5, 6 to these data



until the FeO content of the mantle reaches the present-day value.

As mentioned in recent LHDAC works by Fischer et al. (2015) on the partition of MSE, the oxygen fugacity inside the diamond anvil cell is around  $\Delta IW-1$ , and the partitioning behaviors of Ni and Co change with both pressure and temperature up to  $\sim 50$  GPa. However, we do notice that the effect of  $fO_2$  on the partition of Ni and Co at 25 GPa is quite profound. Both  $D_{(Ni)}$  and  $D_{(Co)}$  increase with oxygen fugacity condition changing from a more reduced condition ( $\Delta IW-3.1$ ) to a relatively oxide condition ( $\Delta IW-1.9$ ) (Fig. 4). The increase of  $fO_2$  will balance off the effect

of high pressure and high temperature. If the  $fO_2$  changed from  $\Delta IW-4$  to around  $\Delta IW-2$  during the accretion of the Earth (Fischer et al. 2015; Wade and Wood 2005), then the partitioning of Ni and Co between metal and silicate increased through time, leading to depletion of Ni and Co in the mantle. Thus, it will need to increase the pressure or temperature to a higher value to explain the “excess” Ni and Co in the mantle. On the other hand, if the Earth’s magma ocean started as a more reduced material ( $< \Delta IW-2$ ), the  $D_{(Ni)}$  and  $D_{(Co)}$  may be smaller than the LHDAC experimental result from Fisher et al. (2015). Along this line, the pressure and temperature condition of the bottom



**Fig. 4** Partitioning of Ni and Co between liquid metal and liquid silicate at 25–100 GPa. The data are from Fischer et al. (2015). The experiments carried out in large volume press (25 GPa) result in oxygen fugacity changing from  $\Delta IW$ –1.9 to  $\Delta IW$ –3.1, and those carried in LHDAC show consistent oxygen fugacity around  $\Delta IW$ –1. LVP: Large Volume Press. LHDAC: Laser-Heated Diamond-Anvil Cell

of the magma ocean constrained by the partitioning behavior of Ni and Co will be smaller than 45–65 GPa and 3500–4000 K. Apparently, more work needs to be done to further constrain the effect of oxygen fugacity on the partitioning behaviors of siderophile elements, especially those with more reduced conditions and high P–T conditions.

### 2.3 The light element content of the Earth’s core

The Earth’s core was proposed to compose of an iron-nickel alloy with a small amount of light elements due to the density deficits of the Earth’s liquid outer core and its solid inner core (Birch 1952, 1964). Candidates for the light elements include sulfur (S), silicon (Si), oxygen(O), carbon (C), phosphorus (P), and hydrogen (H) (e.g., Alfe et al. 2002; Bazhanova et al. 2017; Blanchard et al. 2022; Clesi et al. 2018; Fichtner et al. 2021; Fischer et al. 2020; Kamada et al. 2012; Kinoshita et al. 2020; Mashino et al. 2019; Ozawa et al. 2016; Zhang and Yin 2012; Zhang et al. 2020). As mentioned above, the light element content in the metallic phase shows a different effect on the partitioning behavior of siderophile elements, which is consistent with the assumption that the excess of siderophile elements in the mantle may be related to the composition of the Earth’s core. Brett (1984) found that the increase of sulfur content in the liquid metal can significantly reduce the solubility of HSE in the metal. The addition of light elements will also make MSE less siderophile. For example, the high P–T experiments (up to 25 GPa and 2623 K) by Li and Agee (2001) demonstrated that both  $D_{(Ni)}$  and  $D_{(Co)}$  decrease with increasing sulfur content in the metal. Tuff et al. (2011) investigated the effect of Si on metal-

silicate partitioning in Fe–Ni–Co–Mo–W–V–Cr–Nb–Si system and found that increasing Si content tends to make Ni, Co, Mo, W, and V more lithophile. The LHDAC experiments on the partitioning of MSE mentioned above show that the partitioning of Si between metal and silicate also increased largely with pressure (Fisher et al. 2015; Suer et al. 2021). Therefore, the reduction in  $D_{(Ni)}$  and  $D_{(Co)}$ , which are measured under high P–T conditions, may also be a coordinated effect of the light element content in the “core”.

Jana and Walker (1997) reported the impact of carbon on element partition at 5–8 GPa and 2273–2573 K. When carbon is saturated, Ni and Co become less siderophile, but the siderophile affinity of W and Mo increase with increasing carbon content. Based on the observation that phosphorus becomes lithophile at the carbon saturation condition and the fact that phosphorus is depleted in the mantle, they further concluded that core formation did not occur at carbon saturation. Chabot et al. (2004) did experiments on Fe–Ni–Co–C system at higher pressure and temperature (7 GPa, 2273 K), and showed that the addition of 6.4 wt% carbon in metal can cause both  $D_{(Ni)}$  and  $D_{(Co)}$  decrease 30%. Another siderophile element tungsten (W) is extremely sensitive to the carbon content of the metal alloy, becoming about an order of magnitude more siderophile at carbon saturation (Cottrell et al. 2009).

Given that more than one light element may be present in the Earth’s core (e.g., Hirose et al. 2013, 2021; Li and Fei. 2014; Litasov and Shatskiy. 2016; Li 2021; Poirier 1994), the partition coefficient of siderophile elements in a Fe-light elements system has also been studied. For instance, Buono et al (2013) performed cohenite-bearing experiments and indicated that  $D_{(Ni)}$  decreases as S + C content increases at a pressure between 3–6 GPa. Corgne et al. (2009) carried out calculations to explain the mantle contents of siderophile elements (Ni, Co, V, Mn, Cr, and Nb), based on partitioning and metallurgy data, revealed that Vanadium (V) became significantly less siderophile with the increasing oxygen content of core-forming materials, while the behaviors of Ni, Co, Cr, and Mn are little affected. Also, Corgne et al. (2009) pointed out that the amount of oxygen in the core required by the single-stage model ( $\sim$  2–5 wt%) was insufficient to explain the entire density deficit of the core relative to pure Fe (e.g., Poirier 1994). A combination of oxygen and other light elements should therefore be considered, and Si is one of the most likely candidates, which is consistent with the LHDAC studies that oxygen and silicon are the two most important light elements in the Earth’s core (e.g., Siebert et al. 2011; Fischer et al. 2015).

The light elements in the Earth’s core not only affect the partitioning of siderophile elements between metal and silicate but also strongly restrict the core’s geographical

properties (e.g., sound velocities, conductivity, density). For example, Alfe et al. (2002) investigated the chemical potentials of S, O, and Si in liquid and solid iron by comparing ab initio calculations with seismic data. Assuming that the solid inner core and liquid outer core are in thermodynamic equilibrium, they found that the presence of oxygen in the core is essential to account for the inner-outer core density jump because oxygen partitions into the liquid is much more strongly than sulfur and silicon. Thus, they proposed that the inner core contains  $8.5 \pm 2.5$  at.% S and/or Si and  $0.2 \pm 0.1$  at.% O, and the outer core contains  $10 \pm 2.5$  at.% S and/or Si and  $8 \pm 2.5$  at.% O (Alfe et al. 2002). Morard et al. (2013) calculated the Earth's core composition according to density measurements of liquid iron alloys at high pressure. And they emphasized that a composition of 2 wt% of Si and 6 wt% of S provides the best agreement of the geophysical constraints (Morard et al. 2013). Badro et al. (2014) calculated seismic wave velocities and densities in the Fe–(Ni, C, O, Si, S) system and suggested that oxygen is a major light element in the core, whereas Si, S, and C are not required. They also demonstrated that the concentration of silicon in the outer core cannot be  $> 4.5$  wt%, and the concentration of sulfur must be below 2.4 wt%. On the other hand, Fe<sub>2</sub>S and FeS were proposed to be a stable phase in the Earth's solid inner core (330–364 GPa) based on the evolutionary crystal structure prediction algorithm USPEX (Bazhanova et al. 2017). However, Zhang et al. (2020) simulated the partition of S between solid and liquid iron under Earth's core conditions (150–330 GPa, 4000–6000 K). And they showed that  $D_{(S)}$  is remarkably pressure-dependent when pressures lower than 250 GPa, but almost pressure independent with an averaged value of  $0.75 \pm 0.07$  at a pressure higher than 250 GPa, thus the partition of S was insufficient to account for the observed density jump across the Earth's inner core boundary and its roles on the geodynamics of the Earth's core was overestimated.

Recently, other elements in the core have also aroused concern. Liu et al. (2020) employed first-principles molecular dynamics (FPMD) simulation to study Magnesium (Mg) partitioning between silicate melt and liquid iron under 22.3–120.4 GPa, 3116–4500 K. They found that the equilibrium constants are dependent on temperature and proposed that Mg partitioned into the core during giant impacts and reached a concentration of about 2 wt%, which can precipitate out of the core at around 3.5 Ga, much earlier than the onset of inner core nucleation. During the subsequent evolution of the Earth, Si concentration in the Earth's core will remain constant while Mg and O concentrations decrease greatly. Consequently, the current Si concentration in the core reflects the accretion processes of the Earth while O and Mg concentrations in the core are the combined result of both the accretion and the subsequent

evolution of the Earth's core (Liu et al. 2020). Recently, Wang et al. (2022) have performed thermodynamic integration (TI) calculations based on FPMD simulation to investigate the partition coefficients of noble gases (NG: He, Ne, Ar, Kr, Xe) between liquid Fe and MgSiO<sub>3</sub> melt under core-mantle equilibrium conditions (10–135 GPa, 2300–5000 K). Based on their calculated partition coefficients [ $D_{(Ne)} = 10^{-6} \sim 10^{-3}$ ,  $D_{(Ar)} = 10^{-6} \sim 10^{-2}$ ,  $D_{(Kr)} = 10^{-7} \sim 10^{-1}$ , and  $D_{(Xe)} = 10^{-5} \sim 10^0$  from 2300 to 5000 K, respectively], they hold that Earth's core might have preserved a multitude of noble gases considering the volatile-rich environment where the core segregated (Wang et al. 2022).

#### 2.4 Incomplete core formation hypothesis

The incomplete core formation hypothesis was proposed by Arculus and Delano (1981) and Jones and Drake (1982), assuming that a small portion of S-rich liquid metal and/or S-poor solid metal remain in the mantle during core-mantle differentiation, and the partition of siderophile elements between S-rich metal and silicate differs from its partitioning behavior between S-poor metal and silicate. This hypothesis is very flexible and allows mathematical adjustments to the amount of metal retained to result in the retention of appropriate HSE in the silicate part of the Earth to meet the current abundance. Jones and Drake (1986) modelled inefficient core separation by presuming a bulk composition of the Earth (within the range of chondrite value), a metal to silicate ratio for the Earth (0.3:0.7), advisable partition coefficients for various siderophile elements between solid metal-liquid metal, liquid metal-liquid silicate, liquid metal-solid silicate, as well as solid silicate-liquid silicate. They found that the abundance of any single HSE in the mantle can be well explained by this type of process via adjustment of the proportions of the controlling phases remaining in the mantle after core formation. However, Jones and Drake (1986) noticed when a group of elements is fitted in the proportion of different stages of core formation, the content of other related elements cannot be satisfied at the same time. In other words, the biggest obstacle to this hypothesis is that it does not work systematically for all elements. For instance, suppose that a considerable amount (2.5%) of metal liquid is retained in the mantle, the Co/Ni ratio of the mantle can be kept within 10% of the chondritic mean value. However, this leads to the retention of much more sulfur (6000 ppm) in the mantle than the observed concentration of  $< 300$  ppm.

Moreover, the elevated high P–T experimental exploration of metal-silicate partitioning characteristic of many HSE and MSE supports a deep magma ocean, and the partitioning behavior of elements between liquid metal and

liquid silicate matters much on the abundance of these elements in the mantle. The inefficient core formation hypothesis will be further discussed only if more information about the condition (pressure, temperature, and composition) of the proto-mantle can be constrained.

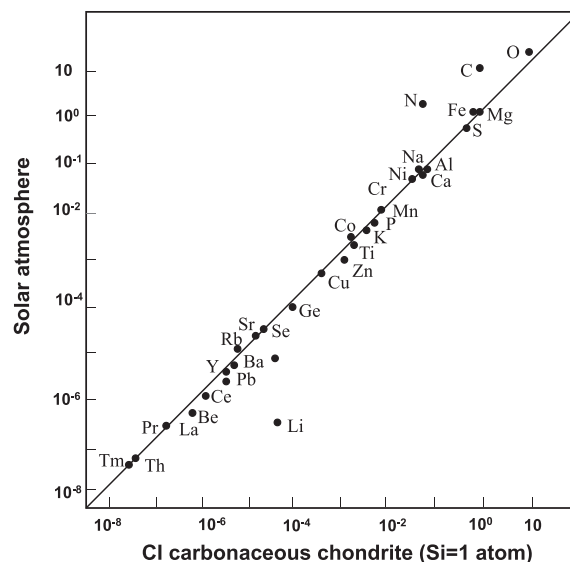
## 2.5 Late Veneer hypothesis

The HSE occurs in approximately chondritic relative proportions in the bulk silicate Earth (BSE) (Fig. 1) (Chou 1978; Becker et al. 2006; Fischer-Gödde et al. 2011; Meisel et al 2001; Morgan 1986), and the absolute abundances are only  $\sim 200$  times lower than bulk CI chondrite abundances (Morgan 1986). These characteristics of the HSE in the BSE do not appear to be the consequence of high-pressure and high-temperature metal-silicate equilibration. Experimental studies have verified that large differences in the metal-silicate partition coefficients of siderophile elements at relevant temperatures and pressures would have resulted in non-chondritic relative abundances in the mantle (Brenan and McDonough 2009; Holzheid et al. 2000; Mann et al. 2012). Instead, the HSE in the BSE may be related to the continued accretion of planetesimals with bulk chondritic compositions after core-mantle differentiation, the late veneer, or the late accretion process (Chou 1978; Kimura et al. 1974). Please refer to Li (2022) in this volume for more details on materials accreted to the Earth after the core-mantle differentiation.

## 3 The formation of proto-Earth

### 3.1 Bulk composition of the Earth

To explore the chemical composition of the early Earth, it would be necessary to know its current bulk composition and formation mechanism. About 4.567 billion years ago, the Earth and other planets formed by the accretion and condensation of primitive solar nebula (e.g., Jacobsen et al. 2008). The bulk composition of the Sun provides clues to the bulk chemical properties of the material in the solar system. Chondrites, which rarely have undergone melting and differentiation since their formation, are considered to be formed very early in the solar nebular. Thus, they can provide direct information on the chemical composition of the solar nebula and planetary bodies (e.g., Kallemeyn and Wasson 1981; McSween 1979; Weisberg et al. 2006). Geochemical studies have revealed that the composition of CI chondrites is almost identical to that of solar photosphere except for the most volatile elements (Fig. 5), which can be regarded as an analogy to primitive solar nebula (e.g., Asplund et al. 2009; Lodders 2003; Palme and Jones 2005). Comparing experimental petrology results with the



**Fig. 5** Comparison of abundances of condensable elements in CI carbonaceous chondrites with abundances in the Sun (Lodders 2003)

composition of basalts and peridotite massifs, Ringwood modeled the chemical composition of the silicate Earth, so-called “the pyrolite model”, which has similar refractory lithophile elemental composition to CI chondrites (Ringwood 1966, 1979). Ringwood’s approach was further developed to estimate the bulk Earth composition by adding back the separated core (32.5% mass of the Earth) (e.g., Morgan and Anders 1980). However, there are some obstacles to the CI chondrite model. For example, the BSE has a higher Mg/Si ratio than CI chondrite (Table 1), the abundance of siderophile elements (especially HSE) in the primitive mantle is “excessive”, the  $^{17}\text{O}$  signature of the Earth and the Moon is distinct from CI chondrite and so on (Fig. 7). Later, a heterogeneous accretion model was developed to answer these questions, especially the late veneer or late accretion process (e.g., Li 2022 in the same volume; Walker 2009). Meanwhile, different approaches using the meteorite data or terrestrial data were advanced to further constrain the bulk composition of the Earth, including the primitive mantle and the core (e.g., Agee 1990; Alexander 2019a, b, 2022; Bouvier and Boyet 2016; Boyet et al. 2018; Dauphas 2017; Li and Agee 1996, 2001; Javoy 1995; Javoy et al. 2010; Mougél et al. 2018; Yoshizaki and McDonough 2021).

#### 3.1.1 The terrestrial model

In the past 20 years, significant progress has been made, which involves the composition of the Earth’s core. High-pressure experiments yield up to date partition coefficients of siderophile elements between the core and the mantle (e.g., Fischer et al. 2015; Li and Agee 1996, 2001; Siebert



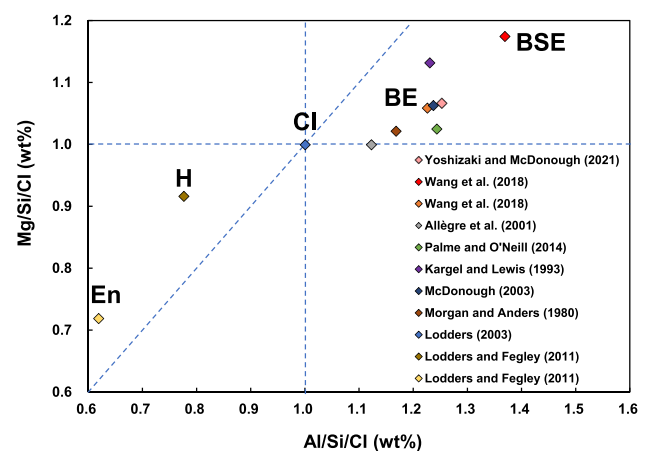
**Table 1** The composition of Earth and chondrites

| wt%                            | Bulk silicate Earth model   |                             |                             |                       |       | Mantle + crust <sup>e,f</sup> | wt%   | Bulk Earth <sup>e,f</sup> | Core <sup>e</sup> | Chondrite <sup>g</sup> |       |       |  |
|--------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------|-------|-------------------------------|-------|---------------------------|-------------------|------------------------|-------|-------|--|
|                                | Pyrolite model <sup>a</sup> | Pyrolite model <sup>b</sup> | Pyrolite model <sup>c</sup> | CI model <sup>d</sup> | wt%   |                               |       |                           |                   | EH                     | L     | CI    |  |
| SiO <sub>2</sub>               | 45                          | 45.16                       | 45                          | 49.9                  | 44.9  | Si                            | 16.10 | 6.00                      | Si                | 17.8                   | 19.5  | 16.0  |  |
| TiO <sub>2</sub>               | 0.20                        | 0.22                        | 0.17                        | 0.16                  | 0.20  | O                             | 29.70 | 0.00                      | O                 | 30.0                   | 35.8  | 29.9  |  |
| Al <sub>2</sub> O <sub>3</sub> | 4.45                        | 3.97                        | 4.40                        | 3.65                  | 4.44  | Al                            | 1.59  | 0.00                      | Al                | 0.9                    | 1.3   | 1.3   |  |
| Cr <sub>2</sub> O <sub>3</sub> | 0.38                        | 0.46                        | 0.45                        | 0.44                  | 0.15  | Cr                            | 0.47  | 0.90                      | Cr                | –                      | –     | –     |  |
| MnO                            | 0.14                        | 0.13                        | 0.11                        | 0.13                  | 0.14  | Mn                            | 0.08  | 0.30                      | Mn                | –                      | –     | –     |  |
| FeO                            | 8.05                        | 7.82                        | 7.60                        | 8.00                  | 8.06  | Fe                            | 32.00 | 85.50                     | Fe                | 31.0                   | 22.7  | 27.7  |  |
| NiO                            | 0.25                        | 0.27                        | 0.26                        | 0.25                  | 0.25  | Ni                            | 1.82  | 5.20                      | Ni                | 1.9                    | 1.3   | 1.6   |  |
| MgO                            | 37.80                       | 38.30                       | 38.80                       | 35.15                 | 37.80 | Mg                            | 15.40 | 0.00                      | Mg                | 11.3                   | 15.7  | 14.3  |  |
| CaO                            | 3.55                        | 3.50                        | 3.40                        | 2.90                  | 3.54  | Ca                            | 1.71  | 0.00                      | Ca                | 0.9                    | 1.4   | 1.4   |  |
| Na <sub>2</sub> O              | 0.36                        | 0.33                        | 0.40                        | 0.34                  | 0.36  | Na                            | 0.18  | 0.00                      | S                 | 6.2                    | 2.3   | 8.0   |  |
| K <sub>2</sub> O               | 0.03                        | 0.03                        | 0.00                        | 0.02                  | 0.03  | S                             | 0.64  | 1.90                      | Total             | 100.0                  | 100.0 | 100.0 |  |
| P <sub>2</sub> O <sub>5</sub>  | 0.02                        | –                           | –                           | –                     | 0.02  | P                             | 0.07  | 0.20                      |                   |                        |       |       |  |
| Total                          | 100.23                      | 100.19                      | 100.59                      | 100.94                | 99.90 | C                             | 0.07  | 0.2                       | Al/Si             | 0.05                   | 0.07  | 0.08  |  |
| Mg#                            | 89.42                       | 89.81                       | 90.19                       | 88.78                 | 89.41 | H                             | 0.03  | 0.06                      | Fe/Si             | 1.7                    | 1.2   | 1.7   |  |
| Mg/Si                          | 1.26                        | 1.27                        | 1.29                        | 1.06                  | 1.26  | Total                         | 99.88 | 99.97                     | Mg/Si             | 0.63                   | 0.81  | 0.89  |  |

<sup>a</sup>Pyrolite model based on peridotites, komatiites and basalts (McDonough and Sun 1995); <sup>b</sup>Least depleted ultramafic xenolith model (Jagoutz et al. 1979); <sup>c</sup>MORB-harzburgite model (Green et al. 1979); <sup>d</sup>Bulk Silicate Earth model based on CI carbonaceous chondrites (Taylor and McLennan 1985); <sup>e</sup>McDonough (2014); <sup>f</sup>Yoshizaki and McDonough (2021); <sup>g</sup>Alexander (2019a; b) (Volatile-free, normalized to total = 100 wt%)

et al. 2011; 2013; Suer et al. 2021) and the light element content of the core (e.g., Badro et al. 2014; Fischer et al. 2014; Jeanloz and Ahrens 1980; Litasov and Shatskiy 2016; Mao et al. 2012; Tateno et al. 2015; Wood et al. 2006; Zhang and Yin 2012; Zhang et al. 2020). These new data are beneficial to reboot the mass balance method on different reservoirs to get the precise composition of the Earth, which used to be difficult due to the incomplete knowledge of the composition deep inside the Earth. Applying recent subduction models (e.g., Poitrasson and Zambardi 2015) and progress on the degree of the mantle homogeneity (e.g., McDonough 2016), the estimation of the primitive mantle composition was also greatly improved. Compiling the enhanced elemental composition of the primitive mantle (e.g. McDonough and Arevalo 2008; Palme and O'Neill 2014) and the core (e.g. Rubie et al. 2011; Zhang and Yin 2012), Wang et al. (2018) concordantly estimated the bulk composition of the Earth through mass balance calculation (“compiling model”). The new compiling results show some differences from the previous study that mainly depends on the relative concentration of trace elements to refractory elemental composition of carbonaceous chondrite “carbonaceous chondrite model” (e.g., Allègre et al. 2001). For example, the “carbonaceous chondrite model” has a similar Mg/Si

ratio to CI chondrite, but its Al/Si ratio is larger than that of CI chondrite, and both Mg/Si and Al/Si ratio are high in the new compiling model (Fig. 6). The bulk Si content of the Earth from the “compiling model” is 16.0 wt%, which is 1 wt% smaller than the “carbonaceous chondrite model”. This is because the new compiling data suppose that Earth’s core contains 4.96 wt% Si, which makes Si the



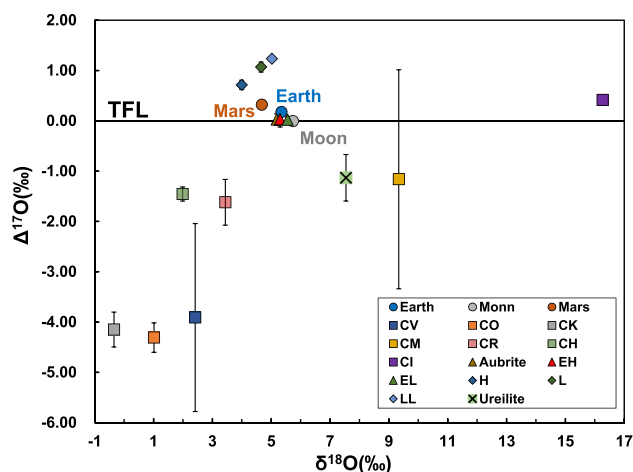
**Fig. 6** The CI chondrite-normalized Mg/Si vs. Al/Si ratios of bulk chondrite (H-ordinary, Enstatite chondrite (En), carbonaceous chondrite (CI), and estimates of bulk Earth (BE) and bulk silicate Earth (BSE) (References as showed in legends)

most abundant light element in the Earth's core (Wang et al. 2018). More recently, Yoshizaki and McDonough (2021) have compared the modeled composition of the Earth with that of Mars and demonstrated that the Earth and Mars are equally enriched in refractory elements ( $1.9 \times \text{CI}$ ) and the bulk Earth may contain 16.1 wt% Si. Accordingly, the Earth's core should contain 4 wt% Si together with 2 wt% O and 1.8 wt% S. As discussed in Lü and Liu (2022, in this volume), the light element content in the Earth's core remains a debate. The silicon and oxygen content in the Earth's core will largely affect the oxygen fugacity of the Earth's lower mantle and further deduction on the material of the Earth's building blocks.

### 3.1.2 The chondritic meteorites model

Although the chemical composition of the Earth mainly depends on the planetary embryos that could be treated as an early form of the proto-Earth, it is difficult to get samples of these embryos. On the other hand, fragments of asteroids, the chondritic materials serve as good samples for interpreting the process of planetary formation since they preserve chemical and isotopic compositions and rarely go through a large degree of melting as the embryos. Chondrites have been divided into two groups carbonaceous (CC) [carbonaceous chondrite (CI, CM, CO, and CV groups)] or non-carbonaceous (NCC) [ordinary (H, L, and LL groups)], Rumuruti, and Enstatite chondrite (EH and EL groups) based on the small but distinct patterns of isotope anomalies (Warren 2011). In addition to isotopic composition, the CC and NCC groups also show different trends in plots of bulk Mg/Si vs. Al/Si, Na/Ti vs. Mn/Na, and moderately volatile elements (Alexander 2019a, b, 2022; Yoshizaki and McDonough 2021). More generally, geochemical 'fingerprinting' of meteoritic materials has indicated that none of the known meteoritic classes corresponds to a hypothetical bulk Earth composition in every aspect (Drake and Righter 2002; Righter et al. 2006).

On the other hand, the CC-NCC dichotomy may reflect the isolation of the inner (NCC) and outer (CC) solar systems (Budde et al. 2016; Kruijer et al. 2017; Warren 2011). And the Earth formed in the inner solar system. Although, the compositions of bulk Earth and bulk silicate Earth have more similar to CCs (e.g., McDonough and Sun 1995; Palme and O'Neill 2014; Wang et al. 2018), the Earth is closer to NCCs in terms of isotopes. Furthermore, some enstatite chondrites show almost identical isotopic composition to the bulk silicate Earth (Figs. 7, 8), thus were proposed to share strong genetic affinities with the Earth (e.g. Dauphas 2017; Walker et al. 2015) or the essential building blocks of the Earth are enstatite chondrite (e.g., Javoy 1995; Javoy et al. 2010; Valdes et al.



**Fig. 7** Oxygen isotopic composition of terrestrial planets and some meteorolites. Data from Clayton et al. (1984, 1991); Clayton and Mayeda (1999); Greenwood et al. (2017); Newton et al. (2000); Tanaka and Nakamura (2017); Tanaka et al. (2021); Young et al. (2016). TFL: terrestrial fractionation line (Clayton et al. 1977). All error bars are two standard ( $2\sigma$ )

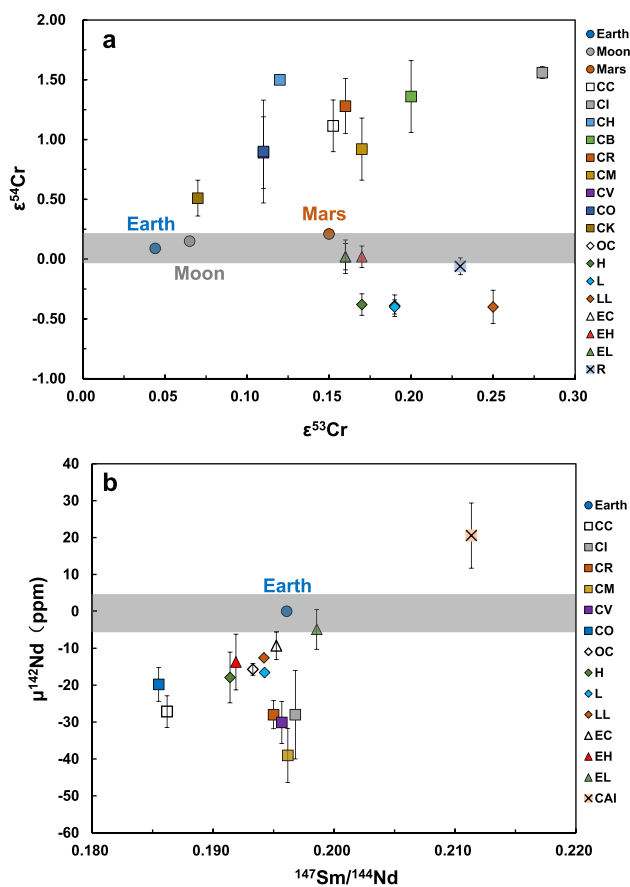
2014). However, the enstatite chondrite model was challenged by stable isotope systematics such as Ca and Si isotopes (e.g., Fitoussi and Bourdon 2012; Savage and Moynier 2013; Shahar et al. 2009; Simon and DePaolo 2010) and by the silicon content of the Earth core (e.g., Hirose et al. 2013; Li and Fei 2014).

In addition, there is no single chondritic model that could perfectly account for how the Earth's redox state evolved to the fayalite-magnetite-quartz (FMQ) of the current mantle, so a joint model was introduced (e.g., Dauphas 2017; Fitoussi and Bourdon 2012), Earth might have accreted from a mixture of the known meteoritic groups, consistent with the substantial radial mixing in the proto-planetary disk that is expected to have occurred during terrestrial planet formation (Canup and Agnor 2000; Chambers 2001).

## 3.2 The building blocks of the Earth

### 3.2.1 The oxidation condition of the early-Earth

The present Earth is an oxidizing planet. In the solar system, only the Earth's atmosphere contains a high concentration ( $\sim 21\%$ ) of  $\text{O}_2$  (e.g., Sun 2020). Based on high-pressure (35–74 GPa) and high-temperature (3100–4400 K) experimental results on the partition of Cr and V between liquid metal and liquid silicates, Siebert et al. (2013) suggested that the Earth's core formed under oxidizing conditions and the Earth's building materials could be as oxidized as ordinary or carbonaceous chondrites. However, the redox state of the proto-Earth and its planetary embryo controls not only the partition of the



**Fig. 8** Chromium (Cr) and neodymium (Nd) isotope value for terrestrial planets and chondrites. The modern terrestrial composition is indicated by the blue circle labeled Earth. All error bars are two standard ( $2\sigma$ ) for individual data points. **a** The  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values for terrestrial planets and chondrites. Cr isotope data are from Kruijjer et al. (2020), Mougél et al. (2018), Qin et al. (2010), Trinquier et al. (2007, 2008), Zhu et al. (2021a, b). The gray band represents the  $2\sigma$  on the  $\epsilon^{53}\text{Cr}$  of Earth (which corresponds to the mean  $\epsilon^{53}\text{Cr}$  of the terrestrial rocks (0.09,  $2\sigma$ )). **b** The  $^{147}\text{Sm}/^{144}\text{Nd}$  versus  $\mu^{142}\text{Nd}$  values for terrestrial planets and chondrites. Nd isotope data are from Bouvier and Boyet (2016), Boyet and Carlson (2005), Boyet et al. (2018), Burkhardt et al. (2016), Carlson et al. (2007), Fukai and Yokoyama (2017), Gannoun et al. (2011), Rankenburg et al. (2006). The gray band represents the  $2\sigma$  on the  $\mu^{142}\text{Nd}$  of Earth [which corresponds to  $\mu^{142}\text{Nd}$  of the JNdi-1 standard ( $0 \pm 5$  ppm,  $2\sigma$ )]

siderophile elements between the mantle and the core but also the component of gases that erupted from the Earth's interior. It was implied that in the early stages of the Earth's evolution, its atmospheric composition is similar to that of Mars, which is dominated by  $\text{CO}_2$  (Canfield 2005). There are also studies that assert that the early stage of the Earth is an extremely reduced environment similar to Mercury (Allegre et al. 1995). The  $f\text{O}_2$  condition of the Earth evolved over time during the core-mantle differentiation, changing from a reduced state to a more oxidized state (Forst et al. 2008; Wänke 1981; Wade and Wood 2005; Wood et al. 2006), and the  $f\text{O}_2$  of the mantle has not

changed much in the last 3 billion years (Berry et al. 2008; Dauphas et al. 2009; Li and Lee 2004). Moreover, gases that erupted from the gradually oxidizing Earth's mantle may have a connection with the Great Oxidation Event. A case in point is that Nicklas et al. (2019) calculated the  $f\text{O}_2$  of the source magma for some old (3.55 Ga) komatitite and picrite samples using the distribution relationship of the  $f\text{O}_2$  sensitive element vanadium (V) between the liquidus mineral olivine and their pairing melt. The results showed that from 3.48 to 1.87 Ga, the mantle was “self-oxidized”, and the  $f\text{O}_2$  increased by  $\sim 1.3$   $\Delta\text{FMQ}$  log units, which provides strong evidence for the mantle to participate in the Great Oxidation Event. Then, some researchers further argued that the decline of oxidizable volcanic gases which formed in a gradually oxidized mantle could have triggered the Great Oxidation (Kadoya et al. 2020). The “self-oxidized” process in the Earth's mantle is powered by the disproportionation reaction of  $\text{Fe}^{2+}$ , which forms metallic Fe and  $\text{Fe}^{3+}$  at lower mantle conditions (e.g., Frost et al. 2004).  $\text{Fe}^{3+}$  is present in bridgmanite and Fe drops into the core, thus the ratio of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in the mantle increases, resulting in relatively high  $f\text{O}_2$  in the lower mantle (Kurnosov et al. 2017; McCammon 1997; Rohrbach et al. 2014; Smith et al. 2016; Wade and Wood 2005). Considering this process powered oxidation during the accretion process, the  $f\text{O}_2$  of early Earth remains unchanged in the first 10% of the accretion (because perovskite is not stable) and then reaches the current core-mantle equilibrium value at the end of the accretion (Corgne et al. 2008). Therefore, the current experimental results on the partitioning of siderophile elements, analysis of samples from deep inside of the Earth, and theoretical modeling of the formation process of the Earth favor a more reduced condition in the early stage of the Earth accretion.

Certainly, there are other suggestions on the redox condition of early Earth. For example, Georg and Shahar (2015) suggested that the oxidation level should be approximately  $\Delta\text{IW} \sim -1.2$  to  $-1.7$ , assuming that MSE like Ni and Co are less siderophile at oxidating conditions. This may not be the case as we discussed previously (Fig. 4). Therefore, quantitative studies on the effect of  $f\text{O}_2$  on partitioning behaviors of siderophile elements at high P–T conditions will help to clear this issue and more work is needed to constrain the Si budget of bulk Earth under reducing conditions.

On the other hand, Huang et al. (2020) performed high-pressure partition experiments on twin elements niobium (Nb) and tantalum (Ta) and found that Nb enters the core more than Ta in the process of core-mantle differentiation, thus reducing Nb/Ta ratio in silicate Earth. Their Nb-Ta data defined the boundary conditions of the redox environment in the early stages of Earth's formation, that is, moderately reduced or oxidized, neither the extremely

reduced nor oxidized environment as previously thought. The redox condition of the early Earth is still an open question, relying on more experimental and cosmochemistry work.

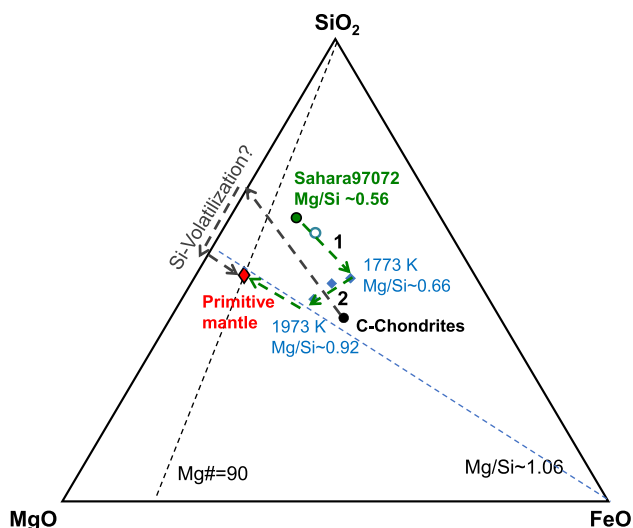
### 3.2.2 The enstatite chondrite model

The debates on the redox environment in the proto-Earth (e.g., Corgne et al. 2008, 2009; Georg and Shahar 2015; Rubie et al. 2004) and  $fO_2$  changes with the evolution of the Earth's mantle (e.g., Frost et al. 2004; Frost et al. 2008; Sieber et al. 2013; Wade and Wood 2005;) call for constructing a model of planetary formation and evolution in a reduced environment. Among all types of chondrites, enstatite chondrites are almost entirely composed of highly reduced and anhydrous high-temperature minerals such as Fe-free (or almost so) enstatite pyroxene (~ 70–80 wt%), Fe-Ni metal (~ 20–30 wt%) and abundant sulfides including troilite, oldhamite (CaS), members of the Fe–Mg–Mn cubic monosulfide solid solution keilite-ninigerite-alabandite (e.g., Norton 2002). The biggest difference between enstatite chondrites and carbonaceous chondrites, which is from an oxidized environment, is that a large amount of monovalent metal iron is preserved in primitive enstatite chondrites (e.g., Casanova et al. 1993; Keil 1989). And the content of FeO in enstatite chondrites is less than 2 wt% (Cloutis et al. 2018). The very low  $fO_2$  of enstatite chondrites (IW–6 to IW–8) and the high temperatures they recorded (980 to 1400 K) (e.g., Fogel et al. 1989; Petaev and Khodakovskiy 1986) imply that they were formed in a strongly reduced environment.

In addition, enstatite chondrites (EH and EL), whose isotopic compositions are closest to the Earth (Figs. 7, 8) (e.g., Bouvier and Boyet 2016; Boyet et al. 2018; Clayton et al. 1984; Gannoun et al. 2011; Mougél et al. 2018; Newton et al. 2000; Steele et al. 2012; Walker et al. 2015), do not show a clear refractory enrichment nor moderately volatile elements depletion. Dauphas (2017) suggested that the Earth's formation process could be divided into three stages. In the first stage, the Earth's formation is nearly 60%, and the main components of the proto-Earth in this stage are very reduced; in the second stage, the Earth is increased from 60% to 99.5%; and the remaining 0.5% as the third stage. The reason for the 60% divide is that previous study has asserted that the material accreted by the Earth could have changed in nature, from more reduced to more oxidized, at 60%–80% accretion (Rubie et al. 2015). The third stage corresponds to the addition of a late veneer after the core-mantle differentiation (Bottke et al. 2010). The accreted material is supposed to be mixture of four components with the isotopic compositions of enstatite

(En), ordinary (O), and carbonaceous chondrites (CI and CO/CV). Compared with the chemical and isotopic composition of the present Earth, Dauphas emphasized that enstatite chondrites are very vital components in all three stages, which strongly supports the homology of enstatite chondrite and the primordial composition of the Earth (Dauphas 2017).

The greatest barrier to making the enstatite chondrite as the building block of the Earth is the chemical composition. For instance, enstatite chondrites have over-abundant volatile elements and lower Mg/Si and Al/Si ratios (Fig. 6) that need to be devolatilized prior to accreting to form the Earth (Javoy et al. 2010). If the Earth and the enstatite chondrites had a common precursor, the secondary event, impacting, or collisional erosion is needed to modify the chemical composition of the enstatite chondrites but keep its isotope character not changed (Jacobsen et al. 2013). The original composition of condensed materials in the solar nebula may be altered as accretion proceeded and eventually grew into planetesimal-size parent bodies (Moynier and Fegley 2015). O'Neill and Palme (2008) proposed that collisional erosion is another process that alters the composition of planetary embryos by the loss of the out layers on the embryos. It is thus necessary to model the “crust”, the outer layer composed of the planetary embryos with enstatite chondrite-like composition. If the planetary embryos have undergone a high-energy impact, it may cause a large degree (if not complete) melting of the whole embryos. Our high-pressure (~ 5 GPa) and high-temperature (over the liquidus of silicate) melting experiments on enstatite chondrite (Sahara 95072 EH3) demonstrated that  $SiO_2$  separates from the silicate liquid when the heating temperature is over liquidus of silicate phases (1973 K). The  $SiO_2$  is the high-temperature polymorph tridymite, indicating that liquid immiscibility happened between silicate liquid and  $SiO_2$  at high-pressure conditions during heating. The Mg/Si ratio in the silicate liquid phase largely increased and got close to the CI chondritic ratio (Fig. 9) (Du et al. 2017, 2019). Considering the low density of  $SiO_2$  phase, it will flow to the shallow level and most likely to the surface (Hirose et al. 2017). If this kind of embryos whose outer layer is rich in  $SiO_2$ , got impacted and the outer layer was removed by erosion, Mg/Si in the left silicate portion will be largely increased, thus an embryo with EH chondritic composition becomes close to CI chondritic Mg/Si ratio. More experiment work will be done along this direction to further explore the pressure and temperature conditions for enstatite chondrite to “lose” its Si, and the differentiation process of a planet with enstatite chondrite composition.



**Fig. 9** The Mg/Si ratio of silicate liquid phase changes through high temperature heating at 5 GPa. During heating, the Mg/Si increased from 0.56 to 0.92 and got close to the primitive mantle ratio (1.06). This image is modified from Du et al. 2017, 2019

#### 4 Summary

Partition coefficients of siderophile elements is a powerful tool to infer the pressure and temperature conditions of the Earth's core formation. High-pressure and high-temperature experiments have made large progress in the partitioning behavior of siderophile elements under different P–T conditions with different metal and silicate compositions. Despite a bulk of experimental data being available to constrain the core-mantle segregating conditions,  $fO_2$  evolution path in these experimental studies is less constrained. The experiments carried out at relatively low pressure (< 25 GPa) show some coordinated variation of partitioning coefficient and  $fO_2$ , but those carried out at higher pressure (30–100 GPa) all indicate relatively oxidized conditions, which may be consistent with the redox condition of the current mantle, but it is less persuasive on the accretion process of early Earth. High-pressure and high-temperature experiments designed to ascertain the partitioning behavior of the same group of siderophile elements under uniform conditions and under different  $fO_2$  conditions will contribute most to solving the excess problem to the most HSE in the Earth's mantle and accurately describe the differentiation of proto-Earth.

Compositional constraints on the Earth's bulk composition rely on indirect approaches, such as geochemical and/or cosmochemical studies on the samples from internal Earth and extraterrestrial samples. Additional chemical analysis on more samples, especially Martian and lunar samples will be very promising in constraining the Earth's building blocks, the process involved in establishing the siderophile elements abundance in the mantle. Given the

probability of a more complicated model of planetary formation occurring in the inner solar system, it will undoubtedly be advantageous to do more experimental studies on the differentiation of small planets or planetary embryos, using different materials as starting composition. Simulations on the formation process of planets will benefit from the outcome of this type of experiment. All of this work will provide information regarding planetary growth and enrich our knowledge of the true process of the Earth formation and differentiation.

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#### Declarations

**Conflict of interest** The author declares that they have no conflict of interest.

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