



Metal–silicate partitioning of sulphur, new experimental and thermodynamic constraints on planetary accretion



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ABSTRACT

Partitioning of sulphur between liquid Fe-rich metals and silicates ($D_S^{met/sil}$) was investigated at temperatures from 1800 °C to 2400 °C, pressures from 2 to 23 GPa and oxygen fugacities from 3.5 to 1.5 log units below the iron–wüstite buffer, using multi-anvil apparatus. The results are combined with previous experimental works to refine a multi-variable thermodynamic model of $D_S^{met/sil}$. Sulphur appears to become more siderophile with increasing pressure and FeO content of the silicate melt, and less siderophile with increasing temperature and with Si, C, O, Fe and Ni contents of the metal. We then modelled the behaviour of sulphur in the course of planetary accretion, using different possible scenarios of mantle dynamics and evolution with time of oxygen fugacity. We investigated three end-member models for metal–silicate segregation of the incoming impactors: (i) the planetary mantle does not mix and is kept chemically stratified, (ii) the magma ocean is continuously mixed chemically, and (iii) both the magma ocean and the solid lower mantle are well mixed.

We show that if S is accreted along the accretion, whatever the oxidation path, its distribution between core and mantle can lead to the observed S concentration of the mantle (200 ± 80 ppm) and to the estimations of S content of the core (from its depletion in the mantle relative to the other elements with the same volatility). In the case of an Earth built with reduced material, to explain the present-day 200 (± 80) ppm S found in the mantle, it is necessary that both the magma ocean and the solid lower mantle mix at each major step of the planetary accretion. S could also be accreted in the last 10 to 20% of Earth's growth and reach its observed present terrestrial abundances if the magma ocean is chemically mixed along the accretion. Consequently, our models show that the S terrestrial abundances do not formally require an S accretion in a late veneer but can be explained by a core–mantle equilibration alone.

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1. Introduction

Early Earth history is marked by one of the most important events: core segregation. This event led to drastic changes of the Earth's internal structure, with formation of quasi-independent chemical reservoirs. It yielded irreversible distribution of all elements between terrestrial reservoirs at the pressure and temperature conditions relevant to the Earth differentiation. Abundances of siderophile (Fe metal-loving) elements in the present-day Earth mantle can thereby be compared to chondrites compositions and experimental results on their partitioning to infer conditions under which iron-rich metals and silicate phases equilibrated.

From experimental metal–silicate partitioning studies of moderately and slightly siderophile elements a growing consensus is emerging indicating that high pressures and high temperatures are required for core–mantle differentiation (e.g. Bouhifd and Jephcoat, 2003, 2011; Chabot et al., 2005; Li and Agee, 1996; Mann et al., 2009; Richter, 2011; Siebert et al., 2011, 2012; Wood et al., 2006). In particular, it has been shown that during the final stages of the Earth's accretion, core–mantle equilibration occurred at pressures between 40 and 60 GPa, which correspond to a base of the magma ocean located at half the depth of core–mantle boundary.

It was suggested that a single-stage formation model remains unlikely considering that Earth's core formation was a continuous process associated to a series of large impact events (Canup, 2008; O'Brien et al., 2006; Wetherill and Cox, 1985). Geochemical arguments based on the isotopic systems ^{107}Pd – ^{107}Ag and ^{182}Hf – ^{182}W (Halliday and Wood, 2009) provide support for a continuous core

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formation where internal pressures and temperatures rose, affecting the degree to which siderophile elements are partitioned into the core. Moreover previous kinetics modelling showed that the time scale of equilibration between the liquid mantle and a molten metal layer at the base of a magma ocean is greater than the time scale of cooling of the magma ocean (Rubie et al., 2003). Therefore, the equilibrium that is recorded by the growing core is likely to have involved falling metal droplets in a magma ocean.

Furthermore, the natural abundances in the mantle of the slightly siderophile elements V, Mn, and Cr have been explained either by an accretion model with a highly controversial constant, progressively increasing or decreasing oxygen fugacity (Siebert et al., 2013; Wade and Wood, 2005), or by their stabilization in deep mantle phases (Righter, 2011). Different mechanisms could account for the f_{O_2} change with the accretion time: (i) the ability of the Mg-perovskite phase to enhance the ferric iron content in the lower mantle (Frost et al., 2004); (ii) the change of the f_{O_2} of the accreted material (Wänke, 1981); (iii) the rise of FeO content of the mantle through silicon solubility in the core (Javoy et al., 2010); (iv) the dissolution of the FeO from the mantle to the core at high pressure and high temperature (Rubie et al., 2004), and (v) the change of thermal expansion of redox equilibria as the pressure increases during Earth's accretion (Righter and Chiorso, 2012). Still, the high mantle abundances of a majority of highly siderophile elements (HSE) cannot result from any of all these models and suggest a subsequent addition to the mantle of an HSE-bearing material as a 'late veneer' (Chou, 1978; Holzheid et al., 2000; Ohtani et al., 1997).

Sulphur is a siderophile, chalcophile and volatile element and is known to be more siderophile with increasing pressure and f_{O_2} and decreasing temperature (Holzheid and Grove, 2002; Mavrogenes and O'Neill, 1999; Rose-Weston et al., 2009). This element is relatively abundant in all types of meteorites (~2 to 6 wt%) (Wasson and Kallemeyn, 1988) but it is present in very low concentrations in the Earth mantle (ranging from ~100 to 300 ppm) (Dreibus and Palme, 1996; McDonough and Sun, 1995). In fact, there is a strong depletion of sulphur in the Earth mantle in comparison to other elements with the same volatility (Zn for instance). If sulphur should follow the classical terrestrial volatility trend, 98% of the terrestrial S would be located in the core, corresponding to an S-content in the core of about 1.9 wt% (Palme and O'Neill, 2003).

A recent study argues that the S, Se and Te abundances found in the mantle can only be explained by their addition in a late veneer, based on new experimental measurements of metal-silicate S partitioning at high pressures and temperatures (Rose-Weston et al., 2009). However, this previous study neglected the effects of oxygen fugacity and chemical compositions of both the silicate and the metal. The presence of C in the metal, in particular, could play a major role on the Mo and W behaviour at the latest stages of the accretion (Wade et al., 2012 and Wood et al., 2013). An assessment of all parameters controlling the metal-silicate partitioning of sulphur is needed to constrain its behaviour during accretion and core segregation, and to tentatively determine its abundance in the core.

Another problem in previous studies is the use of a too high S-content, compared to the terrestrial abundances. For example, Li and Agee (2001b) and Holzheid and Grove (2002) used starting materials with chemical compositions representative of natural carbonaceous and ordinary chondrites. In the recovered experimental charges, the metals contained from 11 to 32 wt% S, which is far above the expected S-content in the Earth's core (Morard et al., 2013; Alfé et al., 2000). As a consequence, the Fe concentrations in the metal were very low (49 to 76 wt%). This can affect the S partition coefficient as well as the abundances in the metallic phase of other light elements (Si, C, O). Consequently, additional

experimental measurements at lower S-content are required to determine whether it is possible, or not, to reach the present-day S abundances in the mantle.

2. Experimental methods

We used starting materials composed of synthetic mixtures of oxides and metal powders with a silicate/metal ratio similar to that of the Earth and enstatite chondrites (Javoy et al., 2010). We varied S contents from 1.6 to 3 wt%, thus at values lower than the 3 to 6 wt% S found in natural EC. We also varied the SiO₂ content in the silicate phase, and the FeS and FeSi contents in the metallic phase (see Supplementary Table S1). To prepare silicate phases, ultra-pure SiO₂, MgO, Al₂O₃, TiO₂ and Cr₂O₃ powders were dried at 1273 K overnight and Na₂CO₃, CaCO₃ and K₂CO₃ powders at 623 K during 4 h. These powders were weighted dry, grinded under alcohol for 1 h, before decarbonation overnight at 1073 K. Iron-rich metals consisted of mixtures of pure powders of Fe₈₃Si₁₇, FeS, Fe, Ni, Co, Fe, Mn and Cr. Silicate and metallic powders were then intimately mixed together before loading in the graphite capsules. A reversal experiment was also performed by loading in the capsule separated layers of the silicate and metallic starting materials, the silicate being loaded at the bottom and the metal at the top, in close contact one with each other.

High-pressure experiments were performed using Kawai type multi-anvil presses at the Laboratoire Magmas et Volcans, Clermont-Ferrand, France. Experiments were carried out at pressures ranging from 2 GPa to 23 GPa and heated to temperatures of 2073 K to 2673 K for time durations ranging from 10 s to 30 min (Table 1). We used Cr₂O₃-doped MgO octahedra as pressure medium with edge lengths of 18 mm, 14 mm and 10 mm, depending on the target pressure. For these octahedral sizes, tungsten carbide cubes presented angle truncations of 11 mm, 8 mm and 4 mm, respectively. Experiments at 16 and 23 GPa were carried out using the 1500-t multi-anvil press calibrated against the ringwoodite decomposition into periclase plus perovskite (Ishii et al., 2011; Katsura et al., 2003) and the perovskite-corundum phase diagram (Kubo and Akaogi, 2000). Experiments at lower pressures were performed using the 1000-t multi-anvil press which calibration is described elsewhere (Hammouda, 2003).

High temperatures were provided using LaCrO₃ furnaces and measured using W₉₇Re₃-W₇₅Re₂₅ thermocouples. When a thermocouple failed, temperature was estimated on the basis of the temperature/electrical-power relationship of other experiments for which the thermocouple was available. After the target temperature was reached and stable for the expected heating duration (Table 1), samples were quenched by switching off the electrical power. The cooling rate is determined from temperature measurements that are recorded automatically every 0.1 s. In most of the experiments, we used a cylindrical zirconia sleeve to ensure a better thermal isolation between the LaCrO₃ furnace and the WC cubes. In this case, the temperature decay indicated a cooling rate ranging from 240 to 750 °/s after electrical power was turned off. In one of the experiments (#1147), in order to obtain a faster quenching rate, we did not use any ZrO₂ sleeve, yielding a cooling rate of 10000 °/s.

3. Analytical methods

3.1. Chemical analyses

Chemical compositions of both metal and silicate phases were quantified using a CAMECA SX100 electron probe micro-analyzer (EPMA) (see Supplementary Tables S2, S3 and S4). To prevent artifacts associated to potential heterogeneous dendritic microstructures of the devitrified melt, chemical analyses were performed

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