Magma Ocean Depth and Oxygen Fugacity in the Early Earth—Implications for Biochemistry

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Abstract A large class of elements, referred to as the siderophile (iron-loving) elements, in the Earth's mantle can be explained by an early deep magma ocean on the early Earth in which the mantle equilibrated with metallic liquid (core liquid). This stage would have affected the distribution of some of the classic volatile elements that are also essential ingredients for life and biochemistry – H, C, S, and N. Estimates are made of the H, C, S, and N contents of Earth's early mantle after core formation, considering the effects of variable temperature, pressure, oxygen fugacity, and composition on their partitioning. Assessment is made of whether additional, exogenous, sources are required to explain the observed mantle concentrations, and areas are identified where additional data and experimentation would lead to an improved understanding of this phase of Earth's history.

Keywords Core · Siderophile · Sulfur · Nitrogen · Carbon · Hydrogen · Redox

Introduction

Early Earth went through a magma ocean phase, with the magma ocean attaining depths of 1000–2400 km (30 to 70 GPa pressures; Siebert et al. 2012; Bouhifd and Jephcoat 2011; Righter 2011; Corgne et al. 2009; Wood 2008; Mann et al. 2009). This is based on the metal-silicate partitioning of siderophile trace elements such as Ni, Co, Mo, W, P, Zn, Cu, Pd, Mn, V and Cr, as accreting metal droplets equilibrated with the surrounding magma down to these depths. As an interesting aside, all of these elements eventually became integral to fundamental biochemical processes. Undoubtedly, this magma ocean stage also helped to establish the concentrations of the more volatile S, C, N and H concentrations in the mantle, because all four of these elements likely partition between the core and the mantle.

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Models for the origin of S, C, N, H in the Earth's mantle are of several kinds: a) models in which most of these partition into the core, and must be replenished by later exogenous contributions (late accretion or late chondritic additions), b) models in which most of these partition into the core, and must be replenished by later indigenous contributions (atmospheric ingassing), and c) models in which most of these partition into the core, but the amount partitioning into the mantle accounts for the bulk silicate Earth (BSE) contents (e.g., Halliday 2013).

To evaluate these models a solid understanding must be obtained for the partitioning of S, C, N and H between metallic liquid and silicate melts across a wide pressure and temperature range corresponding to possible deep Earth conditions. In particular, these elements are sensitive to oxygen fugacity (fO2), and there is a wide range of oxygen fugacities recorded in samples from the inner solar system (Earth, Moon, Mars, comets, and meteorites)– nearly 15 orders of magnitude from IW-6 to IW+9 (Righter et al. 2006). It is not even clear if fO_2 evolved from reduced to oxidized (e.g., Rubie et al. 2011), oxidized to reduced (Siebert et al. 2013), or remained relatively constant (Righter and Ghiorso 2012) during Earth's accretion. In this contribution partitioning data are summarized, and a simple model is presented that includes mass balance and metal-silicate partitioning to illustrate how much S, C, N and H can be in the mantle just after core formation, and whether exogenous or indigenous additional sources of these elements are required.

Sulfur has been studied by a number of authors, and its partitioning between core and mantle as characterized by the partition coefficient D (wt.% element in core/wt.% element in mantle, or D(metal/silicate)) is now known to be dependent upon pressure (P), temperature (T), fO_2, and metallic and silicate melt composition. Li and Agee (2001) explored the effects of temperature and pressure, whereas Malavergne et al. (2014) showed high solubilities in silicate melt at low fO_2. Boujibar et al. (2014) presented an expression for predicting D(S) metal/ silicate as a function of these parameters and here their expression is used to demonstrate the BSE values of 250 ppm S can be attained by metal-silicate equilibrium at the base of a deep magma ocean, where D(S) ~ 200 (Figs. 1 and 2).

Nitrogen solubility in silicate melts has been known for some time (Libourel et al. 2003), and is generally low, unless the fO_2 becomes extremely low - < IW-2. The solubility of N in metal has been studied more recently and is initially pressure sensitive, but less so at higher pressures (Roskosz et al. 2013). The combined effect of the metal and silicate solubilities is moderately siderophile behavior for N, with D(N) between 10 and 20 at IW-2. Such behavior has been argued by Marty (2012) to be an explanation for the depletion of N in the Earth's mantle compared to other noble gases and carbon (Fig. 1). At much lower fO_2, N solubility in silicate melts decreases substantially, so that at these low fO_2, D(N) will be much lower thus allowing a more N-rich mantle.

Carbon has been included in past modelling efforts, and is known to be siderophile, but has only recently become a focus of extensive experimental study (Dasgupta et al. 2013). Carbon is also siderophile, but D(C) can be lowered from values of ~1000 to values closer to 100 by the combined effects of increasing temperature, silicate melt depolymerization, and oxygen fugacity; pressure, on the other hand, promotes siderophility. To illustrate the effect of D(C)= 100 vs. D(C)=1000, we show the calculated mantle contents for each values (Fig. 1). This illustrates that the carbon content of the BSE may be explicable by such a deep magma ocean scenario, but awaits additional work at higher PT conditions to allow more accurate calculations at the extreme conditions.

Hydrogen is also known to be quite siderophile, but its mobility in experimental systems has made detailed studies very difficult. Nonetheless, Okuchi (1997) demonstrated very high solubility in Fe-rich metallic liquids, and showed that up to 95 % of the water in a magma
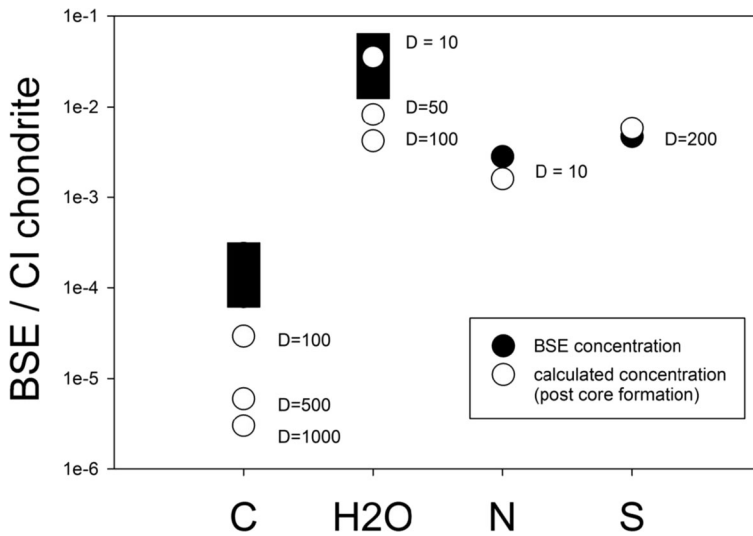
Fig. 1 C, H_2O, N, and S concentrations in the bulk silicate Earth, from Marty (2012) and Palme and O'Neill (2014). Calculated values are based on work of Chi et al. (2014) and Dasgupta et al. (2013) for carbon, Kuramoto and Matsui (1996) for H_2O, Roskosz et al. (2013) for nitrogen, and Boujibar et al. (2014) for sulfur. Bulk Earth values are from Marty (2012) and McDonough and Sun (1995) and are as follows: C=530 ppm, N=1.68 ppm, H_2O=2700 ppm, and S=2 wt.%

ocean could have reacted with Fe metal to form FeH liquid, accounting for 60 % of the density deficit in Earth's core. Kuramoto and Matsui (1996) argued that such an environment may also
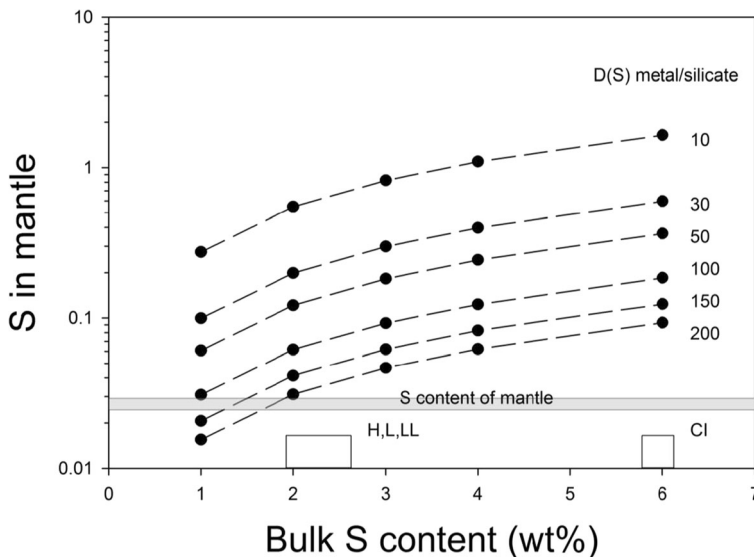
Fig. 2 Calculated S concentrations in the bulk silicate Earth, at various bulk Earth S contents. S content of the Earth's primitive mantle (250 ppm; McDonough and Sun 1995) is a horizontal shaded area; ordinary (H, L., LL) and CI chondrite S contents are indicated and taken from Newsom (1995) compilation. At bulk Earth S content of 2 wt.% and D(S) metal/silicate=200, the Earth's primitive mantle S content can be matched; the value of D(S) is expected for a deep magma ocean scenario for the early Earth (Boujibar et al. 2014)

account for oxidation of Earth's mantle (see below) and obviate the need for late additions of chondritic material. Finally, Nomura et al. (2014) demonstrate that the temperature at Earth's CMB is lower than expected and thus the outer core temperature could be depressed by an impurity such as H. D(H) metal/silicate as high as 100 would leave the BSE with less H_2O than estimates for the bulk mantle, but values as low as 10 (see Kuramoto and Matsui 1996) could be consistent with observations (Fig. 1).

In general, then, low fO_2 conditions (IW-4 to IW-6) tend to favor mantles with low C and H, and relatively high S and N, perhaps like Mercury (e.g., Malavergne et al. 2014). In comparison, high fO_2 conditions (IW-1 to IW-3) tend to favor a mantle with higher H and C, but lower S and N, more like what we consider early Earth-like. In fact, for Earth, the conclusion is that the S and N content of the BSE can be explained by equilibrium partitioning between core and mantle, and do not require an exogenous or indigenous source. The high pressure partitioning behavior of H and C, however, remain incompletely characterized (Fig. 1). There is great potential for the H and C contents of the BSE to be explained via this simple model, but several kinds of information are still lacking.

First, one major question is how low can D(C) metal/silicate become at the conditions thought to exist in the early Earth? Such conditions are currently thought to be near the base of a deep magma ocean (e.g., Righter 2011; Wood 2008), near 3500–4000 K and 40–50 GPa, but our current experimental database extends only to near 3 GPa and <2000 C (Chi et al. 2014; Dasgupta et al. 2013). Second, there is some data at low P, but essentially no data > 7 GPa (Okuchi 1997) for H partitioning between metallic liquid and silicate melt; this is primarily due to the technical challenges offered by these chemical systems. The acquisition of additional data regarding H partitioning will be important with respect to testing the indigenous or exogenous origin of water on Earth. Third, Earth's metallic core likely also contains Si, S and C, with additional H and O. However, most experimental studies have been on simple systems such as Fe-Si, Fe-C, or Fe-S-C (See Hirose et al. 2013; Morard et al. 2013, and references therein). Realistic multi-component systems must be explored so that any significant chemical effects of multi-component systems can be understood for the application to the Earth and its light element-bearing core. So, for example, Fe-Ni-Si-S-C-H-O metallic liquids should be studied when examining metal-silicate equilibria relevant to early Earth.

Fourth, fO_2 at high pressures is not well understood yet is essential to knowing the distribution of C, S, N, and H between the core and the mantle. Scant knowledge of peridotite silicate melt properties at high pressures remains a barrier to detailed understanding of deep Earth redox equilibria. Fifth, the evolution of fO_2 from the conditions of core formation (IW-2) to the Hadean mantle record (FMQ) is clearly important but mechanisms remain uncertain. The specific fO_2 controls important fundamental chemical parameters such as speciation of volatiles in magmatic gases – high fO_2 like FMQ would favor CO_2-H_2O-SO_2 species, while low fO_2 like IW would favor CH_4-H_2-CO species (e.g., Holloway and Jakobsson 1986). Various ideas have been proposed for this early oxidation event, but most have drawbacks. For example, plate tectonics and recycling of oxidized surface materials back into a relatively reduced mantle may be expected to be a cause of long term oxidation of the mantle, but there has been no evidence for this with even the oldest portions of Hadean mantle recording O_2 near FMQ (Trail et al. 2011; Delano 2001; Canil 2002), until the recent work on Hadean zircons suggests a temporal trend (Yang et al. 2014). The dissociation of Mg,Fe-perovskite into Fe^{3+} and Fe metal at the base of the upper mantle was also suggested as an oxidation mechanisms, but it remains uncertain whether the Fe^{3+} produced will be stable or subsequently dissociate into Fe^{3+} and Fe^{2+} in response to local fO_2 imposed (Wade and Wood 2005; Frost

et al. 2004). It is also possible that Fe^{3+}/Fe^{2+} increases with depth in the magma ocean such that convection stirring would lead to a more oxidized mantle overall, but results so far up to ~7 GPa indicate that Fe^{3+}/Fe^{2+} decreases (Zhang and Hirschmann 2013; Righter et al. 2013). Finally, and perhaps most promising, is the possibility that early H_2 loss could lead to rapid and substantial oxidation (Sharp et al. 2013; Hamano et al. 2013). Such a mechanism may also be tied to the explanation for Earth's oceans D/H ratio.

Clearly there are many avenues of research that will help sharpen our understanding of the early Earth and what conditions led to a stable and chemically rich environment for the origin of life.

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