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Melting Phase Relations in the Fe-S and Fe-S-O Systems at Core Conditions in Small Terrestrial Bodies

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Abstract

We report an experimental investigation of phase equilibria in the Fe-S and Fe-S-O systems. Experiments were performed at high temperatures (1400-1850°C) and high pressure (14 and 20 GPa) using a multi-anvil apparatus. The results of this study are used to understand the effect of sulfur and oxygen on core dynamics in small terrestrial bodies. We observe that oxygen has little effect on the liquidus temperature and that the formation of solid FeO grains occurs at the Fe-S liquid – Fe solid interface at high temperature (>1400°C at 20 GPa). Oxygen fugacities calculated for each O-bearing sample showed that redox conditions vary from ΔIW=-0.65 to 0. Considering the relative density of each phase and existing evolutionary models of terrestrial cores, we apply our experimental results to the cores of Mars and Ganymede. We suggest that the presence of FeO in small terrestrial planets tends to contribute to outer-core compositional stratification. Depending on the redox and thermal history of the planet, FeO may also help forming a transitional redox zone at the core-mantle boundary.

1. Introduction

Different light elements (e.g., sulfur, oxygen, hydrogen, nitrogen, carbon, silicon) could have been added to the Fe-Ni metallic core of terrestrial planets during differentiation processes (e.g., Poirier, 1994; Wood et al., 2006). It has been suggested that several wt.% of light elements may compose the core of these planets, such as the Earth, Mars, and Mercury (e.g., Birch, 1964; Dreibus and Wänke, 1985; Harder and Schubert, 2001). Sulfur is thought to be a major light element in terrestrial cores due to its high solubility in liquid iron (Dreibus and Wänke, 1985; Dreibus and Palme, 1996; Allègre et al., 2001) and to the possible segregation of liquid FeS sulfide into the core (e.g., O'Neill, 1991; Laurenz et al., 2016; Rubie et al., 2016). Earth's core density deficit of up to about 10 wt.% compared to the density of a pure Fe-Ni core (e.g., Anderson and Isaak, 2002) is usually assumed to be the result of a combination of several light elements, as S (or Si) alone cannot satisfy the density jump at the inner core boundary (i.e. outer core density deficit) while preserving the (astronomically-determined) mass of the core (e.g., Alfé et al., 2002). One major candidate is oxygen (e.g., Ohtani and Ringwood, 1984; Ringwood and Hibberson, 1991; Badro et al., 2015) because of its abundance in the bulk Earth, its partitioning behavior into metal at core pressure and temperature (Alfé et al., 2002), and because thermodynamic calculations and high-pressure experiments showed a high solubility of S and O in liquid iron (e.g., Urakawa et al., 1987; Tsuno and Ohtani, 2009; Buono and Walker, 2015). Considering a Fe-S-O system, the oxygen abundance in the Earth's present-day core can be as high as ~6 wt.% (McDonough and Sun, 1995; Tsuno et al., 2007; Davies et al., 2015). Because high solubility of S and O in liquid Fe is observed at shallower pressure than Earth's core pressure (e.g., Tsuno et al., 2007), it is possible that the metallic core of terrestrial bodies smaller than the Earth also contains these two light elements in significant amounts.

At the conditions of Earth's inner core boundary, *ab initio* calculations based on density functional theory suggest that oxygen partitions almost entirely into the liquid phase on freezing (Alfé et al., 2002). This partitioning depresses the core melting temperature by 500-1000 K (Davies et al, 2015), which is a key factor in determining the timing of inner core formation. Oxygen rejected from the solid phase as the inner core freezes is lighter than the overlying liquid and must rise, mixing the outer core (Braginsky, 1963). The associated gravitational energy release is the most efficient power source for generating magnetic field and is the dominant contribution to maintaining the present geodynamo (Lister and Buffett, 1995; Nimmo, 2015). It has also been proposed that oxygen accumulates below Earth's core-mantle boundary (CMB), either via chemical reactions with the mantle or by pressure-driven diffusion, creating a stable stratification (Buffett and Seagle, 2010; Gubbins and Davies, 2013; Brodholt and Badro, 2017). However, it is presently unclear whether oxygen plays the same crucial dynamical role in the core of smaller terrestrial bodies (i.e., at smaller pressure than Earth's core pressure) as it does in Earth. This gap in our current understanding of planetary cores at conditions relevant to small terrestrial planets requires the investigation of the crystallization of O-bearing phases and the partitioning behavior of oxygen between these phases. It has been suggested that the core of small terrestrial planets contains only a very small concentration of oxygen, because the temperatures experienced by these small bodies may not be high enough to partition a significant amount of oxygen into the metallic core (e.g., Rubie et al., 2004). However, there is no consensus on the amount of oxygen in the core of these terrestrial planets yet, and other laboratory-based thermodynamic models proposed that a few wt. % O may be stored in their core (e.g., Tsuno et al. 2011). In the present study, we consider the latter hypothesis and examine the effect of oxygen on the crystallization of a Fe-S core in small terrestrial bodies.

Several experimental studies have investigated the effect of oxygen on phase equilibria of the Fe-S system, but only a few of them were conducted at pressures relevant to the cores of small terrestrial planets (i.e. up to a few tens of GPa) and near the liquidus temperature in order to investigate core crystallization processes (Urakawa et al., 1987; Tsuno et al., 2007, 2011; Tsuno and Ohtani, 2009; Buono and Walker, 2015). However, these studies conducted in the Fe-S(-O) systems considered either high S contents (>10 wt.% S in Buono and Walker, 2015 and Tsuno et al., 2011) or high O contents (>8.0 wt.% O in Tsuno et al., 2007; >3.7 wt.% O in Tsuno and Ohtani, 2009) and thus cannot be used to understand the effect of a small amount of light elements on core crystallization. Here, we present phase equilibria experiments in the Fe-S and Fe-S-O systems at 14 and 20 GPa and at high temperatures ($>T_{eutectic}$). We conducted experiments on Fe-S samples containing 1 and 5 wt.% S in order to characterize the meting relationships of core analogues containing a small amount of S. Constraining the shape of the liquidus curve in the Fe-S system is key to understand the crystallization processes of cores and requires further experimental constraint, as previous studies suggested either a parabolic or a sigmoidal shape (Fei et al., 2000; Chen et al., 2008, respectively). Experimental oxygen fugacities are calculated for each sample. Experiments in the Fe-S-O system were conducted at pressure and temperature conditions similar to the experiments on Fe-S in order to allow direct comparison and characterize the effect of a small amount of oxygen (up to 3 wt.% O) on Fe-S phase equilibria. Our results are applied to the cores of Mars and Ganymede in order to constrain the effect of oxygen on the structure and possible evolution of terrestrial cores as well as their magnetic activity.

2. Experimental methods

2.1. Starting materials

Experimental samples consist of Fe-S and Fe-S-O mixtures that were synthesized from FeS and Fe powders in various proportions, with the addition of Fe_2O_3 for the O-bearing materials. Each mixture was placed in a drying oven at about 150°C for several hours and then stored in a desiccator. Five compositions were obtained and atomic proportions are listed in Table 1. No nickel was added to our starting materials as previous work pointed out that adding Ni to the Fe-S system does not significantly affect the liquidus temperature and phase relations of Fe and Fe-S (Stewart et al., 2007; Martorell et al., 2013) though this small effect can be observed (Zhang and Fei, 2008).

2.2. Phase equilibrium experiments

Experiments were performed at 14 and 20 GPa and at temperatures ranging from 1400 to 1850°C. All experiments were performed in a Kawai-type multi-anvil apparatus using tungsten carbide cubes with a corner-truncation edge length of 4 mm and MgO (doped with 5 wt.% Cr_2O_3) octahedral pressure media with an edge length of 10 mm. The samples were placed in either high purity MgO single crystal capsules or Al_2O_3 tubing topped with MgO spacers, and surrounded by a $LaCrO_3$ heater. The assembly was dried in a furnace at 1000°C before the experiment. The thermal gradient inside the sample is estimated to be in the order of 10-20°C/mm (Rubie, 1999, Buono and Walker 2015). Some experiments contained two sample capsules on top of each other that were run simultaneously. A type D $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple was placed in contact with the top MgO spacer through the heater, and in case the thermocouple was lost during an experiment, the power-temperature relationship was used to estimate temperature. Run duration was 20 min at the highest temperatures (1760 and 1850°C) and 30 min at lower temperatures (Table 1). Previous work on the monitoring of thermal and chemical equilibrium in the Fe-S system showed that this is sufficient time at these pressure and temperature conditions to obtain a homogeneous chemical composition, indicating that chemical and phase equilibrium was reached (Chen et al., 2008a). The experiments were ended by quenching, i.e., by turning off the power to the heater. Recovered samples were mounted in epoxy and polished for chemical analyses.

2.3. Analytical techniques

Recovered samples were polished for microscope and electron microprobe analyses at the Bayerisches Geoinstitut. Textural analyses of the quenched samples were used to determine melting relations. Chemical analyses of the recovered samples and MgO capsules were performed using an electron microprobe (Jeol JXA-8200) with 15 kV accelerating voltage and 15 nA beam current. Counting times were 20 s for major elements and 10 s for background. Standards were metallic iron or Fe_2O_3 for Fe (depending on the phase analyzed), FeS_2 for S, MgO or Fe_2O_3 for O, and enstatite for Mg. The ZAF correction method was used for matrix corrections. All solid phases were analyzed using a focused beam. Because sulfide and metallic melts show quench textures, they were analyzed using a defocused beam of 20 μm in diameter. Bulk chemical compositions were obtained by averaging grid analyses (3x3 points along grids of 60μmx60μm). Several of these grids were analyzed and each grid–average was taken as a single analysis from which final averages and standard deviations were calculated (Table 2). This procedure has previously been shown to yield comparable results to estimating bulk compositions via image analysis (Chabot and Drake, 1997).

3. Results

3.1. Sample textures and phase relations

The experimental conditions and observed phase assemblages are summarized in Table 1 and the chemical composition of each phase is listed in Table 2.

3.1.1. Fe-S binary system

Back-scattered electron (BSE) images of several experiments are presented in Figure 1. Samples with Fe-S starting composition either show a single quenched liquid phase or both metallic iron and a liquid phase that quenched to iron dendrites in the Fe-S matrix (Figure 1). Small amounts of oxygen in these experiments were measured in the liquid phase and a few small FeO grains were observed in some retrieved samples (Figure 1c, Table 2). The presence of minor amounts of O in these samples possibly results from interactions with surrounding materials (capsule and/or heater).

Using the textures obtained from experiments at different temperatures, we inferred a portion of the liquidus curve in the Fe-FeS system at 14 GPa and 20 GPa

(Figure 2). At 14 GPa, our results are consistent with the ones by Chen et al. (2008a) at a similar pressure but are different from the predicted liquidus by the thermodynamic model by Buono and Walker (2011). As underlined by Buono and Walker (2011), this can be explained by a change in the thermodynamic behavior of the liquid that occurs above 10 GPa. At 20 GPa, the determination of the liquidus curve from our data at about 5wt.% S does not agree with the predicted liquidus curve from Fei et al. (2000) at 21 GPa: for this composition, Fei et al. predicted a liquidus temperature of 1900 °C, while an additional data point from our experiments suggests a temperature of ≈1700°C (+/-50) that would be consistent with a sigmoidal shape of the liquidus curve, though our data cannot confirm that the shape at 20 GPa is sigmoidal. We observe a steep slope of the liquidus curve between 2000 and about 1600°C and a relatively flat slope near 1500°C. Our data would be consistent with an inflection point at about 7wt.% S. This has previously been observed in the Fe-S system over a wide pressure range for a similar sulfur content (at 14 GPa, Chen et al., 2008a; from 15 to 20.6 GPa, Andrault et al., 2009; from 1 bar to 10 GPa, Buono and Walker, 2011 and references therein) and indicates a non-ideal liquid solution behavior with a metastable solvus beneath the liquidus. Such a sigmoidal shape is characteristic of a metastable miscibility gap (i.e. metastable with respect to solid Fe and liquid) at temperatures below the inflection point of the liquidus (e.g., Buono and Walker, 2011).

Three experiments were conducted with starting materials containing 36.5 wt.% S. Solid FeS was observed in the three experimental products, as is expected from phase equilibria, but the absence of a liquid phase in two of them (S6421 and S6535b) is not in agreement with previous phase diagrams (Fei et al., 2000; Chen et al., 2008a). This might be explained by the fact that these experiments are close to the boundary between FeS + liquid field and the field of single solid solution pyrrhotite $Fe_{1-x}S$ expected at 35 wt.%S (Ehlers, 1972). A small oxidation of Fe into FeO in these experiments leaves the bulk composition with a higher S content (i.e., >36wt.%), and thus, the solids obtained in our experiments are solid phases stable at sulfur contents >35wt.% S.

3.1.2. Fe-S-O ternary system

As illustrated in Figure 3a, samples of Fe-S-O starting composition quenched from above the liquidus temperature present quenched liquid made of Fe-dendrites, Fe-S matrix, and rosaceous FeO grains (compositions listed in Table 2). For samples quenched from below the liquidus temperature, BSE-images show that the phases are metal Fe and solid FeO coexisting with a liquid phase composed of Fe-dendrites and a Fe-S matrix (Figure 3b-f). Several FeO-rich blobs were observed in large metallic iron grains and may represent exsolution products from the Fe-metal phase (Figure 3b). It should be noted that in all Fe-S-O experiments, the use of MgO capsule leads to the formation of a thin ferropericlase layer at the sample-capsule interface, due to the reaction between iron and MgO (Figure 3).

Extensive crystallization of solid FeO at the interface between solid iron and liquid phase (Figure 3c-f) was observed in all oxygen-added experiments except in two runs performed at 20 GPa (Table 1): S6426, which was conducted above the liquidus temperature (Figure 3a) and S6428, which was the experiment performed at the lowest temperature (1400°C, Figure 3b). At lower pressure (14 GPa), a continuous FeO layer was observed at 1400°C. In runs performed at temperatures close to the liquidus (which depends on both composition and pressure: 1600°C at 20 GPa, and 1400-1500°C at 14 GPa), the FeO layer is partially broken up (Figure 3d-f), with one side of the layer showing FeO grains dissociated from the layer and being disseminated into the melt phase. The following observations can be made regarding the stability of the FeO layer: 1) at 20 GPa, the FeO layer is only observed at temperature higher than 1400°C, whereas it is present at 14 GPa and 1400°C and 2) at high temperature, the layer is broken and FeO grains move towards the liquid phase. Further work is required to determine whether or not the texture of the layer depends on its thickness, and if a threshold in the layer thickness exists, above which the layers breaks down into FeO grains. No effect of the bulk oxygen content (up to 3 wt.% O) is observed on the stability of the layer, since experiments containing 0.65 and 3 wt.% O performed at the same *P, T* conditions both present this structure of FeO grains (S6435 and S6433a, Table 1).

Electron microprobe traverses performed across the interfaces between O-bearing samples and the MgO capsule indicate the formation of a nearly continuous layer of ferropericlase (Figures 3e-f and Section 3.2). However, these reaction rims are only about 10 micron thick, and microprobe analyses across the sample and away from this layer showed homogeneous chemistry of each phase throughout the capsule.

3.2. Solubility of oxygen and sulfur in the metal and melt phase

In both Fe-S and Fe-S-O experiments, oxygen content in solid iron is negligible (Table 2), which is in agreement with oxygen contents reported by Tsuno and Ohtani (2009) and Tsuno et al. (2011). The amount of sulfur dissolved in solid iron increases with decreasing temperature from 0.2 to 0.5 at.% S (Figure 4a) and the absence of solubility of S in FeO was observed. These sulfur contents are in agreement with previous studies at comparable pressure (Li et al., 2001; Stewart et al., 2007; Tsuno and Ohtani, 2009). When temperature is below the liquidus, solid iron is in equilibrium with the Fe-S liquid that has less and less sulfur when temperature increases, due to the dilution effect. With increasing temperature, the activity of sulfur in the Fe-S melt decreases, which leads to a decrease in the sulfur content in the coexisting solid iron.

For Fe-S-O experiments crystallizing FeO, the samples are FeO buffered, suggesting that we can constrain the O content of both Fe metal and coexisting liquid in terms of the effects of T and S-content. Sulfur and oxygen solubilities in the liquid phase are presented in Figures 4b and 4c. At low temperature (1400°C), the first liquids produced are sulfur-rich, containing up to 28 at.% S (Figure 4b), which promotes the incorporation of oxygen into the liquid phase. As shown in Figure 4c, the oxygen content in the liquid increases with temperature (from 0.7 to 3.2 at.% on the investigated T range). Increasing temperature increases the ability of the liquid to dissolve oxygen and decreases the sulfur content of the liquid by dilution effect. At higher temperature (>1800°C), a decrease of the oxygen content in both liquid and solid is expected, due to the effect of decreasing the sulfur content.

3.3. Oxygen fugacity determination

For experiments in the Fe-S (-O) system, Fe-metal is generally in equilibrium with an FeO-bearing oxide (either pure FeO or ferropericlase), so that the oxygen fugacity of the sample can be defined by the following redox reaction

$$2Fe_{metal} + O_2 = 2FeO \qquad (1)$$

for which the equilibrium constant can be written as follows

$$K(1) = \log\left[\frac{(a_{FeO})^2}{\left(a_{Fe}^{metal}\right)^2 f_{O_2}}\right] = 2\log\left[\frac{X_{FeO}}{X_{Fe}^{metal}}\right] + 2\log\left[\frac{\gamma_{FeO}}{\gamma_{Fe}^{metal}}\right] - \log f_{O_2}^{exp} \qquad (2)$$

where $f_{O_2}^{exp}$ denotes the oxygen fugacity of the experiment and a_i, X_i and γ_i are the activities, mole fractions and activity coefficients of i (i.e., Fe and FeO), respectively. If pure Fe is in equilibrium with pure FeO (i.e. a_{Fe} = a_{FeO}=1), equilibrium (1) defines the Iron-Wüstite buffer and $K(1) = -logf_{O2}^{IW}$. Substituting this relationship into Eq. (2) yields

$$logf_{O2}^{exp} - logf_{O2}^{IW} = 2log\left[\frac{X_{FeO}}{X_{Fe}^{metal}}\right] + 2log\left[\frac{\gamma_{FeO}}{\gamma_{Fe}^{metal}}\right] = \Delta IW \qquad (3)$$

The oxygen fugacity of the experiments can therefore be expressed relative to the IW-buffer using Eq. (3). In many experiments, pure Fe metal is in equilibrium with pure FeO, so that ΔIW=0. If no pure FeO phase is present to calculate fO_2, we used ferropericlase that formed as a result of the reaction of the sample with the MgO single crystal capsule. Taking into account the activity composition relations in ferropericlase (Frost et al., 2003) and assuming that Raoult's Law is valid (i.e., γ_{Fe}^{metal}=1) (Mann et al., 2009), the experimental fO_2 can be expressed relative to the Iron-Wüstite buffer using the following equation (Mann et al., 2009)

$$\Delta IW = 2log\left[\frac{X_{FeO}^{ferrop.}}{X_{Fe}^{metal}}\right] + \frac{2(11{,}000 + 0.011P)(1 - X_{FeO}^{ferrop.})^2}{RTln10} \qquad (4)$$

with P the pressure (bar), T the temperature (K), and R the universal gas constant. For all samples from the Fe-S system containing small amounts of oxygen, at both 14 and 20 GPa, ΔIW ranges from -0.65 to -0.13 (Figure 5 and Table 2), whereas experiments in the

Fe-S-O system being FeO buffered, ΔIW=0. There is no noticeable effect of temperature on the calculated fO_2, suggesting that the absolute fO_2 of the experiments evolves parallel to the buffer with changing T.

4. Discussion

4.1 Formation and stability of FeO grains at the melt-solid iron interface in laboratory experiments and in planetary cores

We suggest that the formation of FeO results from a compositional gradient in oxygen in the sample initiated by a small thermal gradient across the capsule. When Fe-S-O melt contains metal iron, the melt separates from the residual solid phase due to a small temperature gradient, rather than density contrast (Walker, 2000). The presence of a small thermal gradient would favor the accumulation of solid metal in the cold end of the capsule (Buono and Walker, 2015). The process is independent from the relative density of each phase, as it has been shown that dense solid iron can accumulate at the top of the capsule (Walker, 2000). This observation contrasts significantly with a planetary core, in which the buoyancy force points in the direction of gravity. In terms of oxygen solubility in the liquid, the thermal gradient associated with the accumulation of solid metal in the cold part of the capsule results in a gradient in oxygen solubility within the liquid phase: oxygen solubility in the liquid decreasing with temperature (Figure 4c), it is the smallest at the solid-melt interface, i.e. where temperature is the lowest. Because oxygen solubility is negligible in solid iron, the solid-melt interface starts forming FeO grains. We suggest that the stability of the FeO grains is due to changes in oxygen solubility in the melt, probably as a function of temperature.

The presence of an FeO layer has also been reported by Buono and Walker (2015) at 6-8 GPa and was thought to be immiscible FeO liquid, whereas Tsuno et al. (2011) suggested that FeO is present as a solid phase in their experiments at 5-24.5 GPa. It is reasonable to assume that FeO in our experiments and in these previous studies is solid for three major reasons: 1) The melting temperature of FeO is ≈1470°C at 8 GPa, ≈1650°C at 14 GPa and ≈1950°C at 20 GPa (Fischer and Campbell, 2010), which is a much higher temperature than the one in the experiments of Buono and Walker (<1100°C) and in our experiments; 2) The Fe-oxides in the experiments are slightly non-stoichiometric, which could affect the melting temperature of the system. However, Komabayashi (2014) pointed out that at about 14 GPa on the O-rich side of the immiscibility gap, the lowest melting temperature for an ionic melt at the monotectic point with about 20 wt.% O (corresponding to a composition comparable to the one of our Fe oxides) is ≈1880°C, which is still higher than the temperature of Buono and Walker's experiments as well as our experiments; 3) Textural observations of the quenched samples suggest that the texture of the FeO layer is very different from the one of the quenched ionic liquid shown in Tsuno et al. 2011, and the angular appearance of the FeO grains in the solid Fe metal also suggests that FeO is solid.

The solid/liquid interface being an energetically favorable interface to the formation of FeO grains, FeO crystals can also form at the solid/liquid interface of a partially crystallized Fe-S-O planetary core. Another point in common to a cooling core and the experiments regards the solubility of oxygen in the melt phase, which decreases with temperature (Figure 4c). This eventually results in the crystallization of FeO grains, preferentially at the solid-liquid interface. The formation of FeO grains is expected in the core, as phase equilibria apply both at the capsule scale and the core scale. However, we propose that the stability of FeO grains in a planetary core is due to a mechanism that is different from the one observed in the experiments because of the importance of buoyancy, whereas the driving forces that control the stability of FeO in a capsule are constrained by a small volume of core material and a small thermal gradient.

4.2. Application to planetary cores

4.2.1. The fate of oxygen in a cooling core

The dynamo in a fully or partially liquid core generates an intrinsic magnetic field. Depending on the cooling history of the planet, a dynamo may be powered by compositional convection (e.g., Hauck et al., 2006; Rückriemen et al., 2015), thermal convection (e.g., Stevenson et al., 1983; Williams and Nimmo, 2004; Kimura et al., 2009; Dumberry and Rivoldini, 2015), impact-induced changes in the rotation rate (Le Bars et al., 2011), or mechanical stirring (Dwyer et al., 2011). In all cases, the chemistry and structure of the core plays a critical role (e.g., Breuer et al., 2015). Here we consider a convection-driven dynamo and we use experimental results to assess its evolution during core cooling.

We consider sulfur concentrations in planetary cores to be below the eutectic Fe-S value (from 5 to 15 wt.% S), in agreement with the sulfur content estimated in the core of Mars (e.g., Dreibus and Wänke, 1985, Sanloup et al., 1999) and Ganymede (e.g., Hauck et al., 2006), though a FeS core with 36.5 wt.% S has also been suggested for the latter (Kimura et al., 2009). The eutectic composition varies with pressure, and corresponds to about 15wt.% S at 20 GPa and 18wt.% S at 14 GPa, i.e. at Mars CMB conditions (Figure 2; Fei et al., 2000; Chudinovskikh and Boehler, 2007; Chen et al., 2008a; Buono and Walker, 2015). The eutectic composition is not expected to have less than about 13.5 wt% over the entire depth of the Martian core (Mori et al., 2017). Considering compositions below the eutectic implies that crystallization in the Fe-FeS system produces solid phases (metal iron at high temperature and Fe_3S at low temperature, Figure 2) that are denser than the Fe-S liquid. If oxygen is present in planetary cores (e.g., Rubie et al., 2004, Tsuno et al., 2011), its presence during core crystallization results in the formation of solid FeO coexisting with solid Fe and with little oxygen present in the coexisting liquid phase (Table 2), as observed in our experiments containing 0.65 and 3 wt.% O and in previous works (Urakawa et al., 1987; Tsuno and Ohtani, 2009; Buono and Walker, 2015). As explained above, FeO grains are expected to crystallize at the interface between solid Fe and Fe-S liquid. The fate of this region depends on the thermal structure and crystallization regime of the core as well as the relative density of each phase.

Three possible crystallization regimes have been identified in terrestrial cores for sulfur concentrations below the eutectic, depending on the depth of the intersection of the adiabat with the melting curve (e.g., Breuer et al., 2015): 1) if $\partial T_{liquidus}/\partial P > \partial T_{adiabat}/\partial P$ at all P, a solid inner core grows radially outward, and gravitational energy is provided by sulfur partitioning into the liquid phase; 2) if $\partial T_{liquidus}/\partial P < \partial T_{adiabat}/\partial P$ at all P, crystallization begins at the outermost part of the core and follows an iron "snowing" regime; 3) in case the relative slopes of $T_{adiabat}$ and $T_{liquidus}$ vary with pressure, crystallization begins in the middle of the core and proceeds towards both the center and the CMB.

In a Fe-S-O core, the evolution of each crystallization regime will depend on the relative density of O-bearing and S-bearing phases. Previous work observed that metallic iron is denser than liquid Fe-S and solid FeO at core pressure (e.g., Huang et al., 2011), implying that upon crystallization at any depth, metallic iron will sink towards the center of the planet. Comparison between density studies on FeS liquid, FeS solid, and FeO solid (Sanloup et al., 2000; Balog et al., 2003; Murakami et al., 2004; Kondo et al., 2004; Urakawa et al., 2004; Nishida et al., 2008, Huang et al., 2011) suggests that 1) the density of liquid Fe-S is higher than the density of solid FeS if the sulfur content in the liquid is less than 30wt.%, which is the case for the considered compositions of the planetary cores; 2) little difference exists between the density of FeS solid and FeO solid at P< ≈80 GPa; the Hugoniot curves for FeO and FeS (in the form of FeS-IV) predict only a slightly lower density for FeO than for FeS (about 0.5 g/cc of difference), and experimental data by Huang at al. (2011) report an even smaller density difference; 3) at P>6 GPa and high temperature, solid FeO is less dense than a Fe-S liquid containing 10 wt.% S. Therefore, we consider that the densities of the first phases to crystallize in a Fe-S-O core range as follows

$$\rho_{Fe\ metal} > \rho_{FeS\ liquid} > \rho_{FeO\ solid} \sim \rho_{FeS\ solid}, \quad (5)$$

implying that FeO is expected to migrate upward and potentially pile up at the CMB whereas metallic Fe will tend to sink. This also suggests that if a partially or fully crystallized core contains oxygen that does not significantly partition into the mantle, then the outermost part of it will tend to be enriched in oxygen through time whereas the innermost part will tend to be depleted, independently of the crystallization regime (bottom, top, or middle crystallization).

In case the crystallizing S-bearing phase is Fe_3S (and not Fe or FeS), core dynamics will strongly depend on the resulting density profile of the core, as discussed in detail in Breuer et al. (2015). For instance, in the case of top-down crystallization, solid Fe_3S being denser than the residual fluid (Stewart et al., 2007), it is expected to sink and remelt at depth in a process similar to the iron snow regime (Breuer et al., 2015). However, Fe_3S crystallization results in increasing density with depth due to an increase in S content with depth, which is a gravitationally unstable situation, affecting the long-term dynamics of the core. Comparison of density measurements of FeO and Fe_3S at 300K (Huang et al., 2014 and Kamada et al., 2014, respectively) suggest that Fe_3S is slightly denser than FeO at similar pressure. This suggests that FeO is expected to migrate upward, though core dynamic modeling studies are required to assess the effect of Fe_3S crystallization on FeO upward migration.

4.2.2. The effect of FeO on the heat budget of a cooling core

Like most crystallization reactions, the formation of FeO is exothermic (e.g., Alfè et al., 2002). When scaled to a planetary core, this production of heat from FeO formation may have consequences on the thermal structure and hence the dynamics of the core. The heat of reaction associated to FeO crystallization can provide an entropy source for the dynamo, but a detailed investigation is needed to determine its importance compared to the other entropy sources that depend on the cooling rate.

The presence of solid FeO in a metallic core will also influence the gravitational energy and the latent heat. In our experiments, FeO grains are sandwiched between solid and liquid Fe-S, a potentially gravitationally unstable configuration. In applying this result to planetary cores (Figure 6), we first consider the case where freezing produces solid Fe underlying the FeO layer. Top-down freezing yields continuous crystallization of Fe and also produces FeO grains trapped beneath the CMB owing to its density deficit (assuming negligible mass exchange with the mantle), while the solid Fe falls and remelts, mixing the underlying Fe-S liquid owing to its excess density. The dynamics are expected to be similar to the standard iron snow regime. If freezing initiates at greater depths then solid Fe will fall while the buoyant FeO layer will rise, possibly remelting as discussed below. In this scenario gravitational energy is released as the FeO grains migrate upwards, which can act to power core convection and dynamo action. In a case where freezing produces solid iron laying atop FeO, the configuration is dynamically unstable and mixing between the two solid layers will inevitably ensue. Whether and how a solid inner core grows in these conditions is not known at present.

The production of FeO on freezing leads to the release of latent heat, which may be partially balanced by latent heat absorption if dynamic instability results in remelting of FeO. In bottom-up freezing the latent heat released by freezing out the FeO crystals at the inner core boundary will add to that produced by freezing out FeS solid; both act as power sources for core convection and dynamo action (Gubbins et al., 2003). However, since the FeO grains are lighter than the overlying Fe-S liquid, they will presumably rise and remelt at shallower depth, absorbing latent heat. Remelting at shallow depth is consistent with the melting curve of FeO at low pressure (e.g., Komabayashi, 2014). The net latent heat released or absorbed in this process will depend on the melting gradient, but recent models of a similar process suggest it will be small at the core conditions of small terrestrial bodies, such as Ganymede (Rückriemen et al., 2015). Alternatively, in top-down freezing the latent heat released by FeO formation will not be balanced by remelting since the layer is buoyant. However, latent heat release at the top of the core provides very little entropy even though it may provide a lot of heat, a situation that is likely to stifle dynamo action (Davies and Pommier, in press).

Determining which of these competing effects governs core dynamics will depend on the structure and history of the planet considered. Another effect that could influence dynamo activity is liquid immiscibility, which has not been observed in our experiments but was obtained in previous work conducted at temperature higher than our maximum T (e.g. Tsuno et al., 2007). Early in its history, a core may be entirely molten due to the combined effects of accretionary and radioactive heating. If the cooling of the Fe-S-O core through time is slow and keeps temperature above the liquidus and above 2000°C, then liquid FeO coexists with one or two immiscible liquids (ionic and metallic) at $P<20$ GPa and the immiscibility gap disappears at pressure higher than 21 GPa (Tsuno et al., 2007). If the cooling of a Fe-S-O core through time is fast, then the core crystallizes rapidly and the lack of a significant liquid phase may cause the dynamo to stop. The fluid dynamics also depend on the state of FeO (solid or liquid) as it migrates across the core, and it is unclear how liquid immiscibility in the Fe-S-O system will affect the heat flux of the cooling core.

4.2.3. *Implications for Mars and Ganymede: the effect of oxygen on the magnetic activity of the core*

Past missions have detected different magnetic activities on Mars and Ganymede: Mars does not currently possess an internally-generated magnetic field but likely had an ancient magnetic field (Acuña et al., 1999; Solomon et al., 2005), while Ganymede presents strong magnetic field (Kivelson et al., 1996).

Figure 7 compares the present-day thermal structure of Mars and Ganymede with results of phase equilibria experiments in the Fe-S-O system, and in particular the conditions for which FeO grains are observed from our experiments and previous experimental studies. For each planet, the adiabats come from modeling studies (Breuer et al., 2015 for Ganymede; Williams and Nimmo, 2004, Hauck and Phillips, 2002 for Mars). Considering a Fe-S-O core composition, this figure suggests that the three cores possibly contain FeO today, and may have formed FeO early in their history in case they cooled down rapidly, which seems to have been the case for Mars (Williams and Nimmo, 2004; Breuer and Spohn, 2006).

Being the most oxidized terrestrial body with a high FeO content in the mantle (17.9 wt.% FeO, Dreibus and Wänke, 1985), Mars may have stored a large amount of oxygen in its core. Though several previous studies have found acceptable thermal histories for Mars that involve no core crystallization, some hypothesized a plausible alternative scenario that requires partial crystallization of the core (Stewart et al., 2007), suggesting that Mars may have entered a snow regime in the past (Davies and Pommier, in press). As shown in Figure 6 (top panel), the crystallization of metal iron in a snow regime (possibly containing some FeO exsolution) at the CMB and the formation of solid FeO at the metal iron - liquid Fe-S interface are gravitationally unstable, due to the high density of the metallic phase. The sinking of dense pure Fe would cause the disruption of the FeO layer and the upward migration of less dense FeO (Figure 6, top panel). As a result, if oxygen is present in the Martian core, it has been in the solid form as FeO for most of its time-evolution and the equilibrium state should be one of stable chemical stratification beneath the CMB. Regarding the redox state of the planet's core, it should be close to ΔIW due to the presence of FeO (Figure 5). This value is close to estimates of redox conditions for the mantle, thought to be ΔIW~-1 (e.g., Righter et al., 2016 and references therein; Figure 5), suggesting that the difference in redox conditions between the outer core and the lower mantle may be too small for chemical stratification at the Martian CMB to act as a redox transition zone.

The dynamics of Ganymede's core is poorly constrained and its intrinsic magnetic field (Kivelson et al., 1996) and moment of inertia (Schubert et al., 2004) have been explained both by compositional (Hauck et al., 2006; Bland et al., 2008) and thermal dynamos (Kimura et al., 2009). Our results in the Fe-S-O system suggest that the formation of solid FeO could affect the efficiency of a compositional dynamo, by forming a FeO-rich layer in the outermost core and reducing the thermal gradient across the core by releasing heat. An iron snow regime has been proposed for Ganymede's core (Hauck et al. 2006; Christensen 2015; Rückriemen et al. 2015) and the present-day estimates for the thermal structure of the core (from 1250 to 1750K in the pressure range 6-10 GPa, Breuer et al., 2015) are compatible with the presence of solid FeO (Urakawa et al., 1987). Beside sulfur and possibly oxygen, Ganymede's core, like other terrestrial cores, may contain other volatile elements (such as hydrogen, Shibazaki et al., 2011) and further work is required to assess the effect of these elements on dynamo activity.

5. Conclusions

Phase equilibria experiments in the Fe-S and Fe-S-O systems at 14 and 20 GPa and at temperature up to 1760°C suggest that oxygen has little effect on the liquidus temperature. FeO crystallizes in the form of solid grains at the Fe-S liquid – Fe solid interface. At 20 GPa, this FeO-rich interface is stable from T>1400°C up to 1760°C. Redox conditions vary from ΔIW=-0.65 to 0, based on oxygen fugacities calculated for each sample. Using our experimental results and density constraints, we examine the effect of oxygen in the core of Mars, Mercury, and Ganymede, and suggest that the presence of FeO in small terrestrial planets tends to contribute to outer-core compositional stratification. Depending on the redox and thermal history of the planet, FeO may also help forming a transitional redox zone at the core mantle boundary.

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Figure captions

Figure 1: Back-scattered electron images of run products in the Fe-S system. A) Fe, 5wt.% S, 20 GPa, 1760°C (S6413): fully molten sample showing Fe dendrites in an FeS matrix (dark grey); B) Fe, 5wt.% S, 20 GPa, 1400°C (S6418): large pure iron grains (right) coexist with quenched FeS liquid (left); C) Fe, 1wt.% S, 20 GPa, 1850°C (S6431): the iron matrix (bottom) containing a few FeO grains (black) is overlain by FeS liquid; D) Zoom in from C) in the quenched liquid area showing iron dendrites in an FeS matrix. Area of solid accumulation are expected to be slightly cooler than the top part of the capsule, suggesting that melt separates from the solid phase due to a small temperature gradient rather than density contrast (see text for details).

Figure 2: Phase relations in the Fe-S and Fe-S-O systems at 14 and 20 GPa (based on microprobe analyses on retrieved experimental samples). Each dot indicates the S and O contents in the liquid and is located at the corresponding S content of the liquid phase (except for experiments containing 35wt%S as the liquid phase was not analyzed). The data from two experiments are not plotted (S6433a and S6520a) as bulk melt analyses (defocused beam) were not performed. Grey lines are from previous studies at similar pressure (Fei et al., 2000; Chen et al., 2008a). The phases observed in the Fe-S-O system are labeled in green. Numbers in italic are wt. S in the liquid phase coexisting with metal Fe (Fe-S system). The red dashed line indicates a possible corrected FeS liquidus (see text for details). No significant effect of oxygen on liquidus temperature is observed.

Figure 3: Back-scattered electron images of run products in the Fe-S-O system. A) Sample containing 0.65wt.% O quenched at 1760°C and 20 GPa (S6426). Fe dendrites (light grey) coexist with FeS matrix and FeO (dark grey) is present in the quenched liquid as rosaceous grains; B) Sample containing 3wt.% O quenched at 1400°C and 20 GPa (S6428). FeO is present as isolated grains (dark grey) in solid iron. The absence of an FeO layer at the liquid/solid interface suggests that the layer stability is temperature dependent (see text for details); C) Sample containing 3wt.% O and quenched at 1400°C and 14 GPa showing the presence of a continuous FeO layer at the liquid/solid interface (S6433b); D) FeO layer (gray) in sample containing 3 wt.% O, 14 GPa, 1500°C (H4277); E) and F): destruction of the FeO layer at 14 GPa, 1400°C (S6535a, E)) and 20 GPa, 1600°C (S6520a, F)). Area of solid accumulation are expected to be slightly cooler than the top part of the capsule, suggesting that melt separates from the solid phase due to a small temperature gradient rather than density contrast (see text for details).

Figure 4: Sulfur and oxygen solubilities in solid iron and liquid. A) Amounts of S in the iron metal phase as a function of temperature and comparison with previous studies. O contents in the solid phase were about 0.2 at.% or less. B) Concentration of S in the liquid phase for samples with (filled circles) and without (open circles) oxygen added as a function of temperature at 14 and 20 GPa. A general trend suggests a decrease in S content with increasing the degree of partial melting. C) Concentration of O in the liquid phase as a function of temperature at 14 and 20 GPa. The amount of oxygen in the liquid phase increases up to ~1wt.% with increasing temperature.

Figure 5: Oxygen fugacity expressed relative to the Iron-Wüstite buffer as a function of temperature. Redox conditions were calculated for each sample using the formalism of Mann et al., 2009 based on the FeO content in the MgO capsule (Fe-S system) or considering X_{FeO}=1 (FeO buffered experiments in the Fe-S-O system). Estimates of oxygen fugacity for present-day Martian lower mantle are shown for comparison and come from Righter et al., 2016 and references therein. See text for details.

Figure 6: Evolutionary scenarios of the cooling core of a terrestrial planet, considering a Fe-S-O composition with potentially the addition of other elements (such as Si). Top panel: top-down crystallization (snow regime), bottom panel: bottom-up crystallization (inner core). Both scenarios present stages of gravitational instability and all contribute to decrease the dynamo activity. In a snowing core, the presence of FeO decreases the magnetic activity by reducing the thermal gradient and may cause to the cessation of the dynamo. In an inner core crystallization regime, the presence of FeO at the solid inner core-liquid interface initially helps the dynamo by enhancing convection. The subsequent upward migration of FeO due to density contrast with coexisting phases then weakens the magnetic field. The heat production related to the formation of solid FeO is labeled Q_{FeO}. See text for details.

Figure 7: Pressure-temperature diagram showing experiments from this study and previous works in the Fe-S-O system (green data points), and comparison with the present-day thermal structure of Mars (maroon), Mercury (purple), and Ganymede (orange). Shaded areas are defined by possible adiabats for each planet from previous

modeling studies (Breuer et al., 2015 for Ganymede; Harder and Schubert, 2001 for Mercury; Williams and Nimmo, 2004, Fei and Bertka, 2005, Hauck and Phillips, 2002 for Mars). Fe-S (5wt.%S) melting curve from Chen et al., 2008b; iron meting curve and Fe-S eutectic from Chen et al., 2008b redrawn from Boehler, 1993; Fei et al., 1997. The presence of solid FeO at the solid Fe - liquid interface (green lines) is derived from our experiments and previous studies that observed FeO at the same interface (Buono and Walker, 2015) or not (Urakawa et al., 1987; Tsuno and Ohtani, 2009). The thermal structure of the three bodies considered overlaps the stability field of FeO and may have been compatible with the formation of solid FeO at the solid-liquid interface at some stage of core cooling, depending on the crystallization regime.