

OXYGEN PARTITIONING BETWEEN METALLIC ALLOY AND SILICATE MELTS. A. Ricolleau¹, Y. Fei¹ and V. Castro^{1,2}, ¹Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW, Washington D.C. 20015 (a.ricolleau@gl.ciw.edu, y.fei@gl.ciw.edu), ²Bucknell University, Lewisburg, PA (mvc003@bucknell.edu)

Introduction: In the planetary differentiation process, the metallic alloy segregates from the silicates to form a metallic core and silicate mantle. Earth's core is mainly composed of Fe-Ni alloy. The core density deficit, compared to the density of pure iron, requires the presence of about 10% of light elements in the liquid outer core. Among the likely candidates for the light elements in the core are S, Si, O, C, and H [1]. Previous studies have focused on the possibility of having S-Si and Si-O as the possible light elements in the core. Ternary combinations of light elements still need to be explored.

Some core formation scenarios suggested high temperature conditions which favour a significant portion of oxygen to enter in the core. Recent studies have investigated the solubility of oxygen in iron alloy with oxides melts up to 25 GPa [2, 3] and with silicates melts up to 140 GPa in diamond anvil cell [e.g., 4]. They showed that oxygen solubility increases with temperature, and decreases with pressure up to ~20 GPa and then increases at higher pressure. In order to understand behavior of oxygen during core formation, experiments on iron-silicate melts are required at pressures below 25 GPa. The results obtained under controlled oxygen fugacity and temperature in the multi-anvil apparatus will provide insight to the diamond-anvil cell data and can be compared with results on iron-oxides melts.

In this study, we investigated the solubility of oxygen in metallic alloys, such as Fe, Fe-Ni, Fe-Ni-S, Fe-Ni-S-C, in equilibrium with silicate melts, at 2 and 8 GPa and at 2000 and 2600°C.

Experimental procedure: Melting experiments were performed using several starting compositions (Table 1) including 'devolatilized' chondrite model compositions containing moderate amounts of S (0, 1.4 and 2.7 wt%), simplified compositions in the Mg-Si-O-Fe system, and pure iron. These starting materials were prepared from high-purity oxides, carbonates and metals. The proportions of SiO₂, Al₂O₃, CaO, MgO, NiO, Fe₂O₃, and Fe were chosen to resemble that of CI-chondrite. The relative abundances of metal Fe and Fe₂O₃ vary for the different compositions to be able to cover a range of oxygen fugacity conditions. We first mixed the required proportions of dried SiO₂, Al₂O₃, MgO, NiO, Fe₂O₃, and CaO (as CaCO₃), and the mixture was then slowly decarbonated in air from 600 to 1000°C. The appropriate amounts of FeS and Fe were

then added to the silicate mixture. The starting powders were homogenized under ethanol, dried and stored at 100°C.

Table 1. Chemical composition of starting materials

| wt% | SM1 ^a | SM2 ^b | SM3 ^b | SM4 ^b | SM5 | SM6 | SM7 ^a |
|-----|------------------|------------------|------------------|------------------|-------|-------|------------------|
| Si | 16.80 | 16.69 | 16.07 | 16.06 | - | 13.24 | 12.54 |
| Mg | 15.11 | 15.02 | 14.46 | 15.38 | - | 11.46 | 7.60 |
| Fe | 28.99 | 26.35 | 27.73 | 29.49 | 100.0 | 52.67 | 57.36 |
| S | 1.42 | 1.41 | 2.71 | - | - | - | - |
| Al | 1.34 | 1.33 | 1.28 | 1.36 | - | - | - |
| Ca | 1.47 | 1.46 | 1.40 | 1.49 | - | - | - |
| Ni | 1.69 | 1.68 | 1.62 | 1.72 | - | - | - |
| O | 33.19 | 36.07 | 34.73 | 34.50 | - | 22.63 | 22.50 |

a, b: we added 15 and 30 % of the total iron as an oxides, respectively.

Experiments were carried out at 2, 7 and 8 GPa and at 2000 and 2600°C using piston cylinder apparatus and a 1500-ton multi-anvil press at the Geophysical Laboratory. Piston-cylinder experiments were conducted at 2 GPa using half-inch talc-pyrex (at 2000°C) or talc-LaCrO₃ (at 2600°C) with straight graphite furnace and magnesia spacers. Multi-anvil experiments were carried out at 7 and 8 GPa in 18 mm edge length, cast, finned octahedral made of an MgO-based ceramic, which were contained within tungsten carbide cubic anvils with 11 mm truncated edge length. Outer Zirconia or LaCrO₃ sleeves were used as thermal insulator at 2000 and 2600°C, respectively. Temperature was monitored by WRe5%-WRe26% thermocouple inserted axially above the sample chamber. All runs were heated at the target temperature for 2 min. For the CI melts experiments, we used both C and MgO capsules. For the Fe-silicates melts, we used MgO capsule. All sample were analyzed using the JEOL 8900L electron microprobe at the Carnegie Institution of Washington.

Results and discussion: For the system containing sulfur, in graphite capsule, we observed two immiscible liquids at 2 GPa and one liquid at 8 GPa, which is in good agreement with the study of Corgne et al. [5]. Using MgO capsule, one liquid is observed at all pressures (Fig. 1). In the Fe-S-C system, at 2 GPa, one liquid is S- and O-rich and C-poor, the other is S- and O-poor and C-rich. By mass balance calcula-

tion, we obtained the total amount of oxygen in the metal. The oxygen content in the system containing carbon is lower than that without carbon (Fig. 2). At higher pressure, the oxygen content of the metal decreases. We obtained the partitioning of sulfur for each run and observed almost no change of D_s as the system becomes more reduced. With increasing pressure, the partitioning of sulfur increases as observed by Li and Agee [6].

We performed experiments on CI composition without sulfur in graphite and MgO capsule and observed one metal liquid in both cases. The oxygen content of the metal in MgO capsule (without carbon) is similar to what we measured in the system with sulfur. In graphite capsule, the oxygen content is lower than that in the system with sulfur (Fig. 2). Thus, our preliminary results seem to show that the presence of carbon decreases oxygen solubility in metallic alloy whereas sulfur and carbon will enhance oxygen solubility. In the carbon-free system, the presence of sulfur does not seem to change the oxygen solubility in alloys.

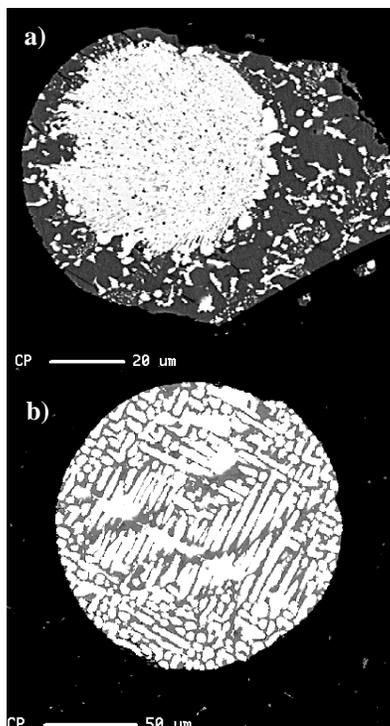


Fig.1: Quenched metallic alloys surrounded by silicate melts from 2 GPa and 2000°C, a) in a graphite capsule, b) in a MgO capsule. We observed two immiscible liquid in the Fe-S-C-O system (a): the bright one is S-poor and carbon rich, the dark one is S-rich and O-rich. In the Fe-S-O system (b), we observed a single metallic melt with dendritic texture.

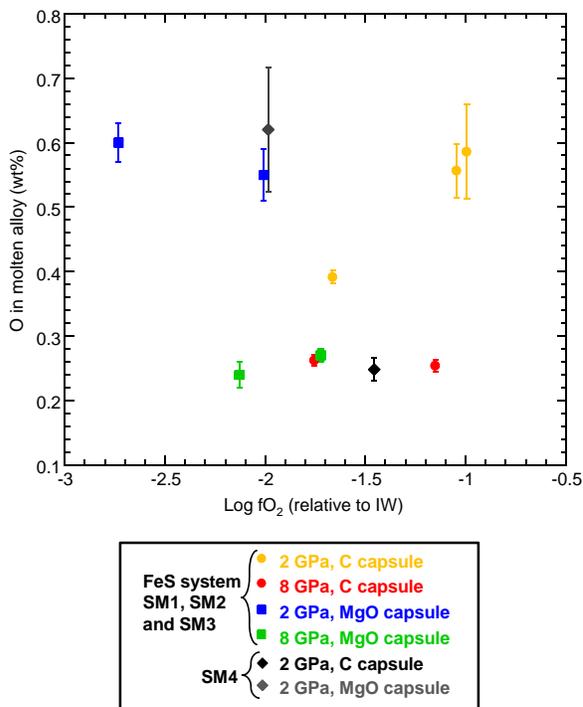


Fig. 2: Oxygen content in metallic alloy measured on samples synthesized at 2000°C and at 2 and 8 GPa in MgO and graphite capsules.

In addition, we have prepared other simplified starting materials with different metal/silicate ratios to understand the behaviour of oxygen in silicate/oxide and metal melts. These experiments have been performed in MgO capsule at 2 and 7 GPa and 2000 and 2600°C. The quenched samples are under chemical analysis. Solubility of oxygen in the metal will be discussed as a function of oxide and silicate melts, oxygen fugacity, temperature, and pressure. The results will be compared with data obtained for the CI-like compositions.

References: [1] Li J. and Fei Y. (2003) *Geochemistry of the Mantle and Core* (ed. R.W. Carlson), pp. 521-546. [2] Rubie D.C. et al. (2004) *Nature*, 429, 58-61. [3] Asahara Y. et al. (2007) *EPSL*, 257, 435-449. [4] Sakai T. et al. (2006) *GRL*, 33, L15317. [5] Corgne A. et al. (2008) *GCA*, 72, 2409-2416. [6] Li J. and Agee C.B. (2001) *GRL*, 28,81-84.