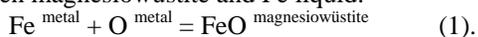


OXYGEN SOLUBILITY IN LIQUID IRON AND CONSEQUENCES FOR THE EARLY DIFFERENTIATION OF EARTH AND MARS. Y. Asahara¹, D. C. Rubie¹, D. J. Frost¹ and F. Langenhorst²,
¹Bayerisches Geoinstitut; Universität Bayreuth, D-95440 Bayreuth, Germany, Dave.Rubie@uni-bayreuth.de,
²Institut für Geowissenschaften; Friedrich-Schiller-Universität Jena, D-07749 Jena, Germany.

Introduction: It has been considered that the Earth accreted from carbonaceous chondrite-like material (e.g., [1], [2]). This hypothesis is based on the observation that the refractory element ratios of Earth's mantle are close to carbonaceous chondrite values, although the ratio of metallic Fe to total Fe is much closer to that of enstatite chondrite (e.g., [3]). Recently, Halliday [4] suggested that the proto-Earth might have been volatile-rich and oxidized, like the current Martian mantle. In this case, it is important to clarify when and how FeO reduction occurred in the Earth. One possibility is during a magma ocean stage, when the segregation of core and mantle material occurred. Rubie et al. [5] suggested that FeO could be partitioned into Fe metal in a terrestrial magma ocean because of very high temperatures. In addition, their experimental data suggested that oxygen solubility in liquid Fe alloy decreases with increasing pressure and that the equilibrium solubility of oxygen in the Earth's core may be close to zero. However, the effect of pressure on oxygen solubility in liquid Fe has been a controversial topic for the last 3 decades. Based on phase relations in the Fe-FeO system, it has been proposed that oxygen solubility in liquid iron increases with increasing pressure (e. g., [6], [7]). On the otherhand, studies of the partitioning of oxygen between magnesiowüstite and liquid Fe suggest that oxygen solubility in liquid iron decreases with increasing pressure. Here we report new data on oxygen partitioning between magnesiowüstite and liquid iron in the Fe-FeO-MgO system, over a wide range of pressures and temperatures (3-25 GPa and 2273-3173 K), which resolve this apparent inconsistency. Using the present results, we discuss the possibility of FeO reduction in early terrestrial and Martian magma oceans and the oxygen content of metallic cores.

Experimental procedure: High-pressure and high-temperature experiments were performed using a Kawai-type multi-anvil apparatus. The starting materials were mixtures of Fe metal and Fe₂O₃ oxide powders with a range of bulk oxygen contents. We used MgO single crystals as sample containers. Chemical analysis and imaging analysis of the recovered samples were conducted with an electron microprobe and a scanning electron microscope.

Results: We consider the reaction of oxygen between magnesiowüstite and Fe liquid:



The distribution coefficient, Kd , of this reaction is expressed as $Kd = X_{\text{O}}^{\text{met}} X_{\text{Fe}}^{\text{met}} / X_{\text{FeO}}^{\text{mw}}$, where $X_{\text{O}}^{\text{met}}$, $X_{\text{Fe}}^{\text{met}}$, $X_{\text{FeO}}^{\text{mw}}$ are the mol fractions of oxygen in metal, Fe in metal and FeO in magnesiowüstite, respectively. $\ln Kd$ increases with increasing temperature over the range of experimental conditions, and shows a linear relationship with $1/T$ at 15-24.5 GPa, and 2273-3173 K. We observe that $\ln Kd$ initially decreases with increasing pressure, reaches a minimum at 10-15 GPa and then increases at higher pressures. This means that the volume change (ΔV) of the reaction changes from being negative at pressures below 10-15 GPa to positive at higher pressures. This can be explained by a difference in the compressibilities of the FeO component in magnesiowüstite and liquid iron respectively.

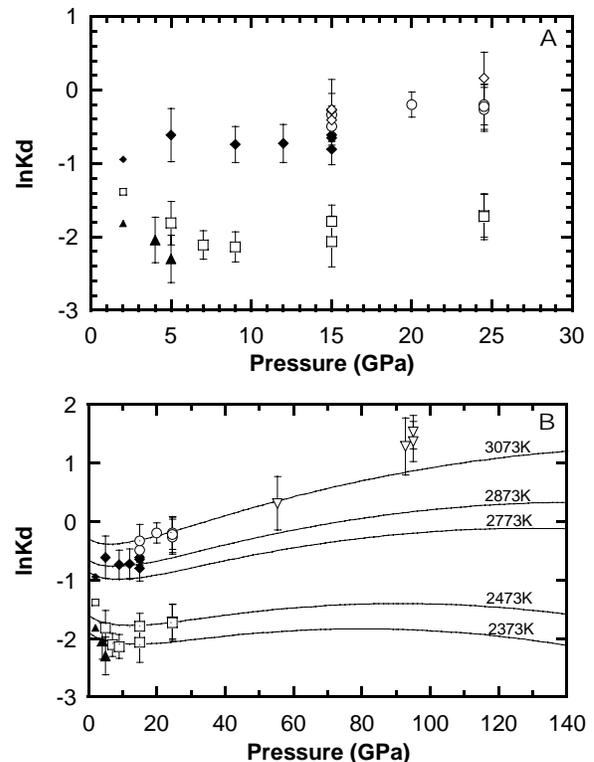


Figure 1. Dependence of $\ln Kd$ on pressure: Data from this study: Filled triangles, 2373 K; open squares, 2473 K; filled diamonds, 2873 K; open circles, 3073 K; open diamonds, 3150 K. Data from [8]: Small filled triangle, 2373 K; small open square, 2473 K; small filled diamond, 2823 K. Open triangles are calculated using the data at 3000-3150 K from [9] and partitioning data for Fe between magnesiowüstite and Mg-perovskite reported by [10].

Discussion: Thermodynamic calculation. We have fitted the new experimental data and higher pressure partitioning results reported by Takafuji et al. [8] using the equation

$$RT\ln K_d = -\Delta H + T\Delta S - \int \Delta V dP \quad (2)$$

where ΔH , ΔS and ΔV are the changes in enthalpy, entropy and volume, respectively, for the oxygen exchange reaction (1) and R is the gas constant. Activity coefficients of oxygen in metal, Fe in metal and FeO in magnesiowüstite were assumed to be unity. To evaluate $\int \Delta V dP$, we used an equation of state for the FeO component in liquid Fe that, together with the equation of state of wüstite, is consistent with the observed pressure dependence of $\ln K_d$. Obtained parameters for the equation of state of FeO component in liquid Fe are: $V_{0,2000K} = 14.14$ (cm³/mol), $K_0,2000K = 48$ (GPa), $K'_0 = 8.5$. The values $\Delta H_{0,2000K} = 1.66 (\pm 0.07) \times 10^5$ J/mol and $\Delta S = 52 (\pm 2)$ J/K/mol are also obtained by the fit. The resulting fit is shown in Fig. 1.

FeO reduction in a magma ocean. We examine the consequences of the partitioning of oxygen between liquid iron and peridotite-like liquid in a magma ocean following Rubie et al. [5] using the thermodynamic parameters obtained in this study.

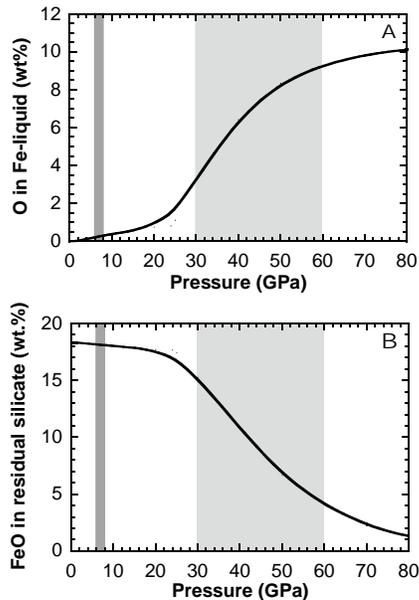


Fig 2. Results of the metal-silicate separation model for Earth and Mars: Light and dark shaded regions represent the estimated range of magma ocean depths for Earth (e.g., [11]) and Mars [12], respectively.

We assume that the temperature at the base of the magma ocean is defined by the peridotite solidus [13], and, for simplicity, that the conditions of equilibration

between metallic liquid and silicate liquid are approximately those at the base of the magma ocean. We assume a model primitive composition for Earth and Mars which has the major elements Si, Al, Mg, Fe, and Ca in carbonaceous chondritic proportions. The initial oxidation state of the model material is defined as $\text{Fe}^{2+} : \text{Fe}^0 = 0.4 : 0.6$. This oxidation state is similar to that of the current Martian mantle (18 wt.% FeO). The results are shown in Fig 2. The oxygen concentration in liquid Fe in the magma ocean increases with increasing depth (Fig. 2A) and, consequently, the FeO concentration in the residual silicate melt decreases (Fig. 2B). At around 50 GPa, the FeO content in the silicate liquid is reduced to about 8 wt.%, which is comparable to the FeO concentration of Earth's mantle. The model also explains the different mass fractions of the cores of Earth (~30% of the total planet) and Mars (~20%) because more metal segregates from the magma ocean on Earth than on Mars. These results are consistent with those of Rubie et al. [5], though the pressure dependence of oxygen solubility in Fe liquid is completely different above 15 GPa. This is because the effect of temperature on oxygen solubility is much larger than that of pressure. However, because oxygen becomes more soluble in Fe liquid with increasing pressure, at conditions of the Earth's core-mantle boundary (e.g., 2773 K and 136 GPa), magnesiowüstite should coexist with liquid Fe containing 5-7 wt.% of oxygen.

The present results suggest that the difference between Earth and Mars in terms of mantle FeO contents and mass fractions of metallic cores can be explained by differences in the pressure and temperature conditions under which metal and silicate segregated in a magma ocean. The low FeO content of Earth's mantle could be the result of metal-silicate equilibrium in a deep terrestrial magma ocean. According to these results, oxygen must be an important light element in the Earth's core, but not in the Martian core.

References: [1] Ringwood A. E. (1997) *Origin of the Earth and Moon*. Springer-Verlag, New York, 295. [2] Allègre C. et al. (2001) *EPSL* 185, 49-69. [3] Asahara, Y. et al. (2004) *PEPI* 143-144, 421-432. [4] Halliday A. (2004) *Nature* 427, 505-509. [5] Rubie D. C. (2004) *Nature* 429, 58-62. [6] Ohtani E. et al. (1984) *EPSL* 71, 94-103. [7] Kato T. and Ringwood A. E. (1989) *PCM* 16, 524-538. [8] Ohtani, T and Ringwood, A. E. (1984) *EPSL* 71, 85-93. [9] Takafuji, N. et al. (2005) *GRL* 32, 6313, doi: 10.1029/2005GL022773. [10] Kesson, S. E. et al. (2002) *PEPI* 131, 295-310. [11] Chabot, N. L. Et al. (2005) *GCA* 69, 2141-2151. [12] Righter, K. et al. (1998) *GCA* 62, 2167-2177. [13] Zerr, A. et al. (1998) *Science* 281, 243-247.