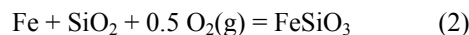
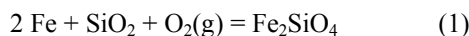


## OLIVINE-ORTHOPYROXENE EQUILIBRIUM IN METAL-RICH SYSTEMS: APPLICATIONS TO ACHONDRITES AND EQUILIBRATED CHONDRITES.

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**Introduction:** Olivine and orthopyroxene are major minerals in every type of stony meteorite. The majority of achondritic meteorites and silicate-bearing iron meteorites have experienced high temperatures. If these temperatures persisted for an extended period of time then the iron contents of olivine and orthopyroxene should be in equilibrium. In their study of ungrouped clasts and chondritic meteorites, [1] suggested that the equilibrium compositions of olivine and orthopyroxene should fall on a mixing line between LL chondrites and aubrites. Here we show that this is not necessarily the case and that a range of FeO contents in olivine and orthopyroxene can be in equilibrium with each other. The key parameters that determine the equilibrium Fe content in these minerals are temperature, oxygen fugacity ( $f_{O_2}$ ), and silica activity ( $a_{SiO_2}$ ).

**Methods:** The mole fractions of Fe in equilibrated olivines ( $X_{Fa}$ ) and orthopyroxenes ( $X_{Fs}$ ) in systems where metal is stable are determined by the following two reactions:



Equilibrium constants for these reactions can be expressed as:

$$\log K_1 = \log a_{Fa} - 2 \log a_{Fe} - \log a_{SiO_2} - \log f_{O_2} \quad (3)$$

$$\log K_2 = \log a_{Fs} - \log a_{Fe} - \log a_{SiO_2} - 0.5 \log f_{O_2} \quad (4)$$

These equilibrium constants can be expressed as a function of temperature. We used thermodynamic data from [2] to derive the following expressions:

$$\log K_1 = \frac{2.97 \times 10^4}{T} - 7.85 \quad (900 < T < 1150 \text{ K}) \quad (5)$$

$$\log K_1 = \frac{2.98 \times 10^4}{T} - 8.00 \quad (1150 < T < 1450 \text{ K}) \quad (6)$$

$$\log K_1 = \frac{2.45 \times 10^4}{T} - 4.40 \quad (1450 < T < 1700 \text{ K}) \quad (7)$$

$$\log K_2 = \frac{1.49 \times 10^4}{T} - 3.98 \quad (900 < T < 1150 \text{ K}) \quad (8)$$

$$\log K_2 = \frac{1.49 \times 10^4}{T} - 4.00 \quad (1150 < T < 1400 \text{ K}) \quad (9)$$

Equations (3-9) allow us to calculate values for  $a_{Fa}$  and  $a_{Fs}$  as a function of temperature,  $f_{O_2}$ ,  $a_{SiO_2}$ , and  $a_{Fe}$  (assumed to be unity). However, we are interested in determining values for  $X_{Fa}$  and  $X_{Fs}$ . The olivine and orthopyroxene solid solutions are non-ideal, requiring us to determine activity coefficients. We determined analytical expressions for the activities of fayalite ( $a_{Fa}$ ) and ferrosilite ( $a_{Fs}$ ) in olivine and orthopyroxene, respectively, following the solid solution models of [3]. The expression for  $a_{Fa}$  is relatively simple because disorder between the M1 and M2 octahedral sites is not a factor:

$$a_{Fa} = \exp\left(\frac{8.50}{T} + \frac{2.44 \times 10^3}{T} \cdot (1 - X_{Fa})^2 + 2 \ln(X_{Fa})\right) \quad (10)$$

The expression for  $a_{Fs}$  is similar. However, because disorder between the M1 and M2 sites in orthopyroxene is important it must be taken into consideration. We quantify the effect of this disorder defining a disorder temperature ( $T_d$ ) and express  $a_{Fs}$  as:

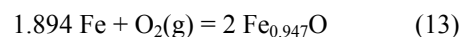
$$a_{Fs} = \exp\left(\frac{46.4}{T_d} + \frac{1.57 \times 10^3}{T_d} \cdot (1 - X_{Fs})^2 + 2 \ln(X_{Fs})\right) \quad (11)$$

We express the disorder temperature as a fifth-order polynomial of the form:

$$T_d = T + C_1 X_{Fs} + C_2 X_{Fs}^2 + C_3 X_{Fs}^3 + C_4 X_{Fs}^4 + C_5 X_{Fs}^5 \quad (12)$$

In equation (12)  $T$  is the actual temperature and the constants have the following values:  $C_1 = 6.77 \times 10^1$ ;  $C_2 = -3.04 \times 10^3$ ;  $C_3 = 5.92 \times 10^4$ ;  $C_4 = -1.56 \times 10^5$ ;  $C_5 = 1.10 \times 10^5$ .

Since we are interested in systems where iron metal is stable, we calculate  $f_{O_2}$  values relative to the iron-wustite (IW) buffer:



Using thermodynamic data from [2] and assuming that  $a_{Fe} = a_{Fe_{0.947}O} = 1$ , we express the  $f_{O_2}$  of this buffer as a function of temperature:

$$\log f_{\text{O}_2, \text{IW}} = \frac{-2.75 \times 10^4}{T} + 6.69 \quad (900 < T < 1150 \text{ K}) \quad (14)$$

$$\log f_{\text{O}_2, \text{IW}} = \frac{-2.76 \times 10^4}{T} + 6.80 \quad (1150 < T < 1450 \text{ K}) \quad (15)$$

$$\log f_{\text{O}_2, \text{IW}} = \frac{-2.67 \times 10^4}{T} + 6.17 \quad (1450 < T < 1700 \text{ K}) \quad (16)$$

**Results:** We plot the results of our analytical expressions for the activities of fayalite and ferrosilite in Figures 1 and 2. The solid symbols on these plots represent the values for these quantities determined using the MELTS calculator [4]. The analytical expressions that we have developed reproduce the results of MELTS within 5% for opx and within 1% for olv.

If an equilibrium temperature can be determined than the equations outlined above allow the calculation of  $f_{\text{O}_2}$  and  $a_{\text{SiO}_2}$  for each equilibrated meteorite class. We use the equations to determine these values for equilibrated ordinary chondrites (EOCs), silicates in IAB iron meteorites, and Aubrites (Table 1). For the

EOCs and the Aubrites we used compositions and assumed equilibrium temperatures consistent with prior petrologic studies [5]. Temperatures for the silicates in IAB meteorites were determined by considering equilibrium between chromite and olivine [6]. The results of our calculations show that these meteorites are equilibrated, and that the variation in  $X_{\text{Fs}}/X_{\text{Fa}}$  ratios can be attributed to different  $f_{\text{O}_2}$  and  $a_{\text{SiO}_2}$  values. Further, the calculations show the  $X_{\text{Fs}}$  greater than  $X_{\text{Fa}}$  can occur in meteorites whose bulk composition is reduced.

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**References:** [1] Kallemeyn and Wasson (1985) *GCA* **49**, 261-270. [2] Barin (1995) *Thermochemical Data of Pure Substances*, VCH. [3] Sack and Ghiorso (1989) *Contrib. Mineral. Petrol.* **102**, 41-68. [4] [www.geology.washington.edu/~ghiorso/MeltsWWW/Melts.html](http://www.geology.washington.edu/~ghiorso/MeltsWWW/Melts.html). [5] *Planetary Materials* MSA Rev. Min. v 36 [6] Benedix, Lauretta, and McCoy (2002) *LPSC XXXIII* #1317.

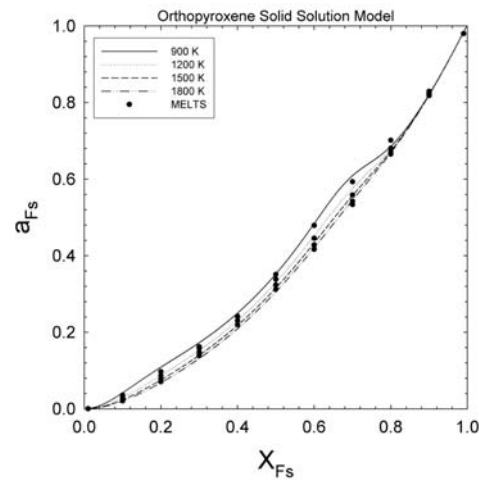
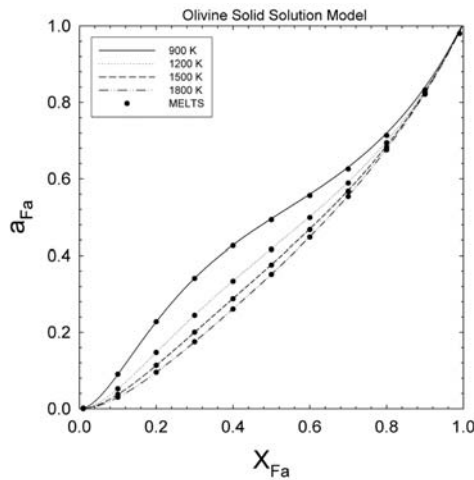


Table 1. Equilibrium Conditions Based on Olivine and Orthopyroxene FeO Contents

	$X_{\text{Fa}}$	$X_{\text{Fs}}$	T (K)	$a_{\text{Fa}}$	$a_{\text{Fs}}$	$\log f_{\text{O}_2}$	$\log a_{\text{SiO}_2}$
Equilibrated Ordinary Chondrites							
LL6 - low	0.26	0.22	1173	0.21	0.11	-16.95 (IW - 0.18)	-1.16
LL6 - high	0.32	0.26	1173	0.27	0.15	-16.96 (IW - 0.19)	-1.04
L6 - low	0.22	0.19	1173	0.17	0.09	-16.93 (IW - 0.16)	-1.27
L6 - high	0.26	0.22	1173	0.21	0.11	-16.95 (IW - 0.18)	-1.16
H6 - low	0.16	0.15	1173	0.11	0.06	-16.93 (IW - 0.15)	-1.46
H6 - high	0.20	0.18	1173	0.15	0.08	-16.97 (IW - 0.19)	-1.29
IAB Silicates							
Copiapo	0.06	0.08	1655	0.01	0.02	-10.95 (IW - 0.99)	-1.33
Caddo County	0.04	0.07	1616	0.01	0.01	-11.46 (IW - 1.1)	-1.43
Udei Station	0.05	0.06	1637	0.01	0.01	-10.94 (IW - 0.81)	-1.64
Aubrites							
Bustee	0.02	0.07	1773	0.00	0.01	-11.75 (IW - 2.9)	-0.49