

DEVELOPMENT OF AN IRON BASED GEOBAROMETER

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INTRODUCTION

The effects of oxygen fugacity and temperature on equilibrium redox conditions in the geochemical standard basaltic compositions JB-1 and W-1 were investigated to provide a basis for the development of a geobarometer. Oxygen fugacity for a given atmospheric composition increases with increasing temperature at constant atmospheric pressure. The ratio of ferric to ferrous iron was used to measure the redox condition within a melt at equilibrium under an imposed oxygen fugacity and known temperature. Sack *et al* (1980), and Schreiber *et al* (1986), observed a definite correlation between increasing oxygen fugacities and decreasing redox values. The correlation is supported by experimental data obtained in this study (Table 1). Temperature effects on the equilibrium redox state of the melt are positively correlated; as temperature increases the redox ratio within the melt increases. This relationship reflects the effect of temperature on oxygen fugacity, in which higher oxygen fugacities are correlated with higher temperature (Sack, 1980). The relationship between oxygen fugacity and equilibrium redox values at known temperatures as observed in experimental data has permitted development of a graphical geobarometer (Figure 2). The barometer operates on the premise that given the redox state of a rock in nature, equilibrium oxygen fugacity conditions responsible for the redox state can be determined if the melting temperature of the rock is known.

EXPERIMENTAL PROCEDURE AND ANALYSIS

The procedure followed for sample preparation and collection of data involves a series of furnace runs at atmospheric pressure to fuse the powdered samples into glass beads. Dissolution of these beads and subsequent titration of the solution measures the concentration of ferric ions in the bead at equilibrium.

Two-hundred milligrams of the powdered geochemical standard was placed in a shallow graphite crucible containing a five millimeter diameter platinum wire loop. The crucible was heated in a DT-31 bulk furnace at 1200 degrees C for one minute and then removed to quench the sample at room temperature, producing a glass bead. The glass bead was suspended in a DT-28 vertical tube furnace at the desired temperature and oxygen fugacity conditions for four hours to ensure redox equilibrium between the melt and the imposed atmosphere. Previous studies had indicated achievement of redox equilibria within four hours. Oxygen fugacity conditions within the furnace were controlled by mixtures of carbon dioxide and carbon monoxide gases. Samples were run at CO₂/CO ratios of 50/50, 95/5, 100/0, and in air at 1200, 1275, and 1375 degrees C. Similar experimental runs were completed on both standard compositions.

After reaching equilibrium, samples were taken from the furnace and quenched at room temperature. The samples were removed from the platinum loop and ground into a fine powder using a clean alumina mortar and pestle. Ten to fifteen milligrams of the powder was placed into a covered plastic vessel and flushed with argon gas to remove excess oxygen. Ten milliliters of 1:1 H₂SO₄:H₂O solution was then added to the vessel and allowed to react with the glass for five minutes while being stirred with a magnetic stirring rod. Five milliliters of 1:1 HF:H₂O solution was then added and the mixture was stirred for an additional ten minutes. Four grams of crystalline boric acid was added and allowed to react for five minutes with the solution to complex any excess fluoride in the solution that might interfere with the subsequent titration.

The resulting solution contained Fe (II) and Fe (III) ions in the ratio in which they existed in the melt at equilibrium with the imposed atmosphere. Fifty microliters of 0.2M o-phenanthroline indicator was added to the solution, giving it a red-orange color. The sample was titrated using 0.00125M Ce (IV) sulfate solution. The amount of titrant used in reaching the colorless endpoint was recorded and compared to the amount necessary to neutralize a blank sample. Fe (II) in solution was calculated by equation 1.

$$[\text{Eq. 1}] \quad \text{Fe (II)} = \frac{\text{ml. Sample} - \text{ml. Blank}}{\text{mg. Sample}} * .00698$$

The equilibrium redox ratio was then calculated as the amount of Fe (II) divided by total Fe minus Fe (II).

an experimental time series, R is the gas constant, and Do is the pre-exponential factor. The activation energy, the energy required to drive the diffusion process, determined for each composition is as follows:

An₈₀ Di₂₀ 79.34 Kcal/mole

An₁₀₀ 156.35 Kcal/mole

References

Schreiber, H., Kozak, S., Fritchman, A., Goldman, D., and Schaeffer, H., 1986, Redox kinetics and oxygen diffusion in a borosilicate melt. *Physics and Chemistry of Glasses*, v. 27, no. 4, p. 152-177.

Schreiber, H., Kozak, S., Trandel, B., and Schreiber C., 1986, Oxygen diffusion in SRL waste glass melts. *Advances in Ceramics*, v. 20, Nuclear Waste Management II, p. 125-132.

TABLE 1 (Raw Data)

<u>Log fO₂</u>	<u>W-1</u> <u>Log of Redox</u>	<u>JB-1</u> <u>Log of Redox</u>
11.0	0.53	0.44
8.4	0.47	0.55
5.8	-0.17	0.03
0.7	-0.73	-0.75
10.0	0.54	0.67
7.5	0.45	0.53
5.0	-0.12	0.04
0.7	-0.50	-0.59
8.6	0.29	0.44
6.4	0.46	0.32
4.0	0.00	-0.05
0.7	-0.50	-0.54

1200C

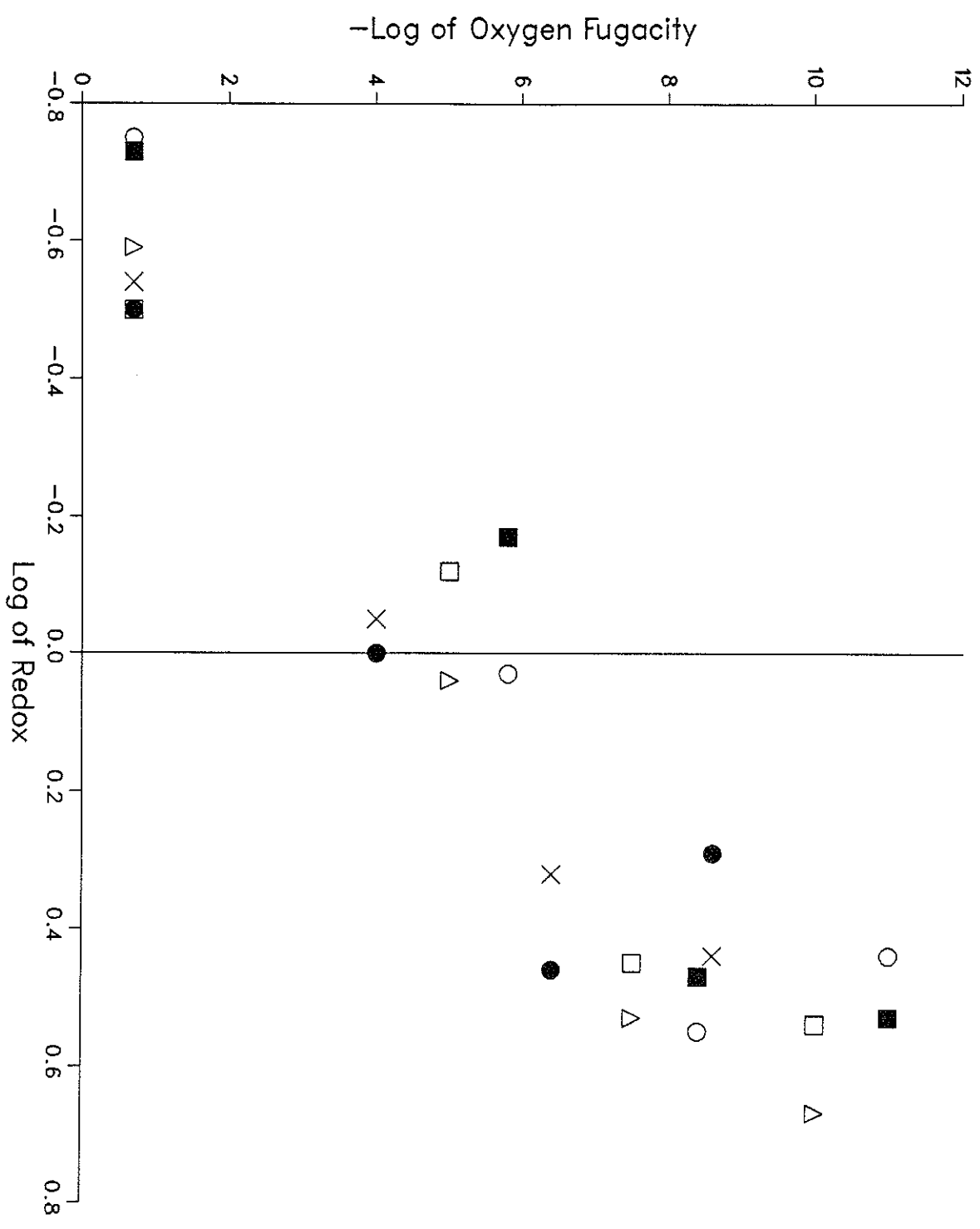
1275C

1375C

TABLE 2 (Average Slopes)

<u>W-1</u> <u>-Log fO₂</u>	<u>JB-1</u> <u>-Log fO₂</u>	<u>W-1</u> <u>Log of Redox</u>	<u>JB-1</u> <u>Log of Redox</u>
10.2	9.2	0.53	0.44
9.8	9.9	0.47	0.55
5.0	6.2	-0.17	0.03
0.8	0.6	-0.73	-0.75
9.1	9.5	0.54	0.67
8.4	8.5	0.45	0.53
4.2	5.0	-0.12	0.04
1.4	0.5	-0.50	-0.59
6.6	7.8	0.29	0.44
7.9	6.9	0.46	0.32
4.5	4.3	0.00	-0.05
0.75	0.74	-0.50	-0.54

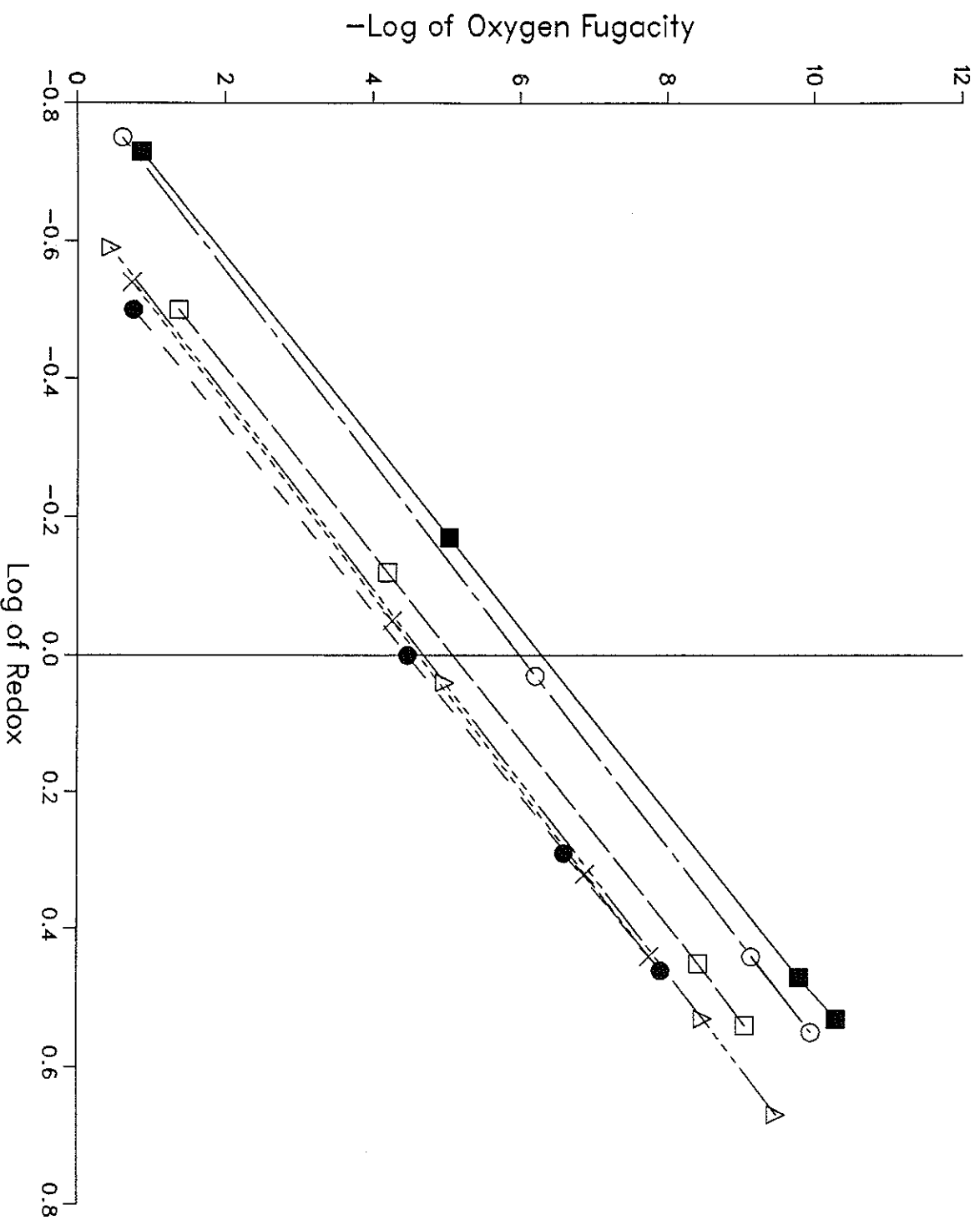
Figure 1 Raw Data
 W-1 and JB-1 at 1200, 1275, and 1375 degrees C
 Log of Redox vs. -Log of Oxygen Fugacity



Legend

- W-1 1200 degrees C
- W-1 1275 degrees C
- W-1 1375 degrees C
- JB-1 1200 degrees C
- △ JB-1 1275 degrees C
- × JB-1 1375 degrees C

Figure 2 Average Slope Plots
 W-1 and JB-1 at 1200, 1275, and 1375 degrees C
 Log of Redox vs. -Log of Oxygen Fugacity



- Legend
- W-1 1200 degrees C
 - W-1 1275 degrees C
 - W-1 1375 degrees C
 - JB-1 1200 degrees C
 - △ JB-1 1275 degrees C
 - × JB-1 1375 degrees C

DEVELOPING THE GEOBAROMETER

The proposed geobarometer is similar to other barometer models using the redox state of a multivalent cation to suggest imposed oxygen fugacity conditions. One such model proposed used Eu (II)/Eu (III) ratios in plagioclase and coexisting magmatic liquids. Drake (1975) proposed an empirical relationship between redox states within the melt and within plagioclase phases as an indicator of imposed oxygen fugacity conditions. The barometer proposed in this study approached the problem from a graphical, as well as empirical, viewpoint. Collected equilibrium redox values were plotted with their corresponding oxygen fugacity conditions as $-\log$ of oxygen fugacity vs. \log of redox (Figure 1). General trends for the plots of W-1 and JB-1 at each of the temperatures describes a linear relationship between \log of redox, and $-\log$ of oxygen fugacity at equilibrium. Figure 2 depicts the average slopes of 7.43 for W-1 samples, and 7.17 for JB-1 samples through the data points. The slopes were generated as averages of three best fit slopes for each composition. Best fit slopes varied from 7.86 to 7.18 for W-1, and from 6.88 to 7.56 for JB-1. The average slopes were used in the linear equation $y=mx + b$, where y is $-\log$ of oxygen fugacity, m is the average slope, x is the experimentally determined equilibrium redox value, and b is the y intercept taken from the best fit plots for each composition and experimental temperature. M , x , and b were considered known values and used to calculate $-\log$ of oxygen fugacity for corresponding \log of redox values (Table 2).

The theory behind the geobarometer lies in the linear relationships between oxygen fugacity and redox values at known temperatures. The equilibrium redox value for a given composition and temperature fall along a line as a function of the imposed oxygen fugacity. Application of the geobarometer involves experimental determination of the equilibrium redox ratio for a given multivalent cation within the sample. The model is not limited to Fe (II)/Fe (III) ratios. Schreiber *et al* (1986), have shown the given linear relationship using a variety of multivalent cations. The sample is ground to a fine powder and fused into a glass bead above the sample's melting point. The equilibrium redox ratio for the sample can be determined at a known oxygen fugacity using the experimental procedure already described. A second equilibrium redox ratio is then determined from the powdered sample at a different known oxygen fugacity and the same temperature. The two equilibrium redox values are plotted with their corresponding oxygen fugacity values in $-\log fO_2$ vs. \log of redox space. The experimentally derived points describe a line along which the equilibrium redox-oxygen fugacity value of the fresh rock lies. The equilibrium redox ratio can then be determined for a powdered sample without fusing it into a glass bead. This determined ratio is the actual redox ratio state of the fresh rock; it is also the redox state of the original melt at equilibrium before cooling occurred. $-\log$ of oxygen fugacity can be picked from the line at the corresponding redox ratio. Imposed oxygen fugacity conditions at which the sample rock reached equilibrium are then calculated from the $-\log$ of fO_2 value.

Constraints on this model relate to two necessary assumptions in its development. The first assumes that no changes occur in the equilibrium redox ratio as the rock crystallized from its liquid state (Sack, 1980). Secondly, it must be assumed that the observed equilibrium redox ratio has not been changed by alteration of the rock after it has cooled. Such alteration generally causes oxidation rather than reduction (Sack, 1980). An assumed equilibrium pressure of one bar is also necessary, as the experiment was conducted at this pressure. Sack *et al* (1980), have shown that these assumptions are basically legitimate by agreement of calculated fO_2 values with known values for experimental data. Development of an equation relating imposed oxygen fugacity and temperature to equilibrium redox values has not been completed in this project. Further work on a thesis project will accomplish this, and also will examine samples with known equilibrium oxygen fugacity values to reinforce the barometer's validity.

REFERENCES CITED

- Drake, M. J. , 1975, The oxidation state of europium as an indicator of oxygen fugacity. *Geochimica et Cosmochimica Acta*, v. 39, pp. 55-63.
- Sack, R. O. *et al.*, 1980, Ferric-ferrous equilibria in natural silicates at 1 bar. *Contrib. Mineral Petrol.*, v. 75, pp. 369-376.
- Schreiber, H. L. *et al.*, 1986, Redox kinetics and oxygen fugacity in a borosilicate melt. *Physics and Chemistry of Glasses*, v. 27, pp. 152-175.