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THE FAYALITE-MAGNETITE-QUARTZ ASSEMBLAGE BETWEEN 600° AND 800°C.†

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ABSTRACT. The f_{O_2}-T curve for the assemblage fayalite–magnetite–quartz has been determined between 600°C and 800°C by means of hydrothermal experiments in which temperature, total pressure, and hydrogen pressure are the independent variables. Combining these new data with that of certain earlier high-temperature investigations, the oxygen fugacity of the assemblage at 1 bar over the range 600° to 1100°C can be described by

$$\log f_{O_2} = \frac{-25{,}738}{T} + 9.00\ (\pm\ 0.10)$$

The determined equilibrium is in reasonable agreement with the available thermochemical data.

INTRODUCTION

The stability of fayalite with regard to oxidation and reduction reactions has been of interest in petrologic studies since Bowen and Schairer's (1932) classic study on the system FeO-SiO_2. In recent years the assemblage fayalite–magnetite–quartz has been an important reference assemblage in experimental systems (Eugster, 1957).

Previous studies have been chiefly concerned with the olivine-liquid equilibria (Bowen and Schairer, 1932; Darken, 1948; Muan, 1955; Muan and Osborn, 1956; Spiedel and Muan, 1967; and Nafziger and Muan, 1967). Schenk, Franz, and Leymann (1932), Cirilli (1946), Taylor and Schmalzried (1964), Schwerdtfeger and Muan (1966), and Fisher (1967) have all examined subsolidus relationships.

In this study we have examined the univariant equilibria

$$\underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{quartz}}{3SiO_2} = \underset{\text{fayalite}}{3Fe_2SiO_4} + O_2$$

as a function of oxygen pressure and temperature in the range 600°C to 800°C, making use of a hydrogen diffusion membrane developed by H. R. Shaw (1963, 1967).

EXPERIMENTAL TECHNIQUES

The experiments were carried out in "cold seal" pressure vessels (Tuttle, 1949) with the modification designed by Shaw (1963, 1967). The principle of the experiment is simple. A platinum membrane, permeable to hydrogen, is used to control the hydrogen pressure in the inert-gas

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pressure medium inside the vessel, in our case, argon. The sample being investigated is placed in the vessel inside a platinum capsule containing H_2O. The hydrogen pressure at fixed total pressure determines the oxygen fugacity of the experiment by specifying the fugacity of hydrogen across two membranes. Thus the variables in the experiment are temperature, hydrogen pressure, and total pressure.

Temperature calibration and control.—The cold-seal vessels were probed with a sheathed chromel-alumel thermocouple at 1 atm to examine the thermal gradients. The determination showed a maximum gradient of 2°C over the sample in the pressure vessel. Calibration of the entire measuring circuit was achieved by melting NaCl (800.5°C) in evacuated silica capsules in the pressure vessel at 1 atm. Determinations were made at 2°C intervals leading to a calibration of ± 1°C. With the Leeds and Northrup K13 potentiometer employed here, precision of temperature measurement is ± 0.25°C (± 0.01 mv).

Controllers used in the study were of both 2-step proportional and fully proportional type, and control in most instances was better than ± 2°C. Hence the temperature uncertainties presented are due to gradients (± 1°C), calibrations (± 1°C), and control.

Pressure calibration and control.—Hydrogen pressure was monitored on a 16-inch, 2000 psi, Cu-Be, bourdon gauge manufactured by the Heise Bourdon Tube Co. This gauge was calibrated against another similar gauge which had been calibrated by D. C. Presnall of the Geophysical Laboratory against a dead-weight, piston gauge. The comparison indicated that the maximum deviation was 5 psi. Argon pressure was measured on a 16-inch, 40000 psi, Heise gauge which was protected from the hydrogen-argon medium by mercury and oil U-tubes connected in series. Pressure was obtained by using an air-operated diaphragm pump thus avoiding contamination of the gas media.

The major variation in gas pressure was caused by variations in the ambient temperature of the laboratory. These variations, about 1 percent of the measured pressure, were the most serious of the entire study.

As will be seen, none of the above variations prove consequential in terms of the f_{O_2}-T curve established by these experiments, and the method appears to have great value for future studies.

Starting materials.—The materials used in the investigation were synthetic fayalite, quartz, and magnetite made from a variety of starting materials. Magnetite was made by reduction of Fe_2O_3 (Baker's C. P.). Quartz was supplied either as natural material from Lake Toxaway or as recrystallized SiO_2 glass (Corning Glass Works Optical Grade Silica Glass Lump Cullet #7940). Fayalite was crystallized hydrothermally from a mixture of SiO_2 glass and $FeC_2O_4 \cdot 2H_2O$. A synthetic fayalite produced at 1 atm by S. W. Richardson of the Geophysical Laboratory was also used as a starting material. All these materials gave completely consistent results. The d_{130} spacings for various fayalites used in the study are given in table 1.

TABLE 1

d_{130} values for fayalites used in this study

d_{130}	Starting material	Remarks
2.828_0	Quartz-hematite	1 atm reducing furnace
2.826	Quartz-hematite	1 atm reducing furnace
2.826_6	$2FeC_2O_4 \cdot 2H_2O + SiO_2$ glass	Hydrothermal recrystallization
2.826	$2FeC_2O_4 \cdot 2H_2O + SiO_2$ glass	Hydrothermal recrystallization
2.826	Synthetic fayalite	No reaction
2.825	Synthetic fayalite	No reaction
2.829	Synthetic fayalite	No reaction
2.825_5	Synthetic fayalite	No reaction
2.828	Synthetic fayalite	No reaction
2.826	Synthetic fayalite	No reaction
2.825	Synthetic fayalite	Partially oxidized
2.827	Synthetic fayalite	Partially oxidized
2.824	Synthetic fayalite	Partially oxidized
2.827	Synthetic fayalite + quartz + magnetite	Partially oxidized
2.825	Synthetic fayalite + quartz + magnetite	No reaction
2.825	Quartz + magnetite	Hydrothermal recrystallization
2.765_5*	$2MgO + SiO_2$ glass	Hydrothermal recrystallization

*For comparison only.

DETERMINATION OF EQUILIBRIUM

Experimental technique.—Paired capsules of magnetite plus quartz and of fayalite were subjected to the conditions of the particular experiment. When one member of a pair reacted to the other assemblage, the unreacted member was judged to be the stable assemblage.

The time delay of hydrogen diffusing through the controlling membrane was avoided by filling the entire high-pressure line with hydrogen at the desired pressure before starting the experiment. The detailed chronology of a typical run is as follows:

1. Load capsules and seal pressure vessel.
2. Fill vessel with hydrogen at desired pressure.
3. Pump high-pressure medium (argon) into vessel to desired total pressure.
4. Fill control tube supporting the membrane with hydrogen at desired pressure.
5. Heat pressure vessel to desired temperature.
6. Adjust and maintain experiment at desired P, P_{H_2}, T.
7. Quench pressure vessel.
8. Release H_2 control pressure.
9. Release argon-hydrogen medium.
10. Unload experiment.

Position of the equilibrium.—Table 2 lists the results of the critical experiments. This study did not contain a single point that crossed the curve metastably although several experiments very near the curve did not react. The precision of the study was limited by variations in pressure due to ambient temperature variations.

TABLE 2

Experiments defining the position of the univariant assemblage quartz-fayalite-magnetite

T, °C	P_{TOTAL}, bars	Duration, days	γ_{H_2O}*	P_{H_2}, bars	log K_w**	log f_{O_2}***	Stable condensed assemblage
594 600	800 ± 14	7	0.67	11.03 ± 0.07	12.03 ± 0.01 11.96	-20.79 ± 0.03 -20.65 ± 0.03	Fayalite
595 599	807 ± 14	7	0.67	9.17 ± 0.14	12.02 11.97	-20.61 ± 0.03 -20.51 ± 0.03	Magnetite + quartz
689 693	800 ± 3	8	0.79	11.79 ± 0.07	10.58 10.51	-17.80 ± 0.015 -17.66 ± 0.015	Fayalite
690 696	804 ± 10	9	0.79	10.90 ± 0.07	10.57 10.48	-17.70 ± 0.02 -17.52 ± 0.02	Magnetite + quartz
702 710	1889 ± 117	6	0.69	21.7 ± 0.2	10.40 10.29	-17.44 ± 0.04 -17.22 ± 0.04	Fayalite
701 713	2000 ± 41	7	0.68	19.8 ± 0.7	10.41 10.25	-17.35 ± 0.04 -17.03 ± 0.04	Magnetite + quartz
793 797	803 ± 3	4	0.87	13.9 ± 0.2	9.26 9.23	-15.20 ± 0.02 -15.14 ± 0.02	Fayalite
797 803	800 ± 7	5	0.88	12.8 ± 0.2	9.23 9.16	-15.06 ± 0.02 -14.92 ± 0.02	Magnetite + quartz

*Values calculated from Sharp (1962) by use of relation $\gamma_{H_2O} = \frac{1}{P} \exp\left(\frac{G_p - G_{1\ atm}}{RT}\right)$.

**JANAF, 1965.

***The f_{O_2} reported is that expected at 1 bar: $\log \frac{f_{O_2}(P_2)}{f_{O_2}(P_1)} = -\frac{\Delta\bar{V}(1 - P)}{2.303RT}$; $\Delta\bar{V}$ = -17.945 cc/mol O_2 at 25°C of the solids in the reaction

$2Fe_3O_4 + SiO_2 \rightleftharpoons 3Fe_2SiO_4 + O_2$ (Robie, Bethke, and Beardsley, 1967).

The limits of uncertainty are expressed in four values for each experiment and plotted accordingly in figure 1. As the slope of the equilibrium constant for H_2O is subparallel to that for the fayalite oxidation reaction under investigation here, the temperature uncertainty has a small effect on the location of the equilibrium throughout the entire range of the study.

Calculation of all the data to a 1 bar base by means of the relation,

$$\Delta \log f = -\frac{\Delta V_s\,(1-P_{exp})}{2.303\ RT}$$

where ΔV_s is the volume change of the solids for the reaction and P_{exp} is the pressure of the experiment in bars, and plotting fugacity rather than pressure of oxygen, results in a curve expressed as follows:

$$\log f_{O_2} = -\frac{25{,}660}{T} + 8.92.$$

Such an expression implies that the variations in enthalpy of reaction are smaller than could be detected in this study.

Evaluation of f_{O_2} from experimental data.—In order to evaluate properly the errors inherent in each experiment, the method of calculation is given in detail for the 2000 bar run that contains the largest total uncertainty for f_{O_2}. The initial data are: $P_{H_2} = 19.8 \pm 0.7$ bars; $P_{TOTAL} = 2000 \pm 41$ bars; $T = 701°C$ to $713°C$. Inasmuch as hydrogen behaves ideally at low pressures (Shaw and Wones, 1964), $P_{H_2} = f_{H_2}$ on the hydrogen side of the membrane. When membrane equilibrium occurs, f_{H_2} on the hydrogen side must equal f_{H_2} on the argon and hydrogen side. The same holds true for the capsule membrane. So $f_{H_2} = 19.8 \pm 0.7$ and $\log f_{H_2} = 1.296 \pm 0.015$. Inside the water-bearing capsules $f_{H_2O} = (\gamma_{H_2O})\ X\ (P_{TOTAL} - P_{H_2})$. At these low hydrogen concentrations, the Lewis and Randall rule concerning the mixture of real gases may be used (Shaw, 1967). The fugacity coefficient of H_2O (γ_{H_2O}) has been determined from Sharp's (1962) compilation of the thermodynamic properties of water: $\log f_{H_2O} = \log (0.68)\ (1980 \pm 41) = 3.13 \pm 0.01$. The remaining value required is K_W (JANAF, 1965), determined either by graphical or numerical interpolation: $\log K_W = 10.25;\ 10.41 \pm 0.01$. The uncertainties come from (1) variations in H_2 pressure during experiment, $\delta \log f_{H_2} = 0.015$; (2) variations in total pressure during experiment; (3) uncertainties in the fugacity coefficient of water; (4) uncertainties in the equilibrium constant for water due to interpolation:

$$\log f_{O_2} = 2[\log f_{H_2} - \log f_{H_2} - \log K_W] = 2[3.13\text{-}1.30\text{-}10.25] = -16.84$$

$$\delta \log f_{O_2} = 2[(\delta \log P_{TOTAL})^2 + (\delta \log f_{H_2})^2 + (\delta \log K_w)^2 + (\delta \log \gamma_{H_2O})^2]^{1/2}$$

$$= 2[(0.01)^2 + (0.016)^2 + (0.01)^2 + (0.01)^2]^{1/2} = 0.04$$

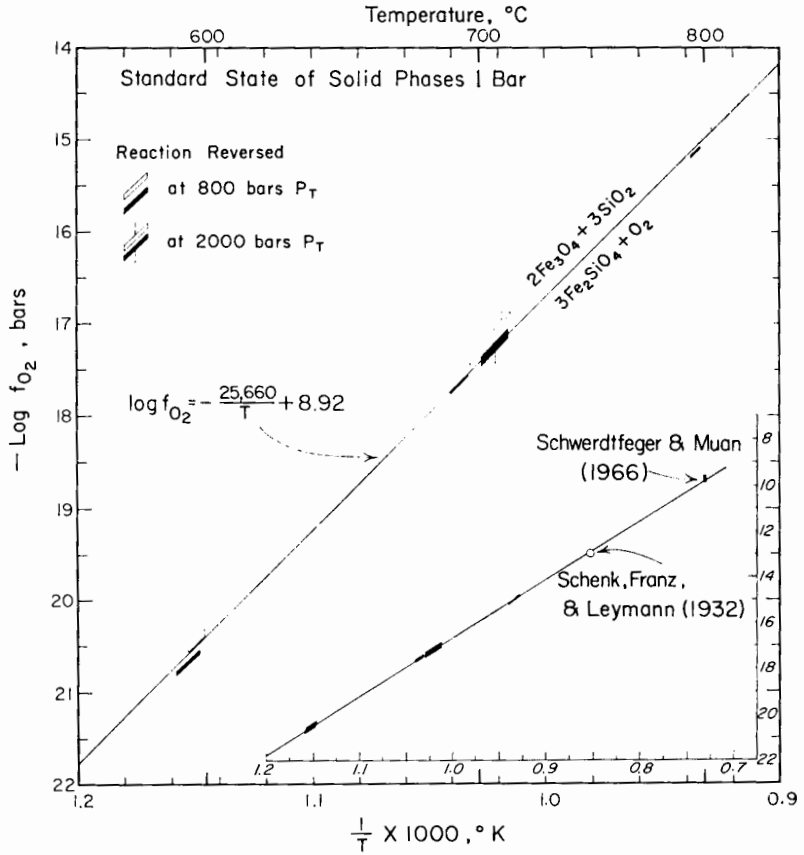

Fig. 1. f_{O_2}-1/T plot for fayalite-quartz-magnetite equilibrium at 1 bar total pressure. Inset shows data from this study plotted along with selected high temperature data.

The temperature variation also affects K_W, so that two values of oxygen fugacities must be calculated, one at each limit of the range of the temperature of the experiment. Therefore, in our example:

$$\log f_{O_2}^{713} = 2 \log f_{H_2O} - \log f_{H_2} - \log K_W^{713} = -16.84 \text{ (2000 bars)}$$

and

$$\log f_{O_2}^{701} = -17.16 \text{ (2000 bars)}$$

Comparison with other experimental data.—Previous determinations of f_{O_2} for fayalite oxidation are listed in table 3. Our experiments agree with those of Schenk, Franz, and Leymann (1932) and Schwerdtfeger and Muan (1966) (see inset, fig. 1). As these investigations were carried out at 1 atm using CO/CO_2 gas mixtures, it would appear that the equilibrium is well known between 600°C and 1100°C. Combination of our data with

those of these investigators can be represented by the equation (at 1 bar total pressure)

$$\log f_{O_2} = -\frac{25{,}738}{T} + 9.00\ (\pm\ 0.10).$$

This may seem surprising because no account has been made of thermal expansion or compressibility of any of the phases, changes in silica polymorphs up to 1100°C, or a reported second-order transition in magnetite at 623°C (Robie and Waldbaum, 1968). All these factors are below the detection limits of this study. The uncertainties in the data of Cirilli (1946) could not be evaluated and seem too high in f_{O_2}.

TABLE 3

Comparison of log f_{O_2} of the quartz-fayalite-magnetite equilibrium as determined by various investigators. Reference is 1 atm total pressure.

600°C	700°C	800°C	900°C	1000°C	1100°C		
-20.48	-17.45	-14.98	-12.94	-11.21	-9.75	This study	
			-13.94	-12.12	-10.60	Taylor and Schmalzried	(1a)
			-13.50	-11.64	-10.12	Taylor and Schmalzried	(1b)
			-12.88	-10.86	-9.18	Cirilli (1946)	(2)
					-9.76	Schwerdtfeger and Muan (1966)	(2)
			-12.98			Schenk, Franz and Leymann (1932)	(2)
-21.00	-18.05	-15.65	-13.70	-12.20	-10.65	Robie and Waldbaum (1968)	(3a)
-20.60	-17.65	-15.11	-13.20	-11.40	-10.10	Robie and Waldbaum (1968)	(3b)

(1) E.M.F. measurements of Fe-Fe_2SiO_4-SiO_2 equilibrium to establish free energies of reaction to which is added the free energy for magnetite from (a) Robie and Waldbaum (1968); (b) JANAF tables (1966).

(2) CO/CO_2 measurements at 1 atm.

(3) Calculations from tabulated free energies (a), but using the JANAF (1966) value for magnetite (b).

Comparison with thermochemical data.—Taylor and Schmalzried (1964) report data on the free energy of the reaction

$$Fe_2SiO_4 = SiO_2 + 2Fe + O_2$$

determined by E. M. F. measurements at 900°C to 1100°C. A comparison with our results is made possible by adding the free energy of formation of magnetite to that of the above reaction:

$$3Fe_2SiO_4 = 3SiO_2 + 6Fe + 3O_2$$
$$6Fe + 4O_2 = 2Fe_3O_4$$
$$3Fe_2SiO_4 + O_2 = 2Fe_3O_4 + SiO_2$$

The data for magnetite have been taken from the compilation by Robie and Waldbaum (1968) and from the JANAF tables (1966). The results in log f_{O_2} plot between 0.5 (JANAF, 1965) and 1.0 (Robie and Waldbaum, 1968) orders of magnitude below the results obtained in this study and those obtained by Schwerdtfeger and Muan (1966).

Robie and Waldbuam's (1968) tabulation of thermochemical data provide a check of free energies determined calorimetrically versus those

determined in this study. Table 3 lists the resulting calculation of f_{O_2} values. The results are in better agreement at low temperatures than at high temperature. By using the magnetite values from the JANAF (1966) tables, the discrepancy can be halved, so it would appear that the JANAF (1966) magnetite tabulation is in better agreement with our data than that tabulated by Robie and Waldbaum.

The enthalpy of reaction obtained in this study is 117.8 ± 2.5 kcal, whereas that obtained by thermochemistry is 119.1 ± 2.0 kcal at 800°K and 115.5 ± 2.0 kcal at 1400°K. There should be a change in slope relating to the quartz-tridymite inversion, but the data are not precise enough to distinguish that detail.

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