The Ferric-Ferrous Ratio
of Natural Silicate Liquids Equilibrated in Air

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Abstract. Results of chemical analyses of glasses produced in 46 melting experiments in air at 1,350° C and 1,450° C on rocks ranging in composition from nephelinite to rhyolite have been combined with other published data to obtain an empirical equation relating $\ln(X_{Fe_2O_3}^{liq}/X_{FeO}^{liq})$ to T, $\ln f_{O_2}$ and bulk composition. The whole set of experimental data range over 1,200–1,450° C and oxygen fugacities of $10^{-9.00}$ to $10^{-0.69}$ bars, respectively. The standard errors of temperature and $\log_{10} f_{O_2}$ predictions from this equation are 52° C and 0.5 units, respectively, for 186 experiments.

Introduction

In many rocks or experimental charges which contain a mixture of crystals and quenched liquid (glass), the Fe_2O_3/FeO ratio in the glass will be unknown unless it can be calculated from experiments designed to show the dependence of this ratio on other variables. These variables are temperature, oxygen fugacity, composition of the silicate liquid, and pressure. A purely empirical relationship connecting these variables at 1 bar has been given by Sack et al. (1980) in the form:

$$\ln(X_{Fe_2O_3}^{liq}/X_{FeO}^{liq}) = a \ln f_{O_2} + \frac{b}{T} + c + \sum_i d_i X_i \qquad (1)$$

where a, b, c and d_i's are constants obtained by regression of ferric/ferrous data on liquids quenched to glasses, and X_i's are the mole fractions of the metal oxides. For example, Sack et al. equilibrated 57 lavas ranging from silica-poor types such as potash ankaramites, to basalts and rhyolites above their respective liquidus temperatures at oxygen fugacities defined by quartz-fayalite-magnetite (QFM). These experimental data were combined with similar published results on natural liquid compositions (Kennedy (1948), Fudali (1965), Shibata (1967), Thornber et al. (1980)), almost all of which were obtained at oxygen fugacities close to QFM. Of the 143 sets of data regressed by Sack et al., only 6 compositions represented natural liquids equilibrated in air, which we assume to be 0.21 bars of oxygen at any temperature.

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We therefore decided to equilibrate a range of lava types in air above their respective liquidus temperatures, 1,350–1,450° C, and combine these new results with those considered by Sack et al. to refine the regression coefficients a, b, c and d_i of Equation 1.

Experimental Procedures

Forty-six wet chemically analysed rocks ranging in composition from ugandite to rhyolite were used as starting materials in our experiments. Powdered rock samples were mixed with a few drops of polyvinyl alcohol solution and pressed to form rock tablets 2.5 cm in diameter. Small chips from these were fused to Pt90%–Rh10% wire loops (0.25 mm O.D.) and five to six samples at a time were placed at the hot spot of a quench furnace with a vertical alumina muffle tube. Two 0.5 cm holes on top and at the bottom of the furnace provided entry and exit ports for the air with which samples were equilibrated. A Pt90%–Rh10% thermocouple was placed in the center of the samples and temperature was monitored continuously. In runs lasting up to 70 h, the temperature fluctuation was $\pm 2°$ C of the set run temperature.

Several wire loops used in the earlier, preliminary experiments were analysed for iron with the electron microprobe. Within the precision of the probe measurements, there was no iron detected in these wire loops, suggesting that loss of iron to sample holders is not a serious problem in experiments conducted in air, although this is not the case at lower oxygen fugacities (Sack et al. 1980).

At the end of the run the charges were quenched in water, the glasses were crushed under acetone and three to four pieces were mounted in epoxy for microprobe analysis. Glasses were analysed for SiO_2, TiO_2, Al_2O_3, FeO_t (total iron), MnO, CaO, Na_2O, K_2O, Cr_2O_3 and P_2O_5 using the 8-channel ARL-SEMQ microprobe in the Department of Geology and Geophysics at the University of California, Berkeley. An accelerating voltage of 15 KV, a sample current of 0.03 µA and a 10 s integration time were used in all analyses. X-ray measurements were corrected following the procedure of Bence and Albee (1968). Standards used included enstatite (Si and Mg), anorthite (Ca and Al), rutile (Ti), hematite (Fe), rhodonite (Mn), albite (Na), orthoclase (K), apatite (P) and chromite (Cr). Six to ten points were analysed on each glass chip and the data were averaged.

Comparison of wet chemical and microprobe analysis of several samples (Sack et al. (1980); also Table 3) indi-

Table 1. Analyses of Glasses in Weight Percent

Sample #	1	2	3	4	5	6	7	8
Identifier	CAM-49	121	3114	NIC-8	867-114	780-U-111	780-U-105	20424
SiO_2	72.21	71.03	69.15	61.59	58.06	43.68	39.50	38.98
TiO_2	0.26	0.28	0.49	0.67	0.85	4.42	5.64	2.93
Al_2O_3	14.04	8.03	11.26	15.66	15.44	9.89	9.89	13.42
Fe_2O_3	1.13	7.29	5.71	5.08	7.12	10.92	11.66	11.29
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	0.64	1.58	0.71	1.31	2.34	1.83	2.63	1.28
MnO	0.04	0.24	0.27	0.15	0.16	0.02	0.24	0.36
MgO	0.27	0.18	0.21	1.43	3.19	9.00	6.69	5.79
CaO	1.27	0.52	0.40	3.55	6.83	11.38	14.82	16.99
Na_2O	4.04	6.08	5.82	5.66	3.70	2.72	2.27	4.04
K_2O	4.38	3.81	4.38	3.77	1.22	4.11	4.23	2.73
P_2O_5	0.04	0.01	0.04	0.10	0.09	0.03	0.61	0.89
Total	98.32	99.05	98.44	98.88	99.00	98.00	98.18	98.70
$T°$ C	1,342	1,344	1,340	1,344	1,349	1,344	1,350	1,342
Time (h)	23	24	47.5	24	25	24	39.5	23

Sample #	21	22	23	24	25	26	27	28
Identifier	COL-11	1910-199	H-96A	90-05	20424	G-84	KIL-2	944-F
SiO_2	57.07	56.74	56.32	55.63	39.84	51.17	50.29	49.93
TiO_2	0.74	1.23	0.74	0.54	2.97	3.27	3.31	3.31
Al_2O_3	16.91	20.15	16.82	21.31	14.21	12.75	13.91	13.57
Fe_2O_3	4.94	3.72	4.78	2.75	10.72	10.09	9.17	9.89
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	2.11	1.49	2.22	1.06	2.41	4.60	3.45	2.74
MnO	0.12	0.19	0.12	0.18	0.38	0.31	0.17	0.16
MgO	5.87	1.04	6.07	0.72	6.18	4.09	6.01	6.37
CaO	7.42	3.09	7.42	3.21	17.81	8.60	9.78	9.81
Na_2O	3.63	7.13	3.84	3.94	2.80	2.85	2.34	2.64
K_2O	0.95	3.52	0.98	8.91	1.10	0.50	0.54	0.63
P_2O_5	0.00	0.08	0.04	0.04	0.02	0.08	0.05	0.28
Total	99.76	99.38	99.35	98.29	98.44	98.31	99.02	99.33
$T°$ C	1,446	1,428	1,434	1,445	1,447	1,445	1,430	1,434
Time (h)	24	25.5	24	24	24	24	22	24

cates that the accuracy of the latter was within 5% of the amount present for Na_2O, and 2% for other oxides. Continuous movement of the sample under the beam during the analysis assured good recovery of Na_2O values.

The ferrous iron contents (FeO) of glasses were determined using the volumetric and colorimetric procedure of Wilson (1960). The USGS standard BCR-1 basalt sample was included with each set of analyses; the arithmetic mean of five FeO determinations of BCR-1 yielded a value of 8.73% ± 0.12 which compares well with the accepted value of 8.80%.

Ferric iron contents of the glasses (Fe_2O_3) were calculated as follows:

wt.% $Fe_2O_3 = 1.1113$ ($FeO_t - FeO$)

where FeO_t is the total iron determined by the microprobe, and FeO is the ferrous iron determined colorimetrically. All analytical data together with T, f_{O_2} and run times are listed in Tables 1, 2 and 3.

Results and Discussion

The establishment of equilibrium between the melts and coexisting air in these experiments was done by monitoring the variation of the ferrous iron content of the melts with time. A glassy andesite sample with 6.76 wt.% FeO and 2.46 wt.% Fe_2O_3 was melted at 1,350° C in a series of experiments lasting 5, 12, 25, 48 and 70 h and the resulting glasses were analysed for ferrous iron. Table 3 shows the FeO content of these glasses as a function of time. It is clear from these data that this composition equilibrated with air in 5 h (or less) and that the FeO content stayed constant in runs up to and including 48 h. Beyond this time, the FeO content of the melts increased slightly, possibly reflecting the loss of alkalies.

On the basis of these time experiments it was decided to conduct the rest of the experiments for 24 h each. This compares well with 16 h at 1,300° C determined by Kennedy (1948) in his experiments.

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Table 1 (continued)

Sample #	9	10	11	12	13	14	15	16	17	18	19	20
Identifier	121	NZC-4	CAM-49	3114	1004	NIC-8	G-24	TC-19	COL-17	A-1770	G-24	442
SiO_2	72.53	72.51	72.38	69.59	67.72	61.43	60.84	60.28	60.21	59.26	58.64	57.40
TiO_2	0.29	0.24	0.27	0.49	0.73	0.70	0.93	0.75	0.75	2.87	1.13	1.49
Al_2O_3	8.06	10.12	13.94	11.10	11.28	16.40	17.70	19.57	17.36	11.40	17.34	18.50
Fe_2O_3	7.02	5.01	1.09	5.32	5.07	4.76	4.16	3.01	4.19	3.02	4.54	4.04
Cr_2O_3	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
FeO	1.41	1.18	0.63	1.23	1.95	1.66	1.40	0.79	1.96	1.09	1.06	1.55
MnO	0.26	0.12	0.04	0.27	0.22	0.17	0.12	0.20	0.12	0.06	0.12	0.13
MgO	0.05	0.02	0.25	0.22	0.98	1.46	0.91	0.41	3.21	6.96	1.66	1.79
CaO	0.46	0.27	1.23	0.36	2.00	3.70	2.32	0.77	5.64	3.94	2.76	4.05
Na_2O	5.95	4.98	4.21	5.42	4.84	5.17	5.49	8.19	4.43	1.12	5.21	4.81
K_2O	3.54	4.10	4.23	4.23	3.51	3.30	5.56	5.09	1.27	8.91	5.82	4.89
P_2O_5	0.00	0.01	0.03	0.02	0.05	0.10	0.23	0.06	0.11	0.01	0.29	0.44
Total	99.57	98.58	98.30	98.25	98.35	98.85	99.67	99.12	99.25	98.64	98.57	99.09
T° C	1,445	1,454	1,434	1,454	1,430	1,430	1,447	1,447	1,430	1,429	1,429	1,445
Time (h)	24	26	20	26	22	24	22	22	22	22.5	22.5	24

Sample #	29	30	31	32	33	34	35	36
Identifier	94-8	A-1805	766-263	780-U-111	X-973	780-U-105	944-E	780-K-15
SiO_2	49.46	48.78	48.55	44.62	40.86	40.49	38.68	49.24
TiO_2	1.12	2.81	2.20	4.70	4.65	5.96	4.33	1.65
Al_2O_3	18.50	8.80	16.26	10.12	14.67	9.97	21.66	19.78
Fe_2O_3	6.64	5.76	7.71	9.73	10.43	11.62	8.91	6.78
Cr_2O_3	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00
FeO	2.14	1.78	2.90	2.95	2.99	3.27	2.86	2.48
MnO	0.15	0.14	0.17	0.16	0.28	0.26	0.26	0.21
MgO	3.96	11.96	8.34	9.22	6.10	7.10	5.07	3.45
CaO	8.64	12.81	8.53	11.76	14.37	15.53	13.22	8.04
Na_2O	2.49	0.64	3.41	2.14	2.82	1.57	2.37	4.85
K_2O	5.83	3.06	1.39	3.55	0.88	2.89	0.92	2.36
P_2O_5	0.01	0.00	0.05	0.03	0.02	0.00	0.00	0.01
Total	98.94	96.55	99.51	98.98	98.07	98.66	98.29	98.85
T° C	1,447	1,434	1,436	1,445	1,445	1,445	1,445	1,445
Time (h)	22	24	10	24	24	24	24	24

Another important aspect of the experimental run time is its effect on loss of volatiles. In Fig. 1, the loss of Na_2O and P_2O_5 in terms of percent present in the starting material is plotted against time. The loss of Na_2O shows an expected variation, although in our 24 h experiments it was gratifying to see that this loss was slightly under 5%. The loss of P_2O_5, however, is dramatic reaching to 100% in the 70 h experiment.

Analytical data from 46 experiments reported in this paper and 140 from the literature covering the compositional, temperature and f_{O_2} range from rhyolite to ugandite, 1,200–1,450° C, and $10^{-9.00}$ to $10^{-0.67}$ bars respectively, were fitted to Equation 1 using stepwise multiple regression analysis. The multiple correlation coefficient, R, is 0.980. Listed in Table 4 are a, b, c and d_i, the regression coefficients which are statistically significant at the 95% confidence level. Although the Fe_2O_3/FeO ratio in natural silicate liquids is dominantly affected by oxygen fugacity and temperature, the composition of the liquid also contributes

to its variation. For these experiments only 5 constants modifying mole fractions contribute significantly to the ferric/ferrous ratio.

Only the value of a, the constant modifying the natural logarithm of the oxygen fugacity, remains essentially identical (within 0.15%) with that found by Sack et al. In the new regression, constants modifying the mole fractions of SiO_2 and MgO are no longer statistically significant.

One measure of the quality of the fit of the experimental data to Equation 1 is to use the observed values for 2 of the 3 parameters T, f_{O_2}, and Fe_2O_3/FeO in an experiment, and solve for the third. This predicted value can be compared to the actual value of this third parameter in that experiment. When this is done for the 186 experiments used in our regression, the RMS prediction errors are 52° C, 0.5 $\log_{10}f_{O_2}$ units and 0.2 wt.% FeO respectively. This last figure is probably very close to the analytical uncertainty, so we conclude that Equation 1 successfully predicts the behavior of the ferric/ferrous ratio in the experiments.
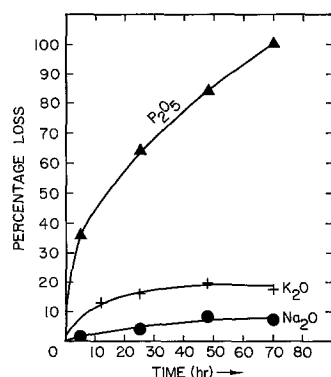
Table 2. Analyses of duplicate experiments in weight percent

Sample #	37	38	49	40	41	42	43	44	45	46
Identifier	IC-2	IC-2	94-8	94-8	G-247	G-247	CSQ-3	CSQ-3	IC-2	IC-2
SiO_2	74.38	72.59	48.28	48.10	56.71	56.44	46.84	46.73	74.22	73.87
TiO_2	0.23	0.24	1.06	1.05	2.40	2.44	2.43	2.45	0.26	0.25
Al_2O_3	12.02	12.13	18.15	18.10	13.84	13.87	15.67	15.58	12.26	12.21
Fe_2O_3	2.09	2.13	7.49	7.39	8.42	8.24	8.58	8.32	2.28	2.24
Cr_2O_3	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01
FeO	1.28	1.38	1.37	1.46	3.74	3.91	2.88	3.04	1.24	1.20
MnO	0.09	0.22	0.25	0.15	0.26	0.26	0.16	0.16	0.10	0.09
MgO	0.10	0.10	3.91	4.02	2.78	2.85	9.48	9.49	0.08	0.09
CaO	1.64	1.60	8.47	8.47	6.22	6.28	9.11	9.13	1.71	1.60
Na_2O	4.32	4.22	2.63	2.63	3.33	3.39	2.98	3.00	4.11	4.14
K_2O	2.72	2.75	6.92	7.10	1.11	1.10	0.92	0.91	2.64	2.64
P_2O_5	0.00	0.02	0.03	0.31	0.02	0.07	0.04	0.03	0.02	0.01
Total	98.89	97.39	98.56	98.78	98.83	98.85	99.10	98.84	98.92	98.35
$T°$ C	1,344	1,342	1,344	1,340	1,443	1,436	1,430	1,430	1,443	1,430
Time (h)	24	23	24	47.5	23	10	24	24	23	22

Table 3. Equilibrium time experiments

SiO_2	58.60	57.61	57.19	58.06	57.92	57.34
TiO_2	0.89	0.82	0.84	0.85	0.83	0.81
Al_2O_3	15.38	15.54	15.62	15.44	15.77	15.73
Fe_2O_3	2.22	7.04	7.28	7.22	7.03	6.80
FeO	6.71	2.23	2.21	2.25	2.34	2.58
MnO	0.18	0.17	0.16	0.16	0.15	0.16
MgO	3.22	3.20	3.27	3.19	3.13	3.27
CaO	7.02	6.71	6.78	6.83	6.85	6.75
Na_2O	3.84	3.77	3.72	3.70	3.52	3.57
K_2O	1.46	1.31	1.31	1.22	1.17	1.20
P_2O_5	0.25	0.18	0.16	0.09	0.04	0.00
Total	99.77	98.68	98.54	99.00	98.66	98.17
$T°$ C	–	1,349	1,349	1,349	1,349	1,359
Time (h)	Initial[a]	5	12	25	48	70

[a] Analysis by wet chemical techniques

Table 4. Regression coefficients with one standard error for Equation 1

Coefficient	Value	Standard Error
a $(a \ln f_{O_2})$	0.2185	0.0044
b $(b/T(K))$	12,670	900
c constant	−7.54	0.55
$d_{Al_2O_3}$	−2.24	1.03
d_{FeO}[a]	1.55	1.03
d_{CaO}	2.96	0.53
d_{Na_2O}	8.42	1.41
d_{K_2O}	9.59	1.45

[a] Total iron expressed as FeO

Note that the standard errors expressed as a percentage of the coefficients are all greatly reduced in comparison to the results of Sack et al. (1980)

Fig. 1. Percentage loss of P, K and Na from initial composition, given in Table 3, as a function of time equilibrated in furnace

As an illustration of an application of Equation 1 we have conducted partial melting experiments on a natural sample, measured the composition of coexisting liquids and olivines and used Equation 1 to compute Fe−Mg distribution coefficients. A ugandite sample was melted in air and at QFM in the temperature range 1,200–1,240° C. The quenched experimental charges contained both olivine and glass, whose compositions were measured on the electron microprobe (Table 5). Because the microprobe can determine only total Fe, we have used Equation 1 and the coefficients in Table 4 to predict the amount of Fe_2O_3 and FeO in the liquids. Note that the olivines equilibrated in air are much more magnesian than those equilibrated at QFM because of the lower FeO contents of the liquids in air.

Based on the measured composition (and predicted Fe_2O_3 and FeO distribution), the K_D for the olivine-liquid Fe−Mg exchange reaction, defined as:

Table 5. Composition of liquids and olivines for ugandite U-50 equilibrated at QFM and in air

	Liquid QFM A	Olivine QFM A	Liquid QFM B	Olivine QFM B	Liquid Air A	Olivine Air A	Liquid Air B	Olivine Air B
SiO_2	42.14	40.08	42.18	39.44	48.21	41.24	42.63	41.78
TiO_2	5.77	–	6.13	–	4.23	–	5.51	–
Al_2O_3	9.40	–	9.78	–	13.69	–	8.79	–
Fe_2O_3	2.66	–	2.68	–	7.23	–	11.73	–
FeO	10.00	14.51	9.69	15.57	0.83	1.59	1.31	1.95
MnO	0.18	0.25	0.18	0.28	0.19	0.28	0.12	0.16
MgO	7.92	45.02	6.94	43.68	7.09	55.91	9.75	55.66
CaO	13.81	0.99	14.57	1.06	10.04	0.45	13.29	0.51
Na_2O	2.51	–	2.72	–	2.54	–	2.18	–
K_2O	4.16	–	4.13	–	3.18	–	2.32	–
P_2O_5	0.64	–	0.58	–	0.38	–	0.18	–
Total	99.19	100.85	99.58	100.03	97.61	99.47	97.81	100.06
$T°$ C	1,234		1,201		1,206		1,225	
$\log f_{O_2}$	−7.89		−8.26		−0.678		−0.678	
K_D	3.92		3.92		4.12		3.84	

$$K_D = \frac{(X_{MgO}^{ol})}{(X_{FeO}^{ol})} \frac{(X_{FeO}^{liq})}{(X_{MgO}^{liq})} \qquad (2)$$

for these liquids was determined (Table 5). The mean K_D's determined at these two oxygen fugacities (3.9 ± 0.0 at QFM, 4.0 ± 0.2 in air) are in excellent agreement, suggesting both that K_D is not strongly dependent upon the Fe_2O_3/FeO ratio in the liquid nor upon the liquid composition (Table 5), and that Eq. (1) and the coefficients in Table 4 accurately predict the actual FeO contents of the liquids.

In summary, these new experimental results on Fe_2O_3/FeO ratios in natural liquids equilibrated in air, equal to an oxygen fugacity of $10^{-0.68}$ bars, essentially sustain the results of Sack et al. (1980), although there are changes in the magnitude of the regression constants of the purely empirical fit equation relating Fe_2O_3/FeO to oxygen fugacity, temperature and liquid composition (Eq. (1); Table 4). Certainly equilibration of lavas in air at above liquidus temperatures does not result in all the iron becoming ferric.

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