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The Oxygen Partial Pressure of the Magma from Mihara Volcano, O-sima, Japan

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After clarifying that the composition of the 1950—1951 lava flow of Mihara Volcano, O-sima, Japan, is completely in the liquid state above 1200°C and at oxygen partial pressures below 10^{-4} atm, the most probable oxygen partial pressure of the magma from Mihara Volcano was estimated to be $10^{-8.0}$ atm. On the basis of the present results as well as those available in the literature, the oxygen partial pressure of the typical tholeiitic basalt magma was deduced to be nearly 10^{-8} atm.

Recently, some attempts have been made to clarify the significance of the oxygen partial pressure of magmas from which various kinds of volcanic rocks are derived by fractional crystallization. Kennedy[1,2] estimated the oxygen partial pressures of magmas on the basis of the mole fraction of ferrous and ferric oxides in rocks, and emphasized that the magmas with a high (FeO)/(Fe_2O_3) ratio will differentiate toward a ferrogabbro, as iron is concentrated in the residual liquid, thus following Fenner's trend[3] of differentiation. Osborn,[4,5] Osborn and Roeder,[6] and Roeder and Osborn[7] studied the fractional crystallization of magma influenced by oxygen partial pressures by extending the fundamental experimental studies established by Muan,[8] and by Muan and Osborn.[9] From the mineralogical and petrological standpoints Yoder and Tilley,[10] and Kuno[11,12] also pointed out the importance of the oxygen partial pressures with regard to the fractional crystallization of magmas. Hamilton *et al.*[13] studied the relationship between the oxygen partial pressure and the solubility of water in basaltic and andesitic magmas by means of hydrothermal high-pressure techniques. Recently, Fudali,[14] from his experimental study, deduced the probable oxygen partial pressures ("oxygen fugacity" in his term) of several basaltic and andesitic magmas.

On the basis of the equilibrium calculations for volcanic gases under magmatic conditions, Krauskopf,[15] Heald *et al.*,[16] and Matsuo[17] have estimated the oxygen partial pressures of magmas.

In the present paper, a new method for obtaining an equilibrated mole ratio of (FeO)/($FeO_{3/2}$) in melted rocks at desired temperatures and at low oxygen partial pressures will be described. The oxygen partial pressure of the typical tholeiitic basalt magma extruded from Mihara Volcano, O-sima, Japan, during the period of 1950—1951 will also be presented on the basis of the equilibrated mole ratio (FeO)/($FeO_{3/2}$) in the quenched rock.

Experimental

General Procedures. Finely-powdered natural and pretreated basalt samples from Mihara Volcano, described below, were heated at 1200 and 1300°C under controlled oxygen partial pressures until equilibrium was attained among the melt and gas phases. The sample was then quenched rapidly in order to analyze the total iron and ferrous iron contents. The quenched samples were also examined under a polarized microscope to check for the presence of any crystal.

Materials. Hypersthene bytownite basalt of Mihara Volcano extruded from the center cone of O-sima during the period of 1950—1951, was chosen.

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1) G. C. Kennedy, *Am. J. Sci.*, **246**, 529 (1948).
2) G. C. Kennedy, *Bull. Geol. Soc. Am., Special Paper*, **62**, 489 (1955).
3) C. N. Fenner, *Min. Mag.*, **22**, 539 (1931).
4) E. F. Osborn, *Am. J. Sci.*, **257**, 609 (1959).
5) E. F. Osborn, *Am. Mineralogist*, **47**, 211 (1962).
6) E. F. Osborn and P. L. Roeder, Rept. Int'l. Geol. Congress, XXI Session, Norden, 147 (1960).
7) P. L. Roeder and E. F. Osborn, *Am. J. Sci.*, **264**, 428 (1966).
8) A. Muan, *Trans. AIME*, **203**, 965 (1955); *Am. J. Sci.*, **256**, 171 (1958).
9) A. Muan and E. F. Osborn, *J. Am. Ceram. Soc.*, **39**, 121 (1956).
10) H. S. Yoder, Jr., and C. E. Tilley, *J. Petrol.*, **3**, 342 (1962).
11) H. Kuno, *ibid.*, **6**, 302 (1965).
12) H. Kuno, *J. Japanese Assoc. Min. Petrol. Econ. Geologists*, **53**, 131 (1965).
13) D. L. Hamilton, C. W. Burnham and E. F. Osborn, *J. Petrol.*, **5**, 21 (1964).
14) R. F. Fudali, *Geochim. et Cosmochim. Acta*, **29**, 1063 (1965).
15) K. B. Krauskopf, "Researches in Geochemistry," Wiley, New York (1959).
16) E. F. Heald and J. J. Naughton, *Nature*, **193**, 642 (1962); E. F. Heald, J. J. Naughton and L. Barnes, Jr., *J. Geophys. Res.*, **68**, 545 (1963).
17) S. Matsuo, *J. Earth Sci., Nagoya Univ.*, **8**, 222 (1960).

TABLE 1. THE CHEMICAL COMPOSITION OF THE 1950—1951 LAVA OF MIHARA VOLCANO AND ITS NORMATIVE MINERALS IN WEIGHT PERCENTAGE

	SiO_2	52.43
	TiO_2	1.57
	Al_2O_3	15.01
	Fe_2O_3	3.08
	FeO	10.14
	MnO	0.12
	MgO	4.81
	CaO	9.73
	Na_2O	1.79
	K_2O	0.35
	P_2O_5	0.14
	$H_2O(-)$	0.28
	$H_2O(+)$	0.08
	Total	99.53
	Fe_2O_3 (total)	14.35
Norm	Q	10.14
	ap	0.34
	il	3.04
	mt	4.64
F	or	2.22
	ab	15.20
	an	31.69
Py	wo	6.38
	en	12.00
	fs	13.33

This specimen was collected by Iwasaki *et al.*[18] The chemical composition is given in Table 1. Pretreated samples were used for shortening the heating times, as will be mentioned later. An extremely oxidized sample with respect to the ferrous-ferric ratio was prepared by heating the sample at 1000°C in air for a long period of time, while a reduced sample was obtained by heating the natural sample at 1000°C in a 1-to-1 mixture of carbon dioxide and hydrogen. The $(FeO)/(FeO_{3/2})$ ratio in these three types of samples were as follows:

original raw sample	4.95
extremely oxidized sample	0.022
reduced sample	24.5

The Control of Atmospheres. Five different atmospheres were chosen in order to obtain different oxygen partial pressures, that is, air, carbon dioxide, and mixed gases of carbon dioxide and hydrogen with CO_2/H_2 ratios of 100, 30, and 8. A gas mixer similar to that described by Darken and Gurry[19] was used to obtain a mixed gas of a desired composition. The linear rate of the gas flow was kept constant at 8.8 mm/sec. The oxygen partial pressure in the gas phase was calibrated by using a oxygen pressure meter made of a $(ZrO_2)_{0.85}(CaO)_{0.15}$ solid electrolyte cell. The principle and the design of the cell have already been reported by several investigators,[20] and some applications to a vertical quenching furnace may be found in a paper by Katsura and Hasegawa.[21] The measured oxygen partial pressures deviated slightly from the values calculated from the thermochemical data at lower temperature and at higher rates of flow. The relationship between the measured and the calculated oxygen partial pressures is given in Fig. 1. In the present study, the measured values were adopted; they are listed in the second column of Table 3.

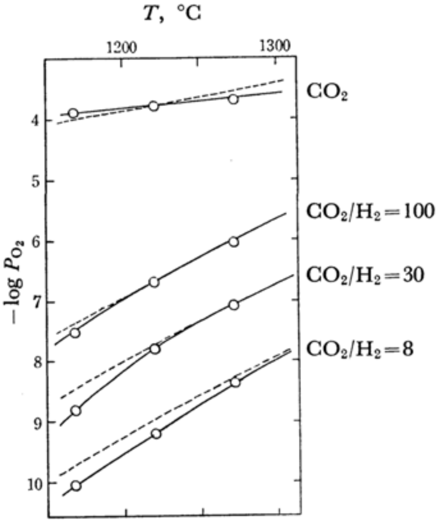

Fig. 1. Oxygen partial pressure data as a function of temperature in various atmospheres calibrated by solid electrolyte cell.
Solid line: Measured by solid electrolyte cell.
Broken line: Calculated from the thermodynamic data summarized by Coughlin (Bureau of Mines, No. 542, U. S. Goverment Printing Office, Washington, D. C. (1954).

Furnace and Temperature Control. The furnace and the temperature control system used in this study were the same as those used by Katsura and Kimura[22]; the furnace temperatures were kept constant within ±2°C.

Chemical Analysis. The ferrous iron was volumetrically determined by using a 0.05 N potassium permanganate standard solution, while the total iron content was photometrically determined by using α, α'-dipyridyl after reducing the total iron to ferrous iron.[18] The ferric iron content was then determined as the difference between the two.

Results and Discussion

The Effects of Sample Containers on Equilibrium Experiments. It is well known that a platinum-made container reacts with iron in samples at high temperatures and low oxygen partial

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[18] I. Iwasaki, T. Katsura, T. Ozawa, M. Yoshida, M. Mashima, H. Haramura and B. Iwasaki, *Bull. Volc. Soc. Japan, Ser. II,* **5**, 9 (1960).

[19] L. S. Darken and R. W. Gurry, *J. Am. Chem. Soc.,* **67**, 1398 (1945).

[20] See a paper by Katsura and Hasegawa, This Bulletin, in press.

[21] T. Katsura and M. Hasegawa, This Bulletin, in press.

[22] T. Katsura and S. Kimura, This Bulletin, **38**, 1664 (1965).

Table 2. The change of total iron content in samples during heating under various oxygen partial pressures (the original sample contains 14.30% iron as Fe_2O_3*)

Starting material	Atmosphere	Temp. °C	Heating time, hr	Total iron as Fe_2O_3*	FeO % wt	Fe_2O_3 % wt	log (FeO)/($FeO_{3/2}$) mole ratio
Original	Air	1300	3	14.1	3.0	10.8	−0.509
Oxidized	Air	1300	3	14.2	2.8	11.1	−0.553
Original	Air	1200	4.5	14.1	2.5	11.3	−0.602
Oxidized	Air	1200	4.5	14.0	1.0	12.9	−1.05
Original	Air	1200	10.5	14.0	1.5	12.3	−0.854
Oxidized	Air	1200	10.5	13.9	1.1	12.7	−1.00
Original	CO_2	1300	3	14.0	7.5	5.7	0.164
Original	CO_2	1300	6	14.4	7.7	5.8	0.176
Oxidized	CO_2	1300	6	14.4	7.3	6.3	0.114
Original	CO_2	1200	7.5	14.2	7.6	5.8	0.164
Oxidized	CO_2	1200	7.5	14.1	3.5	10.2	−0.420
Original	CO_2	1200	16	14.0	6.9	6.3	0.086
Oxidized	CO_2	1200	16	14.2	4.6	9.1	−0.252
Original	CO_2	1200	20	13.8	6.6	6.5	0.053
Oxidized	CO_2	1200	28	14.2	4.9	8.8	−0.208
Oxidized	$CO_2/H_2=100$	1300	6	13.9	9.6	3.2	0.524
Reduced	$CO_2/H_2=100$	1300	9	14.0	10.1	2.8	0.603
Oxidized	$CO_2/H_2=100$	1300	9	14.2	10.3	2.8	0.612
Reduced	$CO_2/H_2=100$	1200	10.5	13·7	10.5	2.0	0.766
Oxidized	$CO_2/H_2=100$	1200	10.5	14.4	8.9	4.5	0.342
Reduced	$CO_2/H_2=100$	1200	20	13.7	10.2	2.4	0.674
Oxidized	$CO_2/H_2=100$	1200	20	14.2	9.5	3.6	0.465
Oxidized	$CO_2/H_2=30$	1200	22	13.5	10.3	2.1	0.740
Reduced	$CO_2/H_2=30$	1200	19	13.4	11.1	1.1	1.05
Reduced	$CO_2/H_2=8$	1300	5	13.0	11.0	0.8	1.184
Original	$CO_2/H_2=8$	1300	5	13.4	11.0	1.2	1.009
Oxidized	$CO_2/H_2=8$	1300	5	13.3	11.0	1.1	1.045
Oxidized	$CO_2/H_2=8$	1300	19	11.4	9.4	1.0	1.021

pressures(23,1,10) to form a Pt-Fe alloy. Muan found a palladium-silver alloy to be suitable for a crucible material in studies of low-melting iron silicates,(24); Fudali(14) used this new container in his recent study. In the present study, a 60%Ag-40%Pd alloy was first tested for runs at 1200°C, and the results were compared with data obtained by using Pt-Rh alloys. At temperatures above 1200°C, the container made of Pt-Rh alloys was better than that made of the Ag-Pd alloy. After a number of preliminary experiments, it was found that the use of an 80%Pt-20%Rh alloy for runs in air, and the use of a 60%Pt-40%Rh alloy for atmospheres of carbon dioxide and for mixed gases of carbon dioxide and hydrogen were the best. The results are given in Table 2, together with the (FeO)/($FeO_{3/2}$) ratio.

As may be seen in Table 2, the loss of iron in samples is minimized except for the case of mixed gas $CO_2/H_2=8$ reacted at 1300°C for 19 hr. This datum is, therefore, omitted for the determination of the equilibrated mole ratio. Also, it may be seen that the loss of iron is smaller in the extremely oxidized samples than in reduced samples.

The Establishment of Equilibrium. Kennedy(1) obtained the equilibrium composition at various temperatures in air, working on the basis of the constancy of the ferrous iron content in samples; Fudali(14) then confirmed the equilibrated compositions by the same method as that of Kennedy,(1) under various oxygen partial pressures ranging from 0.21 atm to 10^{-8} atm. As was made clear by Kennedy and Fudali, it takes a long period of time to approach the equilibrated compositions, even at 1200°C; this will cause an appreciable decrease in the iron content of samples. Thus, it is not sufficient to determine the equilibrated composition from only the constancy of the ferrous iron content; the ferrous iron content should be related to the ferric iron content in order to establish the equilibrated state. In the present study, therefore, the equilibrated state was checked by having constant mole (FeO)/($FeO_{3/2}$) ratio, irrespective of the initial (FeO)/($FeO_{3/2}$) ratios in the starting materials. To minimize the loss of iron in samples,

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23) R. W. Taylor and A. Muan, *Trans. AIME*, **224**, 500 (1962).

24) A. Muan, *J. Am. Ceram. Soc.*, **42**, 344 (1963); *Trans. AIME*, **224**, 1080 (1962).

TABLE 3. EQUILIBRATED LOGARITHMIC MOLE RATIO OF (FeO)/($FeO_{3/2}$) at 1300°C and 1200°C UNDER VARIOUS OXYGEN PARTIAL PRESSURES

Temp. °C	Atmosphere	$-\log P_{O_2}$	log (FeO)/($FeO_{3/2}$) mole ratio	Phase present
1300	$CO_2/H_2=8$	8.0	1.1	G*
1300	$CO_2/H_2=100$	5.7	0.60	G
1300	CO_2	3.6	0.14	G
1300	Air	0.68	−0.53	G
1200	$CO_2/H_2=30$	8.2	0.90	G
1200	$CO_2/H_2=100$	6.9	0.58	G
1200	CO_2	3.9	−0.08	G+Mt**
1200	Air	0.68	−0.94	G+Hm***

* G means Glass.
** Mt means magnetite, less than 0.1% by volume.
*** Hm means hematite, about 5% by volume.

the heating time must be shortened, especially at low oxygen partial pressures; thus the approximation of the equilibrated ratio was made by extrapolating the curves of times *vs.* the ratio from both sides of the reaction as is shown in Fig. 2; the results are given in Table 3 along with the oxygen partial pressure data. In the last column of the table, the phases present under each set of conditions are also summarized. As may be seen in the table, at 1200°C the volcanic rock of the 1950—1951 eruption of Mihara Volcano is in a completely liquid state at oxygen partial pressures below 10^{-4} atm under the present experimental conditions.

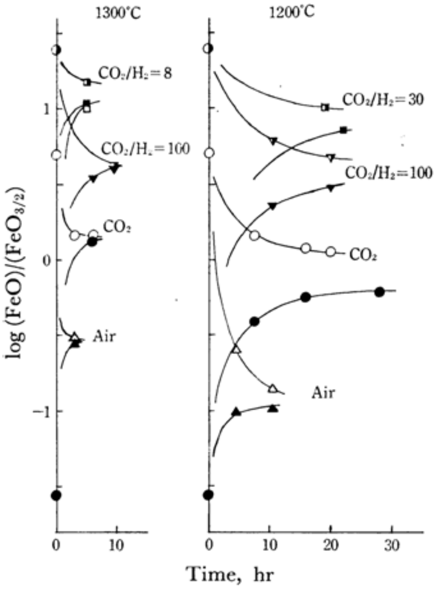

Fig. 2. Logarithmic mole ratio (FeO)/($FeO_{3/2}$) as a function of heating time in various atmospheres at 1300 and 1200°C.
◑ ◨ ⧨: Reduced samples
○ □ ▽: Original samples
● ■ ▼: Extremely oxidized samples

An Estimation of the Oxygen Partial Pressure of the Magma from Mihara Volcano. The experimental results on the equilibration runs given in Table 3 are graphically illustrated in Fig. 3. The gradient of a dotted straight line in Fig. 3, showing the relationship between log(FeO)/($FeO_{3/2}$) and $-\log P_{O_2}$, is 1/4, which is to be expected from the following reaction equilibrium:

$$FeO + 1/4\ O_2 = FeO_{3/2},$$

if it is assumed that the silicate melts are in an ideal solution with respect to the iron oxides. All the data obtained, however, do not fall on lines with this slope. This fact may be attributed to the slight deviation of the activity coefficients of each component from unity. A datum obtained in air at 1200°C deviates appreciably from the lines; this may be due to the presence of some hematite (about 5% in volume) as a first phase crystallized from a liquid.

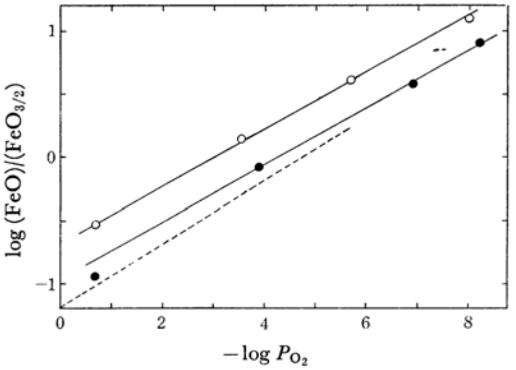

Fig. 3. Variation in mole ratio (FeO)/($FeO_{3/2}$) in melts as a function of oxygen partial pressure.
—○—: 1300°C —●—: 1200°C
The dotted line shows the gradient of 1/4.

From the present results at 1200°C and 1300°C, if one knows the temperature of a magma in the liquid state, together with the ferrous-ferric ratio in a solidified magma, then we will be also to estimate the oxygen partial pressure of that magma, provided that the mole ratio (FeO)/($FeO_{3/2}$) does not significantly change during the period of decreasing temperature. Fudali[14] deduced the oxygen partial pressure of the Kilauean magma of Hawaii to be about $10^{-8.2}$ atm at 1200°C on the basis of the principles of the present study. In his study, Fudali fixed the (FeO)/($FeO_{3/2}$) ratio as 5.12 in the Kilauean basalt magma for a sample of the 1921 eruption; the specimen was not completely in the liquid state at 1200°C and at $10^{-8.2}$ atm P_{O_2}, but small amounts of olivine were crystallized. Heald *et al.*[16] also calculated the oxygen partial pressures of volcanic gases collected from the 1960 Kilauea Iki eruption, and gases from Halemaumau, Kilauea, which were analyzed by Shepherd[25] They obtained the oxygen partial pressure of 10^{-8} atm for the Kilauean basaltic magma at 1500°K.

During the 1950—1951 eruption of Mihara Volcano, many important studies were carried out from the geochemical, geophysical, and geological points of view. Of these, the temperature measurement was directed by Minakami *et al.*[26]; the temperature was recorded to be about 1200°C. The chemical composition of the lava flow was determined in detail by Tsuya *et al.*[27] and by Iwasaki *et al.*[18] The latter authors focused their attention on the iron content of this lava flow and analyzed 159 samples collected systematically from the flow area. They concluded that this lava flow is very homogeneous with respect to the total iron content, the Fe_2O_3 values ranging from 14.2 to 14.4% irrespective of their appearance. The variation in FeO/F_2O_3 in this lava flow is of special importance for the present attempt to estimate the oxygen partial pressure of the magma. The results of Iwasaki *et al.*[18] are shown in Fig. 4 as a frequency histogram of the (FeO)/($FeO_{3/2}$) mole ratio. The mole ratios range from 3.1 to 7.0, a range which corresponds to the oxygen partial pressures ranging from 10^{-6} to 10^{-8} atm from the relationship between log(FeO)/($FeO_{3/2}$) and $-\log P_{O_2}$ at 1200°C in Fig. 3.

If it is assumed that, after extrusion, the solidifying lava may be oxidized to some extent under atmospheric conditions, the most probable (FeO)/($FeO_{3/2}$) ratio in the Mihara Volcano lava immediately after the extrusion will be in the range from 6.5 to 7.0 or more. As the temperature of lava was recorded to be about 1200°C, it may be deduced on the basis of the relationship given in Fig. 3 that the oxygen partial pressure of the magma from Mihara Volcano is $10^{-8.0}$ atm or less.

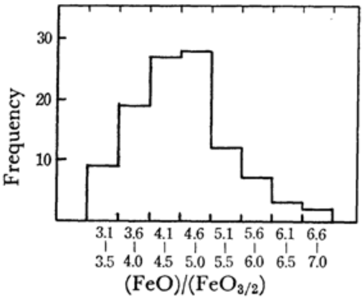

Fig. 4. Frequency histogram of mole ratio (FeO)/($FeO_{3/2}$) in compact solidified lavas extruded during 1950—1951 from Mihara Volcano.

Conclusion

From the foregoing experimental results and discussion, it may be concluded that: 1) an equilibrated mole ratio (FeO)/($FeO_{3/2}$) in rock samples at high temperatures should be determined from both sides of the reaction by extrapolation, as it shortens the heating time and minimizes the loss of iron in samples due to the formation of an alloy with the container; 2) at 1200°C, the volcanic rock of the 1950—1951 eruption of Mihara Volcano is in a completely liquid state at oxygen partial pressures below 10^{-4} atm under the present experimental conditions; 3) the oxygen partial pressure of the magma from Mihara Volcano was estimated to be about $10^{-8.0}$ atm, and 4) by comparing the oxygen partial pressure of the magma from Mihara Volcano with that of the magma from Kilauea Volcano, it seems that the typical tholeiitic basalt magma may be in equilibrium with the gas phase in which the oxygen partial pressure is approximately 10^{-8} atm.

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25) E. S. Shepherd, *Am. J. Sci., 5th Ser.*, **35A**, 311 (1938).

26) T. Minakami, T. Miyazaki and T. Takahashi, *Bull. Earthq. Res. Inst.*, **29**, 359 (1951).

27) H. Tsuya and R. Morimoto, *ibid.*, **29**, 563 (1951); H. Tsuya, R. Morimoto and J. Ossaka, *ibid.*, **30**, 231 (1952).