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On the Estimation of Oxygen Partial Pressure Associated with Lava

By

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Abstract

In this paper the method of estimation of partial oxygen pressure (Po_2) associated with lave is reconsidered on the thermodynamic bases, and some results of experiment to know how Na ion in lave has an effect on the $Fe^{+3}-Fe^{+2}-O^{-2}$ equilibrium are reported.

It is explicit that each lava has its own equilibrium constant of iron redex reactions. Fe^{+3} is more stable than Fe^{+2} with rising temperature in sodium glass and alkalirhyolite at air atmosphere. This is opposite to normal state which Fe^{+2} is more stable than Fe^{+3} with rising temperature.

Besides, the geologic "Po_2-barometer" of olivine and pyroxene is discussed to estimate the oxygen partial pressure associated with lava.

Introduction

Some experimental petrologists have recognized that the oxygen partial pressure is one of the most important factors to be discussed for the petrogenetic investigation of igneous rock. Distinguishable effects of Po_2 may be reflected on the ratio of ferric to ferrous iron of lava.

In 1948 G. C. KENNEDY was the first that treated experimentally a lava as an ideal solution of ferric-ferrous iron ions (KENNEDY, 1955). He applied the equilibrium constant of ferric-ferrous iron ions and oxygen ion obtained at each constant temperature in air to a lava, and estimated that Po_2 may be 10^{-8}–10^{-5} atms at 1000–1400°C in magma. This report is famous for "Fenner trend" and "Bowen trend" as the first proposal of the significance of atmosphere for the differentiation of magma.

OSBORN (1959–62) had evolved petrogenetic discussion based on the MgO-FeO-Fe_2O_3-SiO_2 system studied by MUAN and OSBORN (1956) at controlled Po_2 atmosphere. Although natural lavas are not so simple as explainable by the "simple basalt system", the genetic relations among calcalkaline, hypersthenic, pigeonitic and alkaline rock series in orogenic belt are explained by the relation of Po_2 in the magmas (KUNO, 1965; TANEDA, 1966).

TANEDA (1966) concluded that alkalic rock magmas are produced and crystallized at comparatively high vapor pressure (PH_2O, Po_2, etc.) and low temperature,

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while nonalkalic (tholeiitic, calcalkalic) rock magmas at low vapor pressure and high temperature. FUDALI (1965) has experimentally determined Po_2 equilibrating with the original ratio of ferrous to ferric iron in a natural lavas at 1200°C.

I have reexamined fundamentally the thermodynamic method for estimation of Po_2 used by KENNEDY (1948) and FUDALI (1965), and on the other hand, obtained experimentally some data of the stability of ferric, ferrous iron and oxygen ions in a lava which are affected by coexisting Na ion at different atmosphere such as CO_2/H_2 gas mixture or air. In this paper new method to estimate Po_2 associated with a lava, geologic Po_2-barometer by means of olivine and pyroxene redox reactions, is also discussed.

Acknowledgements

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Estimation of Po_2 based on Equilibrium Relation of Iron-Oxygen in a Lava

Assuming that a lava is a dilute solution of a divalent and trivalent iron ions, we can consider the following reaction.

$$2\,Fe^{+3} + O^{-2} = 2\,Fe^{+2} + 1/2\ O_2 \qquad (1)$$

This ionic reaction (1) may be suitable for a lava of high temperature. We can, however, not measure electromotive forces of (1) in silicate melt at high temperature. We may be able to examine the following reaction (2) through quenching method.

$$2\,Fe_2O_3 = 4\,FeO + O_2 \qquad (2)$$

FUDALI (1965), however, has suggested that the next equation would be more suitable for iron-oxygen equilibrium reaction.

$$4\,FeO_{1.5} = 4\,FeO + O_2 \qquad (3)$$

Here we discuss mainly about the reaction (3) on the basis of thermodynamic theories. Equilibrium constant of the reaction (3) at constant temperature should be

$$Kpo_2 = \frac{(FeO\ mol\%)^4}{(FeO_{1.5}\ mol\%)^4}\,Po_2 \qquad (4)$$

Activities of the ion in melt is assumed to be in accordance with each mol fraction and not affected by confining pressure.

There are two methods to estimate Po_2 in a lava from the equilibrium constant which are a function of oxidation index (O.I.), Po_2 and temperature (T). Here the "Oxidation index" is defined as follows;

$$O.I. = \frac{FeO\ mol\%}{FeO_{1.5}\ mol\%} \tag{5}$$

A. KENNEDY'*s Method*

$$Kpo_2 = F(T, O.I.)_{po_2=const.} \rightarrow Po_2 = F(O.I., Kpo_2)_{T=assumed} \tag{6}$$

Based on this formula, he calculated Po_2 in a lava from Kpo_2 obtained as a function of T, O.I. at constant Po_2 (air). In this case, temperature of lava is assumed by preferable value.

B. FUDALI'*s Method*

It is characteristic of deciding 1200°C as temperature of lava and so the changes of O.I. depend on merely Po_2 or vice versa as represented by the following equation.

$$Kpo_2 = F(Po_2, O.I.)_{T=assumed} \rightarrow Po_2 = F(O.I.)_{Kpo_2=const.} \tag{7}$$

By the equations (4) and (5),

$$1/4 \log Po_2 = -\log. O.I. + 1/4 \log Kpo_2 \tag{8}$$

We can get Po_2 from equation (8) by means of equilibrating a given lava sample at different controlled Po_2 until the original $FeO/FeO_{1.5}$ ratio of lava is maintained.

Here the Po_2 is estimated by two methods above mentioned on a number of

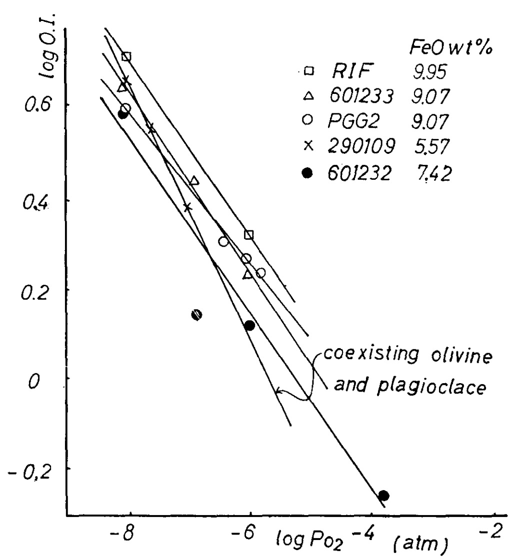

Fig. 1. Relations between oxidation index and oxygen partial pressure in a lava based on the equation (8). Each lave has its own Kpo_2 which is proportionally FeO wt% (R.F. FUDALI 1965).

assumptions. To know the exact temperature of lava is impossible by any geologic thermometer. TILLEY and YODER (1962) reported on the basis of their experiments of basaltic rock melt that crystallization range and appearance of major silicate phases occurred in a comparative narrow temperature interval. It may be possible to calculate within the limits of error ±100°C for basaltic rock.

Each lava has its own peculiar Kpo_2 which is proportionally FeO wt% (FUDALI, 1965). This is non ideal solution because iron ion may be affected by other coexisting ions.

Then equilibrium constant Kpo_2 is not applied to all lavas just as KENNEDY has done. If we dare to estimate Po_2 in the face of danger of assuming a particular temperature of lava, we have to solve the equation (8) for each lava. 290109 (FUDALI, 1965) containing olivine and plagioclace has more steep gradient than complete glass (Fig. 1). This fact is a difficult problem for a lava mostly containing some crystal or microlites. Besides, Po_2 in magma may be variable in the course of crystallization. To what stage of crystallization does the experimentally obtained Po_2 correspond?

Equilibrium Relation of Iron-Oxygen in a Lava

On the grounds of discussions in the preceding section, it has become clear that Kpo_2 obtained from one specimen is not applied to all lavas. Conversely speaking the stability of iron-oxygen is different in each lava which is various in chemical composition and physical conditions.

Now in this section we shall discuss Gibb's energy change of the reaction (3) in a lava and of a reaction (2) in pure oxide. From equation (4),

$$Kpo_2 = \exp - \Delta G/RT \qquad (9)$$

Then

$$\Delta G = -RT \ln Kpo_2 \qquad (10)$$

Data for stability relation between iron and oxygen in a alkali-rhyolite melt and in a tholeiitic basalt melt at air or CO_2/H_2 gas mixture atmosphere are presented in table 1. This alkali-rhyolite contains mainly alkali feldspar and a little of pigeonite and riebeckite. The chemical compositions are also presented in table 1. Experimental method of alkali-rhyolite performed by the writer is similar to FUDALI's Method (1965). Calculation of Po_2 was done by dissociation constant of reaction $2\ CO_2 = 2\ CO + O_2$ and $CO_2 + H_2 = CO + H_2O$ listed in OSBORN and MUAN's paper (1956). For preventing from iron loss to container, Ag-Pd (60:40) arroy container was used, but conical Pt-Rh (80:20) crucible was used above 1200°C. In table 2, the same data about sodium glass (T. BAAK and HORNYAK 1961) and pure iron oxide calculated from COUGHLIN's table (1954) are presented for comparison. Fig. 2 shows the relation among ΔG, T and log Po_2 based on table (1)-(2), but we conveniently consider that Fe^{+2} oxidize to Fe^{+3} as represented $4FeO + O_2 = 4FeO_{1.5}$. In Fig. 2 ΔG calculated from the reaction (2) for the lava more deviate from the ΔG of pure oxide comparing with ΔG calculated from the reaction (3). Consequently the stability relation of iron

Table 1. The iron-oxygen equilibrium in silicate melt

T°c	FeO	Fe_2O_3	Kpo_2	1n Kpo_2	$\triangle G°$	Po_2
(1) Alkali-rhyolite melt in air						
974	.32	1.54	5.99 10^{-4}	−7.42	18.4	0.21*
1051	.39	1.46	1.83 10^{-3}	−6.31	16.6	0.21**
1178	.43	1.38	3.02 10^{-3}	−5.80	16.7	0.21**
1189	.40	1.46	1.84 10^{-3}	−6.30	18.30	0.21
1244	.41	1.45	2.07 10^{-3}	−6.18	18.6	0.21**
1353	.41	1.44	2.11 10^{-3}	−6.16	19.9	0.21
(2) Alkali-rhyolite melt in $10^{-8.0,-8.2}$ Po_2						
1295	1.44	0.30	8.07 $10^{-6.1}$	−11.95	37.2	$10^{-8.1}$**
1351	1.51	.22	3.37 10^{-5}	−10.30	33.2	$10^{-8.0}$
1390	1.60	.12	4.86 $10^{-4.2}$	−8.09	26.7	$10^{-8.2}$
(3) Tholeiitic basalt melt in air (KENNEDY's data 1948)						
1100	0.98	11.50	1.67 10^{-5}	−11.0	30.0	0.21
1200	1.59	10.82	1.49 10^{-4}	−8.81	25.8	0.21
1300	2.35	9.97	9.97 10^{-4}	−6.92	21.6	0.21
1400	3.20	9.02	5.06 10^{-3}	−5.29	17.6	0.21
1430	3.32	8.88	6.26 10^{-3}	−5.02	17.00	0.21

Experimented sample

	(3)	(1)		(3)	(1)
SiO_2	50.87	70.31	MnO	0.88	0.09
TiO_2	.79	.15	MgO	6.25	0.04
Al_2O_3	17.62	15.30	CaO	9.32	0.27
Fe_2O_3	1.60	1.87	Na_2O	2.94	6.37
FeO	9.94	0.66	K_2O	.60	4.27

* exist anorthoclase (high temperature type) and pigeonite
** exist anorthoclase
(1) Analyst; K. ISHIBASHI
(3) Analyst; G.F. GONYER (KENNEDY 1948)

oxide in a lava may be actually represented in reaction (3). This is in accordance with FUDALI's idea that reaction (3) is a much closer approximation to reality.

Most distinguishable facts in Fig. 2 are alkali-rhyolite melt and sodium glass having opposite gradient. The Gibbs energies of reaction (3) increase with rising temperature just in opposite to the free energies for the pure oxide. At another view point, increasing ΔG of pure oxide with rising temperature shows that reaction (3) proceeds spontaneously to the higher reduction state even at constant atmosphere, but in the cases of alkali-rhyolite and sodium glass it is just opposite.

Associating with special high activity energies of sodium in volcanic glass studied by KIRIYAMA (1965) by means of dielectric loss, this abnormal phenomenon may be caused by high contents of sodium ion in alkali-rhyolite and sodium glass. This fact is important to be applied to a lava. We can not say explicitly that in general those lavas with low O. I. show a high oxidation state. Stability of acmite $(NaFe^{+3})SiO_3$ contained in alkali rock may be explained not only by

Table 2. The iron-oxygen equilibrium in silicate melt

	T°c	FeO	Fe_2O_3	Kpo_2	ln Kpo_2	△G°	Po_2
(4)	Na_2SiO_4 glass in air. (T. BAAK and E.J. HORNYAK, 1961)						
	1200	0.179	4.71	6.77 10^{-7}	−14.2	41.6	0.21
	1100	.157	4.74	3.87	−14.8	40.3	0.21
	1000	.143	4.75	2.62	−15.2	38.3	0.21
	900	.137	4.76	2.17	−15.3	35.8	0.21
	1200	.100	2.82	5.01	−14.5	42.5	0.21
	1100	.088	2.84	2.94	−15.0	41.0	0.21
	1000	.078	2.84	1.83	−15.5	39.2	0.21
	900	.074	2.85	1.45	−15.8	36.7	0.21
	1200	.034	.94	5.58	−14.4	42.2	0.21
	1100	.031	.94	3.95	−14.7	40.2	0.21
	1000	.029	.94	2.98	−15.0	38.0	0.21
	900	.028	.94	2.44	−15.2	35.5	0.21
	1200	.005	.097	2.31 10^{-6}	−13.0	38.0	0.21
	1100	.005	.097	2.31	−13.0	38.0	0.21
	1000	.004	.098	9.08 10^{-7}	−13.9	35.2	0.21
	900	.004	.098	9.08	−13.9	35.2	0.21
(5)	Pure oxide (calculated from specific heat capacity)						
	1400			6.14 10^{-6}	−12.0	40.0	
	1200			2.51 10^{-8}	−17.5	51.3	
	1000			1.69 10^{-11}	−24.8	62.7	

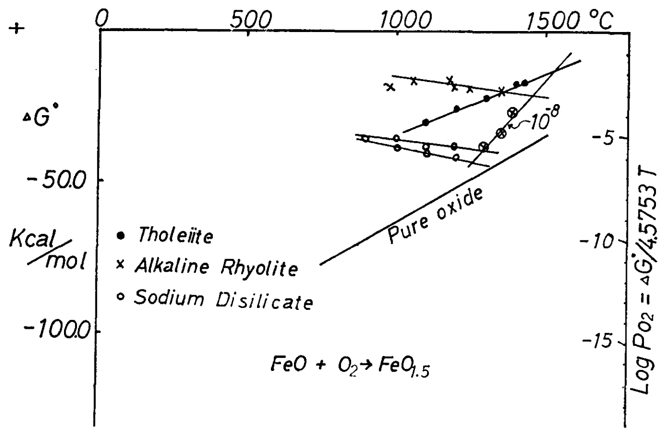

Fig. 2. Relations between stability and oxygen partial pressure in equilibrium with iron ion in a lave. Contrary to pure oxide, Fe^{+3} in soda-glass and alkali rhyolite is more stable than Fe^{+2} with rising temmperature.

high oxygen partial pressure (YAGI, 1966) associated with a lava but also by what Fe^{+3} is more stable than Fe^{+2} at rising temperature. But alkali-rhyolite melt at $10^{-8}Po_2$ has not the same KPo_2 as obtained in air as represented in Fig. 2. This fact should be explained by further study.

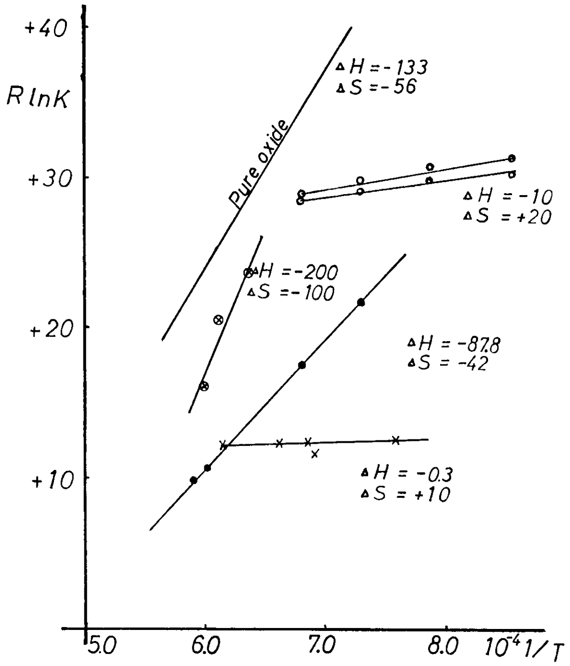

Fig. 3. Thermodynamic properties of the iron-oxygen equilibrium in a lava. Na^+ coexisting with iron is effective to decrease a entropy and heat content changes of reaction $4FeO+O_2=4FeO_{1.5}$. Symboles are same to Fig. 2.

Now we consider the following equation converted from equation (10);

$$R \ln Kpo_2 = \varDelta S - \varDelta H\, 1/T \tag{11}$$

Thermodynamic properties of iron-oxygen redox reaction in a lava are presented in Fig. 3 on the basis of equation (11). Entropy and entalpy changes of redox reaction in alkali-rhyolite and sodium glass at air atmosphere are very different from others. It is characteristic that the heat of oxidation is small and entropy of ferric iron is large.

"Geologic Po_2-Barometer" of Olivine and Pyroxene

Most lavas contain olivine and pyroxene which are closely associated with magnetite rims or exsolution lamellae and others (KUNO, 1950; TANEDA, 1943, 47, 52; SHINNO, 1966; etc.). These phenomena caused by oxidation are applied to estimate Po_2 in lava. Now we have to calculate that how Fe_2SiO_4, $FeSiO_3$ end members of olivine and pyroxene resist to oxygen atmosphere. Next redox reaction of Fe_2SiO_4, $FeSiO_3$ may be considered simply.

$$6Fe_2SiO_4+O_2=2Fe_3O_4+6FeSiO_3 \tag{12}$$

$$4Fe_2SiO_4+O_2=2Fe_3O_4+2FeSiO_3+2SiO_2 \tag{13}$$

$$3Fe_2SiO_4+O_2=2Fe_3O_4+3SiO_2 \tag{14}$$
$$6FeSiO_3+O_2=2Fe_3O_4+6SiO_2 \tag{15}$$
$$3/2Fe_2SiO_4+3FeSiO_3+O_2=4Fe_3O_4+9SiO_2 \tag{16}$$

Thermodynamic data for calculation are obtained from KELLEY (1960) and COUGHLIN (1954). But the data of $FeSiO_3$ were estimated by usual method

Table 3. Thermodynamic constant used in this paper.

Mineral	$\Delta H°298$	$\Delta S°298$	a_0*	a_1*	a_2*	T°K range
Fe_2SiO^4	−346	34.7	36.51	9.36	−6.70	298–1490
$FeSiO_3$**	−279	21	25	5.2	−3	523–1490
Mg_2SiO_4	−508.2	22.75	35.81	6.54	−8.52	298–1800
$MgSiO_3$	−357.9	16.2	24.55	4.74	−6.28	298–1600
$Fe_{0.947}O$	− 63.8	13.74	11.66	2.00	−0.67	298–1650
Fe_2O_3	−196.5	21.5	31.71	1.76		1050–1800
Fe_3O_4	−267.0	35.0	48.00			900–1800
SiO_2***	−205.0	10.2	14.40	2.04		523–2000
O_2	0.0	49.01	7.16	1.00	−0.40	298–3000

* $Cp=a_0+a_1\ 10^{-3}\ T+a_2\ 10^5T^{-2}$

** estimated value, H: HESS Law; S: LATIMER's Method; Cp: SAHAMA and TORGSON's Method.

*** β-cristobalite H=kcal/mol, S=cal/mol

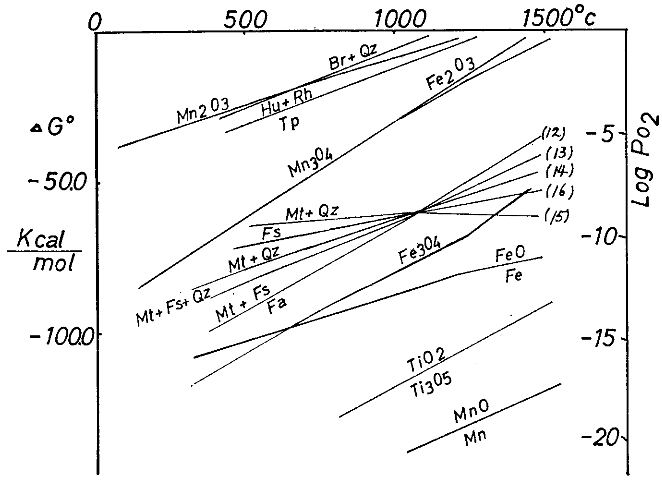

Fig. 4. Relations between staibility and Po_2 in equilibrium with some metal oxides and silicates. Fe^{+2} and Mn^{+2} screened by ortho or meta-silicate persist to more higher Po_2 than Fe and Mn-oxide. Fe_2SiO_4 is more stable than $FeSiO_3$ at high temperature, but the relation is reverse at low temperature. Abbreviations have the following meanings: Br=braunite; Qz=tridymite; Rh=rhodonite; Tp=tephroite; Hu=hausmannite; Mt=magnetite; Fs=ferrosilite; Fa=fayalite. (10)–(14) correspond to each reaction in the text.

and checked by extrapolation of BOWEN and SCHAIRER's experiments (1935) (Table 3).

The above result was shown in Fig. 4 in comparison with other data, related oxide and manganese silicate (MUAN 1959). Stability of Fe_2SiO_4 and $FeSiO_3$ is much affected by temperature and Po_2. $FeSiO_3$ is more stable than Fe_2SiO_4 at a low temperature just as same as Mn-silicate. Fe^{+2} and Mn^{+2} screened by silicate more strongly persist in Po_2 than each oxide as illustrated in Fig. 4. Particularly Mn^{+2} has wider stability fields than Fe^{+2} and accepts much greater stabilizing effect of SiO_2 in comparison with Fe^{+2} as already discussed by MUAN (1957). Assuming that olivines and pyroxenes form ideal solid solution respectively, the chemical potential of Fe_2SiO_4 and $FeSiO_3$ is written by following representation.

$$G_{Fa}=G^0_{Fa}+RT\ln X_{Fa} \tag{17}$$

$$G_{Fs}=G^0_{Fs}+RT\ln X_{Fs} \tag{18}$$

G^0_{Fa}: Chemical potential of fayalite molecule (Fe_2SiO_4) at pure state.

G^0_{Fs}: Chemical potential of ferrosilite molecule ($FeSiO_3$) at pure state.

X_{Fa}: mol. fraction of fayalite.

X_{Fs}: mol. fraction of ferrosilite.

Then we can obtain the relation between Fe_2SiO_4, $FeSiO_3$ mol fraction and its equilibrium partial oxygen pressure ($\log Po_2$). From above reaction (12), (13), (14), (15) and (16),

$$\log Po_2\, X^6_{Fa}\, X^{-6}_{Fs}=-\Delta G/2.307\,RT \tag{19}$$

$$\log Po_2\, X^4_{Fa}\, X^{-2}_{Fs}=-\Delta G/2.307\,RT \tag{20}$$

$$\log Po_2\, X^3_{Fa}=-\Delta G/2.307\,RT \tag{21}$$

$$\log Po_2\, X^6_{Fs}=-\Delta G/2.307\,RT \tag{22}$$

$$\log Po_2\, X^{3/2}_{Fa} X^3_{Fs}=-\Delta G/2.307\,RT \tag{23}$$

In Fig. 5 the equilibrium relation based on equations (21) and (22) at constant temperature is shown graphically. If we would attempt to estimate Po_2 associated with a lava based on this relation, we should know both of the crystallizing temperature and mol fraction of olivine or pyroxene in a lava, because the Po_2 is independent of temperature and mol fraction. Although mol fraction of olivine or pyroxene is easily taken by X-ray method or optical method or chemical analyses as far as separation of olivine and pyroxene is done, crystallizing temperature from magma of these minerals is not easily obtained as mention in the preceding section.

In equations (19), (20) and (23) the relation of coexisting olivine and pyroxene at constant or optional temperature which is equilibrium at each Po_2 is shown. The stability relation of these minerals is controlled by the reaction relation of olivine and pyroxene.

Now as distribution function of (Mg, Fe) to olivine and pyroxene in lava is not clarified, we fall into difficulty just as the crystallizing temperature is hard

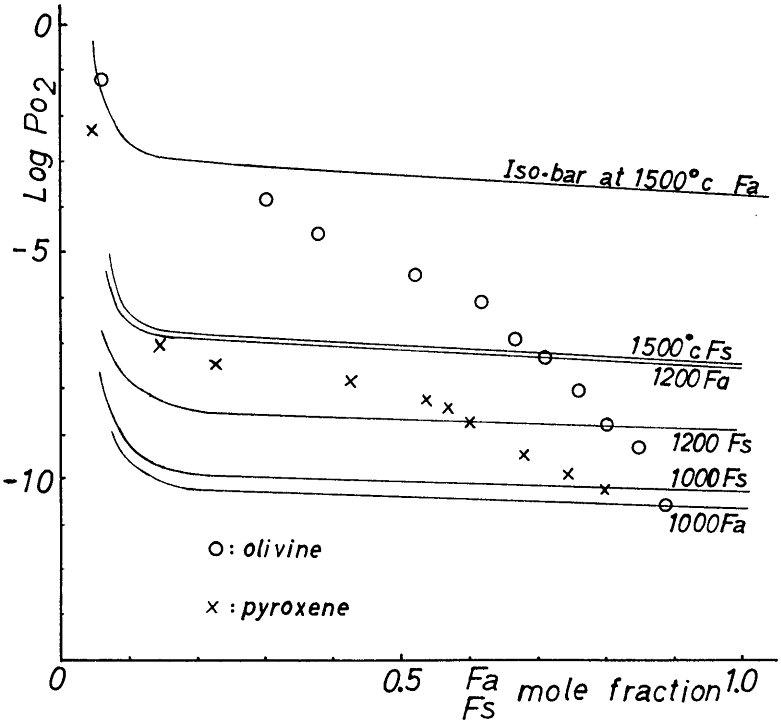

Fig. 5. Theoretical Po_2 equilibrating with olivine and pyroxene based on the equation (14), (15). Calculations are preformed by thermodynamic constant in Table 3. Maximum crystallizing temperature of these minerals is quoted from MgO–SiO_2–FeO ternary system studied by BOWEN *et al.* (1935). But crystallizing temperature of these minerals may be lowered in lave.

to be exactly estimated. These problem may be discussed in more detailed in another paper.

Summary

The possibilities estimating of Po_2 in a lava were discussed by two ways. One is the application of Fe^{+3}-Fe^{+2}-O^{-2} equilibrium relation which may occurred at high temperature. In this case I have discussed about KENNEDY's method and FUDALI's method which are discriminated from each other by the relation between Kpo_2, T and O.I. just as the equations (6) and (7). Consequently it is explicit that a lava has its own equilibrium constant of equation (4) because of an influence of coexisting Na and other ions (Table 1, Fig. 2) or coexisting minerals (Fig. 1).

The other is the application of redox reaction relation of iron-containing minerals. Especially as a lava mostly contain olivine and pyroxene, I have discussed mainly about these minerals on the basis of equations (12)–(16) by means of thermodynamic method. If we take an available information of Po_2 in a lava, it may attribute to know exact temperature of generation of a lava.

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