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Determination of specific component activities in tholeiitic melts: principles and technique

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A method is presented for the determination of *in situ* FeO activities in polycomponent melts. The method utilizes the solubility of iron in platinum according to the equation:

$$\mathrm{Fe_{Pt}} + \tfrac{1}{2}\mathrm{O_2} = \mathrm{FeO_{(melt)}}.$$

The activities of FeO in the melt have been determined by using the following expression.

$$a_{\mathrm{FeO(melt)}} = \frac{p_{\mathrm{O_2}}^{\frac{1}{2}}}{p_{\mathrm{O_2}}^{0\frac{1}{2}}}\, a^0_{\mathrm{FeO}},$$

where a^0_{FeO} is the activity of stoichiometric FeO in the particular iron oxide and $p_{\mathrm{O_2}}^{0\frac{1}{2}}$ is the oxygen pressure in equilibrium with solid oxide and a Pt–Fe alloy containing the same amount of Fe as determined in the melt experiment.

Attention is drawn to the possible errors which may be incurred by extrapolating values of a_{FeO} from simple binary or ternary systems to multicomponent magmatic liquids, due to the presence of component interaction effects.

Introduction

The past five years have seen a marked increase in the use of thermodynamic data to evaluate the rôle of certain important component activities in both natural and synthetic silicate melts. Carmichael & Smith (1970) introduced the concept of silica buffer reactions to calculate the activity of $\mathrm{SiO_2}$, and later workers (Nicholls, Carmichael & Stormer 1971; Nicholls & Carmichael 1972) have expanded the concept to include reactions defining other component activities.

There is, however, a marked paucity of data involving the activities of iron and its oxides in geologic assemblages. The activity of FeO in a melt not only controls the precipitation and composition of iron-bearing oxides and silicate phases, but also the accompanying sulphide assemblages (Haughton, Roeder & Skinner 1974; Shima & Naldrett 1975).

Most of the basic thermodynamic data are available for the systems, Fe–O (Darken & Gurry 1945, 1946) and $\mathrm{FeO{-}Fe_2O_3{-}SiO_2}$ (Schuhmann & Ensio 1951; Michal & Schuhmann 1952; Turkdogan 1962). These systems of metallurgical interest are however relatively simple when compared to the most empirical basalt system, $\mathrm{CaO{-}MgO{-}Al_2O_3{-}SiO_2{-}Fe{-}O}$.

In order to reduce the number of component activity variables in experimental studies of simple silicate systems, two major approaches have been used to fix at least one of the component activities in the melt; either silica activity is fixed at unity by working with silica saturated melts (presence of a solid $\mathrm{SiO_2}$ phase), or the activity of iron itself is fixed at unity by carrying out the experiments in the presence of pure iron (usually pure iron containers are used). Both of these approaches have obvious shortcomings when dealing with the wide compositional ranges of geologic materials.

Roeder (1974) adopted the latter method in determining FeO activities in synthetic basalt melts. Such a technique, however, involves values of p_{O_2} outside the range of terrestrial rock assemblages. The method presented here enables the activities of FeO in silicate melts to be determined within the ranges of p_{O_2} encountered in both terrestrial and lunar assemblages.

THEORY OF THE METHOD

The method employed is based on a modification of the technique used by Abrahams, Davies & Richardson (1960) for the determination of activities of MnO in Mn-bearing silicate melts. The activity of FeO (a_{FeO}) in a silicate melt can be determined from the amount of iron reduced into a thin platinum foil embedded in a silicate melt, when the latter reaches equilibrium with the foil at a given temperature and p_{O_2}. At equilibrium the activity of iron in the platinum is equal to that in the silicate melt:

$$Fe_{(in\ platinum)} + \tfrac{1}{2}O_2 = FeO_{(melt)}, \tag{1}$$

$$K_1 = \frac{a_{FeO(melt)}}{a_{Fe(Pt)}\, p_{O_2}^{\frac{1}{2}}}. \tag{1a}$$

The activity of FeO in the melt can be calculated if the activity of Fe in the platinum alloy in equilibrium with the silicate melt is known, together with the values of the equilibrium constant K_1 at the determined temperatures. A much simpler method was employed by Abrahams *et al.* (1960); for two Pt–Fe alloys of identical composition, one in equilibrium with the given silicate melt and the other in equilibrium with a pure iron oxide (at different oxygen pressures), the activity of Fe will be the same. The activity of FeO in the melt can be determined from the following relation:

$$a_{FeO(melt)} = \frac{p^{\frac{1}{2}}_{O_2(melt)}}{p^{0\frac{1}{2}}_{O_2(oxide)}}\, a^0_{FeO(oxide)}, \tag{2}$$

where p_{O_2} is the partial pressure of oxygen of the melt experiment; $p^0_{O_2}$ the partial pressure of oxygen which would be in equilibrium with pure solid iron oxide and a Pt–Fe alloy containing the same amount of Fe as found in the melt experiment; $a^0_{FeO(oxide)}$ is the activity of stoichiometric FeO in the iron oxide at equilibrium with $p^0_{O_2}$. Values of $p^0_{O_2}$ are determined from a parallel series of experiments, the thin Pt foil being embedded in a pure iron oxide and the system brought to equilibrium at a given temperature and p_{O_2}. The resulting Pt–Fe alloy is then analysed and the Fe content of the alloy plotted against p_{O_2} for various isotherms. The initial calculations at 1300 °C presented here were carried out using the equilibrium Fe/p_{O_2} values determined by Taylor & Muan (1962).

STANDARD STATE OF FeO

The standard state of 'FeO' is taken as wüstite in equilibrium with solid iron at each temperature, and the activity of FeO in this state is set at unity (see Darken & Gurry 1945, p. 1407). As the p_{O_2}–T field of terrestrial rock assemblages is mainly confined to the magnetite stability field, it is necessary to determine the activity of FeO in magnetite relative to the above standard state (i.e. a^0_{FeO} required in equation (2)).

The values of a^0_{FeO} could be determined by a simple manipulation of the following equations:

$$Fe+\tfrac{1}{2}O_2 = FeO, \quad \text{(Standard state)} \tag{3}$$

$$3Fe+2O_2 = Fe_3O_4, \tag{4}$$

to give,

$$3FeO+\tfrac{1}{2}O_2 = Fe_3O_4, \tag{5}$$

$$K_5 = \frac{a_{Fe_3O_4}}{a^3_{FeO}\, p^{\frac{1}{2}}_{O_2}}. \tag{5a}$$

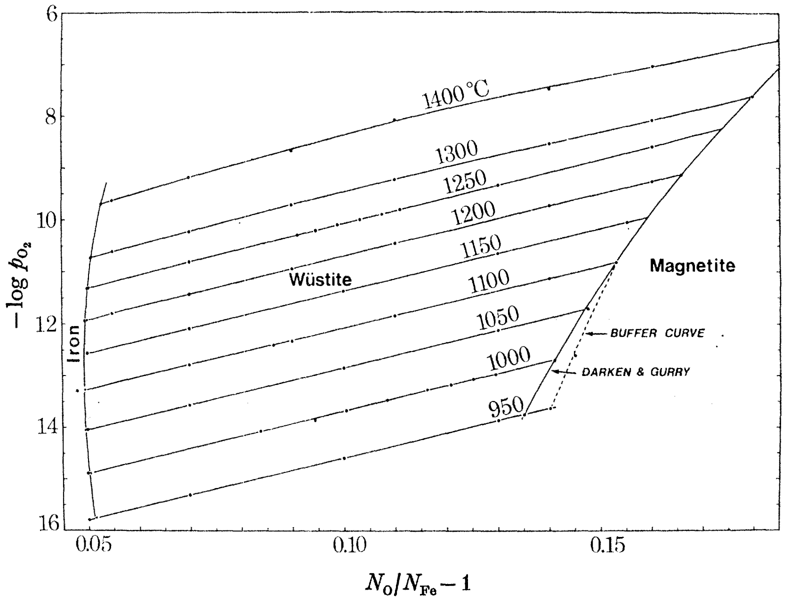

Figure 1. Variation of wüstite composition with p_{O_2}. Data compiled from Darken & Gurry (1945), Swaroop & Wagner (1967) and Rizzio, Gordon & Cutler (1969). The dashed line marked 'buffer curve' was calculated from the data of Eugster & Wones (1962).

Such a method would certainly involve a compounding of errors in the determined equilibrium constants; it was therefore decided to calculate the required equilibrium constants (K_5) from the data of Darken & Gurry (1945) and Swaroop & Wagner (1967). This entailed the integration of a Gibbs–Duhem equation, of the form,

$$\log a^0_{FeO} = -\int (N_2/N_1-1).\, \mathrm{d}\log a_2,$$

where N_2/N_1 is the atomic ratio of oxygen to iron in wüstite and a_2 the activity of oxygen. The lower limit of the integration being the composition of wüstite in equilibrium with iron (standard state) and the upper limit being the composition of wüstite in equilibrium with magnetite. The basic data for the integration are plotted in figure 1.

From the determined values of a^0_{FeO} above and p_{O_2} (Darken & Gurry, 1945) equilibrium constants for equation (5) were calculated at 1000, 1100, 1200, 1300 and 1400 °C. A plot of $\log K_5$ against $1/T$ does result in a straight-line relation (see figure 2). The slight departure from linearity at 1000 °C probably reflects the difficulties in achieving equilibrium at the lower temperatures.

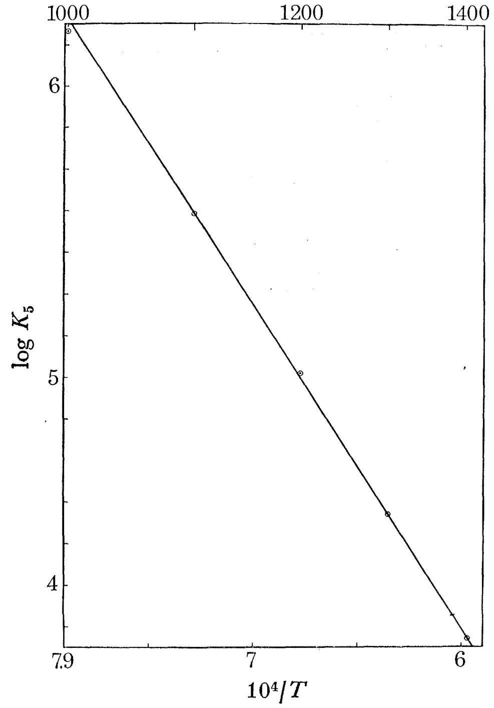

FIGURE 2. Log K_5 against $1/T$ for the reaction $3FeO+\frac{1}{2}O_2 = Fe_3O_4$. $K_5 = a_{Fe_3O_4}/(a^3_{FeO}\cdot f^{\frac{1}{2}}_{O_2})$; $y = 1.5644x-5.6052$.

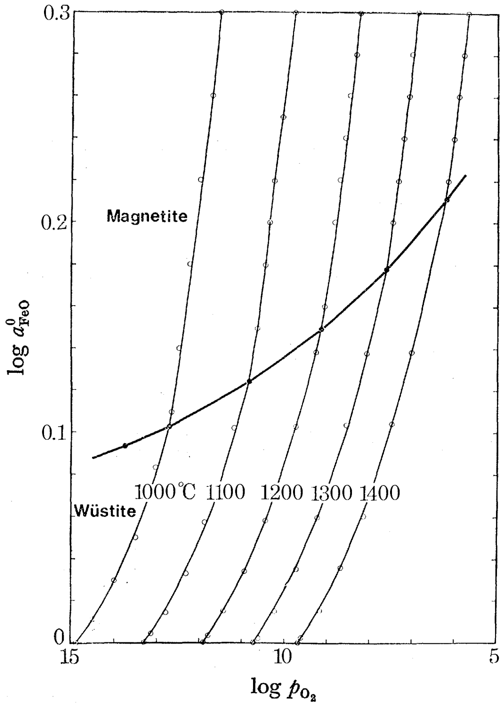

FIGURE 3. Log a^0_{FeO} against log p_{O_2} for solid oxide compositions within the wüstite field and the lower portion of the magnetite field.

With the equilibrium constants for equation (5) and the determined values of $p^0_{O_2}$ the activity of FeO in magnetite can be determined for any p_{O_2} and temperature within the magnetite field. Figure 3 shows a plot of values of log a^0_{FeO} against p_{O_2} for selected isotherms within the stability field of wüstite and part of the magnetic field.

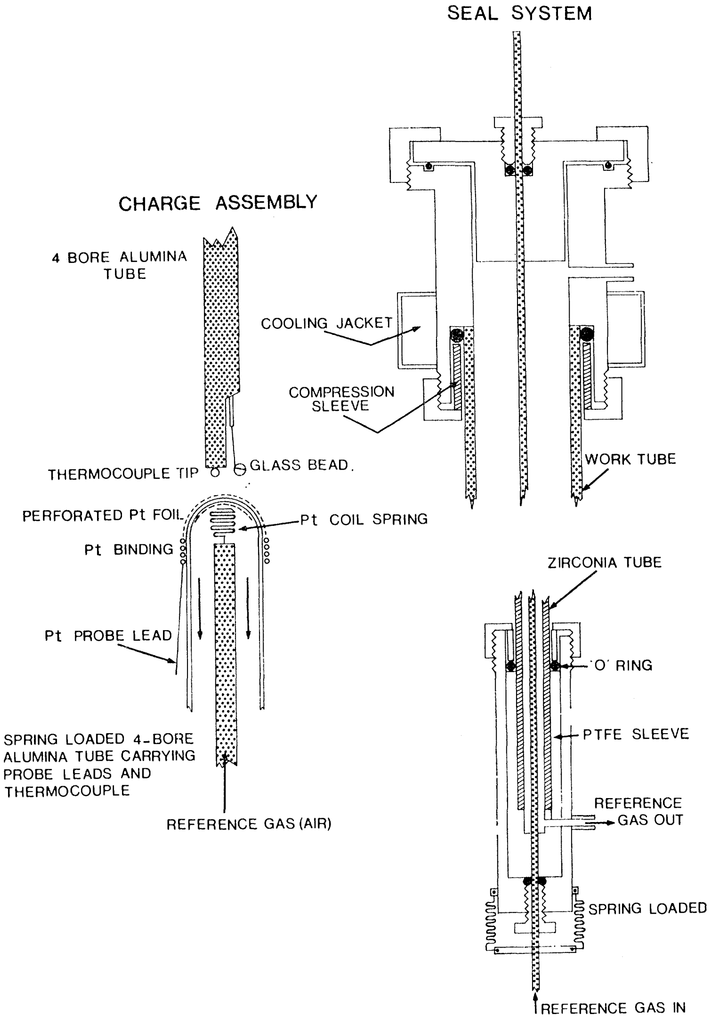

FIGURE 4. The design of seals and charge assembly used in the experiments.

EXPERIMENTAL PROCEDURE

All experiments were carried out in a vertical Pt wound quench furnace equipped for atmosphere control (see figure 4). Pt–Pt 13 % Rh thermocouples were used and periodically calibrated against the melting points of gold (1063 °C) and diopside (1391 °C). The composition of the ingoing gas mixture was controlled either by the hydrogen electrolysis method (Sato 1970), using either N_2, Ar, or CO_2 as the carrier gas, or by conventional flowmeter techniques using CO_2–H_2 mixtures (Darken & Gurry 1945). The partial pressure of oxygen was monitored during all experiments using a calcia-stabilized zirconia oxygen probe (Kiukkola & Wagner 1957), with air as the reference gas. The e.m.f. measurements were made on a high impedance electrometer. A second thermocouple was inserted into the tip of the oxygen probe, the e.m.f.

outputs from both the thermocouples and the electrometer were continuously monitored on a two-channel potentiometric recorder. Values of p_{O_2} were calculated from the following relation:

$$E = 0.0496\,T \log \frac{p_{O_2}}{p_{O_2(\text{air})}}\ \text{mV}.$$

Pure Fe_2O_3, Fe_3O_4, $Fe_{1-x}O_x$, and Fe were used as starting materials for the Pt–Fe alloy calibration runs (Johnson & Matthey, 'Specpure' Fe_2O_3 and Fe sponge were used as the initial source of iron). The starting materials were packed into thin-walled platinum capsules along with a firmly embedded piece of platinum foil (or Pt–Fe alloy). A series of experiments were carried out to determine the necessary run times and platinum foil thicknesses to establish Fe–O equilibria within the charge and to negate diffusion gradients in the platinum foil. The results indicate minimum run times of approximately 18 h and a platinum foil thickness of 0.001 in (weighing 0.2 to 0.5 mg). Equilibria was approached from both directions by using starting compositions of different oxidation states as well as employing Pt–Fe alloys of differing compositions.

The starting materials for the silicate melt experiments were in the form of gels (both oxidized and reduced), glass or glass plus crystals. The investigated compositions were chosen to yield assemblages on or close to the liquidus, which would allow silica activities in the liquid to be determined, i.e. olivine–orthopyroxene–liquid and clinopyroxene–plagioclase–liquid assemblages (see Clarke & Biggar 1972; Tilley, Thompson & Lovenbury 1972). The compositions were then recalculated in terms of the system $CaO–MgO–Al_2O_3–SiO_2–Fe–O$.

Initially Fe saturated platinum capsules were used for the melt experiments, however, due to excessive 'creep' of the iron-rich melts and the resultant dislodgement of the platinum foil from the main bulk of the charge, all subsequent experiments were carried out using the bead technique of Donaldson, Williams & Lofgren (1975), the platinum foil being 'sandwiched' in the initial compressed pellet.

The thin platinum foils from both the oxide and melt experiments were carefully cleared of any adhering charge material by repeated manual teasing and ultrasonic cleaning and mounted edge-on in drilled glass slides. This edge-on mounting was adopted in order to check for any signs of diffusion gradients in the cross-sections of the Pt–Fe alloys. Thin sections of the glassy charges were prepared using a micro-grinding head to enable several charges mounted on a single glass probe slide to be individually prepared. All Pt–Fe alloy foils, glasses and associated crystalline phases were analysed using the 'Geoscan' electron microprobe.

The estimated errors for the experimental run data, given in table 1 are as follows: temperatures are considered to be within ± 4 °C for the thermocouple in the oxygen probe and ± 3 °C for the sample thermocouple. Instrumental errors, including both e.m.f. and potentiometric recorder outputs from the electrometer are estimated at ± 2 mV. Values of p_{O_2} are considered to be better than ± 0.2 log units for the duration of the experiments.

RESULTS, AND COMPARISON WITH OTHER ACTIVITY DATA

Several starting compositions were initially investigated; the results for a series of experiments at 1300 °C on one of these compositions are given to illustrate both the method of determination and the magnitude of values for a_{FeO} in the liquid. The composition P. 1 (see table 1) was chosen, for the initial study at 1300 °C, as it gave a long temperature interval in which only one phase namely olivine was in equilibrium with the liquid, thereby simplifying the rôle of component extraction from the melt. Orthopyroxene appears some 50 °C lower, allowing determinations of a_{SiO_2} to be made using the silica buffer assemblage, $Mg_2SiO_4 + SiO_2$ (liq.) $= 2MgSiO_3$. These data together with data for other compositions are at present being compiled and will be published at a later date.

TABLE 1. DETERMINED VALUES OF $p^0_{O_2}$, a^0_{FeO} AND $a_{FeO(melt)}$ FOR THE P.1. SERIES OF RUNS

(Starting composition: P. 1.: SiO_2 49.186, Al_2O_3 8.984, FeO 14.804, MgO 20.011, Cao 7.013.)

P. 1 series run no.	temp./°C	$-\log p^{\text{exp}}_{O_2}$	mass % Fe in Pt–Fe alloy	$-\log p^0_{O_2}$	$-\log a^0_{FeO}$	$a_{FeO(melt)}$
S.P. 73	1298	2.15	0.28	N.D.	2.4018	N.D.
S.P. 72	1299	6.70	7.10	6.15	0.3506	0.227
S.P. 70	1299	7.55	10.48	6.95	0.3223	0.239
S.P. 71	1299	8.011	12.58	7.40	0.2139	0.303
S.P. 74	1298	8.82	16.23	8.12	0.1473	0.319

TABLE 2. SELECTED COMPOSITIONS OF LIQUIDS AND COEXISTING OLIVINES IN THE P.1. SERIES RUNS

	S.P. 70		S.P. 71		S.P. 72	S.P. 9 (air)	
	glass	olivine	glass	olivine	glass	glass	olivine
SiO_2	53.40	41.17	54.09	41.19	54.00	48.24	42.15
Al_2O_3	11.37	0.02	11.56	0.03	11.26	9.69	1.42
FeO	10.84	9.48	9.72	10.60	10.55	15.56	3.87
MgO	14.35	49.79	14.61	48.19	14.31	16.47	54.78
CaO	8.90	0.36	9.23	0.23	8.92	7.97	0.19
	98.86	100.60	99.21	100.24	99.04	97.93	101.03

The values of $p^0_{O_2}$, a^0_{FeO} and $a_{FeO(melt)}$ are given in table 1. The composition of the liquids and coexisting olivines are given in table 2. Inspection of the data presented in table 1 shows that the determined values of $a_{FeO(melt)}$ do in fact record as might be expected the successive changes in p_{O_2} of the melts.

The only other comparable investigation of a_{FeO} in geologic melts is that of Roeder (1974). A comparison of both sets of data shows that the present determined values are higher than those determined by Roeder for similar compositions.

In determining a_{FeO} Roeder used the following equation:

$$\log a_{FeO} = 12045/T + 0.5 \log f_{O_2} - 2.336,$$

the basic thermodynamic data for which was taken from an original expression used by Schuhmann & Ensio (1951) to calculate a_{FeO} for liquids in the system $FeO–Fe_2O_3–SiO_2$.

In using this equation for polycomponent melts, Roeder has assumed that additional components in the melt have no effect on the activity of FeO. The most important of these additional components being CaO, MgO, Al_2O_3 and TiO_2. Taylor & Chipman (1943) and Turkdogan & Pearson (1953) have shown that additions of both CaO and MgO have marked interaction effects on the liquid ($CaO–MgO–FeO–SiO_2$), the result being to increase the activity of FeO in the liquid by an appreciable amount relative to the system $Fe–O–SiO_2$. The effects of Al_2O_3 and TiO_2 on liquid compositions within the range of geologic interest are very difficult to interpret. Such interaction effects coupled with the higher values of CaO plus MgO in the present investigation could explain the differences between the two sets of data. The possible dangers in extrapolating activity/composition data from relatively simple systems to poly-component melts of geologic interest should not be overlooked in the light of such interaction effects, i.e. the activity of FeO is far from proportional to the product $N_{\mathrm{Fe}}\, N_{\mathrm{O}}$ in the melt.

CONCLUSIONS

The presence of such interaction parameters between components in silicate melts and their final understanding, could possibly help in elucidating some of the problems before igneous petrologists today. It would appear that it is not simply the addition or subtraction of components in a melt which affects the crystallizing assemblage, but the sum total of the resultant interaction parameters of such additions and subtractions. The present investigation does offer a method of determining one important component activity, a_{FeO}, in the presence of such interaction effects.

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