Decomposition of Fayalite (Fe₂SiO₄) in an Oxygen Potential Gradient at 1,418 K

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Abstract. The decomposition of fayalite (Fe_2SiO_4) in oxygen potential gradients is studied at $T = 1,418$ K. The compound will be decomposed into its component oxides wüstite, $Fe_{1-\delta}O$, and silica, SiO_2, by the simultaneous action of two different oxygen partial pressures, exceeding a critical ratio, despite the fact that fayalite is stable at both the lower and the higher oxygen potential. A quantitative analysis of the decomposition process caused by defect fluxes within the bulk Fe_2SiO_4 is given.

I. Introduction

An understanding of solid-state reactions in silicate forming systems is of fundamental interest in solid-earth geochemistry and geophysics. In view of the fact that olivines – besides pyroxenes – are the most abundant minerals in the earth's upper mantle, it is somewhat surprising that only a limited number of reliable experimental results concerning reaction kinetics in MeO/SiO_2-systems ($Me = Mg$, Co, Zn, Sr, Fe) is available in the literature (Brindley and Hayami 1965; Yamaguchi and Tokuda 1967; Borchardt and Schmalzried 1971; Duckwitz and Schmalzried 1971; Lenz et al. 1977; Schmalzried 1978; Hallwig et al. 1982; Hermeling 1984): in such systems olivine-type compounds Me_2SiO_4 form at elevated temperatures besides compounds with other and eventually more complicated structures but likewise simple stoichiometry such as $Me_2Si_2O_6$ or Me_3SiO_5 for instance. However, the experimental results are ambiguous even in such simple silicate systems for many reasons, and a clear-cut conclusion as to the mechanism of olivine-forming reactions can still not be drawn, as was recently emphasized in a review article by Schmalzried (1978).

In the present paper we report another but essentially very similar sort of solid-state reaction, i.e. the decomposition of fayalite (Fe_2SiO_4) according to

$$Fe_2SiO_4 = 2\,'FeO' + SiO_2; \quad \Delta G_1^0 = -\Delta G_{Fe_2SiO_4}^0. \tag{1}$$

(Upper strikes at FeO indicate that not pure but FeO in wüstite is meant, which may be considered as an ordered solid solution in the $Fe-O_2$-system.)

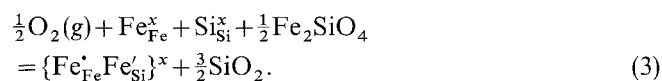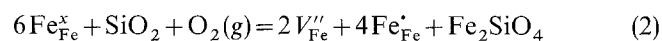It is one of the pecularities of reaction (1) that decomposition proceeds within the fayalite stability field at elevated temperature by means of defect fluxes which drift in the gradient of two different oxygen potentials, μ'_{O_2} and μ''_{O_2}, acting on both sides of a polycrystalline Fe_2SiO_4 disc. This phenomenon was first realized in the case of ilmenite-type $NiTiO_3$ (Schmalzried and Laqua 1981) and is called "kinetic decomposition".

II. Theory

The atomic processes leading to the decomposition of an olivine-type compound by kinetic rather than by thermodynamic effects may be outlined here for the special case of fayalite (Fe_2SiO_4), but one can easily modify and extend the following considerations to other compounds such as Co_2SiO_4 and Ni_2SiO_4, which were also investigated in this context (unpublished work).

At first, it is expedient to deal with the point defect thermodynamics of fayalite recently analyzed in great detail by Nakamura and Schmalzried (1983). From their thermogravimetric measurements in the temperature range $1,000° C \leq T \leq 1,280° C$ the authors conclude, that 3 types of majority defects exist in fayalite: these are doubly charged vacancies, V''_{Fe}, in the octahedrally coordinated iron sublattice, iron-ions, $Fe^{\cdot}_{Fe}$, on iron lattice sites, bearing an excess charge plus one (and which may also be viewed as electron holes $h^{\cdot}$) and, finally, associates, $\{Fe^{\cdot}_{Fe}Fe'_{Si}\}^x$, between $Fe^{\cdot}_{Fe}$-defects and iron-ions, Fe'_{Si}, on tetrahedrally coordinated silicon-lattice sites, which bear one negative excess charge; evidently the associate itself is electrically neutral. (Kröger-Vink notation for defects is used throughout.)

Choosen the oxygen potential p_{O_2} and the silica activity a_{SiO_2} as the independent thermodynamic variables in the ternary system $Fe - Si - O$ at given P and T, the majority defects may form via the following defect reactions (Nakamura and Schmalzried 1983)

$$6\,Fe^x_{Fe} + SiO_2 + O_2(g) = 2\,V''_{Fe} + 4\,Fe^{\cdot}_{Fe} + Fe_2SiO_4 \tag{2}$$

$$\tfrac{1}{2}O_2(g) + Fe^x_{Fe} + Si^x_{Si} + \tfrac{1}{2}Fe_2SiO_4$$
$$= \{Fe^{\cdot}_{Fe}Fe'_{Si}\}^x + \tfrac{3}{2}SiO_2. \tag{3}$$

From reasons which will be more clear later on we have to take into account a fourth, although minority defect, that is silicon on tetrahedrally coordinated in-

terstitial sites, $Si_i^{••••}$, which bears the excess charge plus four. These silicon interstitials may form via the defect reaction

$$2SiO_2 + 2Fe_{Fe}^x + V_i^x = Si_i^{••••} + 2V_{Fe}'' + Fe_2SiO_4. \qquad (4)$$
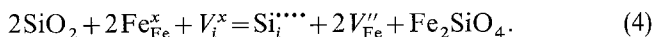
From the mass action law for reactions (2)–(4) we derive

$$[V_{Fe}'']^2 \cdot [Fe_{Fe}^•]^4 = K_2 \cdot p_{O_2} \cdot a_{SiO_2} \qquad (5)$$

$$[\{Fe_{Fe}^•Fe_{Si}'\}^x] = K_3 \cdot p_{O_2}^{1/2} \cdot a_{SiO_2}^{-3/2} \qquad (6)$$

$$[Si_i^{••••}] \cdot [V_{Fe}'']^2 = K_4 \cdot a_{SiO_2}^2. \qquad (7)$$

[ ] designates the site fraction of the corresponding species on their respective sublattice.

Taking into account the electroneutrality condition and bearing in mind that silicon intersitials are minority defects only, i.e.

$$[Fe_{Fe}^•] \cong 2[V_{Fe}''], \qquad (8)$$

on derives from Eqs. (5) and (7) for the oxygen potential dependence of the relevant defect concentrations (Nakamura and Schmalzried 1983)

$$[V_{Fe}''] = 2^{-2/3} \cdot K_2^{1/6} \cdot a_{SiO_2}^{1/6} \cdot p_{O_2}^{1/6} \qquad (9)$$

$$[Si_{Si}^{••••}] = 2^{4/3} \cdot K_2^{-1/3} \cdot K_4 \cdot a_{SiO_2}^{5/3} \cdot p_{O_2}^{-1/3}. \qquad (10)$$

If we define the mole fraction of silicon (n designates the mole number) by

$$\xi = \frac{n_{Si}}{n_{Si} + n_{Fe}} \qquad (11)$$

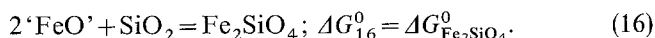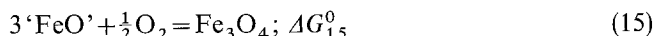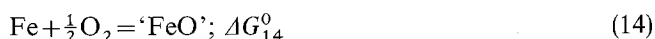then the deviation of ξ from its ideal value in fayalite is given as

$$\bar{\xi} = \xi - \tfrac{1}{3}. \qquad (12)$$

From mass-balance equations for iron and silicon and from site-balance equations for tetrahedrally coordinated lattice sites resp. octahedrally coordinated lattice sites one derives in the well known manner (Schmalzried 1965)

$$\bar{\xi} = \tfrac{2}{9}[V_{Fe}''] - \tfrac{1}{3}[\{Fe_{Fe}^•Fe_{Si}'\}^x]. \qquad (13)$$

In deriving Eq. (13), the approximation $[V_{Fe}''] \ll 1$ has to be taken into account.

Inserting now the defect concentrations $[V_{Fe}'']$ resp. $[\{Fe_{Fe}^•Fe_{Si}'\}^x]$ (Eqs. (9) and (6)) into Eq. (13), this yields a relation which can be used to calculate $\bar{\xi}$, the deviation from ideal stoichiometry, as a function of a_{SiO_2} and p_{O_2}. From a practical point of view it may be expedient in special cases to change one of the independent thermodynamic variables, i.e. to take a_{Fe}, a_{FeO} or $a_{Fe_3O_4}$ instead of a_{SiO_2}; this may be done via the well established two-phase equilibria

$$Fe + \tfrac{1}{2}O_2 = \text{‘FeO’}; \ \Delta G_{14}^0 \qquad (14)$$

$$3\,\text{‘FeO’} + \tfrac{1}{2}O_2 = Fe_3O_4; \ \Delta G_{15}^0 \qquad (15)$$

$$2\,\text{‘FeO’} + SiO_2 = Fe_2SiO_4; \ \Delta G_{16}^0 = \Delta G_{Fe_2SiO_4}^0. \qquad (16)$$

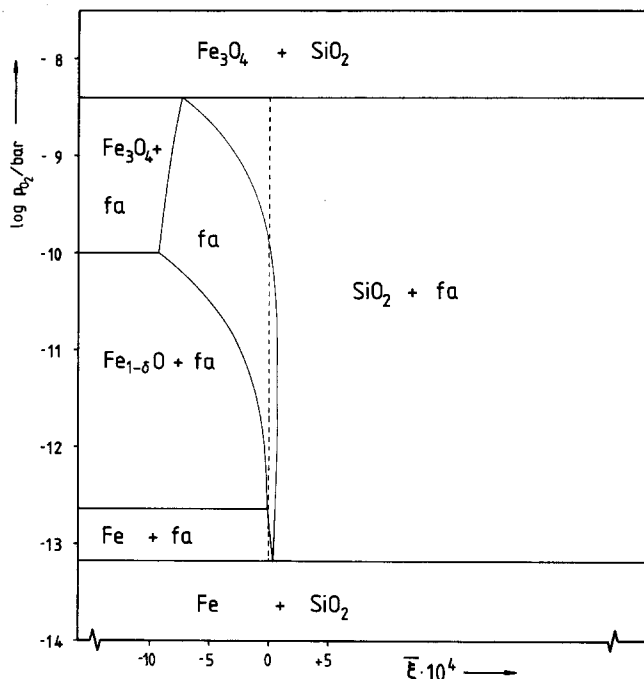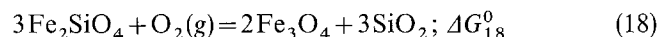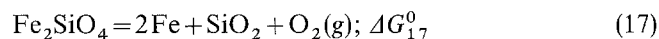Of course, a calculation of $\bar{\xi}$ as a function of p_{O_2}

Fig. 1. Stability region of fayalite at $T = 1,418$ K, calculated from defect equilibrium constants given by Nakamura and Schmalzried (1983); fa = fayalite. Dashed line: $\bar{\xi} = 0$

and a_{SiO_2} (or a_{Fe}, a_{FeO} resp. $a_{Fe_3O_4}$ as well) is possible only if numerical values for the equilibrium constants K_2 and K_3 are known. These values ($K_2 = 5.14 \cdot 10^{-8}$, $K_3 = 50.93$; $T = 1,403$ K) taken from Nakamura and Schmalzried's paper (1983) were used to derive the stability field of fayalite at $T = 1,418$ K, which is the temperature established in our experiments (see Fig. 1). The equilibrium pressures $\log p_{O_2}^{(17)} = -13.17$ and $\log p_{O_2}^{(18)} = -8.40$, which represent the three-phase equilibria

$$Fe_2SiO_4 = 2Fe + SiO_2 + O_2(g); \ \Delta G_{17}^0 \qquad (17)$$

$$3Fe_2SiO_4 + O_2(g) = 2Fe_3O_4 + 3SiO_2; \ \Delta G_{18}^0 \qquad (18)$$

under the assumption that only pure solid phases coexist were taken from the same paper (Nakamura and Schmalzried 1983) as well as the oxygen equilibrium pressures for the two-phase equilibria (14) and (15), given as $\log p_{O_2}^{(14)} = -12.64$ and $\log p_{O_2}^{(15)} = -10.01$ at $T = 1,418$ K (solid-phase activities again are taken to equal one).

If now, in an appropriate experimental arrangement, a single crystalline sheet or a polycrystalline disc of fayalite, say about 800 μm thick, is positioned between two different oxygen partial pressures p_{O_2}' and p_{O_2}'' ($p_{O_2}' > p_{O_2}^{(17)}$, $p_{O_2}'' < p_{O_2}^{(18)}$; see Fig. 1), the defect equilibria (2)–(4) will be established at both surfaces of the crystal. Therefore, defect-concentration gradients develop throughout the bulk crystal and cause (constant a_{SiO_2} anticipated) 1. a flow of vacancies V_{Fe}'' from the higher to the lower oxygen potential side (see Eq. (9)), 2. a flow of holes $h^•$ and associates $\{Fe_{Fe}^•Fe_{Si}'\}^x$ from the higher to the lower oxygen potential side (see Eqs. (8) and (6)) and 3. a flow of silicon interstitials $Si_i^{••••}$ from the lower to the higher oxygen potential side (see Eq. (10)).
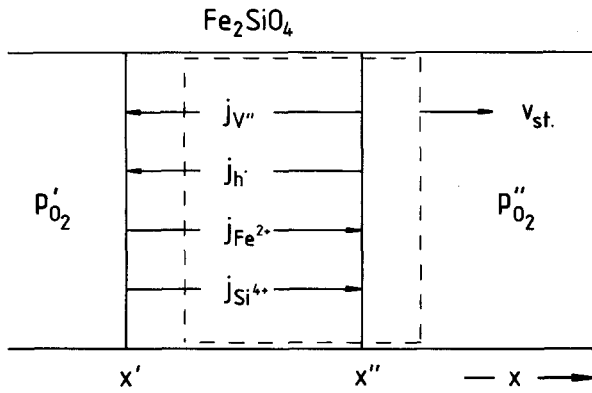
Fig. 2. Schematic representation of the species fluxes in bulk fayalite, induced by the action of different oxygen partial pressures at opposite crystal surfaces $(p''_{O_2} > p'_{O_2})$. The dashed line indicates the crystal movement after attaining steady state conditions (v_{st} = stationary crystal velocity)

In what follows, the flux of associates through the bulk Fe_2SiO_4 will be neglected with regard to the fluxes of vacancies and holes; this seems to be reasonable because of the very low vacancy concentration in the silicon sublattice of fayalite (Sockel 1974) and in view of the fact that silicon vacancies are the only defects which may render the associates mobile. On the other hand, there is some experimental evidence (see later) that the flux of silicon interstitials cannot be neglected despite their minor concentration as compared with $[V''_{Fe}]$ and $[h^{\cdot}]$. Therefore, as to describe the experimental situation correctly, we have to consider the fluxes, which are depicted schematically in Fig. 2.

It must be pointed out here that vacancies moving from one side of the crystal to the other side simultaneously transport Fe^{2+}-ions into the opposite direction. In consequence, both the Fe^{2+} as well as the Si^{4+} ionic fluxes have the same sign, going from the lower to the higher oxygen-potential surface of the fayalite crystal as can be read from Fig. 2.

Concerning the mobility of iron and silicon ions within the Fe_2SiO_4 lattice, we know from tracerdiffusion measurements in olivine-type silicates (Co_2SiO_4: Windhager and Borchardt 1975; Mg_2SiO_4: Hallwig et al. 1982; $(Fe_xMg_{1-x})_2SiO_4$: Hermeling and Schmalzried 1984) that the Me^{2+} cations are mobile via vacancies, while Si^{4+} ions move via (likely tetrahedrally coordinated) interstitial sites, whereby the diffusivities of the respective lowervalence cation exceeds by far the diffusivity of Si^{4+} ions. Thus we conclude that an analogous relation, i.e.

$$D_{Fe^{2+}} > D_{Si^{4+}} \qquad (19)$$

holds for fayalite too.

Therefore, if by action of an oxygen potential gradient iron and solicon cations are transported in the same direction (from the lower to the higher oxygen potential side) but with different jump frequencies (see Fig. 2), the faster moving iron ions will accumulate at the (higher) p''_{O_2}-side, until saturation is reached ($\mu_{FeO} = \mu_{FeO}^{max}$) and wüstite precipitates as a second phase according to

$$6Fe_{Fe}^x + O_2(g) = 2\,'FeO' + 2V''_{Fe} + 4Fe_{Fe}^{\cdot}. \qquad (20)$$
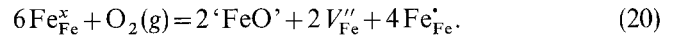
At the same time, silicon ions will be found enriched at the (lower) p'_{O_2}-side and after attaining saturation here ($\mu_{SiO_2} = \mu_{SiO_2}^{max}$), silica segregates as a third phase according to

$$2V''_{Fe} + 4Fe_{Fe}^{\cdot} + Fe_2SiO_4 = 6Fe_{Fe}^x + SiO_2 + O_2(g). \qquad (21)$$
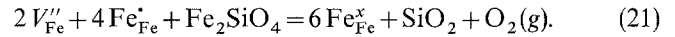
One concludes from this qualitative treatment that fayalite, thermodynamically stable at both p'_{O_2} as well as p''_{O_2}, can decompose into its component oxides 'FeO' and SiO_2, if different oxygen potentials, the so-called critical ratio of which will be calculated below, act at the same time at locally separated surfaces of the compound. It is an interesting feature of this phenomenon that during fayalite decomposition and solely caused by the flux of vacancies and holes, oxygen will be transported from the higher to the lower oxygen potential side by operation of reactions (20) and (21) despite the fact that oxygen is practically immobile within the anion-lattice of fayalite (Reddy et al. 1980; Hallwig et al. 1982).

In order to solve the problem quantitatively one starts with the following flux equations (Schmalzried et al. 1979)

$$j_i = -\frac{c_i D_i}{RT}\frac{d\eta_i}{dx}; \qquad i = Fe^{2+}, Si^{4+}, h^{\cdot}. \qquad (22)$$

(x is the space coordinate of the one-dimensional transport problem; η_i is the electrochemical potential of the electrically charged species i; c_i = concentration of species i in mole per cm^3; D_i = diffusivity of species i, R = ideal gas constant, T = temperature in Kelvin.)

Taking into account the semiconducting property of fayalite, which is a p-type conductor (Sockel 1974) one can replace the electrochemical potentials η_i of the cations Fe^{2+} and Si^{4+} by the chemical potentials μ_i of iron and silicon in their electrically neutral form (Schmalzried and Laqua 1981)

$$j_{Fe^{2+}} = -\frac{c_{Fe}D_{Fe}}{RT}\frac{d\mu_{Fe}}{dx} \qquad (23)$$

$$j_{Si^{4+}} = -\frac{c_{Si}D_{Si}}{RT}\frac{d\mu_{Si}}{dx}. \qquad (24)$$

After a steady-state is reached (that means both μ_{Fe} and μ_{Si} will be independent of time at fixed positions within the bulk fayalite relatively to the oxygen lattice as reference frame), the following condition must hold

$$\frac{j_{Fe}}{c_{Fe}} = \frac{j_{Si}}{c_{Si}} = const. \qquad (25)$$

(c = concentration in moles per cm^3).

Taking into account the condition of locally established thermodynamic equilibrium

$$\mu_{Fe} + \mu_O = \mu_{FeO} \qquad (26)$$

$$\mu_{Si} + 2\mu_O = \mu_{SiO_2} \qquad (27)$$

as well as the Gibbs-Duhem equation

$$c_{FeO}d\mu_{FeO} + c_{SiO_2}d\mu_{SiO_2} = 0 \qquad (28)$$

one derives $(c_{FeO} = 2c_{SiO_2})$ from Eqs. (23)–(28)

$$d\mu_{FeO} = \frac{D_{Fe} - 2D_{Si}}{D_{Fe} + 2D_{Si}} d\mu_O. \qquad (29)$$

Equation (29) relates the change in the chemical potential μ_{FeO} to the change in the local oxygen potential μ_O, caused by the oxygen potential gradient. Integration of (29) between μ'_O and μ''_O resp. μ'_{FeO} and μ''_{FeO} (i.e. between both crystal surfaces at positions x' resp. x'' in the space coordinate x) yields

$$\Delta\mu_O = \frac{\bar{D}_{Fe} + 2\bar{D}_{Si}}{\bar{D}_{Fe} - 2\bar{D}_{Si}} \Delta\mu_{FeO}. \qquad (30)$$

The bar on the diffusivities indicates that appropriate mean values have to be found in order to solve Eq. (29) by integration, because D_{Fe} and D_{Si} are unique functions of p_{O_2} and a_{SiO_2}

$$D_i = D_i^0 \cdot f(p_{O_2}, a_{SiO_2}). \qquad (31)$$

Relation (30) describes the extent of the demixing process, observable as chemical potential difference $\Delta\mu_{FeO}$ of the component FeO, which is produced by the action of two different oxygen partial pressures

$$\Delta\mu_O = \mu''_O - \mu'_O = \tfrac{1}{2} R T \ln(p''_{O_2}/p'_{O_2}) \qquad (32)$$

on both sides of the fayalite crystal. The maximum difference $\Delta\mu_{FeO}^{max}$ the fayalite compound can withstand without decomposition is given from simple thermodynamic principles as

$$\Delta\mu_{FeO}^{max} = \mu''_{FeO} - \mu'_{FeO} = -\tfrac{1}{2}\Delta G^0_{Fe_2SiO_4} + R T \ln a''_{FeO}, \qquad (33)$$

because a'_{SiO_2} equals one after a'_{FeO} has approached its minimum value. a''_{FeO} means the FeO activity in fayalite coexisting with wüstite under the given experimental conditions of p''_{O_2} resp. T. Finally, inserting Eq. (32) and (33) into (30), this yields

$$\ln\left(\frac{p''_{O_2}}{p'_{O_2}}\right)_{crit} = \frac{\gamma+2}{\gamma-2}\left(\frac{-\Delta G^0_{Fe_2SiO_4}}{RT} + 2\ln a''_{FeO}\right). \qquad (34)$$

$\Delta G^0_{Fe_2SiO_4}$ is the standard Gibbs-energy of Fe_2SiO_4-formation according to Eq. (16); γ stands for the ratio $\bar{D}_{Fe}/\bar{D}_{Si}$ of the respective mean diffusivities. From (34) one concludes that the critical ratio $(p''_{O_2}/p'_{O_2})_{crit}$ of the oxygen partial pressures, necessary to decompose fayalite into wüstite and silica depends simultaneously on the diffusivity ratio of iron and silicon and the thermodynamic stability of the compound itself.

A graphical representation of Eq. (34) based on $\Delta G^0_{Fe_2SiO_4}$ (1,418 K) $= -14.49$ kJ $\cdot$ mol^{-1} taken from Nakamura and Schmalzried (1983) is given in Fig. 3. As can easily be recognized, the greater the difference in the diffusivities of the cations (i.e. the greater γ is) the smaller is the oxygen-potential ratio necessary to decompose fayalite kinetically. Two limiting cases have to be considered. First, if one assumes that silicon ions are totally immobile within the fayalite lattice (i.e. $\gamma \to \infty$) and assuming $a''_{FeO} = 1$ for the sake of simplicity, a mini-
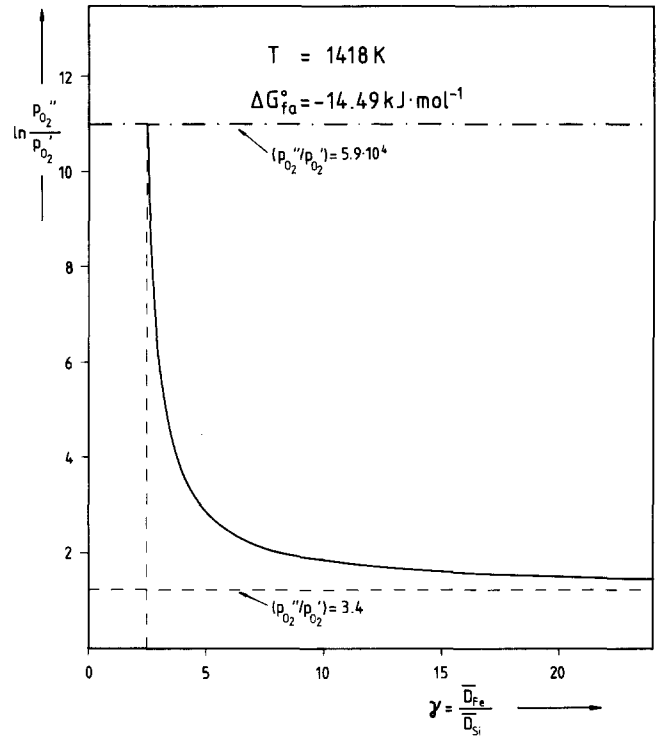

Fig. 3. Dependence of the critical oxygen-partial pressure ratio $(p''_{O_2}/p'_{O_2})_{crit}$ from the diffusivity ratio $\bar{D}_{Fe}/\bar{D}_{Si}$ according to Eq. (34). (For the sake of simplicity $a''_{FeO} = 1$ is assumed.)

mum value 3.4 results for $(p''_{O_2}/p'_{O_2})_{crit}$ from Eq. (34), which then reads for this special case

$$R T \ln(p''_{O_2}/p'_{O_2})_{crit} = -\Delta G^0_{Fe_2SiO_4} + 2 R T \ln a''_{FeO}, \qquad (34\,a)$$

i.e. the critical ratio of oxygen partial pressure is solely governed by the thermodynamic stability of fayalite. Secondly, because fayalite will be oxydized according to Eq. (18) as soon as $\log p''_{O_2}$ exceeds -8.40 at 1,418 K and will be reduced according to Eq. (17) as soon as $\log p'_{O_2}$ is below -13.17, the crystal cannot be exposed to oxygen partial pressure ratios greater than $p''_{O_2}/p'_{O_2} = 5.9 \cdot 10^4$. Inserting this value into Eq. (34), one finds the smallest ratio of diffusivities $\bar{D}_{Fe}/\bar{D}_{Si}$, which allows kinetic decomposition to proceed is 2.5.

Now we will analyze the situation that holds, if the experimentally fixed ratio $(p''_{O_2}/p'_{O_2})_{exp}$ is not sufficient to decompose fayalite kinetically, i.e. $(p''_{O_2}/p'_{O_2})_{exp} < (p''_{O_2}/p'_{O_2})_{crit}$. In this case the reaction

$$2\,Fe_{Fe}^x + Si_i^{\cdots\cdots} + 2\,O_2 = Fe_2SiO_4 + 2V''_{Fe} + 8h^\cdot + V_i^x \qquad (35)$$
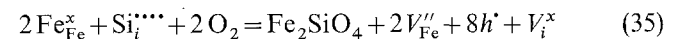
will proceed from the left to the right-hand side at the higher (p''_{O_2}) and from the right to the left-hand side at the lower (p'_{O_2}) oxygen-potential surface. That means, crystal-lattice sites are created at the p''_{O_2}-side by incorporation of gaseous oxygen and they are annihilated at the p'_{O_2}-side, because oxygen escapes from the crystal lattice into the gas phase. Both these processes result in a movement of the Fe_2SiO_4-crystal as a whole from the lower to the higher oxygen potential side, despite the fact that oxygen-ions are immobile within the close-packed anion-lattice.
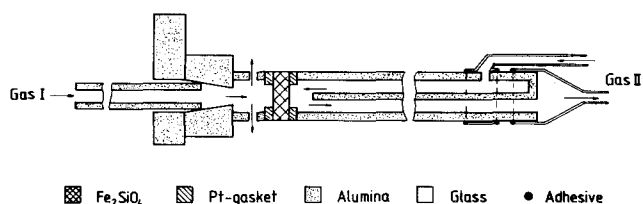
Fig. 4. Experimental assembly for placing fayalite in an oxygen potential gradient. (Gas I, II: CO/CO_2 mixtures with adjustable oxygen activities)

The resulting crystal velocity v_{st} can easily be calculated from the steady state condition Eq. (25) ($v_{st} = j_{Fe}/c_{Fe} = $ const) and Eqs. (23), (26) and (29); one finds ($\Delta x = x'' - x'$, see Fig. 2)

$$v_{st} = \frac{2}{\Delta x} \cdot \frac{\gamma}{\gamma + 2} \bar{D}_{Si} \ln \left(\frac{p''_{O_2}}{p'_{O_2}} \right). \tag{36}$$

It is obvious from Eq. (36) that for any given oxygen partial pressure ratio it is the slower moving cation that governs the stationary crystal velocity, which can experimentally be determined as will be seen later. Again, i.e. in the course of the crystal movement, oxygen molecules will be transported from the higher to the lower oxygen-potential side as described above.

III. Experimental Procedure

Fayalite (Fe_2SiO_4) samples were prepared by mixing powders of Fe_2O_3 (p.a. FLUKA), Fe (p.a. MERCK) and quartz (RIEDEL-DE HAEN) in such portions that the overall mole-ratio n_{Si}/n_{Fe} equals 1.001, i.e. the SiO_2 activity was fixed by a small deviation from stoichiometry, so that the given composition lies already outside the one-phase field of fayalite (Nakamura and Schmalzried 1983). These mixtures were homogenized under acetone in an agate ball mill for 12 h, dried in air at 150° C and pelletized to small discs (10 mm in diameter resp. 6 mm high) under pressures of 1.7 kbar. The pellets were than heated at 1,150° C for 10 days under a CO/CO_2-atmosphere ($\log p_{O_2} = -10.95$) in a platinum boat prereacted with Fe_2O_3 to ensure iron saturation of the platinum walls. After cooling to room temperature, the samples were again ground under acetone repelletized and further heat-treated for 10 days under the same conditions as above. The mean grain size of the samples was 30–50 μm; the density was about 90 percent of the theoretical (X-ray) density. All samples were brownish-yellow in colour. By X-ray diffraction (Guinier-method) no other phases except fayalite could be detected, but *electron probe microanalysis* (EPMA) revealed traces of SiO_2, indicating, that the fayalite phase was saturated with silica, that means a_{SiO_2} equals one.

Flat discs about 700 μm thick were cut from the samples, precision-ground (0.25 μm diamond paste) on both sides and inserted into the apparatus shown schematically in Fig. 4. Because of the special design of this apparatus, constructed from alumina ceramics, we were able to establish different oxygen partial pressures at both surfaces of the samples via CO/CO_2-gas mixtures. These mixtures were prepared in appropriate ra-

tios with the help of high accuracy mechanical pumps. A gas stream velocity of about 6–10 l/h was used throughout. The actual oxygen partial pressure was sensored with CaO-stabilized ZrO_2-solid state galvanic cells at the inlet and the outlet of the reaction chamber. The temperature was measured with a Pt – Pt 10 percent Rh thermocouple; temperature fluctuations were within $\pm 0.2°$ C of the set temperature. After cooling the reaction apparatus to room temperature, the samples were embedded in resin, ground perpendicular to the pellet axis and investigated by means of optical microscopy, EPMA, and *secondary electron microscopy* (SEM).

In EPMA measurements K_α-lines of iron and silicon were registered; the respective X-ray intensities were transformed to mole fractions using $Fe_{1-\delta}O$, Fe_3O_4, SiO_2 and Fe_2SiO_4 samples as standards, their respective compositions being exactly known from wet chemical analysis.

IV. Results and Discussion

The experimental results are summarized in Table 1. It is a general feature of all the experiments performed that the respective lower oxygen partial pressure p'_{O_2} was fixed at a constant value, while the higher p''_{O_2} was systematically changed until the wüstite phase could be detected by optical microscopy and electron microprobe analysis. The absolute values of the lower oxygen potential p'_{O_2} were located at two different positions $-p'_{O_2}$(I) and p'_{O_2}(II) - within the fayalite-phase field ($-13.17 < \log p'_{O_2}$(I) $< \log p'_{O_2}$(II) < -8.40), as can be read from Table 1.

At first, the results taken from runs 1–9 (index I is used for these runs) will be analyzed. Here, the lower oxygen partial pressure $\log p'_{O_2}$(I) is about -12.9. (Small deviations from a nominal constant value are due to fluctuations in the gas-phase impurity content, which is not exactly the same in different CO- resp. CO_2-charges.) If one now raises the higher oxygen partial pressure, starting with $\log p''_{O_2}$(I) $= -12.49$, the fayalite remains stable up to $\log p''_{O_2}$(I) $= -12.10$; at oxygen partial pressures equal or higher than $\log p''_{O_2}$(I) $= -11.99$ the fayalite will be found decomposed at the end of the experiment. This can be seen from the SEM pictures, given in Fig. 5. Regions containing a second resp. third phase have developed, i.e. wüstite at the higher oxygen potential surface and silica at the lower one, which is strongly fissured in accordance with theoretical considerations by Martin and Schmalzried (1985) concerning the stability of moving phase boundaries. The experimental p''_{O_2}(I)$/p'_{O_2}$(I) ratio, which has led to decomposition of fayalite within its thermodynamic stability range and which is termed the "critical" ratio according to Eq. (34) was estimated to be 6.8. At first, one comment concerning the reliability of this striking result seems necessary.

As the phase diagram (Fig. 1) shows, fayalite exhibits a small but distinct range of nonstoichiometry, extending for instance, at $\log p_{O_2} = -12.07$ (an arbitrarily chosen value) from $\xi = 6.75 \cdot 10^{-5}$ (two-phase equilibrium fayalite/SiO_2) to $\xi = -3.17 \cdot 10^{-4}$ (two-phase equilibrium fayalite/$Fe_{1-\delta}O$). In view of these extremely small values, one may argue that evaporation effects on crystal surfaces could eventually be respon-

Table 1. Summary of experimentally established oxygen-partial pressure ratios (p''_{O_2}/p'_{O_2}) and respective phases, identified by optical microscopy and EPMA after reaction time t

No	T/K	$\log p'_{O_2}$	$\log p''_{O_2}$	p''_{O_2}/p'_{O_2}	t/h	Identified phases
1	1,417.2	-12.85	-11.30	36	147	fa, "FeO", SiO_2
2	1,418.1	-12.84	-11.64	16	123	fa, "FeO", SiO_2
3	1,418.0	-12.84	-11.99	7.1	144	fa, "FeO", SiO_2
4	1,416.3	-12.91	-12.10	6.44	146	fa
5	1,418.3	-12.91	-12.18	5.37	144	fa
6	1,418.3	-12.89	-12.19	5.08	139	fa
7	1,417.9	-12.84	-12.18	4.64	144	fa
8	1,421.0	-12.88	-12.23	4.54	146	fa
9	1,416.3	-12.94	-12.49	2.84	144	fa
10	1,422.1	-11.54	-10.79	5.63	144	fa, "FeO", SiO_2
11	1,416.8	-11.55	-10.88	4.69	146	fa, "FeO", SiO_2
12	1,418.4	-11.53	-10.97	3.61	144	fa, "FeO", SiO_2
13	1,418.3	-11.55	-11.08	2.94	140	fa, "FeO", SiO_2
14	1,418.3	-11.54	-11.17	2.32	99	fa, "FeO", SiO_2
15	1,418.3	-11.53	-11.17	2.28	143	fa, ("FeO"), SiO_2
16	1,418.4	-11.53	-11.23	2.02	144	fa

sible for the development of a second phase in our decomposition experiments. Say, for instance, 'FeO' would evaporate more quickly from the sample surface as compared to SiO_2 at the lower oxygen potential side, then the fayalite (starting with $\xi = 0$) will become SiO_2-enriched ($\xi > 0$) until silica exsolves as a second phase.

Concerning this, we could demonstrate, however, that such evaporation effects, if realistic at all, must be negligible small; in fayalite crystals, exposed as long as 170 h ($T = 1,418$ K) against two identical oxygen partial pressures at both crystal sides ($\log p''_{O_2} = -12.07$), making use thereby of the same experimental arrangement as in the decomposition runs, no SiO_2 segregation in near surface regions could be detected.

On the other hand, one may argue that very small deviations from stoichiometry could exist in fayalite samples prior to the action of oxygen potential gradients, originating from sample preparation and sintering procedures. Assuming an iron-rich composition, say $\xi = -4 \cdot 10^{-4}$, one reads from Fig. 1 that the fayalite stability field extends from $\log p_{O_2} = -10.63$ (fayalite/$Fe_{1-\delta}O$) to $\log p_{O_2} = -8.78$ (fayalite/SiO_2) for this arbitrarily chosen nonstoichiometry. Samples, annealed at $T = 1,418$ K during sintering at oxygen-partial pressures between both these limiting values remain single-phased although nonstoichiometric. But, if in the course of a decomposition run an oxygen partial pressure of (for instance) $\log p_{O_2} = -12.07$ acts at one sample surface, one instantly crosses the two-phase boundary line (as Fig. 1 shows) and wüstite is stable now in equilibrium with fayalite. Therefore, an exsolution of $Fe_{1-\delta}O$ has to occur from the otherwise single-phased fayalite. However, we believe from the following reasons that this effect plays no important role in our decomposition experiments; first, the amount of exsoluted wüstite is expected to be extremely small in view of the narrow ranged fayalite stability field and secondly, the wüstite phase, if observable at all in an optical microscope, must be dispersed homogeneously throughout the sample rather than forming a distinct

surface layer, as it does in our experiments. Thus, we are sure that decomposition of fayalite occurs solely by "kinetic" effects as outlined in the foregoing sections.

Inserting now the experimental value $(p''_{O_2}(I)/p'_{O_2}(I))_{crit} = 6.8$ into Eq. (34), taking into account $\Delta G^0_{Fe_2SiO_4} = -14.5$ kJ·mol^{-1} (Nakamura and Schmalzried 1983) and $a''_{FeO} = 0.955$ for the activity of FeO in wüstite at $T = 1,418$ K and $p''_{O_2}(I) = 9.1 \cdot 10^{-13}$ bar (Darken and Gurry 1945), one estimates the ratio of the mean diffusivities of iron and silicon in fayalite to be $\gamma(I) = \bar{D}_{Fe}/\bar{D}_{Si} = 7.8$. Before analyzing this result, one has to remember that both the above diffusivities $\bar{D}_i$ are mean values not only because we have neglected the dependence of D_i on the thermodynamic variables a_{SiO_2} and p_{O_2} during integration of Eq. (29), but also from the fact that polycrystalline samples were used in our studies. From measurements of interdiffusion coefficients $\bar{D}$ in olivine single crystals as a function of the $Fe/(Fe + Mg)$-ratio (Buening and Buseck 1973), it is known that the diffusion is anisotropic with $D_c = 3.5 D_b$, $D_a = 4.3 D_b$. Therefore, the diffusivities $\bar{D}_i$ are only mean values for the crystallographic **a**-, **b**- and **c**-directions in the fayalite lattice.

Nevertheless, we conclude from the above result that the diffusivity of silicon in fayalite as compared to the iron diffusivity is by far not as small as one expects from literature data. For instance, tracer diffusion measurements in Co_2SiO_4 ($p_{O_2} = 0.21$ bar (air), $a_{SiO_2} = 1$, $T = 1,418$ K) yield $\gamma = \bar{D}_{Co}/\bar{D}_{Si}$ to be about 110 (Windhager and Borchardt 1975); in Mg_2SiO_4 (forsterite), the value for $\gamma = \bar{D}_{Mg}/\bar{D}_{Si}$ is about 30 in air at $T = 1,418$ K (Hallwig et al. 1982).

The relatively small γ-value, emerging from the present decomposition experiments, may be explained by the fact that tracer-diffusion measurements, cited from the literature, were performed in air, while our runs were carried out in oxygen partial pressure ranges as low as about 10^{-13} bar. Therefore, in view of the p_{O_2}-dependencies of the defect-concentrations (setting a_{SiO_2} to be one), the iron diffusivity via iron vacancies has to decrease with decreasing oxygen partial pressure
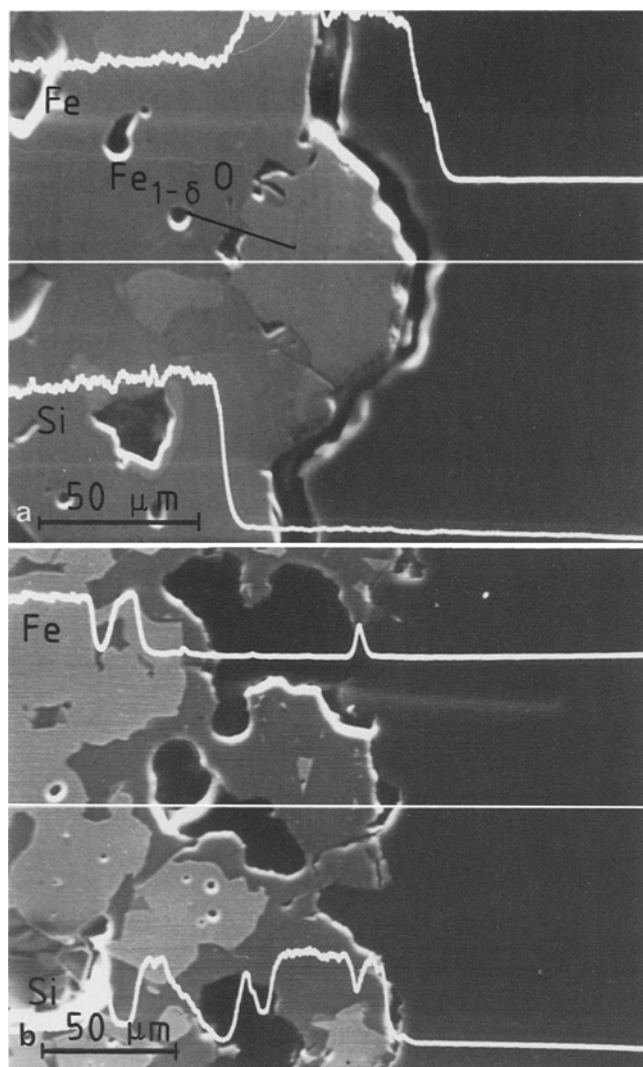
Fig. 5 a, b. SEM pictures of polycrystalline fayalite after opposing to oxygen-partial pressure ratios greater than the critical value given by Eq. (34). a Largely extended wüstite phase formed at the higher oxygen potential surface (p''_{O_2}); b Silica phase formed at the strongly fissured low oxygen potential surface (p'_{O_2}) of the same fayalite crystal as shown in a

Fig. 6. Phase diagram of the second kind for the system Fe—Si—O. —··—··—: Single phase fayalite; —·—·—: Three phase equilibrium $Fe_2SiO_4/Fe_3O_4/SiO_2$ (upper line) resp. $Fe_2SiO_4/Fe/SiO_2$ (lower line); — —: Two phase equilibrium $Fe_{1-\delta}O/Fe_3O_4$ (upper line) resp. $Fe/Fe_{1-\delta}O$ (lower line). The respective critical oxygen partial pressures, experimentally determined in series I (o) and series II (■) experiments, are indicated

Fig. 7. SEM picture of fayalite polycrystal, showing the movement of the high oxygen potential surface relatively to inert Pt-markers prior to decomposition

(Eq. (9) yields $D_{Fe} \propto p_{O_2}^{1/6}$), while at the same time the silicon diffusivity via silicon interstitials will increase (Eq. (10) yields $D_{Si} \propto p_{O_2}^{-1/3}$).

This argument, if correct, leads to the expectation that decomposition runs, carried out in higher oxygen-potential ranges as compared to about 10^{-13} bar must yield higher values for the diffusivity ratio of iron and silicon, and it is exactly this, what we have found in a second series of decomposition experiments (runs 10–16), indexed II in the following.

In these experiments the lower oxygen-partial pressure $\log p'_{O_2}(II)$ was fixed at about -11.52, as can be seen from Table 1, while the higher $\log p_{O_2}(II)$ was systematically changed until the wüstite phase could be detected at the higher oxygen potential side; this was the case at $\log p''_{O_2}(II) = -11.17$, which yields a critical ratio $(p''_{O_2}(II)/p'_{O_2}(II))_{crit} = 2.29$ and which is indeed substantially smaller than the 6.8 value found in our first series experiments.

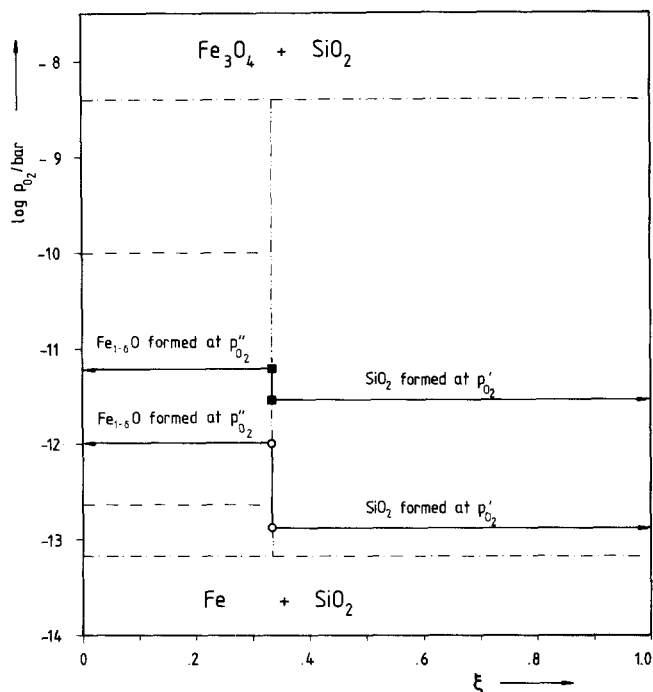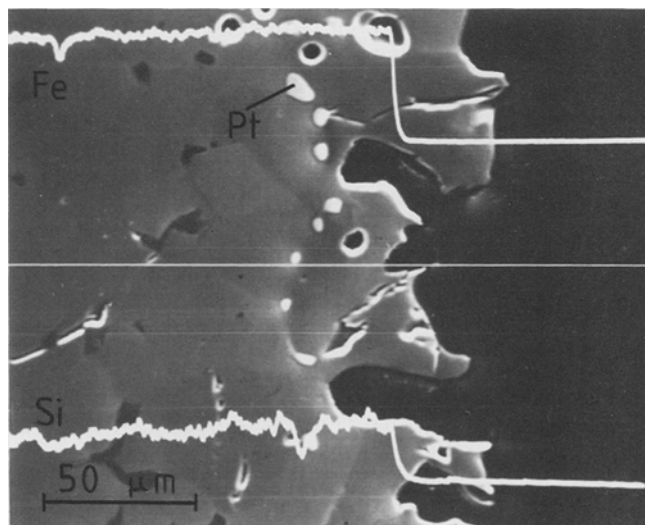Underlying the assumption, that $\bar{D}_{Fe} \gg \bar{D}_{Si}$ holds within the oxygen partial pressure range that operates in our second series experiments, we derive from Eq. (34a) $\Delta G^0_{Fe_2SiO_4} = -12.9 \text{ kJ} \cdot \text{mol}^{-1}$, based on $a''_{FeO} = 0.875$ ($T = 1,418$ K; $p''_{O_2}(II) = 6.70 \cdot 10^{-12}$ bar) taken from the paper of Darken and Gurry (1945). This value is only slightly more positive ($+1.6 \text{ kJ} \cdot \text{mol}^{-1}$) than the

$\Delta G^0_{Fe_2SiO_4} = -14.5 \, \text{kJ} \cdot \text{mol}^{-1}$ given by Nakamura and Schmalzried (1983), thus supporting our assumption of increasing iron and decreasing silica diffusivities with increasing oxygen potentials.

For a better understanding of the foregoing the oxygen partial pressures $p'_{O_2}(I)$, $p''_{O_2}(I)$ and $p'_{O_2}(II)$, $p''_{O_2}(II)$, which represent the respective critical ratios experimentally determined in series I and II experiments are drawn into a phase diagram of the second kind for the Fe−Si−O system. From Fig. 6, two essentials may be summarized; 1. both critical oxygen partial pressure ratios operate within the fayalite stability field, which is limited by the upper resp. lower line, representing the three-phase equilibria Fe_2SiO_4, Fe_3O_4, SiO_2 and Fe_2SiO_4, Fe, SiO_2 respectively; 2. the critical oxygen partial pressure ratio clearly decreases going from the lower to the upper part of the fayalite stability field.

At the end of this chapter we try to analyze the movement of a fayalite crystal in oxygen potential fields. According to theory (see Eq. (36)), after attaining a steady state, the crystal moves with constant velocity v_{st} from the lower to the higher oxygen potential side as long as the acting oxygen potential field is smaller than the critical ratio. We have estimated the stationary velocity v_{st} by use of the so-called marker technique. In such studies, traces of platinum paste (Pt particles suspended in organic liquids) were brought onto the fayalite crystal surface with the aid of a small brush before inserting the sample into the reaction apparatus. After the organic part of the paste was decomposed at the high reaction temperature, some very small platinum particles of about 2 μm diameter have formed. During the decomposition runs, these particles remained fixed within the immobile oxygen lattice. So one can take the time-dependent distance between the higher oxygen potential surface and the marker line, representing the initial surface, as an indication of the crystal movement and therefore as a measure of the crystal velocity v_{st}. Mean values of about $5 \cdot 10^{-9} \, \text{cm s}^{-1}$ were derived for v_{st} from first series runs. Inserting this value in Eq. (36), taking into account the experimentally derived $\gamma(I) = 7.8$, one finds the mean diffusivity of silicon $\bar{D}_{Si}$ to be about $10^{-10} \, \text{cm}^2 \, \text{s}^{-1}$ in the oxygen potential range of about $3 \cdot 10^{-13}$ bar. This value seems to be very high as compared to silicon diffusivities from tracer experiments in Co_2SiO_4 (Windhager and Borchardt 1975) and Mg_2SiO_4 (Hallwig et al. 1982), which yield $\bar{D}_{Si}$ in the order of $10^{-14} - 10^{-15} \, \text{cm}^2 \, \text{s}^{-1}$. Again, it must be emphasized that these measurements were made in air ($p_{O_2} = 0.21$ bar), but according to defect thermodynamics (see Eq. (10)) we expect a strong oxygen potential dependence (a_{SiO_2} taken to be one) for the silicon diffusivity, which has to increase with decreasing p_{O_2}.

Finally, if one takes $\bar{D}_{Si} \approx 10^{-10} \, \text{cm}^2 \, \text{s}^{-1}$ from measurements of the stationary crystal velocity, one is able to calculate the mean diffusivity of iron in fayalite from $\gamma(I) = \bar{D}_{Fe}/\bar{D}_{Si} = 7.8$ to be $\bar{D}_{Fe} \approx 8 \cdot 10^{-10} \, \text{cm}^2 \, \text{s}^{-1}$. Comparing this with tracer diffusion data (Hermeling and Schmalzried 1984) which yield $\bar{D}_{Fe} = 3 \cdot 10^{-10}$ $\text{cm}^2 \, \text{s}^{-1}$ ($T = 1,130^\circ$ C; $p_{O_2} = 10^{-12}$ bar) one concludes, that both values are in fairly good agreement, mani-festing therefore the relatively high silicon diffusivity in fayalite at low oxygen partial pressures.

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