TABLE I continued

(d) Flexural strength ($N\,mm^{-2}$)

Water–powder ratio	Control	Impregnated	Strength factor
0.50	0.74	2.78	3.75
0.60	0.67	2.98	4.45
0.70	0.40	2.75	6.88
0.80	0.32	1.41	4.40

(e) Abrasion resistance % weight loss

Water–powder ratio	Control	Impregnated	Strength factor
0.50	6.4	0.9	7.1
0.60	8.6	1.1	7.8
0.70	9.2	1.7	5.4
0.80	9.3	1.9	4.9

(f) Polymer loadings

Water–powder ratio	% Polymer absorbed
0.50	21.9
0.60	28.3
0.70	35.4
0.80	41.7

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Correlations between oxygen transport phenomena in non-crystalline silica

The mobility of oxygen in fused silica is evident in a variety of phenomena such as permeation of O_2 gas, oxidation of silicon surfaces, and O_2/SiO_2 isotope exchange. However, a mechanistic relationship between all these processes has not yet been presented. The formation of amorphous silica scales during oxidation of silicon is known to be rate-controlled by permeation of molecular O_2 through the SiO_2 layer [1]. On the other hand, oxygen tracer diffusion coefficients as measured by isotopic exchange techniques are said to be uncorrelated to O_2 diffusion-controlled phenomena [2]. However, there should be a common underlying mechanism for the transport of oxygen because all the processes have uniformly low activation energies, depend linearly on the partial pressure of oxygen (p_{O_2}), as well as having algebraic relationships between their respective rate laws. All these observations can be understood if the transport of oxygen involves the interaction of O_2 molecules dissolved in SiO_2 with oxygen of the silica network (lattice oxygen).

Haul and Dümbgen [3] were the first to relate permeability of O_2 gas to diffusion coefficients measured by gas/solid isotope exchange. In their model interstitially dissolved O_2 acts as a defect by which lattice oxygen migrates. The diffusion of lattice oxygen (D_O) then, can be related to O_2 permeability (P_{O_2}),

$$P_{O_2} = D_{O_2} c_{O_2}/7.6 \qquad (1)$$

by

$$D_O = D_{O_2} c_{O_2}/c_O = 7.6 P_{O_2}/c_O \qquad (2)$$

where P_{O_2} is in units of cm^3 gas (STP) sec^{-1} for a 1 mm thick wall, $1\,cm^2$ area at 10 Torr gas pressure difference; D_{O_2} is the diffusion coefficient of molecular oxygen in $cm^2\,sec^{-1}$; c_{O_2} and c_O are the concentrations of oxygen in units of cm^3 gas (STP) per cm^3 solid for dissolved O_2 and lattice oxygen in SiO_2 respectively.

The oxidation rate of silicon to silica (parabolic regime) is correlated with O_2 permeability [4], because the oxidation proceeds by diffusion of dissolved O_2 through the SiO_2 layer to the SiO_2/Si interface. Dankwerts [5] has shown that parabolic oxidation of surfaces can be described by a rate constant:

TABLE I Comparison between ^{18}O-tracer diffusion, oxygen permeation, oxygen diffusion in SiO_2 glass, and oxidation of silicon

D_O, k_O (cm^2 sec^{-1})	Q (kcal mol^{-1})	T (° C)	Pressure dependence	Reference
^{18}O-tracer diffusion (D_O)				
2.0×10^{-9}	$29.0 \pm 2.0 \pm 2.0$	850–1250	$D_O \propto p_{O_2}$	[6]
$(4.4 \pm ^{14}_{3}) \times 10^{-11}$	19.7 ± 4.0	1150–1430	–	[7]
O_2 permeation (P_{O_2})				
	31.4	840–940	–	[8]
	22.0*	900–1100	$P_{O_2} \propto p_{O_2}$	[9]
O_2 diffusion (D_{O_2})				
2.8×10^{-4}†	27.0	900–1100	–	[10]
Parabolic rate constant for oxidation of silicon in O_2 (k_{SiO_2})				
2.0×10^{-9}‡	28.5	800–1200	$k_{SiO_2} \propto p_{O_2}$	[1]
2.0×10^{-9}	31.0	900–1150	$k_{SiO_2} \propto p_{O_2}$ flow system	[11]
1.0×10^{-10}	23.0	950–1100	$k_{SiO_2} \propto p_{O_2}$ manostatic	[11]
1.2×10^{-9}	27.6	900–1300	– r.f. heating	[12]
1.1×10^{-9}	28.0	900–1250	– resistance heating	[12]

$D_O, k_O \mathrel{\hat{=}}$ pre-exponential factor, $Q \mathrel{\hat{=}}$ activation energy
*Revised value 27 kcal mol^{-1} [10].
†Calculated from data given in [10].
‡Calculated from data given in [1].

$$k_{SiO_2} = 2D_{O_2} c_{O_2}/c_O, \tag{3}$$

provided that the solubility of O_2 is sufficiently small, i.e. $c_{O_2} \ll c_O$*; k_{SiO_2} is in units of cm^2 sec^{-1}.

Equations 1 to 3 show clearly that D_O, D_{O_2}, P_{O_2} and k_{SiO_2} are all interdependent and that the equations can be rearranged. For instance, P_{O_2} and k_{SiO_2} are solely dependent on tracer oxygen diffusivity (D_O) in SiO_2.

$$P_{O_2} = c_O D_O/7.6 \tag{4}$$

$$k_{SiO_2} = 2D_O \tag{5}$$

Thus tracer diffusion studies are in fact more useful in elucidating oxygen transport processes than was stated by Meek [2].

It follows from Equations 4 and 5 that P_{O_2}, k_{SiO_2}, and D_O should have the same temperature dependence. D_{O_2} is expected to have that same temperature dependence (see Equation 2) but reduced by the heat of solution of O_2 in SiO_2, which, however, is small [10]. Table I lists data from the literature which show that the four rates do have the same low activation energies (20 to 30 kcal mol^{-1}) within experimental error. Not included in Table I are experiments which show higher activation energies of 71 [13] and 55 kcal mol^{-1} [3] for tracer diffusion because they were influenced by phase-boundary reactions [6, 7]. Table I also shows that oxygen transport in SiO_2 is directly proportional to p_{O_2}, in marked contrast to the $p_{O_2}^{-1/2}$ dependence found for oxygen diffusion in K_2O-SiO_2 glasses [14]. The mechanism of oxygen transport must therefore differ when network-modifying cations are present in the SiO_2 network. Diffusion in the multicomponent silicates occurs not via interstitially dissolved O_2 molecules as in pure SiO_2, but via oxygen vacancies [14]. The activation energies of oxygen diffusion in silicate glasses [14] are much higher than that of SiO_2 glass because diffusion by oxygen vacancies requires the

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*c_{O_2} (900 to 1100° C) = (1.7 to 2) × 10^{-3} cm^3 gas (STP) per cm^3 SiO_2 [10]
c_O = 821 cm^3 gas (STP) per cm^3 SiO_2, i.e. $c_{O_2}/c_O = 2.1 \times 10^{-6}$

breaking of Si–O bonds. The outlined diffusion mechanism in SiO_2 also seems to hold for high temperature (1100 to 1500° C) corrosion of SiC and Si_3N_4 during which SiO_2 layers form. Activation energies of 20 to 30 kcal mol^{-1} were observed in the oxidation (parabolic regime) of SiC [15, 16] and around 25 to 35 kcal mol^{-1} for pure Si_3N_4 [17, 18]. The activation energy for the oxidation of impure Si_3N_4 increases with impurity content [19]. Instead of pure SiO_2, the impure Si_3N_4 forms silicate glass layers that presumably have higher activation energies of tracer oxygen diffusion.

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Kinetics of solid state $NiFe_2O_4$ formation at 700 to 1400° C

Ferrites are fabricated by heating powders, and many processing variables, e.g. powder purity, size distribution, type, etc., effect the reaction rate [1]. Activation energies for $NiO + Fe_2O_3 = NiFe_2O_4$ have varied from 105 and 185 kJ mol^{-1} [2] and 225 to 293 kJ mol^{-1} [3]. In the present work spectrographically pure (J. Matthey) NiO and Fe_2O_3 with sieved particle sizes of 15.6 to 33.0 μm were used. Equimolar amounts were mixed by hand for over 1 h, pressed in a steel die without binder or lubrication to form a pellet 10 mm diameter and 4 mm thick, placed in a recrystallized alumina boat, and fired in air within a temperature variation of ±3° C. The amount of $NiFe_2O_4$ formed was measured by the force in a magnetic field. Chamfered pole pieces of an electromagnet gave a region of constant field gradient and a double pan chemical balance was used to measure the force. A phosphor bronze cantilever was used to prevent the specimen being attracted to either pole. Its stiffness could be neglected during weighing when the specimen returned (checked by a cathetometer) to a null position. A Cu specimen holder was used to hold about 100 mg powdered sample. The force per unit mass of sample versus mol% $NiFe_2O_4$ in a range of NiO, Fe_2O_3 and $NiFe_2O_4$ mixtures was linear and used to determine the unknown amount of $NiFe_2O_4$ in a sample.

Compacting pressures in the range 10 to 100 MPa did not affect the amount of $NiFe_2O_4$