

TABLE 4. RESULTS OF EXPERIMENTAL RUNS AT 1 ATM

T (°C)	Conditions of run -log f_{O_2} (bars)	time (hrs)	Phases present*
1,255	7.48	31	gl
1,250	6.94	24.5	gl
1,241	7.68	65	gl, pl
1,238	7.08	24.5	gl, pl(tr.)
1,189	3.84	41	gl, pl
1,169	3.93	50	gl, pl, il
1,164	8.08	48	gl, pl
1,144	4.05	30.5	gl, pl, il, mt(sa)
1,144	8.99	61	gl, pl
1,142	7.62	52	gl, pl
1,137	8.48	49.5	gl, pl, opx
1,136	7.70	48.5	gl, pl, opx(tr.)
1,134	9.13	58	gl, pl, opx
1,123	7.90	48	gl, pl, opx
1,120	4.19	34.3	gl, pl, opx, il, mt
1,117	8.01	49	gl, pl, opx, il(tr.)
1,109	8.90	55	gl, pl, opx
1,107	8.17	50	gl, pl, opx, il
1,103	9.60	59.5	gl, pl, opx
1,099	9.02	64.5	gl, pl, opx, il(tr.)
1,090	9.81	73	gl, pl, opx, il(sa)
1,086	9.26	68	gl, pl, opx, il
1,079	8.63	53	gl, pl, opx, cpx(sa), il, mt(sa)
1,072	9.49	55.5	gl, pl, opx, il, cpx(sa)
1,070	10.13	102	gl, pl, opx, il, cpx
1,059	9.70	60.5	gl, pl, opx, cpx, mt, il
1,042	10.60	105	pl, opx, cpx, il, mt

*gl = glass, pl = plagioclase, opx = orthopyroxene, cpx = clinopyroxene, il = ilmenite-hematite solid solution, mt = magnetite-ulvöspinel solid solution, tr. = trace, sa = small amount.

judged to be of lesser value. Volcanic rocks are known to be oxidized by subsolidus reactions with gases; even ignoring that problem, the relation of the Fe₂O₃/FeO ratio of a rock, which is a subsolidus ratio or a hypersolidus ratio quenched from an unknown temperature, to a ratio at an assumed liquidus, is not clear. Nevertheless, the range of values deduced by Fudali (1965) for some basalts and andesites (Fig. 5) is within our limits.

Control of Oxygen Fugacity

It is also of interest to evaluate the controls of f_{O_2} in magmatic processes, and in turn to

evaluate the relation of values of Figure 5 to values at higher liquidus temperatures and the extent to which f_{O_2} may vary during fractional crystallization. Various aspects of this subject have been discussed by Carmichael and Nicholls (1967), Anderson (1968), Mueller (1969, 1971), Osborn (1969), and Hamilton and Anderson (1967) among others.

As pointed out by Mueller (1969), two reactions are important in controlling f_{O_2} of a melt, the oxidation of FeO to Fe₂O₃, and the H₂O gas reaction. These may be combined in one equilibrium constant:

$$K = (a_{FeO_{1.5}}/a_{FeO})^2 (f_{H_2}/f_{H_2O}). \quad (1)$$

Whether the first ratio or the second controls f_{O_2} of the melt is simply a question of which is the larger O₂ reservoir. Mueller (1969) and Hamilton and Anderson (1967) argue that in closed systems the second term is the more important when "significant" amounts (probably more than one percent) of H₂O are present. In open systems, the FeO_{1.5}/FeO ratio of the magma is even more likely merely to reflect, rather than control, f_{O_2} .

Now consider four cases of f_{O_2} variation in a system whose components are an anhydrous rock composition and one or more volatile species; two cases involve a magma system closed and two involve a system open to the wall rocks.

1. The system is closed, and the melt contains a negligible amount of H₂O. In this case, f_{O_2} is controlled by the ratio (FeO_{1.5}/FeO), which has been considered for a melt without crystals by Anderson (1968). He found a slope ($d \log f_{O_2}/d(1/T)$) = -3.0×10^4 reasonable. Such a curve for an arbitrary (FeO_{1.5}/FeO) ratio is plotted in Figure 6. If crystal-liquid equilibria are not considered, fractionation along such a curve would lower f_{O_2} relative to the QFM buffer. The effects of crystallization of ferromagnesian silicates and oxides on the (FeO_{1.5}/FeO) ratio has been considered in model systems such as MgO-FeO-Fe₂O₃-SiO₂ (Osborn, 1959). Closed-system fractionation by silicate removal may initially raise (FeO_{1.5}/FeO) and, accordingly, raise f_{O_2} , relative to the curve shown, but eventually, subtraction of magnetite will lower (FeO_{1.5}/FeO) and lower f_{O_2} , as discussed above. Subtraction of an iron-rich phase is needed (somewhat paradoxically) to produce the iron-enrichment trend.

2. The system is closed, but f_{O_2} is controlled

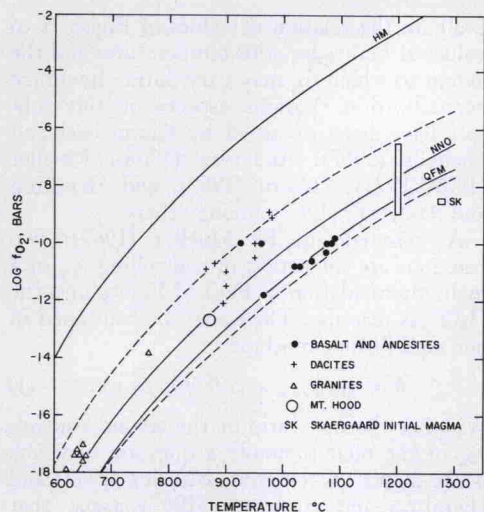


Figure 5. Estimates of f_{O_2} and temperature in basaltic and calcalkaline magmas. Dotted lines identical to lines in Figure 3. Data from Carmichael (1967), Carmichael and Nicholls (1967), Buddington and Lindsley (1964), and Williams (1971). Bar at 1,200°C from Fudali (1965).

by the ratio (f_{H_2O}/f_{H_2}). H_2O may be dissolved in the melt and may also be present in a fluid consisting of H_2O or H_2O and CO_2 . Figure 6 contains contours of (f_{H_2O}/f_{H_2}), calculated from thermodynamic data (K_W) of Robie and Waldbaum (1968). Because f_{H_2O} and f_{H_2} in a fractionating magma change with temperature and total pressure, we continue to make the simplifying assumption of ideal mixing of the gases, in order to calculate f_{O_2} changes.

To illustrate, consider a H_2O -saturated magma initially at the QFM buffer at 1,227°C and 5 kb total pressure. We use the assumption of ideal mixing and the definition of partial pressure:

$$f^{H_2O}/f^{H_2O} = X^{H_2O} \equiv P_{H_2O}/P_{total} \quad (2)$$

$$f^{H_2}/f^{H_2} = X^{H_2} \equiv P_{H_2}/P_{total} \quad (3)$$

It should be noted that pressures are *partial* pressures, in accordance with assumptions of ideal mixing, rather than P_{eH_2O} used elsewhere in this paper.

At 1,227°C, the ratio (f^{H_2O}/f^{H_2}) is defined by K_W and f_{O_2} . Because f^{H_2O} and f^{H_2O} can be obtained from tables (Shaw and Wones, 1964; Holloway and others, 1971), equations (2) and (3) may be solved simultaneously to obtain X^{H_2O} and X^{H_2} , remembering that $X^{H_2O} + X^{H_2} = 1$. Now, those mole frac-

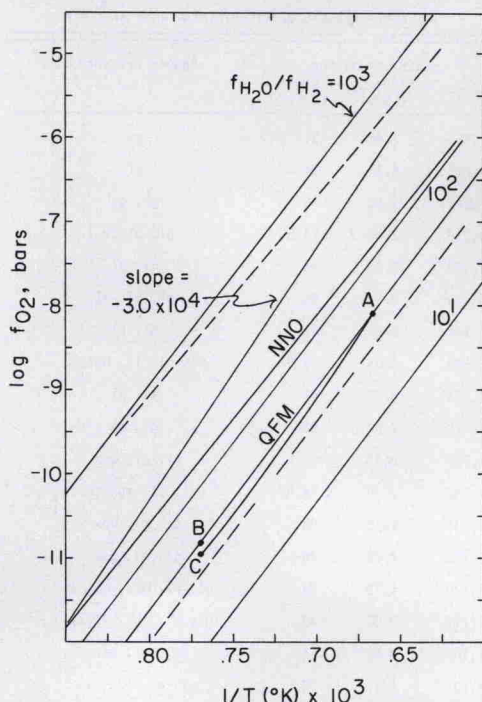


Figure 6. Equilibrium f_{O_2} for various f_{H_2O}/f_{H_2} ratios as a function of temperature. Dotted lines identical to estimate of natural range of f_{O_2} in Figure 3.

tions, known at one temperature in the system, remain constant at another temperature if the gases mix ideally ($[\delta \ln a_i / \delta T]_{x_j} = [\delta \ln x_i / \delta T]_{x_j} = 0$); therefore values of f^{H_2O} and f^{H_2} at any other temperature can be calculated and, from those fugacities and K_W , f_{O_2} . Two cases are presented in Figure 6, A-B, a trend along which a magma cools from 1,227°C to 1,027°C at a total pressure of 5 kb, and A-C, a trend along which a magma cools from 1,227°C to 1,027°C while total pressure drops from 5 kb to 1 kb. Trend A-B is identical to the QFM trend, and A-C nearly parallels QFM. The trend of a differentiating H_2O -undersaturated magma should also nearly parallel QFM, for if a reservoir of H_2O and CO_2 is present, we may write that

$$P_{H_2} + P_{H_2O} = P_{total} - P_{CO_2}; \quad (4)$$

this case is then analogous to those discussed above, inasmuch as the right-hand term is constant at constant pressure. Therefore, f_{O_2} will follow one of the trend lines. If no CO_2 is present, and H_2O is present only in solution in melt, both f_{H_2O} and f_{H_2} will increase as