



Figure 7. Oxygen fugacities produced in a magma by exchange of H₂ with wall rocks. Trends a, b, and c refer to case 3 in text.

anhydrous phases crystallize, probably in a nearly constant ratio, again resulting in a trend parallel to one of the lines shown.

3. The system is open, but the magma exchanges only H₂ with the wall rocks. Assuming H₂ can diffuse with ease, this case is likely in two instances: one, when H₂O is the only volatile species and there is no fluid phase. To exchange with wall rocks, H₂O must diffuse through the magma, a very slow process (Burnham, 1967). In the second instance, a fluid phase exists but has no passage to the wall rocks because of an impenetrable barrier, perhaps a rind of solidified magma.

Calculation of f_{O_2} is simplified by use of a model in which $P_{total} = 5$ kb, magma temperature is constant at 1,200°C, except at its margins, wall rocks are at 600°C, and the magma-wall-rock contact is at 900°C. In the wall-rock reservoir, $P_{H_2O} + P_{H_2} + P_{CO_2} = P_{total}$, and the solid Fe-bearing phases of the wall rocks control f_{O_2} of the entire system, wall rocks plus magma. Two typical wall-rock assemblages are biotite-K-feldspar-magnetite (+ quartz) and orthopyroxene-quartz-magnetite; the f_{O_2} buffering reactions are the oxidation-dehydration of annite to K-feldspar and magnetite, and the oxidation of ferrosilite to magnetite and quartz. Data on natural biotites indicate that they buffer f_{O_2} near NNO (Dodge and others, 1969). Calculation of the

FeSiO₃ reaction from thermochemical data of Williams (1971), assuming $X_{FeSiO_3} = 0.2$ and $X_{Fe_3O_4} = 0.4$ in natural assemblages, yields f_{O_2} within 0.2 log units of NNO at 600°C. Such buffers then define the f_{H_2O}/f_{H_2} ratio of the wall rocks.

Three examples, which span a reasonable range of geologic conditions, illustrate the calculations:

a. Consider that in the magma and wall rocks the only volatile species are H₂O and H₂. If the wall rocks contain an assemblage such as biotite-K-feldspar-magnetite, their f_{O_2} is near NNO, which at 600°C controls log $f_{O_2} = -18.92$ and $P_{H_2} = 9.8$ b. In wall rocks at the contact at 900°C, log $f_{O_2} = -10.91$. That value is calculated by the same method outlined in section 2, assuming H₂O and H₂ exchange throughout the wall-rock reservoir. As Figure 7 shows, wall rocks are locally oxidized, relative to NNO, near the contact. Because f_{H_2} is equal in wall rocks and magma at the contact, and because f_{H_2O} is nearly equal in the magma at the contact at 900°C log $f_{O_2} = -10.91$, a value 0.9 log units greater than the NNO buffer. In the magma at 1,200°C, log $f_{O_2} = -6.20$, a value 1.3 log units greater than NNO (Fig. 7).

b. Consider that in the wall rocks $P_{H_2O} + P_{H_2} = P_{total}$, but that the magma contains 1 wt percent H₂O ($f_{H_2O}^m = 290$ bars at 1,200°C). Because the assumption of ideal mixing certainly does not hold in melts, we shall also require that a fluid phase exist in equilibrium with the magma. Again in the wall rocks at the contact log $f_{O_2} = -10.91$ and $f_{H_2} = 9.8$ b. In the magma at the contact $f_{H_2} = 9.8$ b and, because H₂ behaves nearly ideally, $P_{H_2} = 9.8$ b. From formula (3) we can then calculate that at 900°C, $X_{H_2}^l = 0.002$. At 1,200°C, $X_{H_2O}^l = 290/5,948 = 0.048$. Those mole fractions hold throughout the magma, provided the fluid moves freely. Therefore $X_{CO_2}^l$, at any temperature in the magma, equals 0.95. In the magma near the contact at 900°C, $f_{H_2O}^l = 0.048 \times 5,118 = 245$ b. Log f_{O_2} therefore is -13.55 , considerably less than in wall rocks across the assumed barrier (see Fig. 7). Because we know the fugacities of H₂O and H₂ (9.8 b) at 1,200°C, we calculate that at 1,200°C, log $f_{O_2} = -8.82$, 1.3 log units less than NNO. If the magma were to cool from that temperature, $f_{H_2O}^m$ would increase, because of the subtraction of anhydrous phases, and f_{O_2} would, in relation to NNO, increase. The increase would

be slight, for if magma temperature fell to 1,100°C and the H₂O content doubled, probably an unrealistically high increase, then $f_{\text{H}_2\text{O}}^m = 827$ bars; because P_{H_2} continues to be 9.8 b, $\log f_{\text{O}_2} = -9.18$, 0.4 log units below NNO.

c. If the wall rocks contain an impure pore fluid, such that $f_{\text{H}_2\text{O}} = 0.5 \times f_{\text{H}_2\text{O}}^\circ$, and are buffered at NNO, $\log f_{\text{O}_2}$ again is -18.92 at 600°C, but $f_{\text{H}_2} = 4.9$. By reasoning analogous to case b, if the magma contains 1 percent H₂O, $\log f_{\text{O}_2}$ in the magma is -8.22 at 1,200°C, 0.7 log units less than the NNO buffer.

In summary, H₂ diffusion through a magma and equilibration with fluid in cooler wall rocks will control f_{O_2} within 1.3 log units of the wall-rock buffer curve under a variety of geologic conditions except, as we note below, at shallow depths. In the most probable cases, such as b and c, in which the magma contains only 1 or 2 percent of H₂O, f_{O_2} is lowered in the magma. In any case, f_{O_2} should fall in the range between the dotted lines on Figure 6. Differentiation of a magma would proceed generally along a path with a slightly shallower slope than the wall-rock buffer curve, but would depend somewhat on initial and final H₂O contents of the magma.

4. The system is open, and the magma exchanges H₂O and H₂ with wall rocks. If exchange is complete, f_{O_2} values must lie on a curve such as A-B (Fig. 6), as calculated in example 2. If exchange is incomplete, then $f_{\text{H}_2\text{O}}$ in the magma near the contact generally is less than $f_{\text{H}_2\text{O}}$ in the wall rocks near the contact (unless fluid in the wall rocks is very impure). In that case, f_{O_2} in the magma is less than that defined by a curve parallel to A-B (as in case 3b). If both H₂O and CO₂ are exchanged, the same types of situations apply, but f_{O_2} values will be slightly higher, analogous to case 3c.

Case 4 illustrates that H₂O which may enter a magma need *not* be oxidizing if it is in equilibrium with silicate-oxide assemblages. In the usual case of H₂O diffusion into a melt, f_{O_2} is lowered, relative to some buffer, rather than raised.

Summary

We have shown that in a variety of geologically possible situations, f_{O_2} in a magma within the crust is controlled largely by the initial FeO_{1.5}/FeO or $f_{\text{H}_2\text{O}}/f_{\text{H}_2}$ ratio of the magma

or by the f_{O_2} buffering assemblage of the wall rocks. Differentiation of the magma or exchange of fluid with wall rocks will move f_{O_2} no more than 1.3 log units from the original buffer. Various geobarometers indicate that initial f_{O_2} values in magmas and f_{O_2} values in normal wall-rock assemblages are near NNO. Only unusual conditions can move f_{O_2} in a magma very far away from that buffer.

Unusual conditions may be encountered near the roofs of shallow magma chambers. Because waters are more oxidized at higher levels, either by meteoric water influx or by equilibration with oxidized sediments, exchange of H₂O or H₂ would oxidize the magma. Exchange of H₂O would also be facilitated by extensive fracture development, a common feature of chamber roofs. Extensive fractionation of a magma does not take place at such depths, however, but rather at deeper levels under conditions specified above.

We have previously shown that iron-titanium oxide phases are not stable at temperatures of silicate liquids in andesite melt, under a variety of conditions, when f_{O_2} values are near NNO. We have also argued that to produce andesite by fractional crystallization of basalt, iron-titanium oxide must precipitate with the silicates. This basic inconsistency raises very serious questions about the fractional crystallization hypothesis.

WATER-UNDERSATURATED MELTING IN CALC-ALKALINE MELTS

Melting relations in the system andesite-H₂O-CO₂ are a guide to melting behavior in the H₂O-undersaturated region of most calc-alkaline melts, especially to behavior in the presence of a complex fluid phase. Figure 4 contains *T-X* sections showing melting relations for rock systems with a fluid phase containing one species (H₂O) soluble in silicate melt and one (CO₂) essentially insoluble in the melt. From Figure 4 and data on the relative proportions of phases in run products, we can also construct an isobaric section of the system andesite (Mount Hood)-H₂O (Fig. 8), in which H₂O is the only volatile species. Although Figures 4 and 8 show the same melting curves, their differences should be explicitly stated. The abscissa in Figure 4 is fluid composition, which is directly related to $f_{\text{H}_2\text{O}}^f$ and therefore to $f_{\text{H}_2\text{O}}^m$ and to the H₂O content of the melt, but is related to bulk composition of