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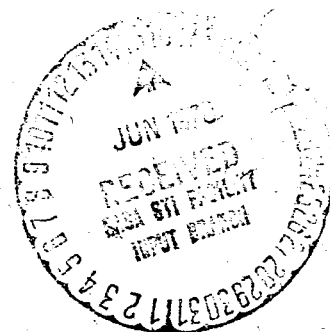
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OXIDATIVE CAPACITY OF MAGMATIC COMPONENTS

ROBERT F. MUELLER

MAY 1970



GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

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ABSTRACT

The capacity of magmatic components such as dissolved or precipitated ferrous and ferric iron compounds and water to control the oxygen fugacity of magmas is treated from a theoretical standpoint. Stoichiometric calculations indicate that in relatively anhydrous magmas, such as those of the Skaergaard complex, the oxygen fugacity is determined by the reaction of ferrous and ferric iron if these are abundant relative to the quantity of dissolved water. However if the quantity of water is high relative to iron, as in the calc-alkali batholiths, the oxygen fugacity is likely to be determined by the dissolved water of a given H_2O/H_2 ratio and by the tendency of H_2O to react with the Si-O-Si bridges of the silicate melt.

OXIDATIVE CAPACITY OF MAGMATIC COMPONENTS

INTRODUCTION

In recent years it has been stated by a number of authors that the oxidation states of certain magmas (including both the melt and crystalline precipitates) can be attributed to a buffering effect of the iron components. Thus it was suggested by Wones and Eugster (1965) that the magmas of the Southern California batholith were buffered by "anhydrous mineral assemblages." More recently Dodge, Smith and Mays (1969) interpreted the rocks of the Sierra Nevada batholith in much the same way. Since this question has an important bearing on the origin of batholiths and other planetary problems it is worthwhile to determine the extent to which this mechanism is operative.

The application of the buffer mechanism in mineral chemistry (Eugster, 1957) depends on obtaining a univariant relation between the oxygen fugacity and the temperature at some fixed phase composition. A necessary requirement, whether the buffer system is internal or external to the system under study, is that the quantity of buffer be large enough to prevent exhaustion. An analogous effect may also be obtained through other techniques such as equilibrating gas mixtures with the system under study. This was the technique employed by Muan and Osborn (1956) in their important study of the system $\text{MgO} - \text{FeO} - \text{SiO}_2 - \text{Fe}_2\text{O}_3$. These authors deduced that if a melt were crystallized at constant total composition of the condensed phases (melt and crystals), so that no oxygen was added to or subtracted from the equilibrated gas, the oxygen

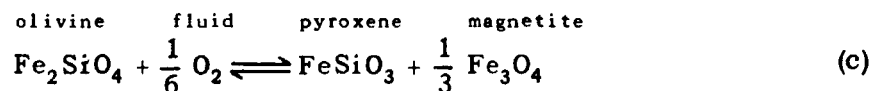
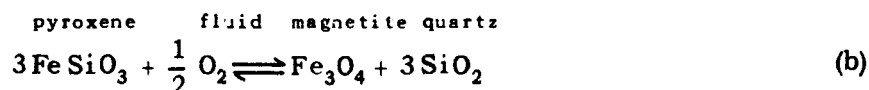
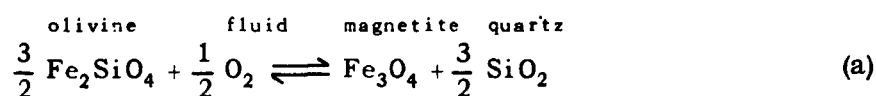
fugacity would decrease with the temperature in a manner analogous to that of a buffer system. Osborn suggested that a relatively anhydrous magma of basaltic composition, which crystallized as a closed system, would also behave in this manner and would give rise to the gabbroic series of differentiates such as those of the Skaergaard complex (Wager and Deer, 1939). Furthermore in these differentiates the steady decrease in oxygen fugacity with crystallization would be accompanied by both absolute iron enrichment of the melt and by relative iron enrichment (as expressed by the atomic ratio $\text{Fe}/(\text{Fe} + \text{Mg})$) in both the melt and the precipitating crystals. It is clear that if natural anhydrous magmas behave in this manner their ferrous and ferric constituents act analogous to internal buffers. The application of this idea to the Skaergaard complex is entirely reasonable since it agrees with the thermochemical data of Fig. 1 and is corroborated by the detailed mineral compositions as determined by Wager and Deer (1939).

Osborn (1959) also proposed an origin for the calc-alkali series of differentiates which characterize the batholiths and large segments of continental rocks in general. This hypothesis again draws on the system $\text{MgO} - \text{FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2$, but depends now on open system behavior in which the oxygen fugacity is constrained to remain constant or even to increase as crystallization occurs. As a result there is a precipitation of magnetite and a corresponding enrichment of the melt in silica. Osborn therefore argued that the silica enrichment, which also characterizes calc-alkali differentiation, is attributable to the maintenance of relatively high oxygen fugacities by oxidizing constituents such as water which are dissolved in the melt. However he made no attempt to show that Po_2 did in fact remain high during calc-alkaline differentiation or that

the dissolved water in these magmas could act as an oxidizing agent. Unfortunately subsequent experimental work has virtually been confined to anhydrous systems so that it has not been possible to determine the oxidative characteristics of hydrous plutonic magmas from direct experiments.

REPRESENTATIVE MAGMATIC MINERAL REACTIONS

There are a number of well known reactions which may be used to define the oxidation and hydration states of magmas and which illustrate the point we wish to make here. Some of these are as follows:



Reaction (a) is well known through its utilization in experimental buffer systems. However its use in natural rocks is restricted to quite reduced assemblages in which the olivine is sufficiently iron-rich to coexist with free silica. For this reason reactions (b) and (c) are more useful since they are applicable to a wider range of conditions.

It may be shown that for the pure system $\text{FeO} - \text{O}_2 - \text{SiO}_2$ the oxygen fugacity temperature curves for all three reactions virtually coincide with curve

(a) as shown in Fig. 1. The applicability of reactions (b) and (c) to the pyroxenes will of course depend on the stability of FeSiO_3 with respect to pressure (Lindsley, Speidel and Nafziger, 1968). However this stability field is probably expanded to much lower pressures than that of pure FeSiO_3 by only modest amounts of MgSiO_3 (Olsen and Mueller 1966). It appears that in at least some batholiths these minimal pressure requirements were met since quite iron-rich pyroxenes are present (Fig. 2).

Wones and Eugster (1965) have given an extensive discussion of the stability relations in the system phlogopite-annite and reaction (d). Although the biotites of batholiths deviate somewhat in composition from the phlogopite-annite series, it is likely that their oxidation relations are similar. Fig. 2 indeed shows that all the ferromagnesian minerals follow similar variation trends with respect to $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ and that their Fe^{2+} - Mg distribution coefficients do not differ from unity by much more than a factor of 2. Consequently it appears in each mineral $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ reflects the oxygen fugacity in approximately the same way.

Reference to Fig. 1 shows that in the case of the anhydrous reactions (a), (b) and (c), Po_2 must decrease substantially to maintain a constant composition of the silicates as the temperature decreases during crystallization-differentiation. It also shows that if $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ increases during differentiation, as is implied by Fig. 2, Po_2 must decrease even more than for a constant $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ ratio.

EVIDENCE FOR THE OXIDATION STATES OF CALC-ALKALINE MAGMAS

Some time ago it was shown by Larsen and Draisin (1948) and by Larsen and Schmidt (1958) that in the Southern California and Idaho batholiths the

atomic fraction $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ of the pyroxenes, biotites and hornblendes all increased systematically in the apparent differentiation sequence gabbro-granite (Fig. 2). More recent data such as those of Best and Mercy (1967) confirm this effect in other plutons.

Recently also thermochemical data for the assemblage orthopyroxene-magnetite-quartz (Reaction (b)) were utilized to calculate the oxygen fugacities as a function of the mineral compositions (Mueller 1967, 1969). It was concluded from this study that in the Southern California batholith the systematic change in $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ shown by Fig. 2 might correspond to as much as a ten order of magnitude decrease in oxygen fugacity between the gabbros and granites. A large part of this decrease in oxygen fugacity is attributable to the normal variation with temperature at a constant activity ratio $a_{\text{H}_2\text{O}}/a_{\text{H}_2}$ in the magma. However Fig. 1 indicates that such a constant ratio might correspond to a decrease in $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ of orthopyroxene (and olivine) since curve (a) has a steeper slope than the curves of constant $\text{H}_2\text{O}/\text{H}_2$. Therefore the increase in $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ observed may well correspond to a decrement in Po_2 in addition to that already implied by a constant $a_{\text{H}_2\text{O}}/a_{\text{H}_2}$ ratio. Consequently it is possible that $a_{\text{H}_2\text{O}}/a_{\text{H}_2}$ actually decreased during differentiation, and that this decrease is attributable to the strong reaction of H_2O with the Si-O-Si bridges of the silicate melt (Mueller, 1969). Interestingly enough the same reaction can also account for the very existence of the calc-alkali series since it greatly enhances the solubilities of the quartzo-feldspathic constituents relative to those of the ferromagnesian constituents (Mueller, 1969). As a consequence enrichment of the melt in quartz and feldspar occurs during differentiation. As far as the oxygen fugacity is concerned in this scheme it bears little relation

to any possible buffering effect of the ferromagnesian minerals since their abundances are usually too low, as we shall show presently. Indeed the ferromagnesian mineral compositions may be regarded as simply reflecting the oxidation state engendered by the fluid interactions within the melt.

STOICHIOMETRY OF OXIDATION

The control of oxygen fugacity through buffer systems depends not only on the proper choice of reactions but also on a sufficient quantity of buffer being presented to prevent exhaustion by the reactions. Consequently the oxidative capacity of magmatic components such as crystalline precipitates or dissolved iron depends greatly on their quantity relative to the quantity of the competing oxidant such as dissolved water or carbon dioxide. In the case of relatively anhydrous magmas such as those of the Skaergaard complex the ferromagnesian components were adequate to provide something approaching a true buffer capacity except that we have little reason to believe that the system remained univariant since the silicates increased in iron content. However as the water content is increased the capacity of the ferromagnesian constituents to control the oxygen fugacity is diminished.

To illustrate the oxidative capacity of the components of a typical hydrous calc-alkali magma we may consider a system of the composition of granodiorite with the following characteristics:

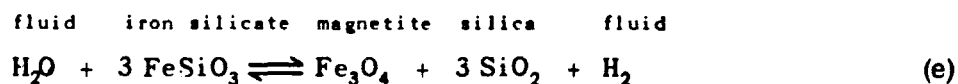
3 wt percent H_2O

$T \sim 1000^\circ K$

10 wt percent ferromagnesian minerals

$$\frac{H_2O}{H_2} = \frac{100}{1}$$

For purposes of the calculation it is helpful to convert the components to molecular values. According to Shaw (1965) 3 weight per cent H_2O is approximately equivalent to 10 mole percent H_2O in a melt with a composition corresponding to the region of the temperature minima in the system $Ab-Or-SiO_2-H_2O$. We shall assume the same data apply to the granodiorite composition. Fig. 2 shows that in this composition range, with $An \sim 30$, the parameter $Fe^{2+} / (Fe^{2+} + Mg) \sim 0.5$ in the ferromagnesian silicates. However in a complex silicate such as mica or hornblende the quantity of $FeSiO_3$ is even more diluted by constituents such as Al_2O_3 . Now it is apparent that the quantity of the Niggli formula unit $1/2 Fe SiO_3$ is less than the weight percent of the same constituent so that an assumption of a 6 mole percent value of $1/2 Fe SiO_3$ in the granodiorite represents a safe upper limit. We may now rewrite reaction (b) as a prototype of the limiting reaction for oxidation:



We assume that this reaction represents the general oxidation of ferrous silicate in all the ferromagnesian minerals. Then for each unit of $1/2 FeSiO_3$ that reacts, one unit of H_2O is destroyed and one unit of H_2 is formed. Consequently if 6 mole percent $1/2 FeSiO_3$ reacts it will use up ten percent of the H_2O present and the final ratio is

$$\frac{H_2O}{H_2} = \frac{90}{11}$$

Thus to decrease H_2O/H_2 by one order of magnitude it is necessary to oxidize all the ferrous silicate present in the granodiorite magma.

If the ratio H_2O/H_2 is decreased during calc-alkaline differentiation by the oxidation of ferrous silicate there is no evidence for it. Indeed we have already seen evidence (Fig. 2) that $FeSiO_3$ accumulates in the melt and the precipitating crystals as differentiation proceeds just as it did in the Skaergaard complex. Thus it appears that as the water content of a magma rises the iron compounds have less effect and something akin to the role of a buffer is played by the fluid constituents of the magma. To a first approximation the oxygen fugacity of the magma is at each stage of differentiation controlled by a_{H_2O}/a_{H_2} ratio of the dissolved fluid. This ratio is in turn determined by the initial condition and by the differential loss of H_2 and H_2O during differentiation. However, it is also determined by the differential interaction of H_2O and H_2 with the melt components (Mueller, 1969) and more particularly with the Si-O-Si bridges whose number steadily increases as differentiation proceeds.

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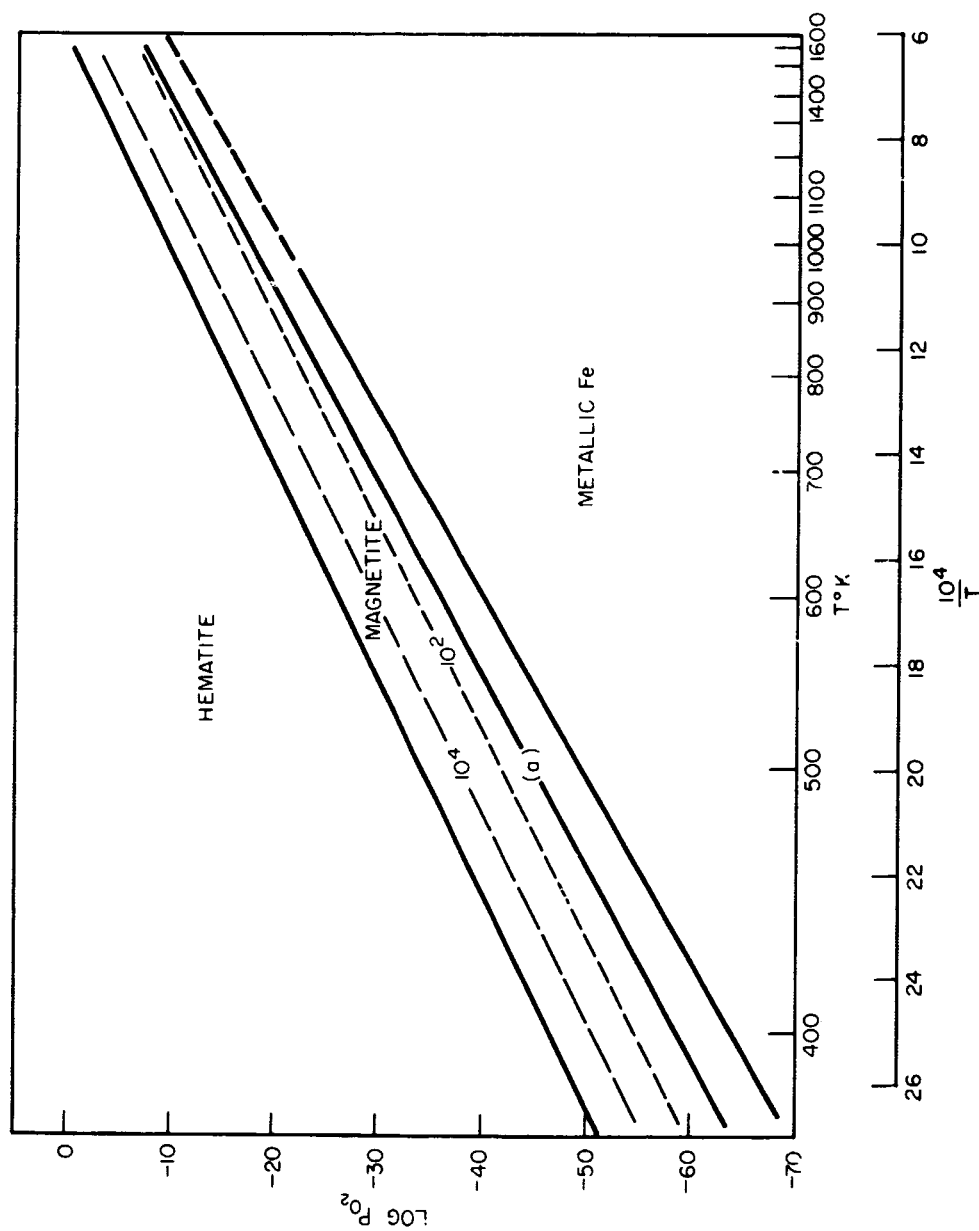


Figure 1. Oxygen fugacity as a function of temperature for three heterogeneous reactions as shown by curve (a) and for the decomposition of water as shown by the dashed lines. The numbers refer to constant H_2O/H_2 ratios assuming perfect gaseous mixtures. The data have been superimposed on the phase boundaries for the pure system $Fe-O$, but the field of wüstite is not shown.

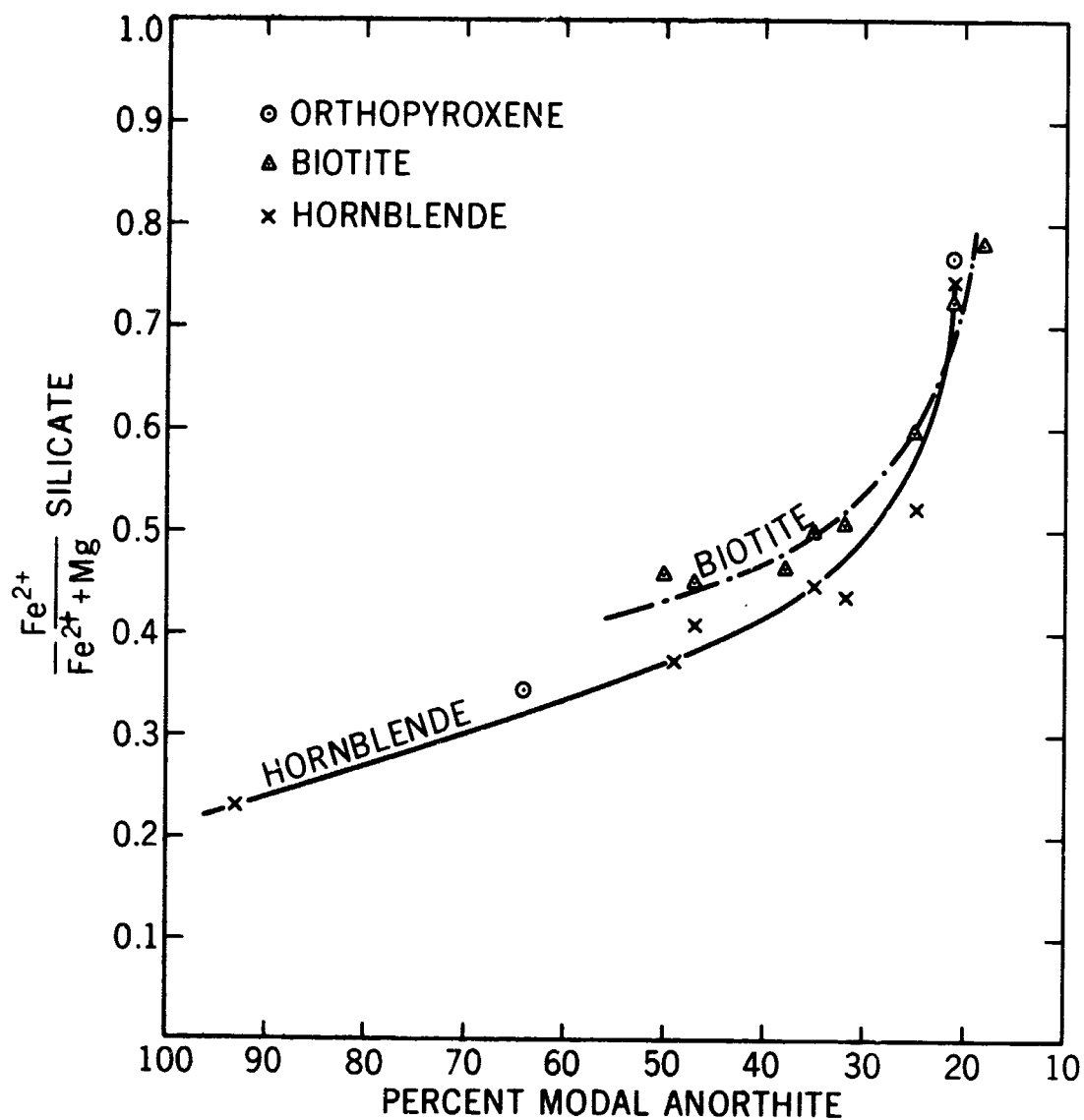


Figure 2. Atomic fraction $\text{Fe}^{2+} / (\text{Fe}^{2+} + \text{Mg})$ as a function of the anorthite content of plagioclase for minerals from the batholith of Southern California. Data are from Larsen and Draisin (1948).