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OXIDATION IN HIGH TEMPERATURE PETROGENESIS

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ABSTRACT. A study has been made of a variety of metamorphic and magmatic rocks to determine how oxidative processes are reflected in their mineral assemblages. In this study particular attention is paid to solid solutions.

Field and experimental evidence agree with theory as to the responses of ferromagnesian solid solutions to compositional changes of the coupled gas phase. Typical of these responses are the increases shown by the ratios Fe_2O_3/FeO and $MgO/(MgO + FeO)$ with increasing P_{O_2}.

Attention is also directed to the consequences of the normally low values of P_{O_2}/P_{H_2O} to gaseous transport by bodily flow and diffusion in regional metamorphism.

Examples of oxidative and related processes are drawn from regionally metamorphosed iron formations of Quebec and the Lake Superior region, from numerous contact metamorphic deposits, from the extrusives of the San Juan region of Colorado, and from other magmatic provinces. A thermodynamic unity of response to oxidative processes is shown by these different rock types.

INTRODUCTION

Viewed in its broadest sense the process of oxidation[1] is the fundamental reaction of petrogenesis. Ironically in the case of the highly oxidized crust of the Earth, consisting largely of oxygen and metallic ions of fixed valence state, this is apt to be forgotten. In the science of metallurgy and in the study of metallic ore deposits the effects of oxidative processes are often obvious because of the conspicuous interactions of oxide and metallic phases. However, in "ordinary" rocks as well, oxidative reactions manifest themselves in subtle and often intriguing ways. This is especially true of rocks which contain phases, such as the ferromagnesian silicates, which show extensive solid solubility of the ferrous iron and magnesian components.

The effects of oxidation may be expected to assume importance in any environment that contains substantial amounts of elements with variable valence states. Rocks falling into this category are very abundant and include representatives from nearly every petrogenic environment. Of peculiar interest in this respect are the meteorites and other extraterrestrial bodies now increasingly under investigation. Evidence of reactions between the condensed phases of these bodies and various gases may be of great significance in the study of their gravitational and temperature history. Equally interesting are the terrestrial iron-rich representatives of regionally and contact-metamorphosed rocks and the magma series and their consolidated equivalents.

This paper will be confined to the study of terrestrial metamorphic and magmatic rocks. The object here is to define more precisely the role in petrogenesis of high temperature oxidative reactions connecting gases and phases showing solid solubility, but some consideration will also be given to magmatic differentiation. Although the simultaneous consideration of such broad categories as metamorphic and magmatic rocks may seem overambitious, it is hoped that such a treatment will reveal the underlying thermodynamic unity of oxidative processes in those widely varying rock types.

[1] Here the term oxidation is used in a sense which includes reduction as well.

OXIDATION IN REGIONAL METAMORPHISM

Environmental conditions.—In order to understand the effects of oxidation in regional metamorphism it is necessary to consider the conditions which particularly characterize this environment. Geologic evidence leads to the conclusion that, in contrast with contact metamorphism, relatively uniform conditions of pressure and temperature over wide regions and isolation from the atmosphere are characteristic.

One of the most interesting questions with respect to this environment concerns the role of an oxygen-containing gaseous phase. Evidence that such a phase must arise frequently during the course of development of most dynamothermally metamorphosed rocks is the presence of healed and partially healed fractures of every age. These as well as intergranular imperfections seem to assure the presence of at least some gas at every stage. It would seem that only the presence of a liquid phase under high pressure could prevent the appearance of a gas. However, even under these conditions oxygen would exert its influence through the medium of the liquid solution.

Mineral indicators of P_{O_2}.—In the gaseous phase oxygen exerts a partial pressure along with such gases as H_2O, CO_2, H_2, and CO. The relations between these gases and the coexisting solid phases are of great consequence to the ultimate mineralogy. Among the most significant mineral assemblages are those containing magnetite and hematite. The significance of these oxides lies in their wide occurrence and that they may, when associated, define P_{O_2} as a univariant function of the temperature. Under these circumstances the system is said to be buffered with respect to oxygen. Over the greatest part of the temperature range of regional metamorphism the actual value of P_{O_2} for the system hematite–magnetite is vanishingly small, of the order of 10^{-40} to 10^{-10} atmospheres. An important consequence of these low pressures is that only small quantities of oxides need react to bring about relatively great changes in P_{O_2}. The practical aspects of such systems are attested by the fact that they have been used (Eugster, 1957) to control P_{O_2} in experimental work.

The pertinent reaction for the hematite-magnetite association is the following:

$$\underset{\text{hematite}}{Fe_2O_3} \rightarrow \underset{\text{magnetite}}{2/3\ Fe_3O_4} + 1/6\ O_2 \quad . \qquad \textbf{(a)}$$

The equilibrium curve for this reaction is shown in figure 1.[2] This curve puts limits on the partial pressure of oxygen in rocks which contain one or more of these oxides in equilibrium with the gas. Thus, if we know that a magnetite-bearing rock crystallized in the neighborhood of 500°C, we see from figure 1 that P_{O_2} was probably less than 10^{-19} atmospheres. Conversely if the same rock contained hematite, we should suspect that P_{O_2} was greater than 10^{-19} atmospheres. Of course these conclusions require that the magnetite and hematite concerned be pure compounds as written in reaction (a). This requirement is more apt to be met in hematite than in magnetite, as the latter may under certain conditions dissolve considerable amounts of MgO or other oxides depending on their concentration in the system and the temperature.

[2] This curve is calculated from the equation $\log P_{O_2} = \dfrac{-119240 + 67.62T}{2.303\ RT}$ (see Kubascheuski and Evans, 1958).

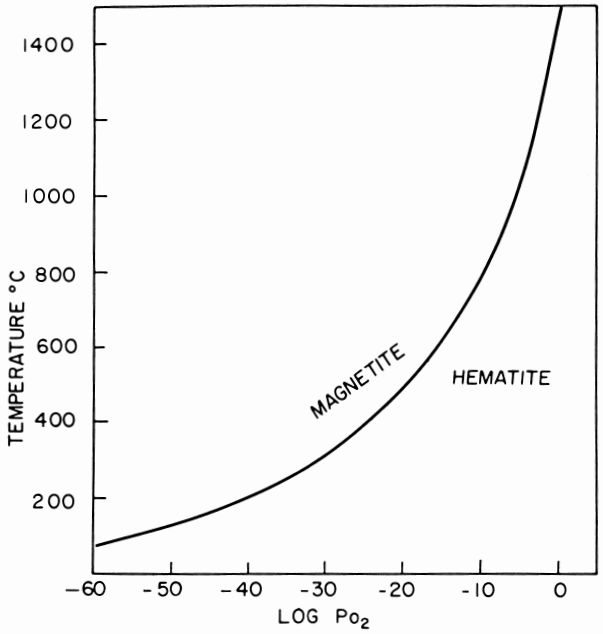

Fig. 1. Stability fields of magnetite and hematite.

Correlation of P_{O_2} with crystalline phases may also be extended to the silicates which form solid solutions. Consider the following mineral assemblages which occur in the Quebec iron formation (Mueller, 1960):

1	2	3
actinolite	actinolite	actinolite
talc	talc	talc
magnetite	hematite	magnetite
hematite	dolomite	quartz
calcite	quartz	
dolomite		
quartz		

We wish to compare these three assemblages to see how the atomic ratio MgO/(MgO + FeO) of actinolite is related to the different values of P_{O_2} implied by the different oxides present. The pertinent reactions are as follows:

$$\underset{\text{ferrotremolite}}{1/5\ Ca_2Fe_5Si_8O_{22}(OH)_2} + \underset{\text{hematite}}{Fe_2O_3} + \underset{\text{talc}}{1/3\ Mg_3Si_4O_{10}(OH)_2} \rightarrow$$

$$\underset{\text{tremolite}}{1/5\ Ca_2Mg_5Si_8O_{22}(OH)_2} + \underset{\text{magnetite}}{Fe_3O_4} + \underset{\text{quartz}}{4/3\ SiO_2} + 1/3\ H_2O\ , \qquad \text{(b)}$$

$$\underset{\text{ferrotremolite}}{1/5\ Ca_2Fe_5Si_8O_{22}(OH)_2} + \underset{\text{talc}}{1/3\ Mg_3Si_4O_{10}(OH)_2} + 1/4\ O_2 \rightarrow$$

$$\underset{\text{tremolite}}{1/5\ Ca_2Mg_5Si_8O_{22}(OH)_2} + \underset{\text{hematite}}{1/2\ Fe_2O_3} + \underset{\text{quartz}}{4/3\ SiO_2} + 1/3\ H_2O\ , \qquad \text{(c)}$$

ferrotremolite talc

$$1/5\ Ca_2Fe_5Si_8O_{22}(OH)_2 + 1/3\ Mg_3Si_4O_{10}(OH)_2 + 1/6\ O_2 \rightarrow$$
tremolite magnetite quartz
$$1/5\ Ca_2Mg_5Si_8O_{22}(OH)_2 + 1/3\ Fe_3O_4 + 4/3\ SiO_2 + 1/3\ H_2O \quad . \quad (d)$$

It should be noted that the end members of the solid solution series actinolite as well as talc, quartz, and water enter into all three reactions with the same stoichiometric coefficients, and that in fact the three reactions differ only by multiples of reaction (a). All of the mineral components which enter into the three reactions occur in assemblage 1, and from this consideration it is apparent that in a thermodynamic sense all three reactions take place in this assemblage without the appearance of additional phases. However only reaction (c) may occur in assemblage 2 and only (d) in 3.

According to thermodynamics these reactions have corresponding equations involving the law of mass action. Since, however, tremolite and ferrotremolite as such do not occur in these rocks, but rather as mutually dissolved components of actinolite, their concentrations in this solid solution play an important role in the equations of equilibrium. This concentration may be expressed as $MgO/(MgO + FeO) = Xact$. Because the actinolite solid solution is probably approximately ideal, it may be shown (Mueller, 1960) that the two following equations provide a comparison of oxidizing conditions in assemblages 2 and 3 with those in the complete assemblage 1:

$$\frac{P_{O_2}{}^{1/4}}{(P'_{O_2})^{1/4}} = \frac{Xact\ (1-X'act)}{X'act\ (1-Xact)}\ , \quad (1)$$

and

$$\frac{P_{O_2}{}^{1/6}}{(P''_{O_2})^{1/6}} = \frac{Xact\ (1-X''act)}{X'act\ (1-Xact)}\ . \quad (2)$$

Here the single-primed symbols refer to assemblage 2, the double-primed ones to 3, and the unprimed to 1. It may be seen that these equations compare the composition of actinolite in the three assemblages in terms of P_{O_2}. In deriving these equations it was assumed (on the basis of other evidence) that P_{H_2O} and P_{CO_2} as well as the temperature were essentially the same where the three assemblages were formed, and that the environment differed only with respect to P_{O_2}.

Equations (1) and (2) refer a system in one oxidation state (assemblage 2 or 3) to a thermodynamically more restricted system in another oxidation state (assemblage 1). In terms of oxidation the reference system here is actually that involved in reaction (a) which is a subsystem to assemblage 1. That is, assemblages 2 and 3 fall in the stability fields of hematite and magnetite respectively, and the composition of actinolite varies accordingly.

The mineral assemblages 1, 2, and 3 illustrate the response of silicates containing ferrous iron and magnesium to different oxidizing conditions, the effect being an increase of the equilibrium concentration of magnesium with increasing oxygen pressure. How this is reflected in other assemblages of the Quebec iron formation is shown in figure 2.

Normally, however, another process plays a part in the response of iron-bearing silicates to varying P_{O_2}. This is the increase in the ratio Fe_2O_3/FeO with increasing P_{O_2}. Since, however, P_{O_2} is related to P_{H_2} by the reaction H_2O

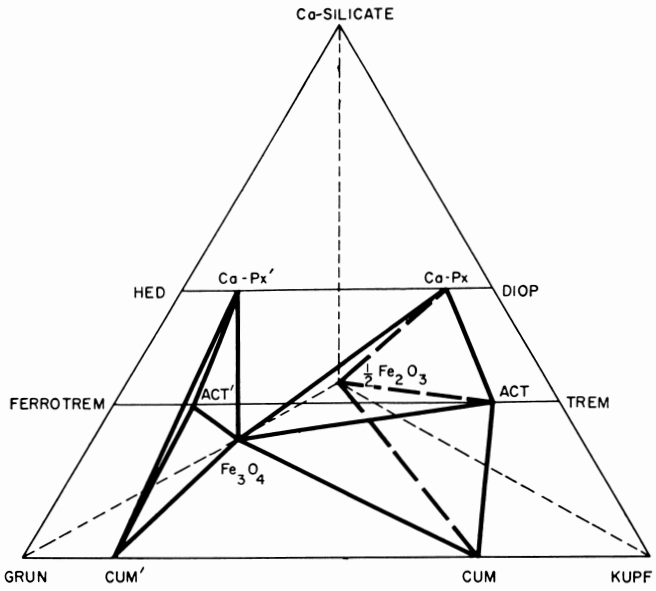

Fig. 2. Tetrahedron showing compositional relations of mineral assemblages from the Quebec iron formation (Mueller, 1960). Mineral symbols are as follows: kupf = kupfferite, grun = grunerite, trem = tremolite, ferrotrem = ferrotremolite, diop = diopside, hed = hedenbergite, cum = cummingtonite, act = actinolite, and Ca-px = Ca-pyroxene.

$\rightarrow \frac{1}{2}O_2 + H_2$, a loss of hydrogen may accompany an increase in Fe_2O_3/FeO in certain hydrous minerals. It is possible that the latter effect may account for certain brown hornblendes poor in hydrogen which characterize certain deepseated metamorphic rocks (Turner and Verhoogen, 1951). We shall return to this subject when the effects of oxidation on volcanic rocks are discussed.

To illustrate further the importance of oxidation in regional metamorphism we consider the Precambrian iron formations of the Lake Superior region. James (1955) has studied the progressive metamorphism of iron formations in northern Michigan and has divided these rocks on the basis of original sedimentary content, into sulfide, carbonate, silicate, and oxide facies. These sediments are represented by their metamorphosed equivalents ranging from chlorite- to sillimanite-rank metamorphism. An interesting feature of this metamorphism is that there appears to have been little change in the degree of oxidation during progressive metamorphism. Thus the original sulfide-organic carbon rocks of the sulfide sedimentary facies are represented by pyritic and graphitic slates in the higher metamorphic equivalents. Similarly the slightly oxidized magnetite-carbonate-greenalite-chert sediments are represented by magnetite-grunerite-quartz assemblages in the high-rank rocks. In this case there have been reactions between carbonate and silica to form grunerite without significant change in oxidation state. In the case of the originally more highly oxidized ferric oxide-chert-calcite-magnetite sediment, the end product of metamorphism is a specular hematite-quartz-magnetite-calcite assemblage.

Here again there has been little or no change in the degree of oxidation, and apparently P_{O_2} was kept high enough throughout metamorphism to prevent the formation of ferrous silicates. It is interesting in this connection that the occurrence of contemporaneously crystallized cummingtonite and hematite is very rare both in the Lake Superior region and in Quebec. Where this association does occur in the Quebec iron formation, the cummingtonite is found to be Mg-rich in accord with the principle already illustrated for actinolite. This feature is also shown by figure 2.

The relative stabilities of hematite and magnetite in regional metamorphism is sometimes a subject of speculation. It is obvious that this problem can be meaningful only in relation to figure 1. although in regional metamorphism the high pressures acting on the solid phases will alter this picture somewhat. It is also clear that in many cases the solubility of such oxides as MgO in magnetite may have to be considered. However, hematite is known to persist, and, as indicated above, iron formations seldom show any obvious reduction during progressive metamorphism, whereas great losses of H_2O and CO_2 often characterize these rocks under the same conditions. This differential degassing has a ready explanation if the equilibrium concentrations of the gases are taken into account. Bowen (1940) and Weeks (1956) have discussed a variety of univariant metamorphic reactions involving CO_2. From these reactions it may be seen that the equilibrium pressures of CO_2 in the carbonate-silicate reactions are usually of the order of 1 to 10^3 atmospheres at ordinary metamorphic temperatures. Similarly P_{H_2O} seems to be of the same general magnitude for many metamorphic dehydration reactions (Fyfe, Turner, and Verhoogen, 1958). These partial pressures are enormous when compared with the equilibrium values of P_{O_2} for reaction (a) as shown by figure 1. An important consequence of this is the following: If the equilibrium P_{H_2O} is only one atmosphere (a conservative value) over the hydrous silicates of a given rock, the ratio $P_{H_2O}/P_{O_2} \approx 10^{20}$, if magnetite and hematite are also present and acting as buffers. If magnetite alone is present this ratio may be even greater. Thus if the gases escape by mass movements along openings such as fractures, they will be lost in the ratio of their concentration or P_{H_2O}/P_{O_2}. Thus dehydration will greatly dominate reduction. The same argument also applies to P_{H_2}/P_{H_2O}, which will also generally be low as demanded by the equilibrium constant for the decomposition of water.

If on the other hand gases are lost by diffusion along intergranular boundaries, the relative rates of diffusion of the different species will play a part. If dm/dT is the material transferred across a unit area perpendicular to X per unit time,

$$\frac{dm}{dT} = -D \frac{dc}{dx} \tag{3}$$

is an expression for gaseous diffusion. Here D is the coefficient of self-diffusion, and dc/dx is the concentration gradient. The following relation also holds:

$$D = 1/3(\bar{v}\lambda) ,$$

where $\bar{v}$ is the mean molecular speed, and λ is the mean free path. Now since

$\bar{v}$ is a function only of the temperature and λ depends on the total molecular concentration. D is practically independent of the concentration for a gas with a low partial pressure. However, dc/dx is a function of c. Consequently dm/dT of gases such as O_2 and H_2 might be expected to be very small in regions buffered by such systems as magnetite-hematite, although it would be somewhat higher for hydrogen than for oxygen. As a result of these relations it may be concluded that oxide systems, once established in a particular part of a rock, are resistant to change by oxidation unless exposed to such over-riding effects as contact with the atmosphere or large volumes of highly oxidizing fluids. This, then, appears to be a logical explanation for the persistence in metamorphic rocks of distinct layers of minerals of various oxidation states.

Also it seems possible that conditions might sometimes arise under deep-seated metamorphism, such as might be encountered in the granulite facies, when P_{O_2} might be very low, perhaps corresponding almost to the stability field of metallic iron. Under these conditions P_{H_2} will be substantial, and consequently the differential loss of hydrogen by minerals might be an important factor.

Thus it seems that certain elements such as oxygen may be transported in significant quantities only if they are combined with another element to form a compound of high equilibrium partial pressure, for example, water. This aspect of diffusion has been discussed by Ramberg (1952).

OXIDATION IN CONTACT METAMORPHISM

General features.—Physico-chemical conditions in the vicinity of igneous intrusive bodies are likely to be characterized by a greater irregularity than those of regional metamorphism. Near the contact steep gradients in temperature, stress, and fluid pressures may be expected. Temperatures near these molten bodies of rock will be higher than any except those encountered under the highest grade of regional metamorphism. Pressure, on the other hand, may be considerably lower, as the majority of recognized contact phenomena probably occurred under relatively shallow conditions. This is especially true for the extensive group of contact rocks of the western United States discussed in this paper. Many of these rocks are regarded on the basis of geologic evidence to have formed at less than a mile below the surface (Lindgren, 1928).

One of the most characteristic features of contact deposits is the widespread associated metasomatism which sediments near the contact have undergone. Heavy metals, silica, alumina, and sulfur have been introduced in great quantities at the expense of original sedimentary constituents such as CO_2. It should not be assumed, however, that metasomatism is any more prevalent in contact metamorphism than in regional metamorphism; it is simply true that the original unaltered sediments are more easily recognized for comparison in the case of contact metamorphism.

Contact metamorphic phenomena undoubtedly accompany every type of intrusion ranging from plutonic to shallow depths. It therefore might be expected that a sequence of contact phenomena that is the result of varying degrees of influence by the atmosphere should be realized. Increasing evidence of oxidation accompanied by loss of CO_2 should therefore characterize this se-

quence in general. The possible change of mineralogic assemblages and the change of composition of individual mineral species as reflections of these varying physico-chemical conditions in the sequence of environments is our concern here.

Characteristics of contact metamorphic mineral assemblages.—The contact metamorphic rocks which have received the greatest amount of attention are those associated with economic mineral deposits, especially in the western United States. The type of intrusion associated with these contacts is typically a small stock or a dike of Tertiary age. The intruded sediments were usually relatively unmetamorphosed before the intrusion.

Some of the most spectacular contact effects are achieved in carbonate-rich sediments. The chemical system involved in such contacts is usually dominated by the following components: CaO, MgO, FeO, Fe_2O_3, SiO_2, H_2O, and CO_2. It is seen that this system is identical to that of the carbonate iron formation discussed in the previous section on regional metamorphism. It will therefore be instructive to compare the two types of rocks. An additional important component, which often occurs in contact rocks, is Al_2O_3. This component appears to be essential in the formation of epidote, a common contact mineral. Other components such as S, Cu, etc., account for economic minerals, but these will not be considered here since they enter into the silicates in only small amounts.

One of the most common types of contact metamorphic assemblages in the western United States is that depicted in figure 3. The components of this figure are the same as for figure 2 except that Al_2O_3 is considered together

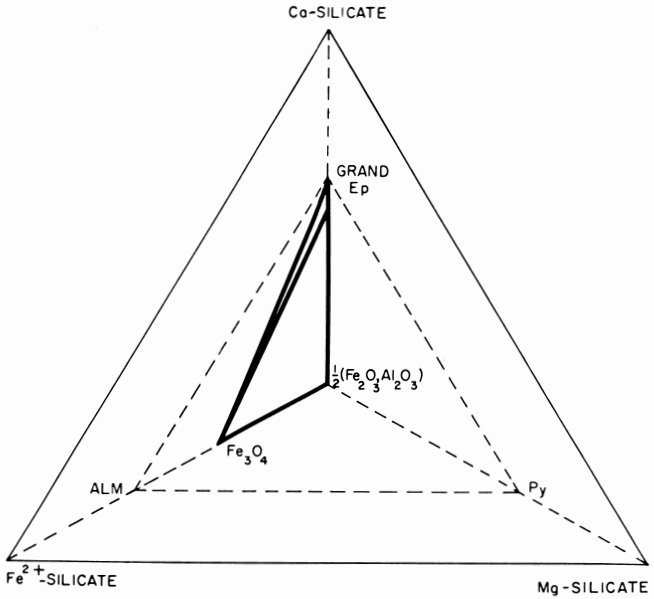

Fig. 3. Tetrahedron showing typical magnesium-poor contact metamorphic mineral assemblages. Mineral symbols are as follows: alm = almandine, py = pyrope, grand = grandite (andradite-grossularite), and ep = epidote.

with Fe_2O_3. The plane Alm-Py-Grand represents the garnets with the respective end members almandine, pyrope, and grandite (andradite-grossularite) as corners. Typical representatives of the assemblage epidote-grandite-magnetite are widespread in the Glifton-Morenci district of Arizona (Lindgren, 1905). The assemblage as shown in figure 3 is magnesium-poor. The exclusion of the possibility of the association grandite-epidote-hematite in figure 3 is only apparent because this figure does not differentiate between Fe_2O_3 and Al_2O_3 and does not show the component H_2O. The latter assemblage is, in fact, common and illustrates the fact that diagrams such as figure 3 should be regarded only as aids to presentation. Few if any conclusions regarding equilibrium mineral association may be drawn from them. Figure 3 does, however, illustrate the highly oxidized nature of this assemblage. Analyses of garnets from these assemblages show them to be nearly pure andradite (Lindgren, 1905). The widespread occurrence of these assemblages in the western United States is in harmony with the shallow nature of the contact phenomena.

If Mg is an important component, additional assemblages similar to those of figure 4 will result. Figure 4 is based on the same components as figure 3 but shows in addition the solid solutions actinolite and Ca-pyroxene. The small distorted tetrahedron of figure 4 shows the assemblage garnet-Ca-pyroxene-actinolite-hematite. Such minerals as quartz and calcite, although not shown in figures 3 and 4, are possible additional phases. The actual position of the tie line connecting Ca-pyroxene and actinolite in figure 4 is taken from a representative occurrence of this assemblage at Iron Mountain, Missouri (Allen and Fahey, 1952, 1956). The atomic ratio $MgO/(MgO + FeO)$ is essentially the same in both minerals and is equal in this case to approximately 0.72. The relation $(MgO/(MgO + FeO))$ Ca-pyroxene $= (MgO/(MgO + FeO))$ actinolite was also found for these coexisting species in the Quebec iron formation (fig. 2). This seems to imply either that the two occurrences were formed near the same temperature or that the distribution of Mg and Fe^{2+} is not very sensitive to temperature.

One of the most interesting things about figure 4 is the actual magnitude of $MgO/(MgO + FeO)$. To see what is involved here we consider the following reactions:

$$\underset{\text{ferrotremolite}}{1/5\ Ca_2Fe_5Si_8O_{22}(OH)_2} + 2/5\ CO_2 + 1/4\ O_2 \rightarrow \underset{\text{calcite}}{2/5\ CaCO_3} + \underset{\text{hematite}}{1/2\ Fe_2O_3} + \underset{\text{quartz}}{8/5\ SiO_2} + 1/5\ H_2O\ , \qquad \text{(e)}$$

$$\underset{\text{hedenbergite}}{CaFeSi_2O_6} + CO_2 + 1/4\ O_2 \rightarrow \underset{\text{calcite}}{CaCO_3} + \underset{\text{hematite}}{1/2\ Fe_2O_3} + \underset{\text{quartz}}{2\ SiO_2}\ . \qquad \text{(f)}$$

Since ferrotremolite and hedenbergite are components of actinolite and Ca-pyroxene respectively, it is obvious that the composition of the latter minerals may be expected to be complex functions of the temperature and the partial pressures of H_2O, CO_2, and O_2. Thus the actual positions and slopes of the tie lines of figure 4 also depend on these variables. Reactions (e) and (f) indicate

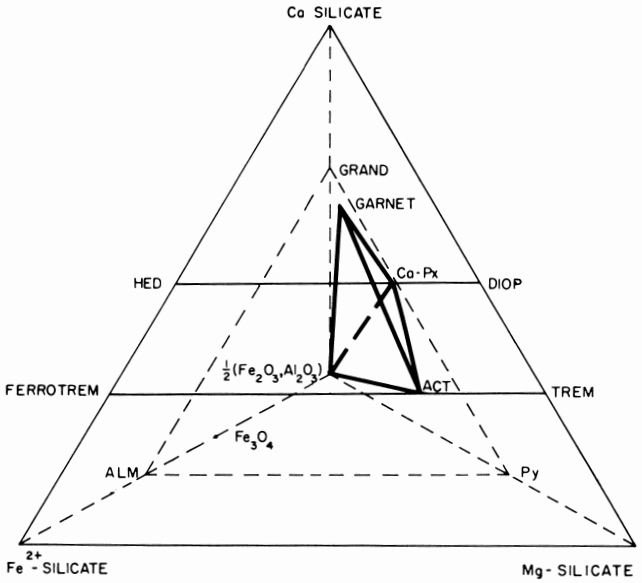

Fig. 4. Tetrahedron showing typical magnesium-rich contact metamorphic mineral assemblage. Mineral symbols are as follows: alm = almandine, py = pyrope, grand = grandite (andradite-grossularite), hed = hedenbergite, diop = diopside, ferrotrem = fertotremolite, trem = tremolite, Ca-px = Ca-pyroxene, and act = actinolite. Compositions of the coexisting minerals are taken from Allen and Fahey (1952, 1956).

that, if the temperature and P_{H_2O} and P_{CO_2} are held constant, increasing P_{O_2} leads to a decrease of the equilibrium concentration of Fe^{2+} in actinolite and Ca-pyroxene. However, if P_{H_2O}, P_{CO_2} and T are allowed to vary, their individual or combined effects may cancel out the effect of P_{O_2}. Thus each mineral assemblage must be studied in terms of the total environment. However it is still possible and even probable that in a large number of occurrences of a given assemblage there will be a statistical correlation between MgO/(MgO + FeO) and P_{O_2}. The statistical nature of such a correlation would not be due to any caprice on the part of nature but would rather conform to definite and expectable variations in the other variables.

An examination of the literature of contact metamorphism seems to indicate that such a correlation does exist. Unfortunately, adequate descriptions of coexisting minerals and the compositions of those minerals are rare in the literature. However, existing information all points to a relation similar to that shown by the Quebec iron formation. In the assemblages such as those of figure 4, which contain hematite and ferromagnesian silicates, the latter tend to be magnesium-rich. The assemblage of Iron Mountain, Missouri has already been referred to. Also in many of the ore deposits of New Mexico (Lindgren, Graton, and Gordon, 1910), where specular hematite is very widespread, the Ca-pyroxene and actinolite associated with specularite are usually described as "diopside" and "tremolite" or as being virtually colorless (and thus implying low iron). Table 1 shows the occurrence of contact metamorphic minerals in New Mexico by districts, as presented by Lindgren, Graton, and Gordon. The

TABLE 1

Minerals of contact-metamorphic deposits of New Mexico by district (after Lindgren, Graton, and Gordon (1910))

	calcite	quartz	garnet	epidote	wollaston.te	diopside	tremolite	specularite	magnetite	pyrite	chalcopyrite	galena	zincblende	molybdenite	Remarks
Elizabethtown	+		+	+		+	+	+	+	+	+				scapolite and pyrrhotite present
Cimarrocito	+		+	+				+	+	+	+				
Ortiz			+												gold present
San Pedro	+		+		+	+	+	+		+	+				biotite present, vesuvianite reported
Magdelena	+	+		+		+	+	+	+	+	+	+	+		
Jones Camp									+						
Jarilla	+	+	+	+		+	+	+		+	+				
Organ	+	+	+	+		+		+	+	+	+		+	+	bismuth mineral present
Modoc	+			+								+	+		
Tres Hermanas	+	+	+		+	+						+	+		only oxidized zinc ores present
Hanover	+	+	+	+		+	+	+	+	+	+		+	+	hedenbergite, ilvaite present
San Simon	+	+	+	+	+	+				+	+				
Apache No. 2	+		+							+	+				scheelite present
Hachita (Copper Dick)	+		+			+					+				

table does not necessarily imply that the minerals coexist. The relatively highly oxidized character of these deposits is clearly indicated by the mineralogy that corresponds to figures 3 and 4. The writer knows of no instance in the literature where ferromagnesian minerals rich in ferrous iron are described as coexisting with hematite, although such associations have a theoretical possibility of occurrence by certain combinations of variables.

Although ferromagnesian minerals coexisting with hematite tend to be poor in ferrous iron, those coexisting with magnetite are frequently rich in this ion. As examples of the latter we have the magnetite-pargasite-hedenbergite tactites described by Holser (1950) from the Phillipsburg region, Montana, and magnetite-hedenbergite-cummingtonite assemblages from New Mexico (Allen and Fahey, 1957).

It would seem from this cursory examination that the whole subject of the relationships of the silicates to the oxides, sulfides, and other ore minerals of contact metamorphic deposits needs re-examination in the light of modern theoretical and experimental methods.

OXIDATION IN MAGMATISM

Oxidation in differentiating and consolidating magmas as related to environmental complexities.—If an attempt is made to imagine the possible variations of physico-chemical environment in magmatism, it is apparent that a very great variety of such environments with respect to oxidation are possible. This will apply especially to magmas which consolidated eventually to hyabyssal or extrusive rocks. The partial pressure, or more properly, the activity of oxygen may be expected to play an important role in magmatic differentiation wherever iron is a major constituent; but even after consolidation of magmas, oxidative reactions between crystalline phases and gases, especially those derived from, or escaping to the atmosphere, may be expected to work significant modifications in the mineralogy.

In considering the influence of variables such as P_{O_2} on the history of magmas it is well to keep in mind the differences between the possible compositional variability of crystals and liquids. As may be seen by consideration of the many reactions between solids and between solids and gases in metamorphism, crystals have a somewhat restricted latitude of compositional range as compared with liquids. The variability in crystals tends to take the form of well-defined series of solid solutions. For example, Ca-pyroxene may often be considered as a simple solution of Mg and Fe^{2+} end members. Therefore the only possible response to oxidative processes of this mineral series is a change in the ratio $MgO/(MgO + FeO)$. Correspondingly large changes in the ratio Fe_2O_3/FeO may be brought about only by the simultaneous substitution of an ion such as Na^+ for Ca^{2+}. However, in a mineral such as hornblende, as we have seen, change of Fe_2O_3/FeO is also possible by a simultaneous change in the hydrogen content.

Because of their disordered state silicate melts are not thus restricted, and the mutual solubilities of almost all major rock-forming oxides extends over wide ranges of composition. Thus many paths of crystallization are possible along the liquidus during early stages of crystallization. As crystallization pro-

gresses, however, the available paths become more limited due to the simultaneous crystallization of a number of minerals and lead eventually to a small number of univariant paths on which the compositions of the liquid and the coexisting crystals are functions of such variables as T, P_{H_2O}, P_{CO_2}, and P_{O_2}. This is well illustrated in the experimental system MgO–FeO–Fe_2O_3–SiO_2 to be discussed later.

As mentioned above, after consolidation the magmatic rock is subject to continued alteration. This is especially true for siliceous extrusives such as rhyolite, which suffer extensive explosive disruption and fracturing. In these rocks residual fluids and atmospheric gases penetrate along every fracture, and a new mineralogy may develop as a consequence.

The mineralogy of the San Juan extrusives.—One of the most thoroughly studied magmatic provinces is that of the San Juan region of Colorado. Of special importance are the papers by Larsen and Cross (1956) and Larsen, Irving, Gonyer, and Larsen (1936, 1937), which contain a wealth of information on many aspects of magmatism, and especially such as involve the effects of oxidation and loss of volatiles on the mineralogy.

In the San Juan region extensive pyroclastics, flows, and shallow intrusives ranging from basalt to rhyolite developed during Tertiary time. These rocks present to the inquiring mineralogist an almost infinite variety of natural experiments in silicate chemistry. Single flows show evidence in the form of phenocrysts of magmatic differentiation at depth. These phenocrysts also bear witness to subsequent changes in the composition of dissolved volatiles during extrusion. The groundmass mineralogy reflects still later phenomena. Finally there is evidence of extensive reaction between late crystals of fractures and vesicles and gas phase.

One interesting observation made by Larsen, Irving, Gonyer, and Larsen (1936) is that the pyroxene phenocrysts of pyroxene andesites are higher in iron than those of quartz latites and rhyolites. This tendency is opposite to that noted by Larsen and Draisin (1948) in the plutonic rocks of the batholith of southern California and also to that noted by Chapman and Williams (1935) in the White Mountain magma series. Although Larsen considered this trend in the San Juan rocks to be at variance with experimental data of silicate systems, it is really not inconsistent with such data when proper account is taken of oxidation.

Most of the rocks of the San Juan volcanic series are conveniently classified as basalts, latites, quartz latites, and rhyolites, although most transitional varieties may be found. The most abundant minerals are olivine, clinopyroxene approaching pigeonite, orthopyroxene, augite, several varieties of hornblende and biotite, plagioclase, sanadine, quartz, tridymite, cristobalite, and a variety of iron oxides. Olivine and pyroxene are naturally more abundant in basalts, but several varieties of pyroxene also occur in the rhyolites, and olivine is found as phenocrysts in rocks that contain quartz in the groundmass.

The ferromagnesian minerals that crystallized at depth, as represented by phenocrysts, are similar in properties to corresponding plutonic minerals. These unaltered minerals derived from greater depths are best seen in parts of

flow which have reacted least with the gases escaping from the magma or derived from the atmosphere. For example, hornblende in the black glass at the base of some flows is green, whereas the red porous vesicular parts of these flows have basaltic hornblende. A pair of such hornblendes from the Alboroto rhyolitic quartz latite were observed to be identical in composition except that the basaltic hornblende contained little water and its iron was largely ferric. As might be expected, the hydroxyl-bearing ferrous iron phenocrysts such as biotite and hornblende show the greatest evidence of reaction with the residual silicate melt and the escaping gases. As Larsen and others (1936) proved from the chemical analyses, these phenocrysts are oxidized to oxyhornblende and oxybiotite in the lava flows, and every gradation between unoxidized and completely oxidized phenocrysts exists. The following are possible reactions in the formation of oxyhornblende and oxybiotite:

$$\underset{\text{ferrotremolite}}{Ca_2Fe_5^{2+}Si_3O_{22}(OH)_2} \rightarrow \underset{\text{oxyhornblende}}{Ca_2Fe_3^{2+}Fe_2^{3+}Si_3O_{24}} + H_2 \quad , \qquad \text{(g)}$$

$$\underset{\text{annite}}{KFe_3^{2+}Si_3AlO_{10}(OH)_2} \rightarrow \underset{\text{oxybiotite}}{KFe^{2+}Fe_2^{3+}Si_3AlO_{12}} + H_2 \quad . \qquad \text{(h)}$$

Oxidation by loss of hydrogen as shown is compatible with the chemical analyses which show a deficiency of water. However it is seen that loss of hydrogen alone results in the oxidation of only 2/5 of the ferrous iron in hornblende and 2/3 in biotite. Also it must be remembered that the ferrotremolite and annite components are usually mutually dissolved with other components such as tremolite and phlogopite.

From thermodynamic considerations it might be suspected that oxybiotite would be unstable relative to its reaction products as follows:

$$\underset{\text{oxybiotite}}{KFe^{2+}Fe_2^{3+}Si_3AlO_{12}} \rightarrow \underset{\text{sanadine}}{KAlSi_3O_8} + \underset{\text{magnetite}}{Fe_3O_4} \quad . \qquad \text{(i)}$$

The common occurrence of magnetite with partially resorbed phenocrysts of oxybiotite seems to confirm that the right side of reaction (i) is usually favored. It seems probable that oxyhornblende also is unstable since like oxybiotite it usually shows strong resorption.

Larsen and others (1937) point out that the resorption of hornblende gives rise to a pyroxene much poorer in total iron than the hornblende from which it was derived. The sum of the oxidation reactions undergone by hornblende may be roughly represented as follows:

$$Fe^{2+}\text{–rich hornblende} + O_2 \rightarrow \text{Mg-rich pyroxene} + \text{magnetite} + H_2O \quad . \qquad \text{(j)}$$

We see here again the same mechanism which was previously observed in the various metamorphic rocks. Similarly the same process may at times yield secondary hornblendes and biotites which by their paler color indicate a lower Fe-content than the original phenocryst minerals. In the flows of the Hinsdale formation, for example, Larsen and Cross (1956) describe a biotite of the gas cavities which is much lighter in color than that of the phenocrysts. Also hornblende of low iron content ($\alpha = 1.628$, $\gamma = 1.645$) is present in these cavities.

Other descriptions of late-crystallizing, pale-colored biotites are common in the paper by Larsen and Cross.

From these facts we may trace a complex and interesting series of events beginning with the crystallization of ferrous iron-rich phenocrysts at depth. On extrusion of the magma these phenocrysts are partially oxidized to oxybiotite and oxyhornblende by loss of H_2 to the atmosphere. Because of the inherent instability of these oxidized minerals, they are subsequently resorbed into the residual melt and reappear as oxides and Mg-rich pyroxenes of the groundmass, the Mg being derived from the melt or concentrated from the Mg-component of the original phenocrysts. Some of the groundmass pyroxenes may also crystallize directly from the phenocrysts by solid state reactions. Occasionally where P_{H_2O} is high enough, as in confined gas cavities, the Mg-rich biotites and hornblendes form by reaction with the gases. The formation of Mg-rich biotite in cavities left by escaping magmatic gases may be illustrated by the following reactions which also have considerable interest in other petrogenic environments:

$$\underset{\text{annite}}{KFe_3^{2+}Si_3AlO_{10}(OH)_2} + 1/2\,O_2 \rightarrow \underset{\text{sanadine}}{KAlSi_3O_8} + \underset{\text{magnetite}}{Fe_3O_4} + H_2O\,, \qquad (k)$$

$$\underset{\text{annite}}{KFe_3^{2+}Si_3AlO_{10}(OH)_2} + 3/4\,O_2 \rightarrow \underset{\text{sanadine}}{KAlSi_3O_8} + \underset{\text{hematite}}{Fe_2O_3} + H_2O\,. \qquad (l)$$

Of course the annite here must be regarded as being in mutual solid solution with $KMg_3Si_3AlO_{10}(OH)_2$ (phlogopite component). Similarly, sanadine is probably usually in mutual solid solution with an albite component, and even magnetite may dissolve $MgFe_2O_4$ (magnesioferrite) at higher temperatures. It is apparent that reactions (k) and (l) are driven to the right by increasing P_{O_2} and decreasing P_{H_2O}. The same effect is also accomplished by decreasing the total gas pressure. The right side of these reactions will also be favored by the spontaneous mixing of sanadine and magnetite in their respective solid solutions with albite and magnesioferrite.

If we consider a mineral assemblage composed of biotite, sanadine, magnetite, and hematite, the reactants and products of reactions (k) and (l), we have a system of five components[3] and five phases, including the gas. According to the phase rule this system is univariant under constant temperature conditions. Under these conditions the ratio MgO/(MgO + FeO) of biotite is a univariant function of the total gas pressure. Thus a gradually decreasing gas pressure in a gas cavity would be expected to favor a Mg-rich biotite as inferred from the light color of the biotites observed in these cavities.

Reaction (k) has also been studied experimentally by Wones (1958). In these experiments biotite was in equilibrium with sanadine, magnetite, and the fluid phase. The system therefore had a total of five components and four phases, giving three degrees of freedom. Consequently, if P_{H_2O} (substantially the total pressure) and T are held fixed, MgO/(MgO + FeO) in biotite is a univariant function of P_{O_2}. The following relations were observed (table 2):

[3] One possible choice of components according to reactions (k) and (l) is $KAlSi_3O_8$, FeO, Fe_2O_3, H_2O, and MgO.

TABLE 2

Experimental results after D. R. Wones (1958)

T°C	P_{H_2O} psi	P_{O_2} atm	Atomic ratio $Mg/(Mg + Fe^{2+})$
700	30,000	10^{-16}	0.23
700	30,000	10^{-18}	0.13
800	30,000	10^{-14}	0.44
800	30,000	10^{-15}	0.32

These results are perfectly consistent with the thermodynamic theory and the field relations as discussed.

It should be emphasized that here again, as in the case of metamorphic reactions, it will in most cases be impossible to consider oxidation independently from other effects such as hydration. It is usually only under experimental conditions that factors other than P_{O_2} can be held constant. But at times the same result may be studied by the observation in nature of selected mineral assemblages such as those involved in reactions (b) to (d).

The system MgO–FeO–Fe_2O_3–SiO_2.—Oxidative processes in magmatism are greatly elucidated by the study of analogous experimental systems. Therefore, the work of Muan and Osborn (1956) on the system MgO–FeO–Fe_2O_3–SiO_2 is worthy of special attention. This system has features in common with many natural systems. For example, the coexistence of two to three crystalline phases exhibiting extensive solid solubility between Mg and Fe^{2+} end members is characteristic of this important subsystem of petrogeny. These solid solutions coexist with the liquid over a wide range of temperatures and partial pressure of oxygen, and this effectively restricts the total number of solid phases which occur in the system. Thus the changing conditions of T and P_{O_2} are frequently reflected in changes in composition of the phases already present rather than in the disappearance of certain phases and the appearance of new ones.

Muan and Osborn have discussed three idealized types of crystallization. Only two of these types need concern us here; they are as follows:

I. The total composition of the condensed phases remains constant.

II. P_{O_2} remains constant but the total composition of the condensed phases may change.

Condition I is approximated in closed systems when the volume of the gas phase is small. The situation is then analogous to that prevailing in classical phase equilibria studies in nonoxidative systems. Condition II is achieved when the volume of the gas phase is large or when the reacting system is connected to a reservoir of gas of fixed composition.

During strong fractional crystallization under condition I, liquids that begin to crystallize in the primary phase volumes of olivine, pyroxene, magnesioferrite, or silica move toward and eventually reach quaternary univariant lines along which these liquids become enriched in Fe^{2+} and total Fe as crystalliza-

tion proceeds. Along these univariant lines there is a steady decrease in the ratio $MgO/(MgO + FeO)$ and Fe_2O_3/FeO. These same ratios of the contemporaneously separating crystals of olivine, pyroxene, and magnesioferrite undergo corresponding changes. The decrease of these ratios during crystallization is also correlated with a steady drop in P_{O_2}. Thus the general picture of liquidus crystallization in the system $MgO–FeO–Fe_2O_3–SiO_2$ is closely analogous to that in metamorphic rocks and more complex systems of consolidating lavas.

Under condition II, when P_{O_2} is constant during crystallization, the liquids cannot move down the quaternary univariant crystallization paths as discussed above but are confined to the isobaric surface. These liquids tend to become enriched in SiO_2 relative to all other constituents. Under these conditions there is comparatively little change in the ratios $MgO/(MgO + FeO)$ and FeO/Fe_2O_3 of the liquids or contemporaneously separating crystals.

Oxidation in magmatic differentiation.—Recently Osborn (1959) presented an interesting hypothesis which relates possible differentiation paths in a basaltic magma to different values of P_{O_2}. His reasoning is by analogy with the system $MgO–FeO–Fe_2O_3–SiO_2$ as discussed above.

According to Osborn, the types of crystallization in conditions I and II have their counterparts in magmas. Type I crystallization, in which the total composition of the condensed phases remains essentially constant, is thought to be represented by differentiates of nonorogenic zones, and especially the Skaergaard complex, whereas type II crystallization, in which P_{O_2} remains essentially constant, is thought to be represented by the calc-alkali-series of rocks of orogenic zones, and more specifically by the basalt-andesite-dacite-rhyolite series of the Cascade Mountains of Washington and Oregon. All possible gradations between the two types of crystallization conditions would, of course, be possible.

The basis for Osborn's hypothesis lies in the following facts: Fractional crystallization of type I leads in the experimental system to an iron-rich differentiate as it did also in the differentiation of the Skaergaard. Fractional crystallization of type II leads to an iron-poor, silica-rich differentiate in the experimental system. The latter two features are of course also characteristic of the calc-alkali series. Other evidence adduced by Osborn is in the form of similarities shown by subtraction diagrams of the experimental system and those derived from the rocks. In these arguments most of the emphasis is placed on changes in the percentage compositions of oxides and on the ratio $(FeO + Fe_2O_3)/(FeO + Fe_2O_3 + MgO)$.

Attention has already been called to the fact that in the system $MgO–FeO–Fe_2O_3–SiO_2$ liquids undergoing type I differentiation not only become rich in total iron but also show a marked decrease in the ratios Fe_2O_3/FeO and $MgO/(MgO + FeO)$. $MgO/(MgO + FeO)$ of the associated crystals of olivine, pyroxene, and magnesioferrite also changes in harmony with the liquid. This ratio in the crystals may, however, be quite independent of the early history of a magma series, as we have seen in the case of the San Juan lavas. The same may be true of the ratio Fe_2O_3/FeO in both the crystals and the total rock. Thus $MgO/(MgO + FeO)$ in crystals may reflect P_{O_2} conditions during

late stages of consolidation irrespective of previous Po_2 conditions during differentiation, as reflected in the ratio $(FeO + Fe_2O_3)/(Fe_2O + Fe_2O_3 + MgO)$ of the rocks. For example, although the latter ratio may remain constant in an extruding magma, most of the iron of the ferromagnesian silicates might be converted to magnetite or hematite. Thus the ratio $(FeO + Fe_2O_3)/(FeO + Fe_2O_3 + MgO)$ is apt to reflect major differentiation trends more faithfully latter are relatively better indicators of Po_2 conditions during late stages of consolidation of any given rock specimen.

It cannot be denied that the mechanism proposed by Osborn is operative in petrogenesis. Since, however, other crystallization trends may also lead to silica-rich differentiates, some idea of the quantitative contribution of Osborn's mechanism is desirable.

It seems intuitively obvious that, to at least a first approximation, the influence of a subsystem such as $MgO–FeO–Fe_2O_3–SiO_2$ upon a complex magma than either of the ratios $MgO/(MgO + FeO)$ and Fe_2O_3/FeO. However, the must be in some proportion to the quantity of the subsystem contained in the magma. Figure 5 is a plot of some important relations of the system $MgO–FeO–Fe_2O_3–SiO_2$ and a rock series presented for comparison (figures 9 and 11 of Osborn). From figure 5 it is seen that in the example of the experimental system chosen by Osborn for comparison with the rock series the ratio $(FeO + Fe_2O_3)/(FeO + Fe_2O_3 + MgO)$ corresponds to range andesite-dacite. From the rock analyses (Osborn, 1959) we see that the experimental system is

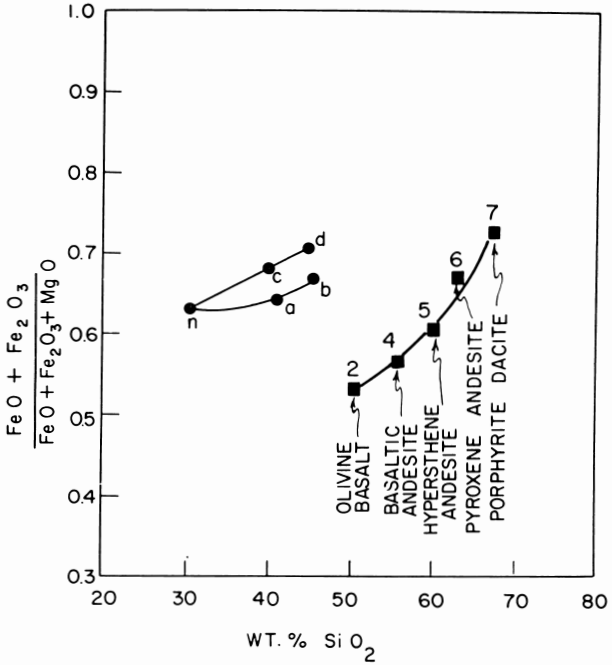

Fig. 5. Comparison of the experimental system $MgO–FeO–Fe_2O_3–SiO_2$ with Cascade volcanics which have been interpreted as a differentiation series. This figure is a composite of figures 9 and 11 of Osborn (1959).

contained in these rocks to the extent of roughly 15 percent during the differentiation interval n-c-d (fig. 5). The question then arises: Is this quantity sufficient to account for the approximately 4.5 percent rise in SiO_2 observed in the differentiation series 6-7 for this range? For the experimental crystallization path n-c-d (constant $P_2 = 0.21$ atm.) it is seen that SiO_2 increases 14.5 percent. If we multiply this figure by 0.15, corresponding to the approximate quantity of experimental subsystem contained in the rocks for the same range in the ratio $(FeO + Fe_2O_3)/(FeO + Fe_2O_3 + MgO)$, we arrive at the conclusion that the 14.5 change in SiO_2 in the subsystem corresponds to a 2 percent change in the rocks. It is obvious that the value calculated in this manner may be brought to better agreement with the observed value by choosing a different crystallization path such as n-a-b in the subsystem. This attempt at evaluating the influence of the subsystem $MgO–FeO–Fe_2O_3–SiO_2$ in natural systems is a relatively crude approximation, but it does seem to indicate that the mechanism proposed by Osborn is capable of producing changes of the right order of magnitude in SiO_2 in complex systems. Since the influence of the subsystem is related to the extent it enters into the composition of the differentiating magma, its influence gradually diminishes during differentiation at constant P_{O_2}. However, in differentiation under conditions of constant total composition, as in the Skaergaard, the influence of the subsystem should increase as differentiation progresses. In the case of the third Skaergaard liquid postulated by Wager and Deer, the system $MgO–FeO–Fe_2O_3–SiO_2$ comprises roughly 50 percent of the magma.

The point has been made here that the calc-alkali magma series appears to include sufficient quantities of the subsystem $MgO–FeO–Fe_2O_3–SiO_2$ to account for changes in SiO_2 on this basis alone. However, it is almost certain that in some differentiating magmas other subsystems, such as the system anorthite-albite, will also contribute heavily to the increase in SiO_2. The effect of these other systems might in many cases dominate over the influence of the system $MgO–FeO–Fe_2O_3–SiO_2$.

GENERAL CONCLUSIONS

It is apparent that manifestations of oxidative processes are widespread in many types of metamorphic and magmatic rocks. In some cases the oxidation reactions involved are between simple oxides or between oxide and metallic phases. Frequently, however, the reactions are very complex, involving changes in composition of complex crystals such as the ferromagnesian silicates. These silicate reactions may also be coupled to the gas phase through reactions involving other gases such as H_2O and CO_2. In the latter case oxidation can seldom be considered separately but must be regarded as simply a contributing factor to the total reaction. When, subject to circumstances defined by the phase rule, oxidative reactions can be isolated for study, they may on occasion be referred to simpler systems for comparison.

Mineralogic response to oxidative processes takes a similar form in all rocks that contain the same or similar mineral series, notably the ferromagnesian silicates. In these minerals the ratios $MgO/(MgO + FeO)$ and Fe_2O_3/FeO increase with increasing P_{O_2}. Similar and related responses are shown by

silicate melts of the system MgO–FeO–Fe_2O_3–SiO_2. These principles have been applied to differentiating magmas by Osborn (1959).

From the nature of the underlying thermodynamic unity of the mineralogic reactions, it seems natural to extend the principles discussed above to any mineral assemblage that implies reaction between solid solutions and gases. Thus, for example, the sulfide and metallic solid solutions, as well as the coexisting ferromagnesian silicates of ore deposits and many meteorites, might be studied with a view of deducing from the phase relations and crystal composition quantities such as the temperature of crystallization and the composition of the gaseous phase.

Although the number and complexity of the phases in natural deposits might at first appear to make analysis impossible, this is partly illusion. The methods of thermodynamics are adequate to cope with systems of great compositional complexity if adequate data are available. Also the presence of additional components in natural systems usually requires the appearance of additional phases which limit the number of degrees of freedom of the system. It is therefore the mineral assemblages with a high ratio of phases to components that are worthy of the closest study and that are most likely to provide clues to the physico-chemical environment of crystallization.

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REFERENCES

Allen, V. T., and Fahey, J. J., 1952, New occurrences of minerals at Iron Mountain, Missouri: Am. Mineralogist, v. 37, p. 736-743.

———— 1956, Actinolite at Iron Mountain, Missouri: Geol. Soc. America Bull., v. 67, p. 1664-1665.

———— 1957, Some pyroxenes associated with pyrometasomatic zinc deposits in Mexico and New Mexico: Geol. Soc. America Bull., v. 68, p. 881-896.

Bowen, N. L., 1940, Progressive metamorphism of siliceous limestone and dolomite: Jour. Geology, v. 48, p. 225-274.

Chapman, R. W., and Williams, C. R., 1935, Evolution of the White Mountain magma series: Am. Mineralogist, v. 20, p. 502-530.

Eugster, H. P., 1957, Heterogeneous reactions involving oxidation and reduction at high pressures and temperatures: Jour. Chem. Physics, v. 26, p. 1760.

Fyfe, W. S., Turner, F. J., and Verhoogen, Jean, 1958, Metamorphic reactions in metamorphic facies: Geol. Soc. America Mem. 73.

Holser, W. T., 1950, Metamorphism and associated mineralization in the Philipsburg region, Montana: Geol. Soc. America Bull., v. 61, p. 1053-1090.

James, H. L., 1955, Zones of regional metamorphism in the Precambrian of northern Michigan: Geol. Soc. America Bull., v. 66, p. 1455-1488.

Kubaschewski, O., and Evans, E. L., 1958, Metallurgical thermochemistry: London, Pergamon Press.

Larsen, E. S. Jr., and Cross, W., 1956, Geology and petrology of the San Juan region southwestern Colorado: U. S. Geol. Survey Prof. Paper 258.

Larsen, E. S., Jr., and Draisin, W. M., 1948, The composition of the minerals in the rocks of the batholith of southern California [abs]: Internat. Geol. Cong. 18th, London 1948, Rept., p. 6-7.

Larsen, E. S., Jr., Irving, J., Gonyer, F. A., and Larsen, E. S., 3rd, 1936, Petrologic results of a study of the minerals from the Tertiary volcanic rocks of the San Juan region, Colorado: Am. Mineralogist, v. 21, p. 679-701.

———— 1937, Petrologic results of a study of the minerals from the Tertiary volcanic rocks of the San Juan region, Colorado: Am. Mineralogist, v. 22, p. 889-905.
Lindgren, Waldemar, 1905, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, 375 p.
———— 1928, Mineral deposits, 3rd ed.: New York, McGraw-Hill Book Company, 1049 p.
Lindgren, W., Graton, L. G., and Gordon, C. H., 1910, The ore deposits of New Mexico: U. S. Geol. Survey, Prof. Paper 68, 361 p.
Muan, Arnulf, and Osborn, E. F., 1956, Phase equilibria at liquidus temperatures in the system MgO–FeO–Fe_2O_3–SiO_2: Am. Ceram. Soc. Jour., v. 39, p. 121-140.
Mueller, R. F., 1960, Compositional characteristics and equilibrium relations in mineral assemblages of a metamorphosed iron formation: Am. Jour. Sci., v. 258, p. 449-497.
Osborn, E. F., 1959, Role of oxygen pressure in the crystallization and differentiation of basaltic magma: Am. Jour. Sci., v. 257, p. 609-647.
Ramberg, Hans, 1952, The origin of metamorphic and metasomatic rocks: Chicago, University of Chicago Press, 317 p.
Turner, F. J., and Verhoogen, Jean, 1951, Igneous and metamorphic petrology: New York, McGraw-Hill Book Company, 602 p.
Weeks, W. F., 1956, A thermochemical study of equilibrium relations during metamorphism of siliceous carbonate rocks: Jour. Geology, v. 64, p. 245-270.
Wones, D. R., 1958, Phase relations of biotites on the join phlogopite-annite [abs.]: Geol. Soc. America Bull., v. 69, p. 1665.
