

## Mineral equilibria in an interdisciplinary perspective<sup>1</sup>

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### Abstract

Experimental studies and interpretations of mineralogical–petrological equilibria involve close interaction with related fields. A quantitative approach to mineralogy requires exacting control of the compositions and external parameters in experimental work and refinement of methods of interpolating and extrapolating data to temperature and pressure regions not readily available for direct experimental observations. Success in these efforts is dependent on more detailed information on the thermodynamic properties of individual phases and improved understanding of the laws governing such relations.

Examples largely from the author's own work are used to illustrate existing or emerging interdisciplinary approaches being brought to bear on mineralogical–petrological problems. Because of relatively extensive information available on thermodynamic properties of many alloy systems at high temperatures and because of the generally very low mutual solubilities between metal and oxide phases, the study of metal–oxide–gas equilibria constitutes a particularly good starting point for determining activities of components in oxide solutions. With the latter as a base, it is shown how one may proceed in successive steps into the more complex silicate systems. It is also inferred that the role of research on mineral equilibria is taking on new dimensions in the applied areas. Existing or future shortages of energy and high-grade raw materials dictate more innovative use and modification of available resources. Solution of such problems requires extensive cooperation and cross-fertilization among several disciplines. Mineralogists–petrologists are in a position to play a key role and should move vigorously in these areas.

### Introduction

During the past decade the field of mineralogy has undergone profound changes toward a multifaceted discipline with rapidly increasing interaction with related disciplines including chemistry, physics, ceramics, metallurgy, engineering, economics, and even sociology. Some of these changes have been caused by circumstances beyond our control, *e.g.*, the energy crisis and the impending shortages of certain critical raw materials. These factors have served to emphasize the critical dependence of society on mineral resources and to recognize the key role of mineralogists. Other changes have resulted from the natural evolution of our field of science. This evolution, however, has been exceptionally rapid during the past decade. The lunar science program, among other

things, has contributed toward a quantum jump in our capabilities. Probably the most important aspect of this evolution is the application of new interdisciplinary tools and new interdisciplinary approaches to the study of the fine structures and energetics of mineralogical systems.

The following discussion will be concerned with selected aspects of “basic science,” as well as problems of a more applied nature. In both these areas, the remarks and the examples given will be heavily colored by the author's background, but it is hoped that the observations made will have some general applicability. Much of the discussion will be concerned with equilibria involving as components oxides of transition metals. These, notably iron oxides, are almost invariably present in natural minerals, and in most experimental work as well as in the interpretation of natural systems we must learn to deal with these oxides if we want to make meaningful interpretations of the processes involved. These

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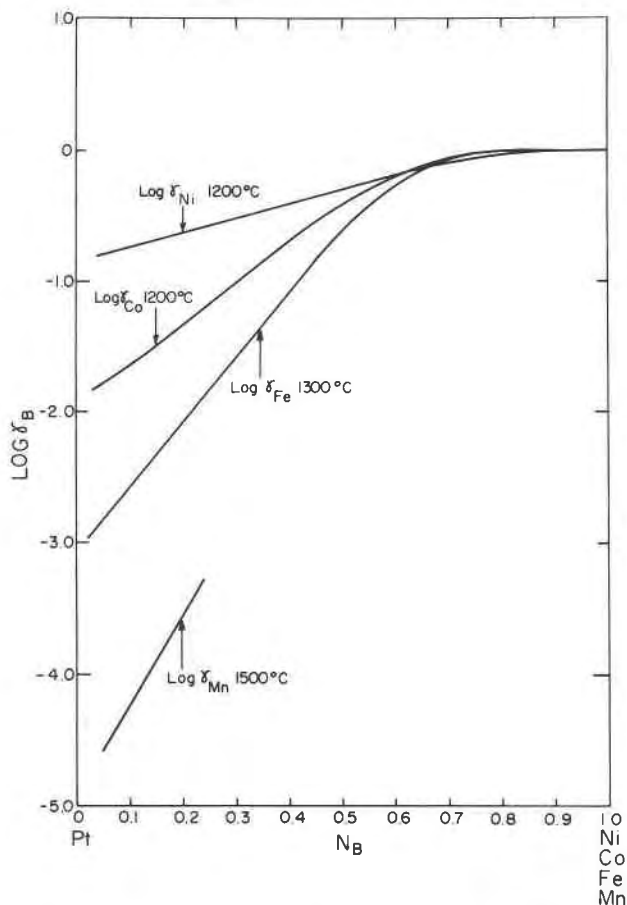


FIG. 1. Summary of activity-composition relations in alloys of platinum with various transition metals (Schwerdtfeger and Muan, 1965a).

oxides are less stable, relative to their constituent elements, than are oxides such as  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ , etc. Hence, equilibria between phases containing transition-metal oxides and their metals (or alloys) become important aspects of reactions where such oxides are involved, especially under the relatively strongly reducing conditions prevailing in many natural minerals and rocks.

#### Equilibria between metal and oxide phases

It is well known among all who have worked experimentally with transition-metal oxides and silicates at high temperatures that success or failure in such experiments often depends on the degree of reaction with the metal of the container. In order to evaluate theoretically the maximum extent of such reactions under equilibrium conditions, an interdisciplinary approach is needed. The equilibrium involves oxide or silicate melts and the alloy of the container, and hence knowledge of the thermodynamic properties of

the alloy phase as well as those of the oxide phase(s) is required. We will first look briefly at the former.

Consider reactions between iron silicates and platinum crucibles. Platinum is, of course, a very attractive crucible material in many respects. However, it has some very undesirable properties relative to its use for containing iron oxides or iron silicates under strongly reducing conditions at high temperatures. This is illustrated in Figure 1 showing activity-composition relations in some Pt alloys at elevated temperatures (Schwerdtfeger and Muan, 1965a). It is seen that there is a very strong negative deviation from ideality (the limiting value of  $\gamma_{\text{Fe}}$  is of the order of  $10^{-3}$ ), hence a very strong tendency for iron to alloy with platinum when iron oxide or iron oxide-containing phases are in contact with platinum at moderately to very low oxygen fugacities. Palladium is somewhat better in this respect, (Fig. 2, Schwerdtfeger and Muan, 1965a) but there still is a large negative deviation from ideality, the limiting value of  $\gamma_{\text{Fe}}$  in the dilute region being  $\sim 10^{-2}$ . This situation improves drastically as Ag is substituted for Pd to form Pd-Ag alloys, as shown by the appearance of a miscibility gap at low Pd contents in the system Pd-Ag-Fe (Fig. 3, Muan, 1962). The Pd-Ag alloys have the additional bonus of providing a ready diffusion path for hydrogen. Thus, the introduction of Ag-Pd alloys as container material for iron oxide-

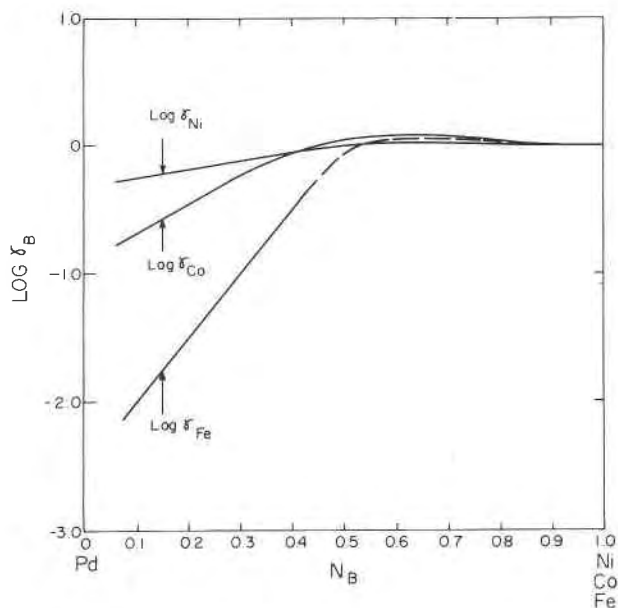


FIG. 2. Summary of activity-composition relations in alloys of palladium with various transition metals (Schwerdtfeger and Muan, 1965a).

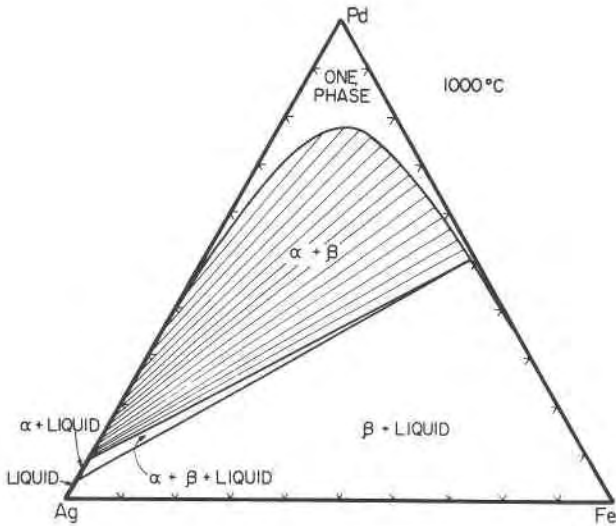


FIG. 3. Miscibility gap in system Ag-Fe-Pd at 1000°C (Muan, 1962).

containing phases opened up new possibilities of experimental research under hydrothermal conditions at controlled oxygen fugacities (see for instance Wones and Eugster, 1965), a necessary condition for meaningful study of systems containing transition-metal oxides of which iron oxides are the most important.

One possible way of circumventing or reducing the degree of reaction with noble-metal containers is to substitute for the oxides of iron either cobalt oxide or nickel oxide. The latter oxides show some similarities in their chemical and crystallographic behavior to that of ferrous iron oxide, while being in some respects easier to handle experimentally. The oxides CoO and NiO are stable in air at temperatures above 1000°C, and the divalent state of these elements is so stable relative to higher valence states that there is little tendency for disproportionation to metal plus a higher oxide as is the case with divalent iron oxide.

In order to define the limiting conditions for such experiments when the samples are held in common noble-metal containers (Pt or Pd), one again needs to know the thermodynamic properties of the alloy phases in question in addition to those of the oxide phases.

Activity-composition relations for a number of the pertinent noble metal-transition metal alloy systems were included in Figures 1 and 2. Combining the information contained in Figure 1 with available stability data for the various oxides (e.g. JANAF tables, 1971), one may construct curves (Fig. 4) showing the maximum concentration of the various transition

metals in platinum in contact with various oxide phases, as a function of oxygen fugacity at constant temperature (1200°C) (Muan and Schwerdtfeger, personal communication). Features to note in particular in this diagram are as follows: The curves for nickel and cobalt are farthest up on the diagrams because of the lower stabilities of these oxides in terms of their elements. However, the divalent oxides of these elements are stable at oxygen fugacities as high as that of air, or even 1 atm. O<sub>2</sub>, at 1200°C and hence can be studied experimentally under those atmospheric conditions with relatively moderate losses to the noble-metal container. Additional features to note in Figure 4 are the positions of the curves for Mn and Cr. In spite of the high stabilities of the oxides MnO and Cr<sub>2</sub>O<sub>3</sub> relative to their constituent elements (see for instance JANAF tables, 1971), the curves for Mn and Cr in Figure 4 are not too far below that of iron. This is because of the extreme degree of negative deviations from ideality in the corresponding alloy systems Pt-Cr (Schwerdtfeger and Muan, 1965b) and Pt-Mn (Abraham *et al.*, 1960). This should serve as a reminder of the necessity to keep a close look at the properties of the alloys formed as oxide mixtures are placed in noble metal containers; relatively high stability

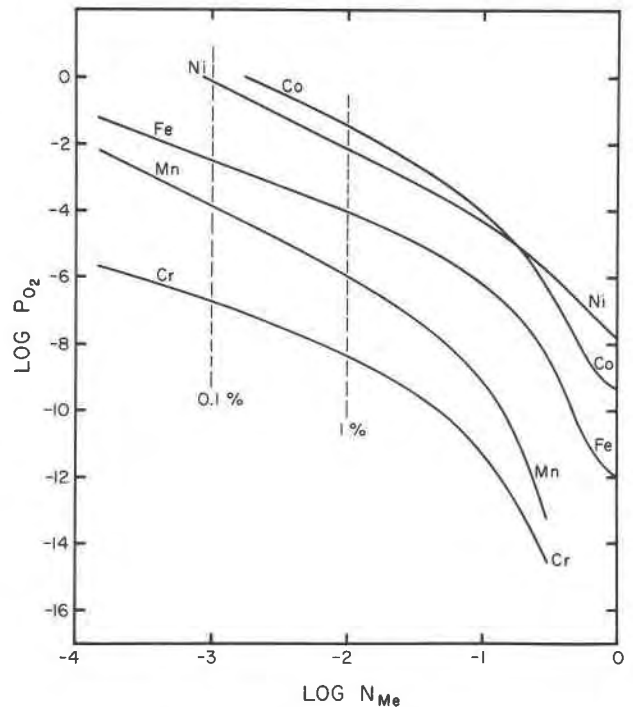


FIG. 4. Curves showing equilibrium concentrations of various transition metals in platinum, in contact with various oxide phases, each of unit activity, as a function of oxygen fugacity at 1200°C (Schwerdtfeger and Muan, personal communication).

of the oxides does not guarantee against composition changes beyond limits of tolerance if highly accurate experimental data are to be obtained.

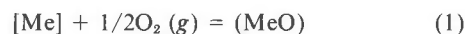
### Thermodynamic properties of oxide and silicate solid solutions

An alternative to experimental studies of iron silicates and other substances for which accurate equilibrium data are difficult to measure experimentally is to calculate the equilibria in the good traditions of the physical chemists. This is a very important part of the evolution which has taken place in mineralogy-petrology during the past decade, and the trend in this direction continues to be very strong.

If we are to use a theoretical approach to ascertain equilibria in mineral systems, to make interpolations among a few scattered experimental data, and to extrapolate experimental data into temperature-, pressure- and composition-ranges not readily attainable experimentally, we have to derive a better understanding of the laws governing the thermodynamic properties of individual oxide and silicate phases, both solid and liquid. In this respect, we seem to be at a turning point in mineralogy and petrology. Whereas during the past 50 years most of the experimental effort has been directed toward delineation of stability relations among phases in multicomponent systems, we see now a supplementary trend toward more detailed studies of chemical properties of individual phases occurring in such systems. Of course it is not practical to study in detail all conceivable systems of importance in mineralogy-petrology. We have to be selective. The selectivity should be directed on the one hand toward establishing some benchmarks involving some of the most common rock-forming minerals, and on the other hand toward working with substances which display as clearly as possible the principles involved. In the latter case, it does not matter whether the substances involved are commonly occurring natural minerals or not—as long as they are suitable model substances for the phenomena involved. Hence, the study of model systems is an important area of mineralogy and petrology.

In the following, we will consider a few examples showing some accomplishments and some challenges in the area of thermodynamic properties of oxide and silicate phases. Because of the generally very small mutual solubilities between oxide and metal phases, one of the most convenient ways of determining activity-composition relations in either phase is to study the distribution of elements between two such coex-

isting phases at known oxygen fugacities according to the reaction



where square brackets indicate the element Me in an alloy phase and the parentheses indicate the conjugate oxide component in an oxide solution. Such equilibria can be studied for instance by EMF measurements involving solid electrolytes (Kiukkola and Wagner, 1957) or by gas-metal-oxide equilibrations in which the oxygen fugacities are determined by mixing gases (e.g.  $\text{CO}_2$  and  $\text{CO}$ ) in controlled proportions (see for instance Darken and Gurry, 1945). If the activity of one of the phases, either the alloy or the oxide, is close to unity, the activity-composition relations of the other phase are derived from well-known, simple equations. By appropriate thermodynamic treatment, the relations, although more complicated, can also be derived quantitatively without *a priori* assumptions when both phases are solid solutions of variable compositions rather than "pure" end members, and when massive oxygen non-stoichiometry exists in the oxide phase. These interrelations have been derived for the system Fe-Ni-O on the basis of data obtained recently in our laboratory (Timucin, Muan and Darken, personal communication). The activity coefficients of the oxide solid solution are expressed by the equations

$$d \ln \gamma_{\text{NiO}} = X_{\text{FeO}} d \ln \frac{X_{\text{FeO}} a_{\text{Ni}}}{X_{\text{NiO}} a_{\text{Fe}}} - (X_{\text{O}} - 1) d \ln f_{\text{O}_2}^{1/2} \quad (2)$$

and

$$d \ln \gamma_{\text{FeO}} = -X_{\text{NiO}} d \ln \frac{X_{\text{FeO}} a_{\text{Ni}}}{X_{\text{NiO}} a_{\text{Fe}}} - (X_{\text{O}} - 1) d \ln f_{\text{O}_2}^{1/2} \quad (3)$$

where  $X$ 's with appropriate subscripts are atom fractions of the various components. It will be noted in the equations above that if  $X_{\text{O}} = 1$ , i.e. in the case of stoichiometric oxide solid solutions, the last term in each of equations (2) and (3) vanishes, leaving a well-known simplified relation for such a case.

Some of the results obtained are illustrated in Figure 5, showing activity-composition relations in the oxide solid solution at 1200°C. Attention is directed toward the "strange" interrelation between the two activity curves. The reason is found in a factor which plays an important role in this system as well as in numerous other oxide systems and hence serves as a good example to illustrate important principles. This

is the non-stoichiometry with respect to oxygen/cation ratios. The oxygen non-stoichiometry becomes very substantial in the "FeO"-NiO solid-solution series because the oxygen fugacity at which oxide and metal coexist in equilibrium, at a given temperature, increases rapidly with increasing Ni/Fe content of the phases. Hence, the cation vacancy concentration, or the  $\text{Fe}^{3+}$  content of the oxide solid solution, initially increases very rapidly with increasing Ni concentration, and greatly suppresses the FeO activity, as is shown in Figure 5. It is to be noted that the limiting tangent to the activity curve of FeO does not follow Raoult's law, because the system is not binary.

In most mineralogical-petrological settings, the oxygen fugacities of course are considerably higher than those prevailing when the oxide phases are in equilibrium with a metal phase. Under these conditions many phases, for instance those containing iron oxides, show high defect concentrations which play an important role in determining thermodynamic and transport properties in such phases. It appears that our ability to map out and understand the fundamentals of point defect concentration in minerals, and their dependence on composition, temperature, and pressure, is going to be an important aspect of mineralogical investigations in the future. Cooperation with ceramists and solid state chemists and physicists will help advance the frontiers of this area of science.

The effects of defect concentration enter dominantly into the mineralogically important spinel group. In addition to the possible non-stoichiometry with respect to oxygen/cation ratios in spinels, a further factor of importance in these minerals is the internal site distribution of the cations. The spinel is a particularly suitable sorting device in which the cations display their individual preferences for octahedral versus tetrahedral coordination. Hence, in addition to the mineralogical importance of spinels *per se*, natural and synthesized spinels are very suitable model substances for studying fundamental aspects of the energetics of formation of ionic phases. It is fortunate that workers in related fields, notably metallurgy, ceramics and solid state chemistry, are also doing a large amount of research on spinel phases because of their key roles in steelmaking and refractory technology, or because of their interesting magnetic properties.

It appears that we are now close to being able to treat these relations quantitatively with a fair degree of accuracy. Modern instrumentation (*e.g.* Mössbauer spectroscopy, neutron diffraction, *etc.*) has opened up new avenues for experimental verification

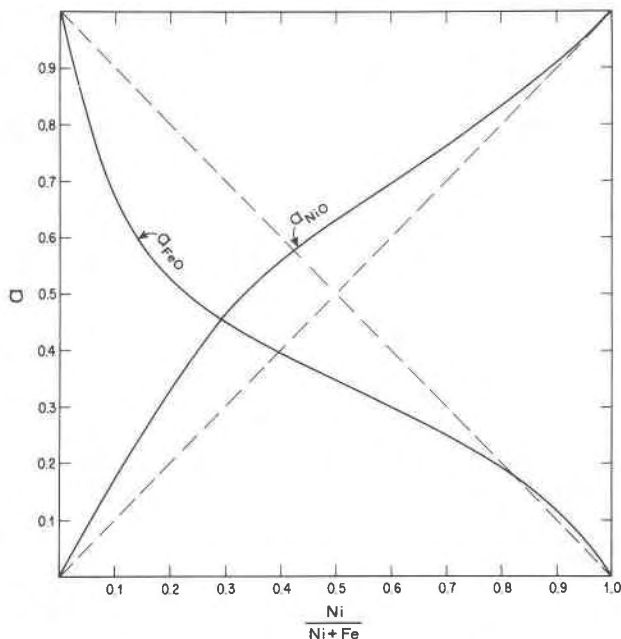


FIG. 5. Activity-composition curves for the oxide components in the system "FeO"-NiO in contact with Fe-Ni alloys at 1200°C (Timucin, Muan and Darken, personal communication).

of the identity and distribution of cations on the various sites in the structure. Hence, the thermodynamic approach has gotten a very powerful ally which makes these approaches far more powerful than either of them would be if used by itself.

The activity-composition relations determined for some key oxide solid solutions, as described above, may be extended to silicate solid solutions by determining directions of conjugation lines between coexisting solid-solution phases (Muan, 1967). What is involved here is a "jump" from one join to another or rather from one two-phase area to another two-phase area. We commonly start with the study of the equilibrium between metal and oxide solid solution, move into the oxide plus orthosilicate solid solution and then proceed into the more complex silicate equilibria. Using an analogue from the Washington scene, we might refer to this as the "domino approach"; we make the system yield step by step.

The quantitative relations attending this situation have been described previously (Muan, 1967). As an example of the application of this method, the data recently made available for "FeO"-NiO solid solutions (see an earlier section of this paper), form a suitable starting point for determination of activity-composition relations in Fe-Ni orthosilicates. The results are shown in Figure 6 (Timucin and Muan, personal communication).

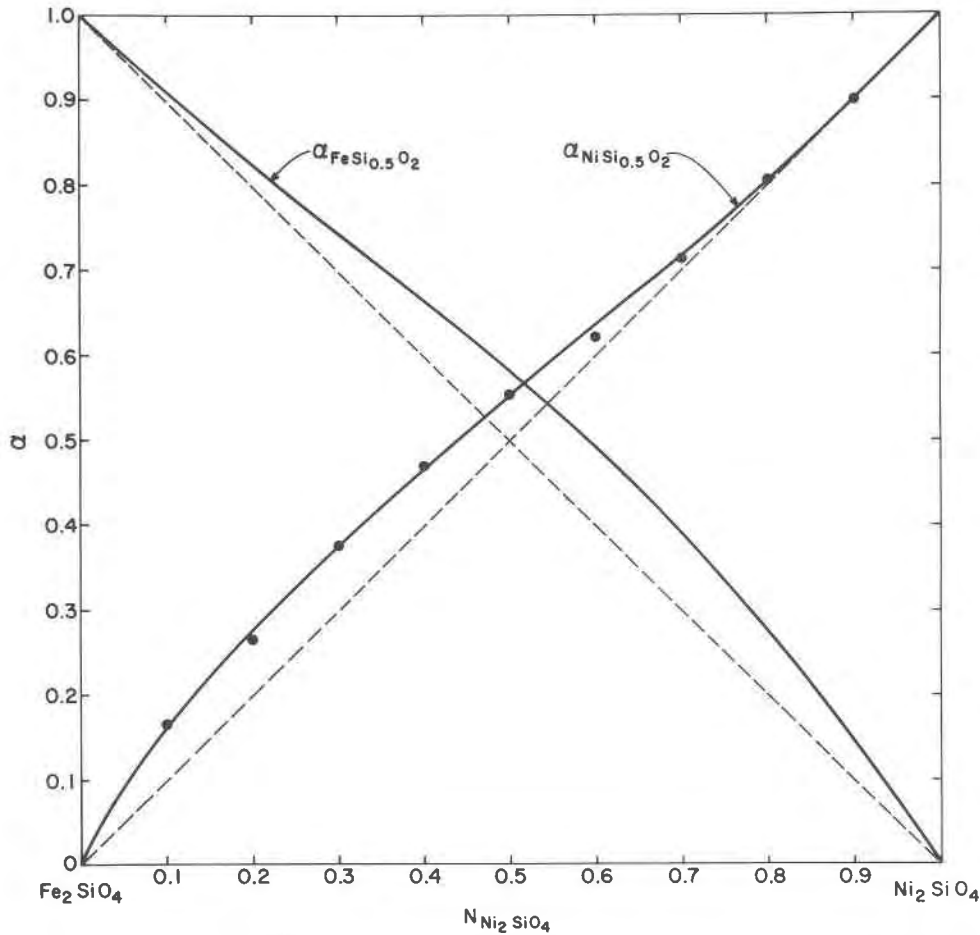


FIG. 6. Activity-composition curve for the system  $Fe_2SiO_4$ - $Ni_2SiO_4$  in contact with metal (Fe-Ni alloys) at  $1200^\circ C$  (Timucin and Muan, personal communication).

As improved and more detailed knowledge of site occupancy distributions becomes available, and as accuracy in the experimental measurements is improved, one can justify the use of more sophisticated ionic models in the interpretation of the data than were used as a first approximation in some of the earliest works on such systems (Schwerdtfeger and Muan, 1966).

In addition to the approaches used above to characterize stable solid solutions, one may, similarly, extrapolate thermodynamic data determined experimentally over a limited composition range to unstable phases which cannot be synthesized and studied in their pure form. This involves "protecting" the unstable phase by dissolving it in a stable phase of the same structure, thus permitting the study of the properties of the unknown (see for instance Muan *et al.*, 1964). Increasing our ability to extrapolate with more confidence and accuracy into the unknown is ob-

viously very important in geosciences because only a very small fraction of the earth is available for direct observation.

#### Solid miscibility gaps in ternary systems

The use of directions of conjugation lines between coexisting solid solutions to derive thermodynamic properties of solid phases can be extended to ternary solid solutions, and yields important information regarding coordination preferences of the cations and immiscibility relations at temperatures too low for equilibrium to be readily attained. For purposes of illustration of the principles involved, we will first select the simplest possible example, namely that of oxide phases with sodium chloride structure and an extensive ternary miscibility gap, as shown for the system  $CaO$ - $MgO$ - $MnO$  at  $1300^\circ C$  in Figure 7 (Woermann and Muan, 1970). The miscibility gap within which two solid-solution phases coexist in

equilibrium originates in the binary join CaO–MgO and gradually closes as MnO is added as a third component, mainly because the  $\text{Mn}^{2+}$  ion is intermediate in size between those of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The tilt of the conjugation lines toward the CaO–MnO join reflects the larger positive deviation from ideality of the activity-composition curve in the system MgO–MnO than in the system CaO–MnO. Indeed, such data have been used to derive approximate activity-composition data for the bounding binary solutions (Woermann and Muan, 1970; Brežný *et al.*, 1970). Although the system used as an example above is unimportant mineralogically, the type of problem described thereby is representative of what is involved in mineral chemistry in general. We deal essentially with an oxygen ion matrix in which various cations are to be distributed among the various sites in the structure. The distribution of the cations is dependent on temperature, pressure, sizes of the cations, and their site preference energies. Many of

the relations seen in the simple system illustrated in Figure 7 are similarly displayed in the more complex mineral systems, but the relations may look more complex because the number of sites and the number of cations to be distributed is larger.

One of the factors involved in determining the extent of the miscibility gaps is the difference in unit cell volumes. We are pleased to note that the Honorary President of our Society, Dr. Wherry, as early as 1923 wrote a paper (Wherry, 1923) entitled "Volume Isomorphism in the Silicates" in which he very perceptively outlined the effects of size factors, based on the very limited data available at that time. Subsequently, of course, Goldschmidt (1926) formulated his ionic size rules for mutual solubility among oxide phases, and at the present time attempts are being made to derive such relations quantitatively. The compressibility,  $\kappa$ , is an important parameter in the equations resulting from a rigorous treatment of this problem. It is hoped that cooperation with colleagues

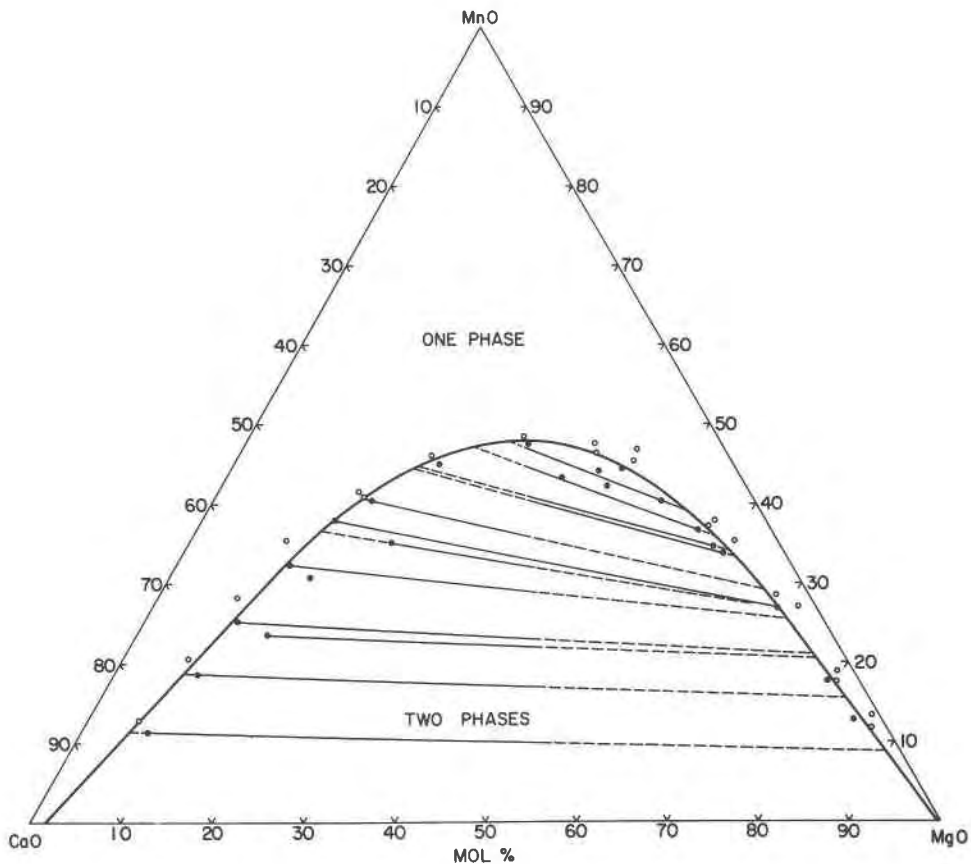


FIG. 7. Diagram showing extent of miscibility gap and directions of conjugation lines within two-phase area of the system CaO–MgO–MnO at 1300°C (Woermann and Muan, 1970).

in geophysics will help produce  $\kappa$ -values of the degree of reliability and accuracy needed for meaningful quantitative derivations of these relations.

### Liquid-solid equilibria in ternary systems

Just as we demonstrated above that solid-solid equilibria are expressions of ion individuality and hence of the thermodynamic properties of phases involving these ions, so we may use observations of solid-liquid equilibria to make similar important deductions regarding properties of the liquid phase. Consider as an example equilibria in magnesium-nickel silicates. The relations of primary interest are best illustrated by drawing fractionation curves along the liquidus surface of the system MgO-NiO-SiO<sub>2</sub>, as shown in Figure 8 (Grutzeck and Muan, personal communication). There is a remarkable curvature on these fractionation curves, characterized by a strong convexity to the right. At low silica contents of the liquid, this corresponds to

an enrichment of Ni in the liquid phase relative to the olivine phase. At higher silica contents, on the other hand, the situation is reversed, *i.e.* there is a depletion of Ni in the liquid phase relative to the olivine phase. These relations may be interpreted in terms of the site preference energies of the ions involved and the changes in structure of the liquid with changing SiO<sub>2</sub> contents. A more detailed discussion of these relations will be presented elsewhere. However, it is emphasized here that in considering the distribution of cations between solid and liquid phases we must keep in mind the changes in structural characteristics of the liquid as the crystallization proceeds.

In order to understand the processes by which minerals crystallize from magmas, we need to know as much as possible about the constitution and properties of the liquid silicates making up these magmas. An obvious starting point is the thermodynamics of the phase involved. Mineralogists and petrologists have made fine contributions to an overall under-

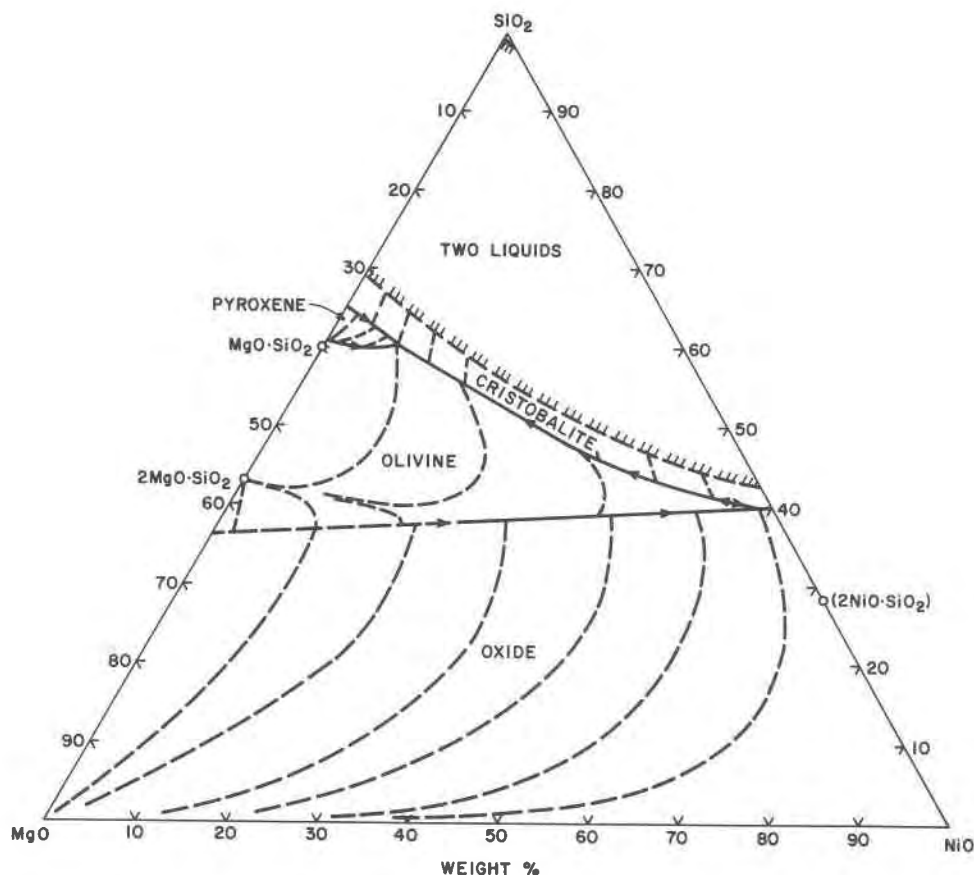


FIG. 8. Diagram showing fractionation curves along the liquidus surface of the system MgO-NiO-SiO<sub>2</sub> (Grutzeck and Muan, personal communication).



standing of phase relations in such systems. Some small steps have also been made toward determining activity-composition relations in some mineralogically-petrologically important solid-solution phases. However, relatively little has been done to delineate activity-composition relations of the components in rock-forming silicate melts. If, for sake of simplicity, we restrict our remarks to water-free systems at a total pressure of 1 atm., it is beneficial to turn to metallurgical literature for preliminary information (see for instance data on the system CaO-"FeO"-SiO<sub>2</sub> by Taylor and Chipman, 1943). A major difference between metallurgical slags, for which a considerable amount of activity-composition data is available, and naturally occurring silicates, is the generally higher silica content of the latter. However, in spite of compositional and structural differences, it is probable that similar experimental approaches will be useful in attempts to further characterize thermodynamically the more siliceous melts of natural systems. Clearly, it is worth-while to keep abreast of work done in the field of slag chemistry.

Similarly, it is highly desirable to interact with glass technologists, who have made extensive studies of very siliceous melts, including extents and mechanisms of solution of H<sub>2</sub>O in silicates.

#### Interrelations with fused salt chemistry

Studies of carbonate equilibria have demonstrated the close link between fused salt chemistry and mineralogical problems. This topic seems particularly apropos for a meeting in Salt Lake City. Flood and coworkers some thirty years ago initiated a series of experimental studies concerned with the equilibrium between CO<sub>2</sub> gas and carbonate melts containing various amounts of so-called "acid oxides," mainly SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>. While primarily aimed at deriving information regarding the relative acid strengths of the latter three oxides, the approach used and the data obtained provide valuable insight into the general thermodynamic properties and hence the ionic configurations of melts. There was nothing new in this; the work (Flood *et al.*, 1947) was undoubtedly inspired by work done by Niggli (1913) during his visit at the Geophysical Laboratory of the Carnegie Institution of Washington some thirty years earlier. However, what was new in the work of Flood and coworkers was that they interpreted their data in terms of ionic models of the melts and the crystalline phases. We see here a very gratifying example of the mutual rewards of interdisciplinary interaction: Ideas

for the experimental work and the definition of the importance of the problem derived mainly from a petrologist's interest in the properties of the magmas from which rocks crystallize. In the hands of physical chemists and fused salt chemists three decades later new dimensions were added to the theoretical treatment of the equilibria.

Work on fused salts, such as the example given above, was the main basis for development of ionic approaches to slag equilibria (see, for instance, Flood and Grjotheim, 1952). A further link in this interdisciplinary chain has been the adaptation of similar ionic approaches to the thermodynamic description of mineralogically important solid solutions (see, for instance, Blander, 1972). It would be unfortunate if we fail to recognize and utilize approaches developed in these related disciplines as we now turn to an increasing extent toward quantitative thermodynamic treatment of phenomena involved in geosciences. This is not a one-way street. The scientists in the related fields, for instance in slag chemistry and in glass chemistry, have made extensive use of phase-equilibrium data derived by geoscientists, and will continue to draw on information coming from our field. We should make sure that we do our part of maintaining the flow of scientific information and insight in both directions across the traditional but largely artificial disciplinary boundaries between these fields.

#### Mineral equilibria applied to technological problems

Mineralogists are getting increasingly involved in the solution of pressing technological and societal problems. Not the least among these problem areas is the supply of mineral resources and energy. Nobody today can avoid hearing about the energy crisis. However, equally disturbing are the long-range prospects in the mineral resources field in general, if present trends continue. The rapidly widening gap between this country's mineral consumption and domestic mineral supplies gives reason for grave concern.

Finding solutions to such problems will require supreme effort and ingenuity, not only on the part of economic geologists but also on the part of mineralogists and petrologists. We will have to play an active role in providing the knowledge base necessary to develop the required new technologies. In order to do so, we must develop and strengthen interfaces with other disciplines. Consider an example of a new technology which is being actively considered at the present time: If we are to utilize heat within the earth

as a major source of energy, we need to improve drilling technologies. One new process which seems far out but yet is undergoing serious study both on a laboratory scale and in the field is the hot penetrator, or the so-called subterrene, being developed at the Los Alamos Laboratories and elsewhere. The main idea involved is to melt the way through rocks rather than to break them up mechanically as is done in conventional drilling. The advantage of the subterrene—if it works—is that the drilling presumably would become easier the hotter the rock is, and hence the deeper or the closer to the heat source one gets. The device used in present prototypes is commonly a molybdenum or tungsten penetrator internally heated to a temperature of  $\sim 1500\text{--}1600^\circ\text{C}$ . The silicate liquid formed by melting the rock in the path of the penetrator is partly squeezed into the cracks of the rock, where it serves as anchors for a glass lining which automatically forms as the drill progresses through the rock, in favorable cases.

Not surprisingly, there are some problems associated with this process. One of them is the corrosion of the material used in the hot penetrator. Quantitative evaluations of such reactions, which may be a critical factor in determining success or failure of this new technology, will depend on our ability to understand the physical chemistry of these reactions. Hence, again it becomes a matter of bridge-building between metallurgy and mineralogy-petrology, and we should be involved. Of course, a hole drilled with a molybdenum penetrator is bound to be called a Moho. Perhaps this is a bad omen, but it is a chance we will have to take.

Projects such as the above, even though directed primarily toward solution of practical energy problems, if successful, are likely to open up new frontiers in mineralogical-petrological research. It is hoped, for instance, that this technology will make it possible to drill through the bottom of lava lakes and to the roots of volcanoes, thus permitting mineralogical-petrological sampling and measurements to be made in previously unavailable regions.

Similarly, there are obvious, important interfaces with engineering and other disciplines in attempts to extract geothermal energy in the form of steam either from natural geysers or by circulating water through drill-holes in hot rocks.

There is another area of applied mineralogy where we have not exerted our influence as strongly as we should. This is in the application of mineralogy to industrial problems. The widening gap between mineral demand and domestic supplies dictate a better

utilization of existing raw materials as one means of reducing the discrepancy. An example of an area where mutual benefits have accrued from pursuing research at the border-lines between metallurgy, ceramics, and mineralogy is in the production and application of chrome-magnesite refractories. These are made by mixing and firing magnesite and chrome ore. Mineralogists have a lot to contribute to an understanding of such reactions, and a lot to learn. The chemistry of chrome-magnesite refractories revolves around the spinel phase. The latter is almost ubiquitous in igneous rocks, including lunar rocks. Moreover, the spinels, especially chromites, are among the first phases to crystallize from silicate liquids, even if chromium is present in relatively low concentrations, and hence these phases serve as very valuable built-in indicators of parameters involved in the crystallization of magmas. Much metallurgical-ceramic research on spinels in general and on chromites in particular is carried out at temperatures of  $1600\text{--}1700^\circ\text{C}$ , in other words considerably higher than those considered of primary interest in geosciences. However, this may be more of an advantage than a disadvantage. Reactions in some of these systems are generally very sluggish, and high temperatures are often required in order to attain equilibrium within a reasonable period of time. Moreover, many of the effects we are trying to understand are greatly magnified at high temperatures or extreme oxygen fugacities. A case in point is the role of  $\text{Cr}^{2+}$  in oxide and silicate phases, a question which has been posed in conjunction with the reported occurrence of larger than usual amounts of chromium in lunar olivines and the inference that much if not most of this chromium may be present in the divalent state. One of the problems involved in determining the state of chromium in these olivines is the low concentration ( $<0.1\%$ ) in which chromium is present. By working at very high temperatures and very low oxygen fugacities we may produce phases of far greater  $\text{Cr}^{2+}$  concentrations and thus provide samples better suited for characterization of the chemical properties of this species. Once the character of such an ion has been deciphered, we should be able to predict its behavior under conditions deviating from those under which the particular experiment was carried out and hence make the data more universally applicable.

A striking example of the dominant role of divalent chromium at high temperatures ( $\sim 1600^\circ\text{C}$ ) and very low oxygen fugacities ( $f_{\text{O}_2} = 10^{-12}$  to  $10^{-13}$  atm) is afforded by silicate liquids in the system  $\text{CaO}\text{--}\text{chromium oxide}\text{--}\text{SiO}_2$  (Snellgrove, Darken and Muan, per-

sonal communication). Under these strongly reducing conditions, the liquids can dissolve as much as ~40 wt. percent chromium oxide, as compared to a solubility of only ~5 wt. percent in air. Moreover, 90–95 percent of the chromium present in the silicate melt under the strongly reducing conditions is in the divalent state. Hence, we here have a phase in which massive concentrations of  $\text{Cr}^{2+}$  are present for chemical characterization of this ion.

### Conclusions

Mineralogy, crystallography and petrology are assuming new dimensions. As mineralogists we hold one of the most important keys to understanding our Earth, and to developing, utilizing, and protecting its resources. But we are not using this key to its fullest potential unless we orient ourselves toward active cooperation with other fields. While continuing with pride the classical aspects of our science, we must also open our eyes to the tremendous potential for cross-fertilization with other fields. We must encourage active participation of young people with new ideas in our Society and in our field of science. And we must work together to promulgate basic aspects of our science as well as the applied aspects, for it is doubtful that one can survive without the other. With serious mineral resource shortages ahead we should assert our influence and display our competence more aggressively and with more visibility than we have in the past. We must remember that problems represent opportunities. It appears that we have more opportunities than ever.

### References

- ABRAHAM, K. P., M. V. DAVIES, J. L. BARTON AND F. D. RICHARDSON (1960) Activities of manganese in solid platinum. *Acta Metal.* **8**, 888–890.
- BLANDER, M. (1972) Thermodynamic properties of orthopyroxenes and clinopyroxenes based on the ideal two-site model. *Geochim. Cosmochim. Acta*, **36**, 787–799.
- BREŽNÝ, B., W. R. RYALL AND A. MUAN (1970) Activity-composition relations in CaO–MnO solid solutions at 1100–1300°C. *Mat. Res. Bull.* **5**, 481–488.
- DARKEN, L. S. AND R. W. GURRY (1945) The system iron-oxygen. I. The wüstite field and related equilibria. *J. Am. Chem. Soc.* **67**, 1398–1412.
- FLOOD, H., T. FÖRLAND AND B. ROALD (1947) The acidic and basic properties of oxides. III. Relative acid-base strengths of some polyacids. *Acta Chem. Scand.* **1**, 790–798.
- AND K. GRJOTHEIM (1952) Thermodynamic calculation of slag equilibria. *J. Iron and Steel Inst. (London)*, **171**, 64–70.
- GOLDSCHMIDT, V. M. (1926) Laws of crystal chemistry. *Naturwiss.* **14**, 477–485.
- JANAF Thermochemical Tables, Second Edition, NSRDS-NBS37, Washington, D. C., 1971.
- KIUKKOLA, K. AND C. WAGNER (1957). Measurements of galvanic-cells involving solid electrolytes. *J. Electrochem. Soc.* **104**, 379–386.
- MUAN, A. (1962) The miscibility gap in the system Ag–Fe–Pd at 1000°, 1100°, and 1200°C. *Trans. AIME*, **224**, 1080–1081.
- , R. H. NAFZIGER AND P. L. ROEDER (1964) A method for determining the instability of ferrosilite. *Nature* **202**, 688–690.
- (1967) Determination of thermodynamic properties of silicates from location of conjugation lines in ternary systems. *Am. Mineral.* **52**, 797–804.
- NIGGLI, P. (1913) Phenomena of equilibrium between silica and alkaline carbonates. *J. Am. Chem. Soc.* **35**, 1693–1727.
- SCHWERDTFEGER, K. AND A. MUAN (1965a) Thermodynamic properties of Pt–Ni, Pd–Ni and Pd–Co alloys at 1000 and 1200°C. *Acta Metal.* **13**, 509–515.
- AND — (1965b) Activity measurements in Pt–Cr and Pd–Cr solid alloys at 1225°C. *Trans. AIME* **233**, 1904–1906.
- AND — (1966) Activities in olivine and pyroxenoid solid solutions of the system Fe–Mn–Si–O at 1150°C. *Trans. AIME* **236**, 201–211.
- TAYLOR, C. AND J. CHIPMAN (1943) Equilibrium of liquid iron and simple basic and acid slags in a rotating induction furnace. *Trans. AIME*, **154**, 228–247.
- WHERRY, E. T. (1923) Volume isomorphism in the silicates. *Am. Mineral.* **8**, 1–8.
- WOERMANN, E. AND A. MUAN (1970) Derivation of approximate activity-composition relations in MgO–MnO solid solutions. *Mat. Res. Bull.* **5**, 779–788.
- WONES, D. R. AND H. P. EUGSTER (1965) Stability of biotite: experiment, theory, and application. *Am. Mineral.* **50**, 1228–1272.