

Wallace H. MacLean; Liquidus Phase Relations in the FeS - FeO - Fe₃O₄ - SiO₂ System, and their Application in Geology; Department of Geological Sciences; Degree of Doctor of Philosophy.

ABSTRACT

Activity of FeO is the main factor governing solubility of FeS in silicate liquids containing FeO. In the FeS - FeO - Fe₃O₄ - SiO₂ system, sulfide liquid coexists with silicate liquid when the silicate liquid becomes saturated with FeS. Invariant points in the system are:

(weight percent)					
FeS	FeO	Fe ₃ O ₄	SiO ₂		

(silicate liquid))	
16	57	1	26)	
)	1140 $\pm 5^{\circ}\text{C}$ iron,fa,td,2-L,v
(sulfide liquid))	
83	15	0.5	1.5)	
(silicate liquid))	
10	40	21	29)	
)	1095 $\pm 5^{\circ}\text{C}$ mt,fa,td,2-L,v
(sulfide liquid))	
57	26	15	2)	
63	20	16	1		955 $\pm 5^{\circ}\text{C}$ mt,fa,td,po,1,v
62	22	15	1		945 $\pm 5^{\circ}\text{C}$ ws,mt,fa,po,1,v
62	36	1	1		917 $\pm 3^{\circ}\text{C}$ iron,ws,fa,po,1,v
85	14	0.5	0.5		1075 $\pm 10^{\circ}\text{C}$ iron,fa,td,po,1,v

Sulfide liquid can be formed by oxidation of siliceous iron silicate liquid containing more than 10 weight percent FeS. When fo₂ is buffered above the quartz-fayalite-magnetite assemblage, the magnetite-pyrrhotite-tridymite solidus temperature can be lowered by as much as 65 degrees.

In nature, sulfide liquids can be generated by partial melting of the mantle or by oxidation of magma.

LIQUIDUS PHASE RELATIONS IN THE
FeS - FeO - Fe₃O₄ - SiO₂ SYSTEM,
AND THEIR APPLICATION IN GEOLOGY

by

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Chapter I

Introduction

Magnetite, and less commonly hematite, are constituents of many sulfide ores. Magnetite is also common in dispersed sulfide grains in igneous rocks. Frequently the textural and spatial relations of the associated magnetite, sulfides and silicates in these rocks and ores indicate that they crystallized together, in many cases apparently from a melt. The sulfide grains and ores are cleanly separated from the enclosing silicate rocks and have in many cases been considered to have formed from a separate liquid phase that became immiscible in the parent silicate melt. The present work was conceived as a study of the immiscibility of certain sulfide and silicate liquids and one that would supply data for the interpretation of the separation and crystallization of a sulfide phase in a silicate melt.

During the past sixty years equilibrium phase relations have been worked out for many combinations of the major rock-

forming oxides. Where phase relations have been extended to non-equilibrium conditions, such as crystal fractionation, they have served as a basis for interpreting the crystallization history of the silicate and oxide portions of magmas. In this work, however, few studies have been made of the phase relations of associated sulfides, oxides and silicates. In initial studies the systems are necessarily simple and are chosen to cover many facets of the problem using as few components as possible. For this reason iron is the obvious choice of the metal cations; it is a major silicate component and forms a large proportion of the oxide and sulfide minerals in the earth's crust. In addition, iron has a special significance: under certain conditions it can change its valence state and thereby many of its chemical properties. The effect of this change on the differentiation of magmas is profound (Osborn, 1959). In this thesis it is shown that it may have a similar effect on the separation and crystallization of the sulfide components in a magma.

The phase relations in the system $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ will be correlated in this thesis with those studied in other systems pertinent to magmas. Using these relations and data on the structure and behaviour of silicate and

sulfide liquids, models are presented to illustrate methods by which sulfides crystallize from a simple melt; and, in particular, conditions under which they could separate to form discrete bodies such as some types of sulfide deposits found in nature.

Chapter II

Sulfur In Silicate Liquids

A basic magma may be looked upon as a solution of alkali, alkali-earth and transition-metal silicates and alumino-silicates, plus small amounts of oxides, halides, sulfides, phosphates and others. As the magma cools it becomes saturated in certain phases which separate as solids, liquids or gas. The laws governing the solubility of sulfur in silicate liquids and the separation of a sulfide liquid are considered here.

The immiscibility of sulfide liquids in silicate systems is well established from smelting processes in which a liquid matte of sulfides collects below a silicate slag. This observation was applied to geology by Vogt (1921) to explain

the origin of certain iron-nickel-copper sulfide ore deposits associated with basic plutonic rocks. Vogt further used the concept to explain the polysulfide grains found in the mesostasis of basic rocks and suggested that the sulfides became immiscible as the silica content of the interstitial liquid increased.

There are, however, some arguments against the application of this principle to geologic conditions, at least to the formation of magmatic sulfide ore deposits. The main problem is whether large amounts of sulfides, now occurring as sulfide deposits, were ever dissolved in basic magmas. And if they were, then what were the causes and mechanism of their separation when the magma was intruded?

The factors governing the solubility of sulfides in silicate liquids are reviewed in light of recent studies on the structure and thermodynamic properties of these liquids.

Solubility of sulfur in silicate liquids

For sulfur to dissolve in a silicate liquid it must become bonded to a positively charged ion. To become bonded in this way, and to retain a balanced electrostatic charge in the silicate liquid, it must either displace oxygen or "oxidize" some cation to a higher valence state. In silicate liquids there are three sites in which sulfur may substitute for an oxygen ion: the Me - O - Me, Me - O - Si and Si - O - Si sites (Me = metal cation, see Fig. 1). However, because of

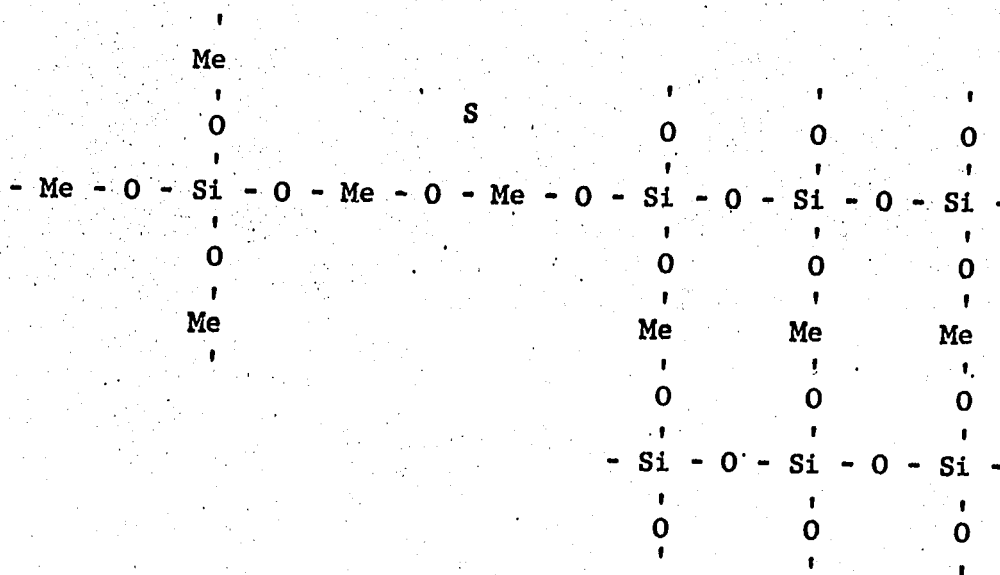


Fig. 1. A diagrammatic structure of a simple silicate liquid containing O^{2-} , SiO_4^{4-} , and $(SiO_3)_n^{2n-}$ anions and metal cations (Me). Sulfur (S) essentially replaces only weakly bonded oxygen in silicate liquids. Si-O bonds are very strong as are Me-O bonds when Me = Mg, Ca, Al, Na, etc. Me-O bonds are weak when Me = Fe^{++} and other divalent transition metal cations. Values of metal to oxygen and metal to sulfur bond energies are listed in Table 1.

the high energy of the Si - O bond relative to Si - S, it is unlikely that sulfur substitutes for oxygen bonded with silicon to any appreciable degree. This is substantiated by the almost complete lack of reaction between molten sulfides and silica glass containers used in high temperature experimental work on sulfide systems.

The Me - O and Me - S relative bond energy values, as given by Nockolds (1966), indicate that the ease with which sulfur can substitute for oxygen in these sites, with the exception of magnesium and aluminum, will be in the decreasing order: Me - O - Me, Me - O - Si and Si - O - Si (see Table 1). In the Me - O - Me sites the tendency for the sulfur to substitute for oxygen increases as cations lower in the columns of Table 1 occupy the Me position. When the number of sulfide ions in the melt becomes greater than the number of sites available in which sulfur can substitute, a separate sulfide phase forms; and, if the temperature of the system is above the melting point of the sulfide phase, the separating sulfide phase will be a liquid. This is the immiscibility that is so often found between liquids having different bond types.

Structure of silicate liquids

Bockris, et al. (1952) demonstrated that silicate liquids are conductors of electricity and thus that the bonding between

Table 1

Comparison of Me - O with Me - S single valence bonding energies (after Nockolds, 1966).

Cation	Single Valence Bonding Energy Me - O(1)	% Ionic Character	Single Valence Bonding Energy Me - S(2)	% Ionic Character	Ratio (1)/(2)
Mg	101	(68)	48	(34)	2.10
Al	100	(60)	48	(25)	2.08
Si	95	(45)	47	(13)	2.02
Ti ^{1v}	87	(51)	43	(16)	2.02
Na	100	(79)	50	(51)	2.00
Ca	200	(77)	50	(47)	2.00
K	90	(82)	45.5	(55)	1.98
Sn ^{1v}	75	(43)	40	(10)	1.87
Cr ¹¹¹	87	(49)	47	(16)	1.85
Zn	85	(51)	46	(17)	1.85
Mn ¹¹	87	(60)	47	(25)	1.85
Ni	84	(47)	46	(14)	1.83
Fe ¹¹	83.5	(50)	46	(15)	1.82
Pb	69	(47)	38	(13)	1.82
Co	83	(47)	46	(14)	1.80
Cu ¹	79	(47)	45	(15)	1.76
Ag ¹	71	(50)	41	(16)	1.73

radicals to be essentially ionic in character. The anions may be simple silicate groups, e.g. SiO_4^{4-} , or polymers of some group, e.g. $(\text{SiO}_3)_n^{2n-}$, the latter collectively called polyanions. In these anions and polyanions the bonds between silica and oxygen are about 50 percent covalent while those holding the anions and polyanions to one another are ionic Me - O bonds.

The ionic liquid may be visualized as having a quasi-crystalline structure. It has no long-range order but retains short-range ordering of its chemical bonds. Each cation is surrounded by about the same number of anions as in the solid, so that "1) for a given stoichiometry, the polyanion charge per mole must equal that of the corresponding cations, and 2) the structures must obey the stereochemistry of the coordinating nonmetal; that is, the Si - O - Si angle in a suggested structure must be near to 140° ." (Bloom and Bockris, 1964, p. 55).

The ionic character of bonds is of great importance in deducing certain physical properties of silicate liquids. According to Myuller (1960), ionic bonds cause higher fluidity, greater diffusion of ions, and, increased rates of chemical reactions. Correspondingly, the short-ranged, localized, covalent bonds result in reduced fluidity, low atomic diffusion rates and low rates of chemical reaction.

Since sulfur can essentially substitute only for oxygen bonded solely to metals in the lower part of Table 1, it is important to be able to determine the proportion of these Me - O - Me groups in the silicate liquid. Their formation is controlled by such factors as (1) the amount of silica in the liquid, (2) the strength and type of bond formed by the metal cations, and (3) the type of anions and polyanions formed. These factors combine to give the silicate liquid a definite structure at constant temperature, pressure and composition.

A model for the structure of silicate liquids has been proposed by Bockris and Lowe (1954) and Bockris, et al. (1955) using combinations of possible anions formed and the measured activities of alkali, alkali-earth and transition metals oxides in silicate liquids. They envisage the silica crystal structure being broken up to form ionic groups which polymerize to increasingly complex polyanions as the silica concentration of the liquid is increased. The anions they find that best fit the experimental data for the silicate liquid are a combination of O^{2-} , SiO_4^{4-} , $(SiO_3)_n^{2n-}$ and $(SiO_{2.5})_q^{q-}$. Table 2 lists the anions predicated for silicate melts by Bloom and Bockris (1964). They point out that other anions may be present but are not needed to satisfy the charge or activity requirements.

Table 2

Polyanions present in liquid silicates comprised of SiO_2 and MeO (after Bloom and Bockris, 1964, and Knapp, 1966).

Composition (mole %)	Dominant Anions
Up to 33% SiO_2 ($2\text{MeO} \cdot \text{SiO}_2$)	O^{2-} , SiO_4^{4-}
From 33% to 50% SiO_2	Polymerization of SiO_4^{4-} anions to $(\text{O}_3\text{Si} - \text{O} - \text{SiO}_3)^{6-}$ anions and chains
At about 50% SiO_2 ($\text{MeO} \cdot \text{SiO}_2$)	Ring formation occurs due to the increase in chain length. $(\text{SiO}_3)_3^{6-}$ and $(\text{SiO}_3)_4^{8-}$ rings are dominant.
From 50% to 67% SiO_2	Larger ring anions are formed.
At about 67% SiO_2 ($\text{MeO} \cdot 2\text{SiO}_2$)	$(\text{Si}_6\text{O}_{15})^{6-}$ and $(\text{Si}_8\text{O}_{20})^{8-}$ anions dominate.
More than 67% SiO_2	(a) MeO = alkali and barium oxides: continued formation of complex silicate anions. (b) MeO = most other metal oxides: two-liquid field; an ionic silicate liquid and a covalent, almost pure, silica liquid.

A different type of silicate anion is discussed by Belov (1959) for coordination with calcium and the alkali cations. According to Belov, these cations with their large ionic radii form much larger octahedra with oxygen than do the smaller ions of magnesium and iron. When silica is added to a melt containing these cations, it coordinates in the form of $\text{Si}_2\text{O}_7^{6-}$ diortho groups around calcium and the other large cations (corresponding to the wollastonite structure). He further suggests that if alumina is present it substitutes for silica in the diortho group to form the AlSiO_7^{7-} anions of the feldspars. These anions probably play the dominant role in lowering the activity of CaO , Na_2O and K_2O in aluminosilicate melts.

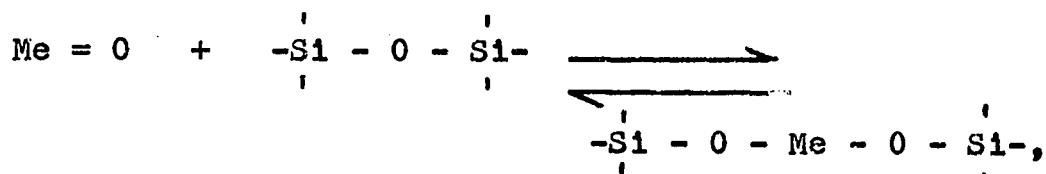
If these proposals are combined, as suggested by Belov (1959), the type of structures formed in natural silicate liquids, i.e. magmas, can be deduced. The small cations of magnesium and iron (and also Mn, Ni, Co, Zn, Cu^{++} , etc.) are coordinated by silica tetrahedra to form olivine-type structures. The larger cations of calcium, potassium and sodium (and also Ba, Sr, Pb, etc.) are coordinated by $\text{Si}_2\text{O}_7^{7-}$ groups to form wollastonite and feldspar-type structures.

Non-ideal silicate liquids:

The solution of silica in oxide liquids is never ideal, and even in dilute solutions all the silicate ions will not

be SiO_4^{4-} or $\text{Si}_2\text{O}_7^{7-}$. Other anions with simple structures will form in small concentrations. The formation of the more complex anions releases an equivalent number of metal cations which will be bonded in the Me - O - Me fashion. The number of ions of any one species in the liquid is proportional to the activity of that species.

In Figure 2, the anion species for the system $\text{PbO} - \text{SiO}_2$ have been estimated by Flood and Knapp (1963) using experimentally determined PbO and SiO_2 activities. It can be seen from this diagram that O^{2-} ions, that is, Pb - O - Pb bonds, are present up to high silica contents. This high activity of the O^{2-} ion appears to be a function of the strength and character of the Me - O bond. In the relation



metal cations that form strong ionic bonds are most effective in breaking the Si - O - Si bridges and in this way share most of their oxygen with silicon.

The bonds between oxygen and the alkali and alkali earth metals are more ionic in character than those with the transition metals. The transition metal cations thus have less tendency to break Si - O - Si bridges and hence would be more

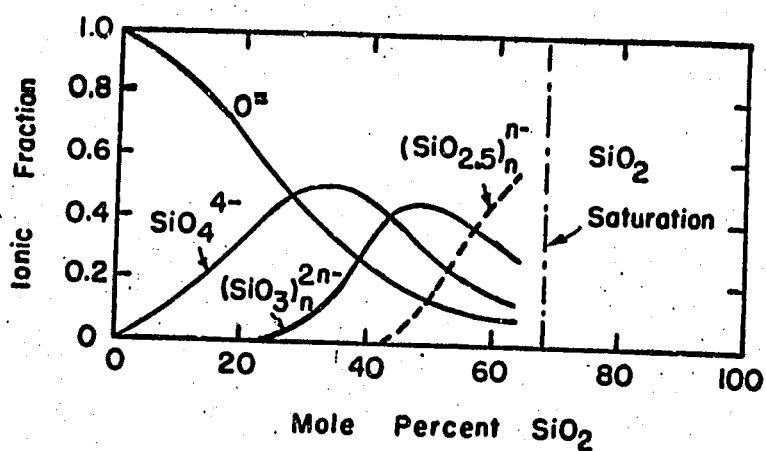


Fig. 2. Ionic fractions calculated from activities of PbO and SiO₂ in the PbO - SiO₂ system. The anions O²⁻, SiO₄⁴⁻, (SiO₃)_n²ⁿ⁻, and (SiO_{2.5})_nⁿ⁻ satisfy the activity requirements but are not necessarily the only anions present. (After Flood and Knapp, 1963)

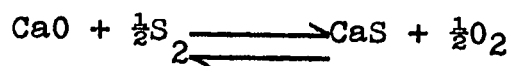
available to form covalent bonds with other anion groups such as the sulfides. A compilation of this data is given in Table 1.

Sulfide-oxide liquids

Most transition metal sulfides, in particular FeS, are metallic-covalent bonded compounds (Pauling, 1960). The iron oxides 'FeO' and Fe_3O_4 have bond types similar to FeS but are more ionic in character (Table 1). When these compounds are melted separately or together they form liquids of low viscosity (comparable to liquid mercury or gallium) whose densities, at least in the case of FeS, are only slightly lower than that of the solids (Ubbelohde, 1965, p. 188). In the solid state these iron oxides and sulfides are almost completely insoluble in each other, but as liquids they are miscible in all proportions. Apparently oxygen and sulfur can substitute freely for each other in the expanded structure of these liquids.

Sulfur capacity of metallurgical slags

There are numerous references in the literature on the activities of oxides in metallurgical slags. Much of the data in these studies was obtained by measuring the capacity of the slags to dissolve sulfur. Rosenqvist (1951) used the equilibrium relation.



to measure the activity of CaO in lime-silica slags around 1500°C, basing his method on the supposition that oxygen is replaceable by sulfur only when it is bonded to calcium ions alone. With an increasing silica content, he found that the amount of CaS formed, and thus the CaO activity, in the slag decreased.

Similar results were obtained by Richardson and Fincham (1954) on calcium, magnesium and iron silicate slags between 1450° and 1650°C.

They found that sulfur can be dissolved in FeO- and CaO- rich slags equally well, but that much less can be dissolved in MgO- rich slags. This result corresponds well with the free-energy data they give for the reactions:



$$\Delta F^\circ 1642 - 2000^\circ\text{K} = +25,280 - 2.41T \pm 3000 \text{ cal.}$$



$$\Delta F^\circ 1023 - 2000^\circ\text{K} = +23,020 - 1.25T \pm 500 \text{ cal.}$$



$$\Delta F^\circ 1380 - 2000^\circ\text{K} = +44,180 - 2.85T \pm 8000 \text{ cal.}$$

However, the amount of sulfide that can be formed in any of these reactions is directly proportional to the amount

of available oxide; that is, proportional to the activity of the oxide. An example of the activities they measured in experimental slags at about 1500°C and having about a 1 : 1 molar ratio of metal oxide to silica is given below:

1) 0.54 molar FeO in FeO - SiO₂ slag; $a(\text{FeO}) = 0.39$

2) 0.50 molar MgO in MgO - SiO₂ slag; $a(\text{MgO}) = 0.10$

3) 0.56 molar CaO in CaO - SiO₂ slag; $a(\text{CaO}) = 0.014$

From these data, Richardson and Fincham conclude that FeO - SiO₂ slags, except when very silica-poor, should be capable of dissolving a much larger quantity of sulfur than CaO - SiO₂ slags; and at any metal oxide-silica ratio, should dissolve more sulfur than MgO - SiO₂ slags. The high FeO activity is reflected in the low free energy of formation value for Fe₂SiO₄ and the instability of FeSiO₃ (Table 3).

The low CaO activity clearly indicates that very little CaS could form even though its free energy value is as favorable as that for FeS. The large negative free energies of formation of the calcium silicates and aluminosilicates listed in Table 4 indicate their stability with respect to CaS and thus the low CaO activities that could be expected in such liquids. The same principle would apply to Na₂O and Na₂S whose free energy values are almost identical. The stability of sodium silicates and aluminosilicates

silicates with respect to Na_2S would indicate that the activities of Na_2O would be very low even in relatively silica-poor liquids.

The low free energies of formation for magnesium silicates are reflected by the activity of MgO cited above. However, the large difference in the free energies between MgO and MgS prevent the formation of any appreciable amount of sulfide.

St. Pierre and Chipman (1956) confirmed much of the activity and sulfur-absorbing capacity data of Richardson and Fincham but maintain that $\text{FeO} - \text{SiO}_2$ slags can hold more sulfur than $\text{CaO} - \text{SiO}_2$ slags only when they contain more than 33 mole percent silica. Studies since that time have been concerned mainly with more accurate calculations of oxide activities but the overall conclusions have not changed.

Summary

As the topics discussed in this section have been taken from diverse fields, they are summarized below to stress their bearing on this study.

- 1) Silicate liquids have ionic bonds, whereas iron sulfide-oxide liquids have metallic-covalent bonds.

Table 3

Free Energy of Formation

Compound	ΔF° 1500°K	Reference
Ca_2SiO_4	-31.9 Kcal	Kay & Taylor (1960)
CaSiO_3	-20.6 Kcal	Kay & Taylor (1960)
$\text{CaAl}_2\text{Si}_2\text{O}_8$	-33.6 Kcal	Kay & Taylor (1960)
Mg_2SiO_4	- 9.4 Kcal	Henderson & Taylor (1966)
MgSiO_3	- 5.1 Kcal	Henderson & Taylor (1966)
Fe_2SiO_4	- 4.0 Kcal	Muan (1966)
FeSiO_3	+ 1. Kcal	Muan (1966)
Na_2SiO_3	-54.1 Kcal	Kelley (1962)
$\text{Na}_2\text{Al}\cdot\text{SiO}_4$	-36. Kcal	Kelley (1962)
$\text{Na AlSi}_2\text{O}_6$	-30. Kcal	Kelley (1962)
$\text{NaAlSi}_3\text{O}_8$	-39. Kcal	Kelley (1962)

- 2) Sulfur substitutes most readily for oxygen in sites where the $\text{Me} - \text{O} : \text{Me} - \text{S}$ bond energy ratio is the lowest.
- 3) Anions that share the largest proportion of their oxygen with metal cations form most readily in silica-poor liquids. With increasing silica content, $\text{Si} - \text{O} - \text{Si}$ bonds form.
- 4) The distribution of ions in silicate liquids is never ideal; thus a number of $\text{Me} - \text{O} - \text{Me}$ bonds are always present. The number of these bonds is proportional to the activity of MeO which, in general, decreases with increasing silica content.
- 5) In slags with equal molar proportions of CaO , MgO and FeO , and more than about 33 mole percent silica, the activities of the oxides are in the general order $\text{FeO} > \text{MgO} >> \text{CaO}$.
- 6) Of the major rock-forming metal cations, ferrous iron forms the weakest and least ionic bond with oxygen, has the lowest ratio of relative bond energies $\text{Me} - \text{O} : \text{Me} - \text{S}$, and has a relatively low free energy change in the oxygen-sulfur substitution.
- 7) From these data it would appear that the solubility of sulfur in a polymetallic silicate liquid, containing more than about 33 mole percent silica, is mainly a function of the activity of ferrous iron.

8) In general, the activity of ferrous iron, and other metal cations, is high in basic melts and low in siliceous ones and the capacity of these melts to dissolve sulfur should be directly proportional.

9) Sulfur in excess of the amount that can substitute in the silicate liquid structure forms a separate sulfide phase that will be an ' immiscible ' liquid if the temperature of the system is above the melting point of this phase.

Extraction of sulfides from a silicate liquid

It would be of considerable geologic interest to know how sulfides could be extracted from silicate liquids and especially if physico-chemical mechanisms exist to make them exsolve at a relatively rapid rate. From the data reviewed in this chapter the most obvious means of exsolving sulfides would be to decrease the activity of metal oxides, and that of the FeO in particular. Some possible mechanisms to achieve this are listed below:

- 1) addition of silica to increase the silicate anion: metal cation ratio.
- ii) addition of oxygen to convert ferrous iron to the ferric state.

iii) addition of other substances to form stable complexes with FeO and the other metal oxides.

iv) precipitation of iron-rich phases other than the sulfides.

Methods i, ii, and iv are examined in the study of phase equilibria in the system FeS - FeO - Fe₃O₄ - SiO₂.

Chapter III

Previous Phase Equilibrium Work

A substantial number of studies have been made on the phase relations in the system $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$. Most of them, however, deal with the $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2$ ternary, while those containing FeS are mainly of a reconnaissance nature.

$\text{FeO} - \text{Fe}_3\text{O}_4$: This join forms a part of the larger system $\text{Fe} - \text{O}$ whose phase relations have been investigated by Darken and Gurry (1945) and Phillips and Muan (1960) among others (Fig. 3). Iron oxide in its lowest oxidation state, wustite, is not stoichiometric FeO but forms a cell deficient in iron. The wustite structure can be considered as a close-packing of oxygen atoms with some of the metal positions of the NaCl arrangement empty. Neutron diffraction studies by Roth (1960) indicate that some iron atoms lie in the tetrahedrally coordinated positions occupied

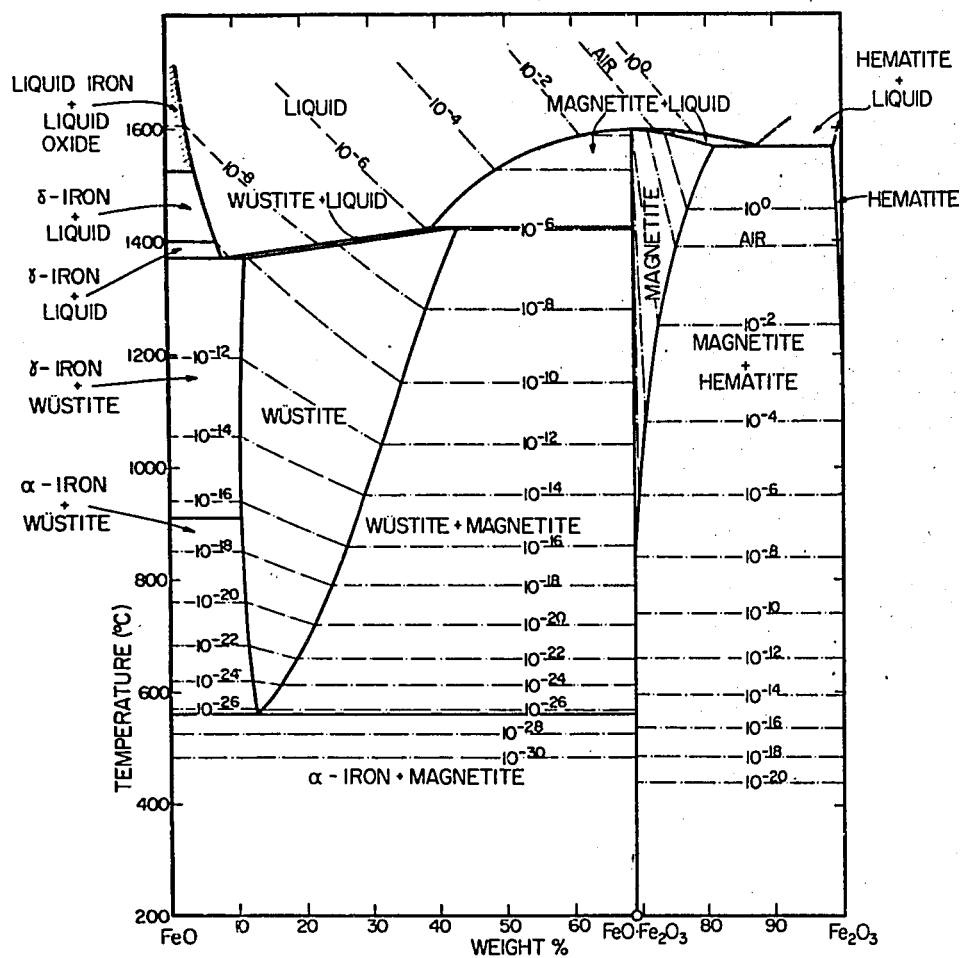


Fig. 3 The FeO - Fe₂O₃ system as compiled by Muan and Osborn (1965), mainly after Darken and Gurry (1945) and Phillips and Muan (1960). Light dash-dot lines are oxygen isobars.

by metal atoms in the spinel structure instead of the octahedrally coordinated positions of the NaCl type arrangement. Darken and Gurry (1945) set the limits of the wustite field between 23.15 and 25.60 percent oxygen whereas stoichiometric FeO would contain 22.27 percent oxygen. (Weight percent is used here and throughout this report unless otherwise stated.). Wustite with an oxygen content greater than about 25.3 percent melts incongruently at 1421°C to yield magnetite plus liquid. Below 560°C, wustite breaks down to form iron and magnetite.

Stoichiometric magnetite (27.63% oxygen) is stable at all temperatures below the liquidus. However, magnetite can become increasingly deficient in iron (max. 28.40% oxygen) at high temperatures in an oxidizing atmosphere (Phillips and Muan, 1960).

FeO - SiO₂: This system was first studied by Bowen and Schairer (1932) using iron crucibles as charge containers. They recognized that wustite was not stoichiometric FeO and that iron was the primary crystallizing phase along a large part of the joinⁱⁿ. Calculating all iron as FeO they give the composition of fayalite as 70.5 FeO, 29.5 SiO₂, melting at 1205±2°C. However, they found that fayalite always contained about 2.25 percent Fe₂O₃.

Small changes have been suggested by Schuhmann and Ensio (1951) and by Allen and Snow (1955) for the $\text{FeO} - \text{Fe}_2\text{SiO}_4$ section of the join. The latter determined the melting point of fayalite at $1204 \pm 2^\circ\text{C}$ and found its composition to change from 70.16 FeO, 0.14 Fe_2O_3 , 29.78 SiO_2 to 63.55 FeO, 2.00 Fe_2O_3 , 34.45 SiO_2 with an increasingly oxidizing atmosphere. They place the eutectic between wustite and fayalite at 75.0 FeO, 3.6 Fe_2O_3 , 21.4 SiO_2 , and $1177 \pm 2^\circ\text{C}$.

$\text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$: Muan (1955) investigated this system thoroughly. The phase relations are shown in Figure 9 and are discussed on page 48.

$\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4$: Vogul and *Fulling (1948) found a simple eutectic melting relation between FeO and FeS at 70 FeS and 920°C , whereas Asanti and Kohlmeier (1951) show it at 60 FeS and 940°C . Ol'shanskii (1951), in a more comprehensive study, determined the eutectic at 65 FeS with the temperature varying from 920°C to 1000°C as the oxygen content of wustite changes from 23.15 to 25.60 percent. Hilty and Crafts (1952), using iron crucibles in a controlled atmosphere of argon determined an eutectic at 920°C involving iron, wustite and troilite at 67Fe, 24 S and 9 O. In a later study Naldrett (1967), using "modified silica tube techniques",

determined the eutectic between iron, wustite, troilite and liquid at $915 \pm 2^\circ\text{C}$ with the composition 68.2 Fe, 24.3 S, 7.5 O. He found " a ternary invariant point where pyrrhotite (composition 62.8 ± 0.2 wt. percent Fe) + wustite \rightleftharpoons magnetite + liquid ", at 934°C and composition 67.3 Fe, 25.1 S, 7.6 O.

FeO - FeS - SiO₂: Ol'shanskii (1951) in his extensive study of the Fe - FeO - FeS - SiO₂ system determined the coordinates of some invariant points which are of interest here since they actually fall within the FeS - FeO - Fe₃O₄ - SiO₂ system. This is due to the wustite he used which contained up to 25.6 percent oxygen. He determined the position of the iron-troilite-wustite eutectic at 28.7 FeO, 6.3 Fe₂O₃, 65.0 FeS and 920°C . This point almost coincides with his iron, troilite, wustite, fayalite quaternary eutectic which contains less than one percent SiO₂. Although he found an immiscibility gap between sulfide and silicate liquids he does not extend it as far as the Fe₂SiO₄ - FeO join. Along the FeS - SiO₂ join he could find no evidence of solubility between silica and FeS even at temperatures approaching 1700°C .

A later investigation by Yazawa and Kameda (1953), using iron and silica containers, shows the immiscibility

gap encroaching well upon the fayalite field. They determined the composition ^{at} ~~of~~ the invariant point, fayalite - silica - two-liquids at 54 FeO, 28 SiO₂, 18 FeS, and 1140°C. The phase relations in this system are discussed on page 50 .

Chapter IV

Experimental Procedures

Introduction

Combinations of iron sulfide, iron oxide and silica were used as starting material in all runs. Appropriate amounts of these materials were weighted out, placed in small alumina containers, and sealed in evacuated silica glass capsules. The sealed charge was suspended in a vertical, platinum-wound resistance furnace, heated at a constant temperature for a specified length of time, then rapidly quenched in water or a 10 percent NaCl solution (see Seybolt and Burke, 1953). Using these techniques the components come to equilibrium with their own gas phase. As long as the vapor space is kept small and the partial pressures of the components remain low it can be treated as a condensed system.

Troilite: Troilite was synthesized by heating iron (99.999% Fe) and sulfur (99.999+%S) in evacuated silica glass capsules at 550°C until all the sulfur had reacted. Subsequently the temperature was raised to 850°C for a few days

to homogenize the material.

Wustite and magnetite: Wustite and magnetite were synthesized in a similar fashion. Iron and reagent grade Fe_2O_3 were heated in evacuated silica glass capsules at 600°C for a few hours to ensure reaction of all the iron. The charge was then reground and heated at 750°C for a few days for homogenization. This technique was followed to avoid reaction with the silica capsule. The composition of each charge was checked using the gravimetric method described by Foster and Welch (1956).

Silica: Powdered silica glass was used as a source of silica. Total impurities, of which Al_2O_3 makes up over half, are approximately 80 parts per million.

Charge Containers

The most difficult experimental problem encountered was that of finding a suitable container to hold the charges. This is undoubtedly the reason for the lack of phase equilibria work in sulfide-oxide-silicate systems. After an extensive search and long testing period, a dense, highly-pure, recrystallized alumina container was found to be suitable for work in most of the system. McDanel AP35 high temperature recrystallized alumina tubes, O.D. 7mm, I.D. 5mm, length 15mm, were the containers used in much of the study. Reaction between the charge and alumina tube was most ex-

tensive when silica was the primary crystallizing phase. In other parts of the system ^{there} was very little reaction with the containers. Some containers were used for as many as ten runs with no noticeable corrosion of the walls.

A series of runs was made with alumina containers along the $\text{FeO} - \text{SiO}_2$ join to check if the amount of alumina going into solution was sufficient to affect liquidus temperatures. The temperatures determined were within $\pm 5^\circ\text{C}$ of those in published data.

Silica glass capsules were used to check the liquidus temperature of points in the system saturated with tridymite. This technique was only partially successful as the liquid continually reacted with the capsules converting the silica glass to tridymite. This resulted in a large mass of tridymite crystals being formed and the liquid became dispersed throughout the walls of the capsule making identification of the phases difficult.

In a similar fashion iron tubes were used to check points in the system in equilibrium with iron. Finally, check runs were made with charges in gold capsules at temperatures below 1025°C in the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4$ system. The results of these runs were within the limit of error of those made in other containers (see Table 4, p.44.)

Temperature Control and Measurement

Sealed charges were suspended in a vertical platinum-wound electrical furnace regulated by an accurate temperature controller. The hot spot in the furnace was uniform within 1°C over a length of 5cm. Temperatures were measured with a Pt : Pt + 13Rh thermocouple and a Rubicon type B potentiometer. The thermocouple was calibrated periodically against the melting point of gold (1063°C).

Identification of Phases

Primary and quench crystals of all phases were easily distinguishable in polished sections using a Zeiss Photomicroscope. Troilite and wustite form crystals with rounded outlines (Plate 1 & 2) whereas crystals of magnetite, fayalite and tridymite have angular outlines (Plates 2, 3 and 4).

A Nonius-Guinier-deWolfe powder X-ray camera was used to detect and identify phases in some of the runs. Shifts in cell parameters of phases were measured with a Phillips Norelco diffractometer.

Chapter V

The System $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$

Introduction

A quaternary system has five independent variables: pressure, temperature and three concentration variables. In systems where vapor pressures are low the vapor phase can be neglected and Gibbs Phase Rule is restated:

$$F + P = C + 1$$

where F = number of degrees of freedom, or variance

P = number of condensed phases present at equilibrium

C = number of components.

Such a system approaches a condensed system. The $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system is not an ideal condensed system as the vapor pressures of both sulfur and oxygen are fairly high in magnetite-rich parts. However, if the vapor space is kept small the amount of sulfur and oxygen lost is insignificant

throughout most of the system.

The phases and compositional extent of the system are outlined in Figure 4. Data for the system was collected on the ternary boundary faces (Figs. 8, 10, and 11), triangular joins within the composition tetrahedron which are hinged along the $\text{FeS} - \text{SiO}_2$ join (Figs. 5 and 6), and on triangular joins parallel to the $\text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ face (Fig. 7). None of these triangular joins are ternary; thus, boundary lines on them represent intersections of quaternary divariant surfaces with the composition plane, and the intersection of a univariant line with the join is a piercing point.

In a large part of this system iron sulfide is soluble in the silicate liquid only to a limited extent, and excess iron sulfide forms an immiscible sulfide-rich liquid. These conjugate liquids will be referred to as 'silicate' and 'sulfide' liquids respectively. The sulfide liquid generally contains from 20 to 35 percent iron oxides and a few percent silicates.

Experimental Results:

Experimental runs were first made on the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4$ system (Fig. 8). The data on these runs and others in the quaternary system are given in the Appendix Tables.

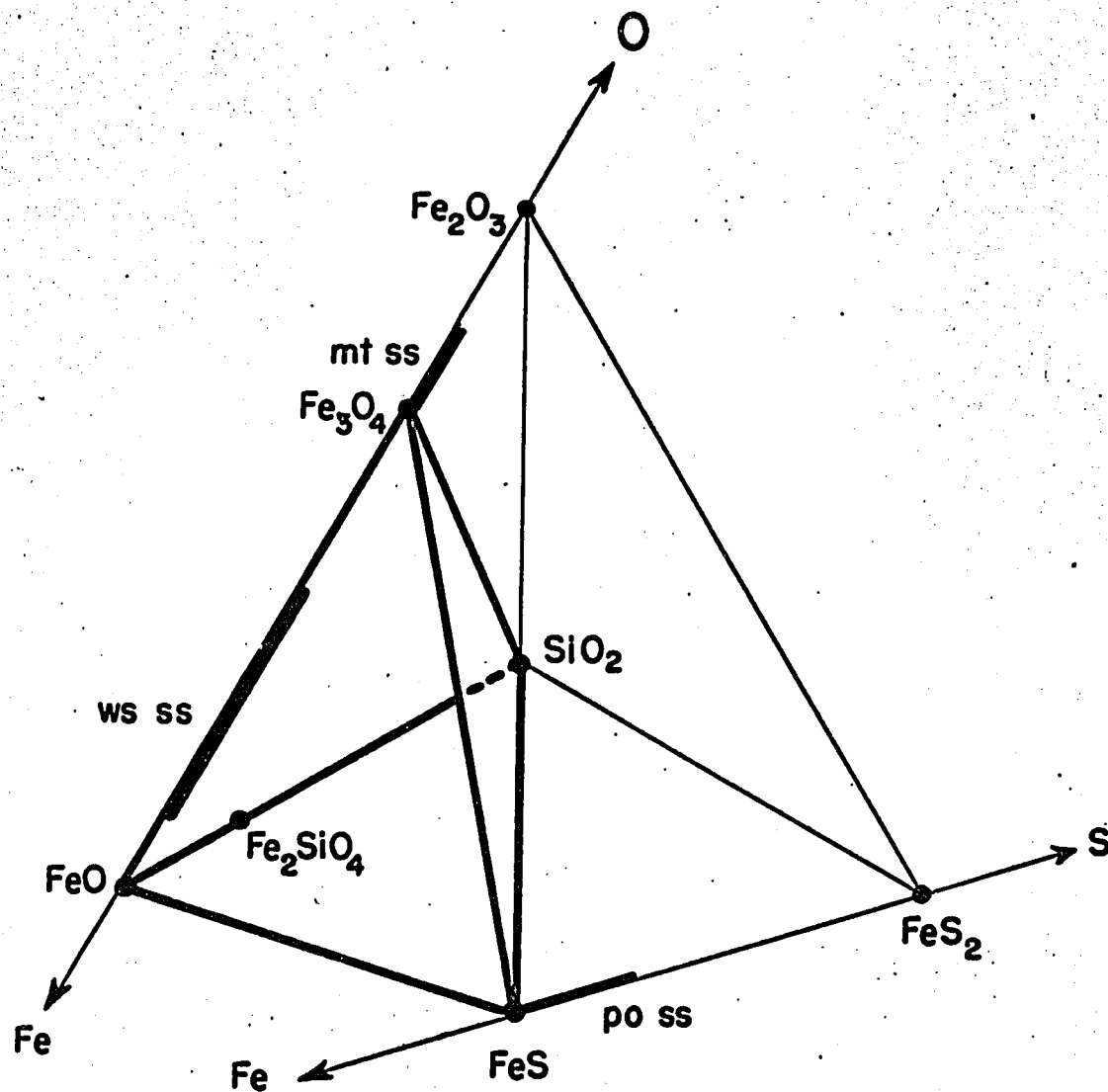


Fig. 4 Diagram showing the position of the $\text{FeS-FeO-Fe}_3\text{O}_4\text{-SiO}_2$ tetrahedron in relation to the Fe-O-S-SiO_2 system.

Liquids formed by melting eutectic mixtures of FeS, FeO and Fe₃O₄ quench to fine intergrowths that have the general appearance of those shown on Plates 1 & 2. If the mixture is not the eutectic composition the quenched liquid may have the same structure, but more often quench crystals* of the phases in excess of the eutectic composition form just prior to the full solidification of the charge (Plate 1c). Pyrrhotite and wustite quench crystals have dendritic forms, while magnetite forms crosses with barbed ends that may be in various stages of infilling growth to octahedra (Plate 3). Winegard (1962) gives a detailed description of the processes involved in the formation of these eutectic intergrowths.

When silica is added to iron oxide - iron sulfide liquids it reacts with FeO to form iron silicate liquids. On cooling these silicate liquids crystallize rapidly making it difficult to quench them to a glass. Quench fayalite crystals are easily distinguished from primary fayalite by their smaller size, elongated habit, and the large number of inclusions they often contain (Plates 3 and 4). Their presence may hinder the recognition of small droplets of immiscible sulfide liquid by growing through the droplet and thus breaking it up.

* Quench crystals form during cooling and are not in equilibrium with the liquid at the temperature of the run.

Furthermore, when fayalite quench crystals, which apparently do not contain any appreciable amount of sulfur, grow in a silicate liquid containing dissolved sulfide they may supersaturate the remaining silicate liquid and cause droplets, i.e., "quench droplets", of sulfide liquid to separate. These quench droplets are sometimes difficult to distinguish from those formed under equilibrium conditions.

Mixtures within the 2-liquid volume, have very sharp liquidus points. A mixture in the silicate-rich part of this volume may be 75 percent crystalline in one run, and in the next run, 5 degrees or less higher, it is completely liquified and separated into the two immiscible phases. Silica-poor mixtures within this phase volume separate readily into two distinct liquid layers, denoting the low viscosity of the silicate liquid formed (Plates 4 and 5). On the other hand mixtures close to the tridymite phase volume yield viscous silicate liquids in which the sulfide liquid occurs as rounded droplets which remain in suspension for a long period of time (Plate 5c). The quenched immiscible sulfide liquids have eutectic intergrowths of iron oxide and iron sulfide and quench-formed crystallites similar to those in the sulfide-oxide and sulfide-oxide-silicate liquids described above.

The depression of the temperature of the iron-wustite-fayalite eutectic by the addition of FeS is 223 degrees (see Table 4). This liquid at the lowest melting point, R, however, contains only about one percent silica. Similarly, the ternary eutectic iron-fayalite-tridymite is depressed 38 degrees and the magnetite-fayalite-tridymite eutectic by 45 degrees to the FeS-saturation points at J and I_A respectively. (Fig. 10, p. 52) These results demonstrate the limited fluxing action of FeS on iron silicate liquids.

In Figures 5 and 6 the Fe_3O_4 : FeO ratio has been increased at intervals that divide the tetrahedron of the FeS - FeO - Fe_3O_4 - SiO_2 system into approximately equal parts. A large proportion of the experimental runs within the quaternary system was made on these joins. The iron oxide in Figure 5 represents the iron-rich end of the wustite solid^{solution} series. Primary phases on this join have stability fields similar in outline to those for the phases in equilibrium with iron (see Fig. 10). However, separating phases do not necessarily lie on this join. For instance, when fayalite or a wustite solid solution precipitates, the liquid moves off the join. Similarly, neither liquid formed from compositions within the two-liquid field lies on the join.

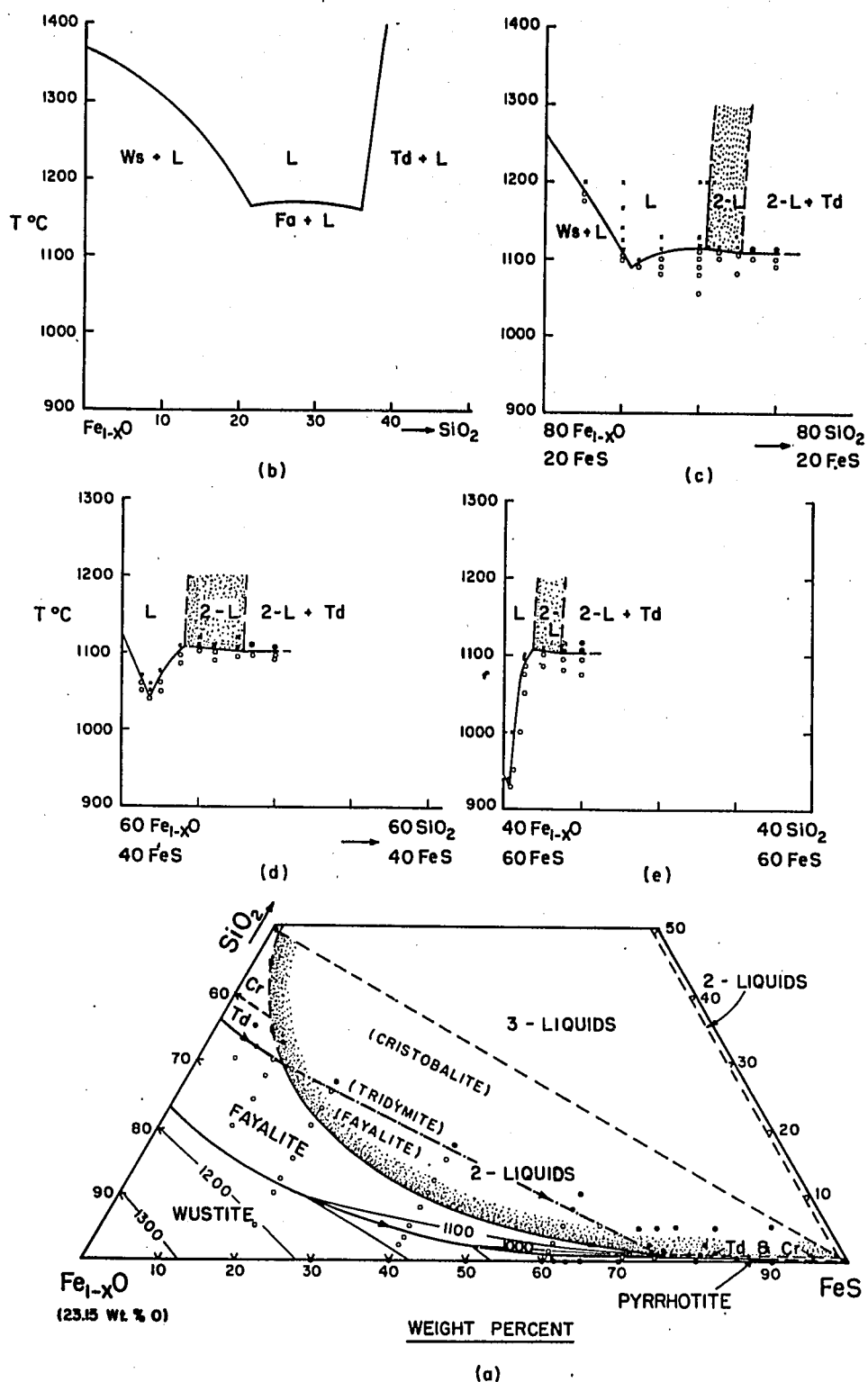
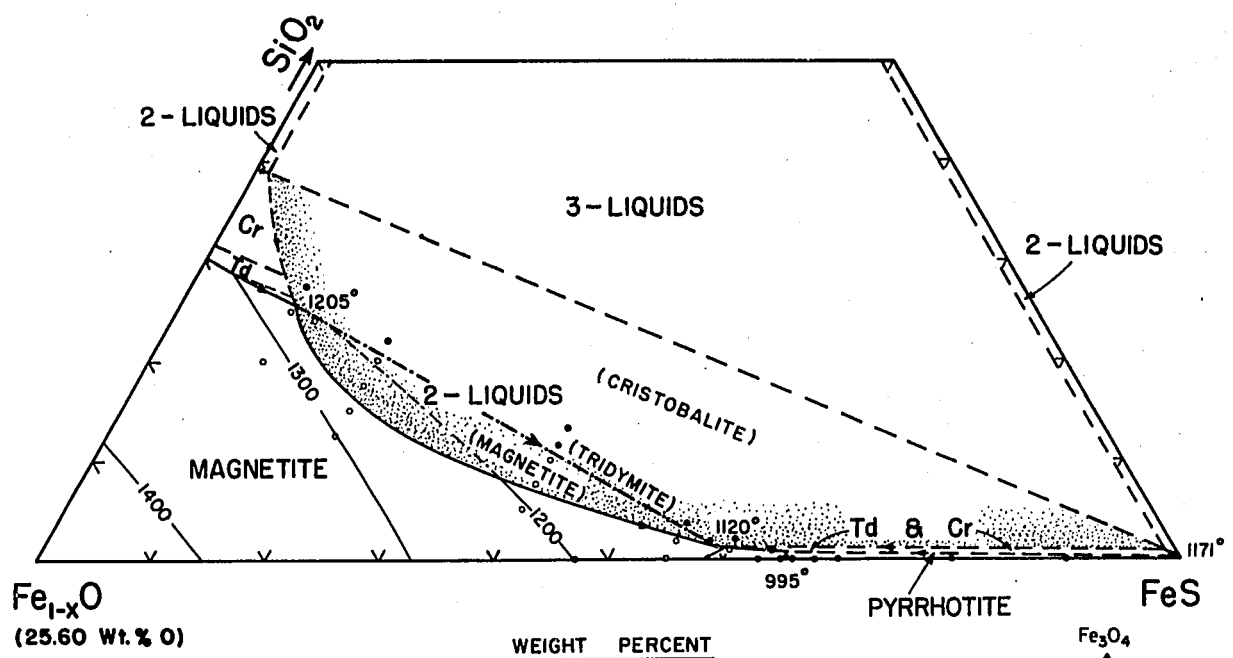
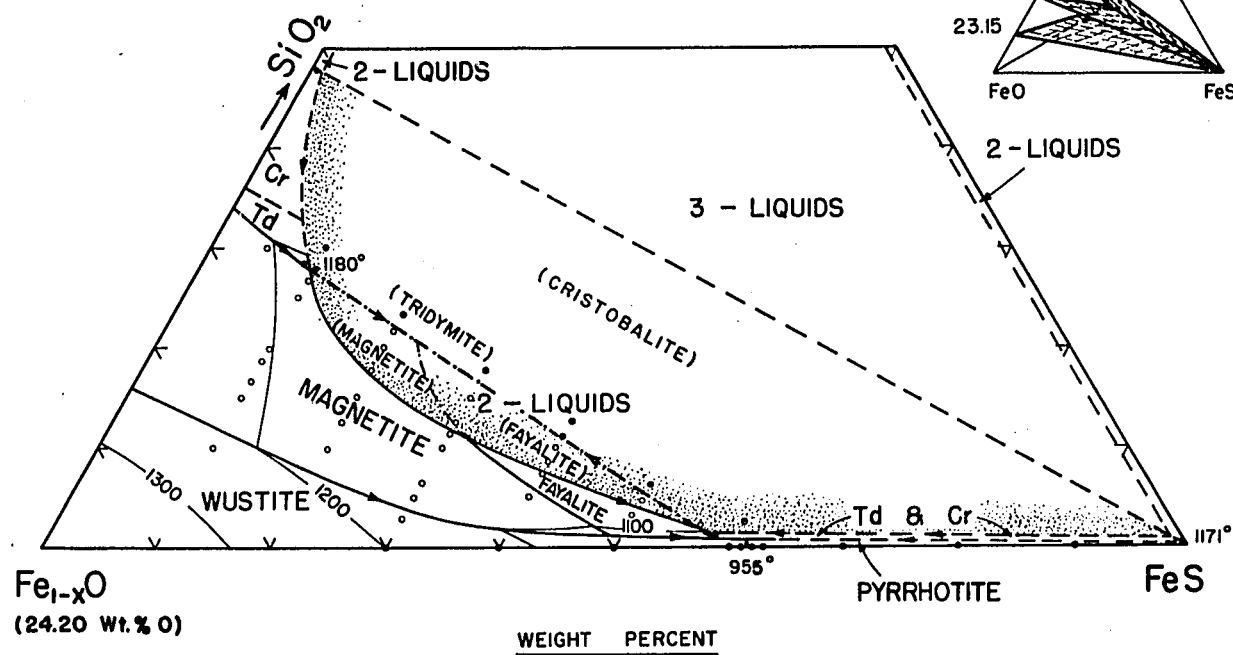


Fig. 5 (a) The join $\text{FeS-Fe}_{1-x}\text{O}$ (23.15 wt.% O) - SiO_2 is not ternary, thus phase boundaries are intersections of quaternary divariant surfaces with the join. The outline of the 2-liquid field is stippled and phases in parenthesis are stable just below this field. The trough formed by the surfaces of fayalite and tridymite with the 2-liquid phase slopes to the right. (See position of this join in the inset in Fig. 6).

(b - e) Cross-sections parallel to the FeO-SiO_2 boundary showing the outline of phase volumes with respect to temperature. Liquids form at low temperatures in section (e) but can dissolve only a small amount of silica below the 2-liquid field. Td = tridymite, Cr = cristobalite, open circles = liquidus, closed circles = liquid + tridymite, + = liquid.



(b)



(a)

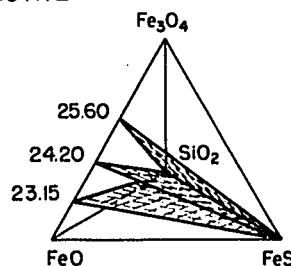


Fig. 6 Triangular joins like Fig. 5a, but with the Fe_{1-x}O end member containing (a) 24.20 and (b) 25.60 weight percent oxygen. The inset at right shows the locations within the quaternary system of the three joins shown in Figs. 5a and 6.

The shape of the two-liquid field in Figures 6a and 6b, ternary joins increasingly richer in Fe_3O_4 ,^{is} similar to that in Figure 5. With the increasing Fe_3O_4 : FeO ratio, magnetite replaces fayalite as the primary phase in contact with the two-liquid field and finally excludes wustite from the join altogether.

The joins in Figure 7 demonstrate the phase relations in the system from a different point of view. These sections, parallel to the $\text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ face (Fig. 9), show the effect of adding FeS to this system. The main feature of interest is the encroachment of the tridymite and two-liquid fields on the fayalite, magnetite and wustite fields with increasing amounts of FeS in the system.

In the cross-sections in Figure 5 a trough is formed by the boundaries of the two-liquid field with fayalite on the one side and tridymite on the other. Quenched runs along the outer edge of the two-liquid field of these sections and in other parts of the system indicate the boundary of the two-liquid field to be essentially vertical. That is, charges just within this field, heated high above the liquidus, show no evidence of homogenization. Alternately, a homogenous liquid cannot penetrate the two-liquid field to any extent upon cooling.

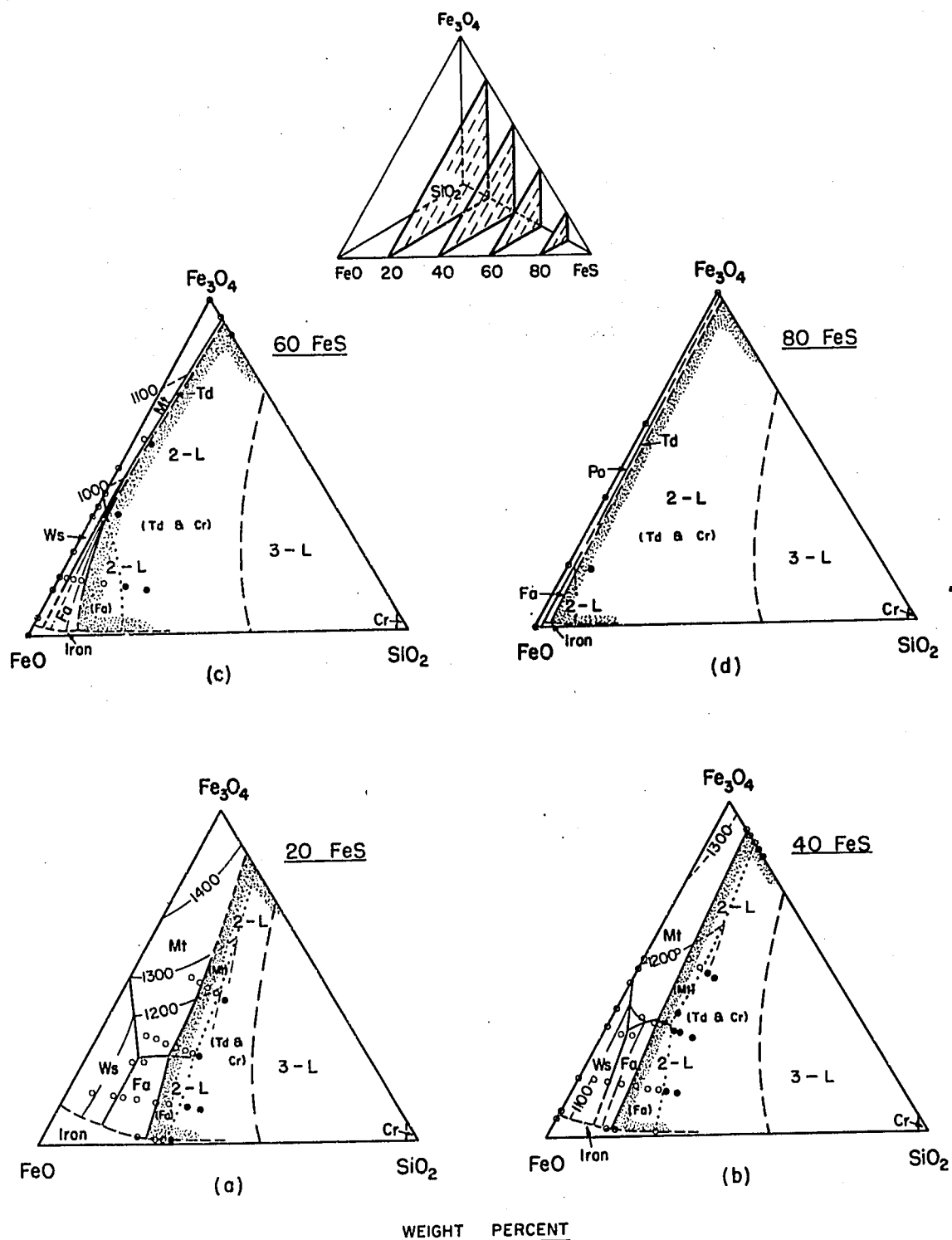


Fig. 7 Projection of the phase relations on the sections shown in the inset onto the FeO - Fe_3O_4 - SiO_2 face of the tetrahedron. The outer edge of the 2-liquid field is stippled. These diagrams illustrate the changes in phase relations caused by the addition of FeS to the iron oxide - silica system.

Coordinates for the ternary and quaternary invariant points in the system are given in Table 4. All the quaternary points, with the exception of I and R, are reaction points; that is, one phase is resorbed at these points by reaction with the liquid. Crystallization paths for various liquid compositions are discussed in the following sections. The boundary ternary systems are discussed first; they are simpler to follow and include many of the relations encountered in the quaternary system.

Crystallization in the Ternary Systems

FeS - FeO - Fe₃O₄ : The system FeS - FeO - Fe₃O₄ (Fig. 8) is not strictly ternary due to the presence of a primary field of iron and the variability of the ratio of iron to sulfur in FeS with increasing Fe₃O₄ content. However, the field of iron presents no difficulties in the interpretation of the system, and it is only in the Fe₃O₄ corner that the divergence of FeS from its stoichiometric ratio is so large that it cannot be ignored.

A pyrrhotite, containing about 48.5 mole percent iron, is stable at the liquidus of FeS (Jensen, 1942), but becomes more iron-rich as the temperature is lowered and reaches FeS (troilite) at about 1070°C. Similarly, in the FeS - FeO - Fe₃O₄ system, with the exceptions noted below, pyrrhotite is

Table 4. Invariant points determined in the FeS - FeO - Fe₃O₄ - SiO₂ system.

Invariant Point	Composition (wt.%)				Temp. °C	Phases present	fo ₂ * (atm.)	fs ₂ ** (atm.)
	FeS	FeO	Fe ₃ O ₄	SiO ₂				
U	70		30		1025 ±5	mt,po,l,v		10 ⁻²
S	62	37	1		920 ±3	iron,ws,po(tr), l,v	10 ^{-16.5}	10 ⁻⁷
T	62	23	15		950 ±5	ws,mt,po,l,v	10 ⁻¹⁴	10 ⁻⁵
P	70		29	1	1020 ±5	mt,td,po,l,v		10 ⁻²
R	62	36	1	1	917 ±3	iron,ws,fa,po(tr), l,v		10 ⁻⁷
Q	62	22	15	1	945 ±5	ws,mt,fa,po,l,v		10 ⁻⁶
N	63	20	16	1	955 ±5	mt,fa,td,po,l,v	10 ^{-13.5}	10 ⁻⁵
O	85	14	0.5	0.5	1075 ±10	iron,fa,td,po(tr), l,v	10 ⁻¹⁵	10 ⁻⁴
I	10	40	21	29)	1095 ±5	mt,fa,td,2-L,v	10 ^{-9.5}	
L	57	26	15	2)				
J	16	57	1	26)	1140 ±5	iron,fa,td,2-L,v	10 ^{-13.5}	
K	83	15	0.5	1.5)				

fa = fayalite, mt = magnetite, po = pyrrhotite, td = tridymite,
tr = troilite, ws = wustite, l = liquid, v = vapor, 2-L = coexisting
silicate and sulfide liquids

* fo₂ values are taken from Figure 3.

** fs₂ values are approximated by extrapolating the data of Toulmin
and Barton (1964) from the Fe - S system.

the stable liquidus phase above 1070°C and troilite the stable phase below this temperature. For convenience we will refer to all these iron sulfides as pyrrhotite. FeS also loses iron to the oxides when magnetite is at the liquidus and becomes continually more iron-deficient as the Fe_3O_4 content of the system is increased. However, the amount of iron lost by the sulfide is small, less than 1 weight percent, even along the FeS - Fe_3O_4 join. The partition of iron between the oxide and sulfide phases can be approximated from the change in composition of pyrrhotite and by the small amount of wustite formed which can be detected microscopically or by the Guinier - DeWolfe X-ray diffraction camera.

The solubility of FeS in wustite and magnetite, and of FeO and Fe_3O_4 in pyrrhotite, was experimentally determined to be markedly less than one-half weight percent. Thus the effect of FeS on the fugacity of oxygen (f_{O_2}) of iron oxides, and of iron oxides on the fugacity of sulfur (f_{S_2}) of pyrrhotite would be negligible except under very high oxygen pressures where species such as SO_2 and SO_3 can form. No trace of these species has been found in this system in the form of iron sulfites or sulfates. The f_{O_2} for various iron oxide mixtures can then be taken directly from Figure 3. Similarly, the f_{S_2} can be approximated by extrapolating

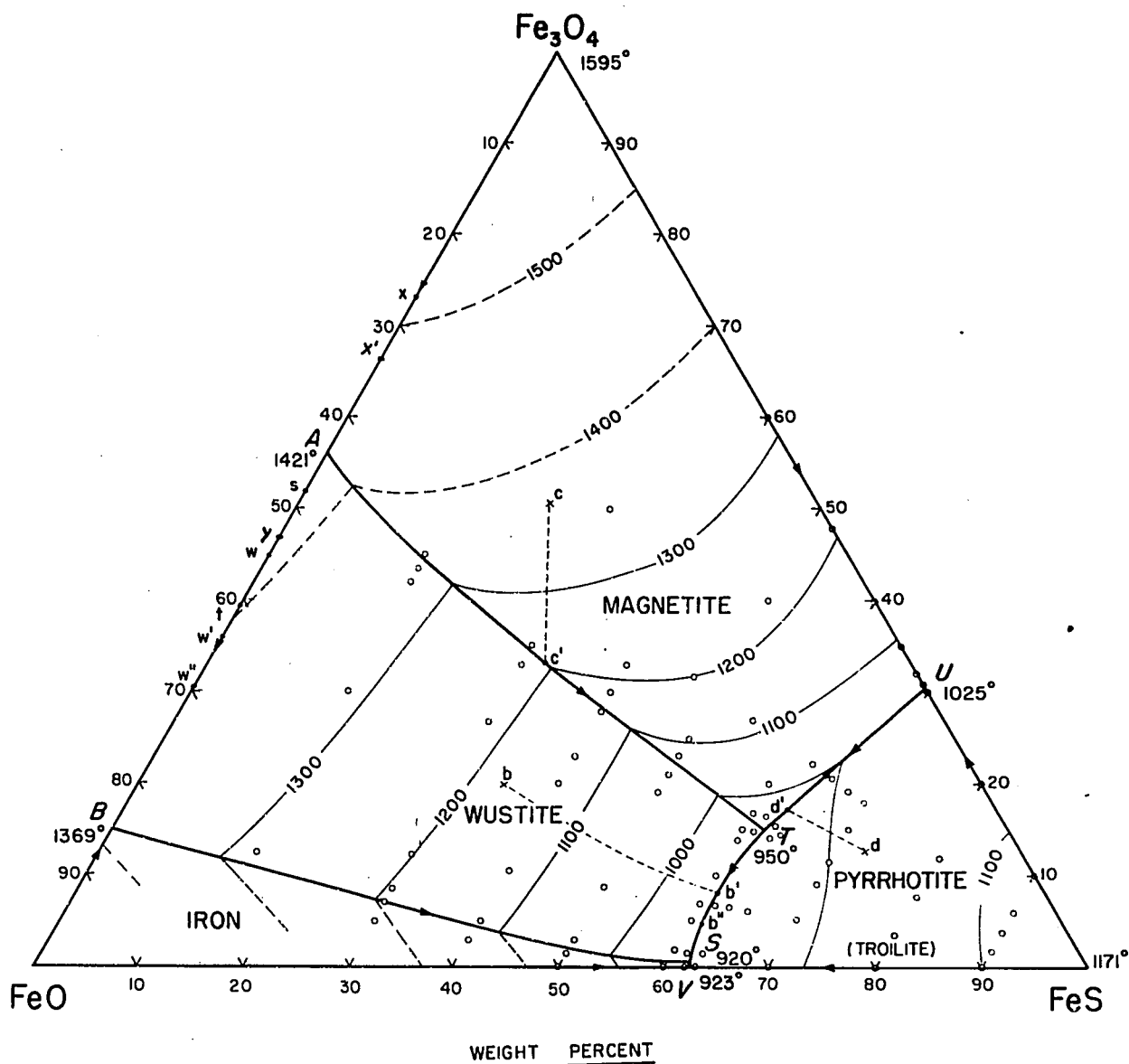


Fig. 8 The FeS - FeO - Fe₃O₄ system. Troilite is the stable phase of iron sulfide at S. AT is a reaction line between magnetite and wustite, and T is a ternary peritectic where, in the presence of pyrrhotite, magnetite reacts with liquid to form wustite containing 24.5 wt.% oxygen. Approximations of f_{O_2} taken from Fig. 3 are $10^{-16.5}$ atm. at S and 10^{-14} at T. Corresponding f_{S_2} values are in the order of 10^{-7} atm. at S and 10^{-5} at T (extrapolated from the data of Toulmin and Barton, 1964). Wustites w, w' and w'' are in equilibrium with liquids b, b' and b''. Magnetite crystallizes from liquid c and reacts with liquid at c' to form wustite of composition s; the final liquid disappears at T. Pyrrhotite crystallizes from liquid d, followed by magnetite at d' and wustite (t) at T.

Toulmin and Barton's (1964) data to liquidus temperatures in the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4$ system. The same reasoning holds for assemblages in the quaternary system since FeS is not measurably soluble in the silicate minerals; f_{O_2} 's are known for the quartz-fayalite-iron and quartz-fayalite-magnetite assemblages. Table 4 includes the f_{O_2} and f_{S_2} at the invariant points where available data was applicable.

Paths of liquids b, c and d are traced on Figure 8 to illustrate the crystallization of liquids in this system. The boundary curve AT is a reaction line and the invariant point T is a ternary peritectic. S is a ternary eutectic point where troilite and wustite form a minimum melting point with iron.

When heat is withdrawn from a liquid of composition b the first crystals of wustite have the approximate composition w and the liquid moves a short distance along the path bb' . With continued loss of heat the liquid moves to b' while the wustite continually changes its composition from w to w' ; the tie line $b'w'$ passes through b at the moment the liquid reaches the univariant line TS at b' . As pyrrhotite separates with wustite the liquid moves down TS toward S. Tie lines now exist between wustite, pyrrhotite and liquid. At b'' the liquid is completely consumed, the final product being a mixture of pyrrhotite and wustite of composition w'' .

The point w'' is fixed by the tie line between pyrrhotite and wustite which must pass through b .

Similarly, a liquid of composition c in the magnetite field precipitates magnetite while the liquid moves along a path to c' formed by projecting a straight line from Fe_3O_4 through c . At c' magnetite reacts with the liquid to form wustite of composition s while the liquid moves along the boundary line AT to the invariant point T . The mean composition of the separated iron oxides as the liquid reaches T is x , on the line $T - x$ which passes through c . As the last of the liquid disappears, the mean composition of the iron oxides is at x' , and the final crystalline solid phases are magnetite, wustite (composition t) and pyrrhotite.

The liquid d in the pyrrhotite field is chosen to demonstrate the primary separation of pyrrhotite and a crystallization sequence in which much of the early formed magnetite reacts to form wustite. With the separation of pyrrhotite the liquid moves from d to d' on the univariant line UT . Magnetite and pyrrhotite separate continually as the liquid moves from d' to the invariant point T . The liquid at T reacts with magnetite to form wustite. The mean composition of the iron oxide when crystallization is complete is represented by the point y , which falls on the Fe_3O_4 side of t , the composition of wustite separating from

melts at T. Thus the final crystalline assemblage is magnetite, pyrrhotite and wustite (24.5 wt.%O).

Fractional crystallization of early formed wustite and magnetite produces liquids rich in iron.

FeO - Fe₃O₄ - SiO₂: The crystallization paths of liquids in this system have been fully discussed by Muan (1955) and some of his results are presented here since they are important to an understanding of the more complicated crystallization history of the FeS - FeO - Fe₃O₄ - SiO₂ system.

In Figure 9 liquid b in the wustite field precipitates wustite of composition w. The liquid moves from b along the curved path to b' on the univariant line CD while the wustite composition changes continually from w to w'. As long as wustite is the only separating phase the tie line between the liquid and wustite must pass through b. At b' fayalite starts to precipitate with wustite, and the liquid moves along DC towards D. Tie lines now exist between wustite, fayalite and the liquid. When the tie line between wustite and fayalite coincides with b, the last of the liquid disappears at b'' and the wustite has a final composition of w''. After the start of crystallization wustite becomes poorer in oxygen until fayalite begins to precipitate. The

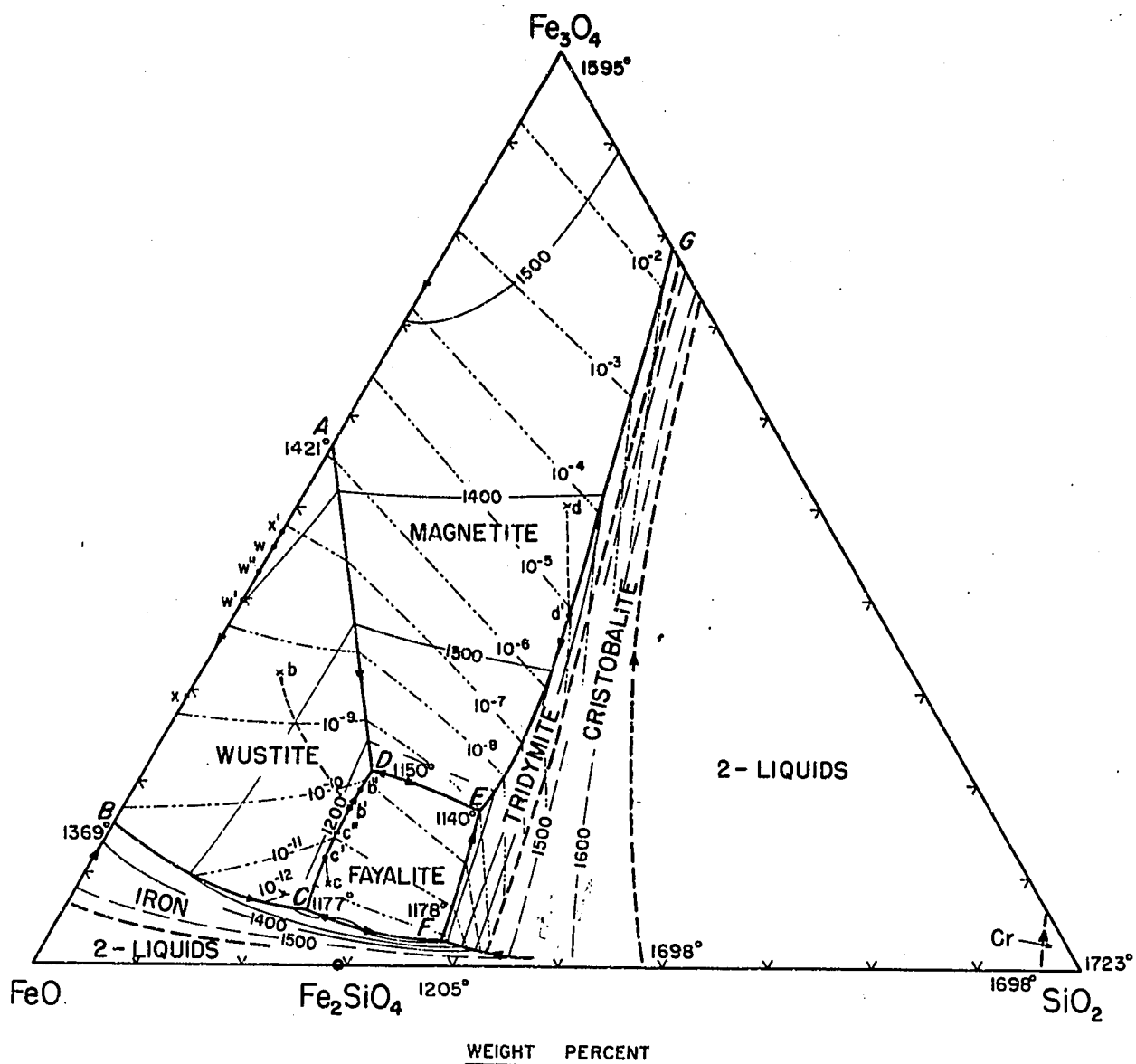


Fig. 9 The $\text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system. Dashed-double dot lines are oxygen isobars. Wustite of composition w is in equilibrium with liquid b , w' with b' , and w'' with b'' . Wustite x is in equilibrium with liquid c' , and x' with c'' . (After Muan, 1955)

reversal in trend at this point is caused by the precipitation of fayalite (Fe_2SiO_4) which enriches the liquid in Fe_3O_4 .

In the fayalite field a liquid of composition c precipitates fayalite and the liquid moves along the extension of the straight line $\text{Fe}_2\text{SiO}_4 - c$ to c' on the univariant line CD. At c' wustite of composition x separates and the liquid moves down CD until the last of it is consumed at c'' . Simultaneously, the composition of wustite changes to x' , determined by the projection of the line $\text{Fe}_2\text{SiO}_4 - c$ to the $\text{FeO} - \text{Fe}_3\text{O}_4$ boundary. The final crystalline aggregate is fayalite and wustite.

Liquids along the join $\text{Fe}_2\text{SiO}_4 - \text{Fe}_3\text{O}_4$ crystallize to mixtures of fayalite and magnetite. Liquids on the SiO_2 side of this join always yield an aggregate of fayalite, magnetite and tridymite. As an example, a liquid of composition d crystallizes magnetite and moves along the line $\text{Fe}_3\text{O}_4 - d$ to d' where it is joined by tridymite. With further cooling the liquid moves along the univariant line GE to the invariant point E where fayalite also separates.

$\text{FeS} - \text{FeO} - \text{SiO}_2$: In the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system, the iron phase volume intrudes to a considerable

extent over much of the $\text{FeS} - \text{FeO} - \text{SiO}_2$ face of the tetrahedron (see Fig. 12). The amount of intrusion is greatest at the FeO apex where it is in contact with the wustite phase volume, and gradually decreases with the addition of FeS and SiO_2 . Ultimately, iron is excluded from the system by pyrrhotite, with which it has a eutectic melting relation. (Pyrrhotite is used here to denote all forms of iron monosulfide though, at temperatures below about 1070°C , troilite is the stable form in equilibrium with iron.) The presence of the iron is due to the non-stoichiometry of both wustite, which is always more iron-deficient than FeO , and fayalite which contains variable amounts of ferric iron (see page 25). Quenched runs on this face of the tetrahedron, with the exception of the pyrrhotite field, thus have iron at the liquidus. The boundaries between iron and other phase volumes can be fixed by determining the temperature at which the last phase in equilibrium with iron disappears. That is, determining the liquidus temperatures of other phases in the presence of iron crystals. This is equivalent to making runs in iron containers which was the method used by Bowen and Schairer (1932) in the system $\text{FeO} - \text{SiO}_2$, and Yazawa and Kameda (1953) in their study of the $\text{FeS} - \text{FeO} - \text{SiO}_2$ system.

The phase relations on Figure 10 are slightly revised after Yazawa and Kameda (1953). Their studies and those in the present work were made on the surface of the iron phase

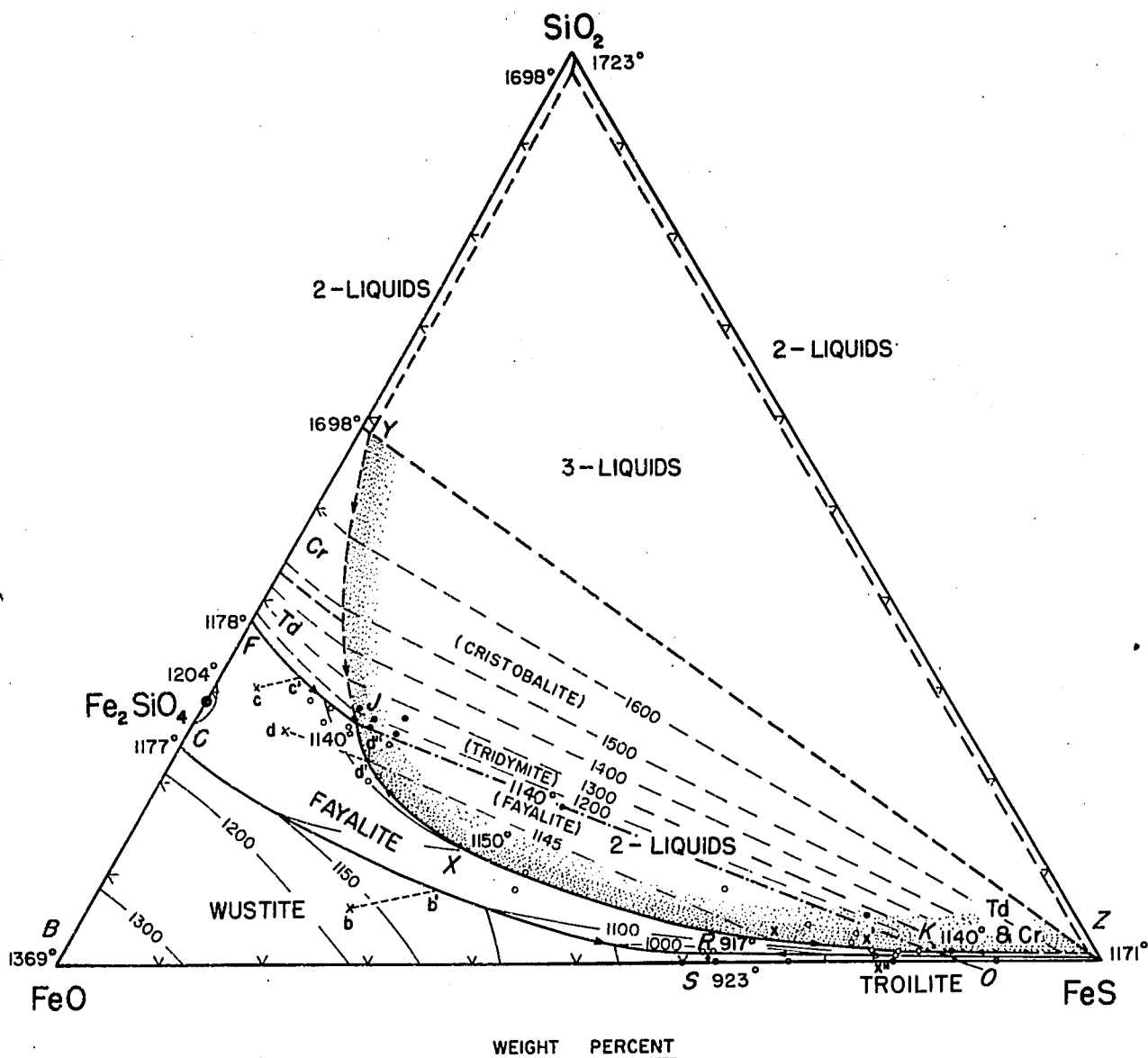


Fig. 10 The FeS - FeO - SiO₂ system revised after Ol'shanskii (1951) and Yazawa and Kameda (1953). All phases are in equilibrium with iron except troilite, thus phase boundaries are projected onto this plane from within the FeS - FeO - Fe₃O₄ - SiO₂ system. The outer edge of the 2-liquid field (silicate and sulfide liquids) is stippled. Contours within the 2-liquid field are on the surfaces between this field and the fields of the crystalline phases (in parenthesis). The surfaces slope inward from X and YZ to the isothermal trough JK. Silicate, silica and sulfide liquids coexist in the 3-liquid field at a temperature of approximately 1675°C. The crystallization of liquids b, c, and d are explained in the text.

volume except for compositions within the pyrrhotite field, and are projected from the Fe apex of Figure 4 onto the FeS - FeO - SiO₂ join. In the summary of crystallization paths of liquids given here, compositions from the FeO - FeS - SiO₂ join are used. Thus, iron is the primary phase on this surface in that part of the system studied except for the primary field of pyrrhotite. The composition of wustite coexisting with iron is very nearly constant over the temperature range in this system.

A melt on the FeS - FeO - SiO₂ join precipitates iron and the liquid moves to b on the iron-wustite phase boundary, where it precipitates wustite and moves to b' on the univariant line CR. Wustite, fayalite and iron separate from b' to R, a quaternary eutectic point, where they are joined by pyrrhotite. The liquid remains at R, the lowest liquidus temperature point in the quaternary system, until crystallization is complete.

Similarly, a melt originating on the FeS - FeO - SiO₂ join precipitates iron and moves to c in the fayalite field of Figure 10. Fayalite and iron precipitate from c to c', on the univariant line FJ, where they are joined by tridymite. With further cooling the composition of the liquid changes from c' to the invariant point J where the silicate liquid is

in equilibrium with iron, fayalite, tridymite and the conjugate sulfide liquid K. When the silicate liquid at J is consumed, the sulfide liquid at K, now having gained a degree of freedom, continues to precipitate iron, fayalite and tridymite and moves along the univariant line KO to the invariant point at O. At O, pyrrhotite precipitates together with iron and fayalite, as the liquid resorbs tridymite. Since the composition of the original melt lies within the triangle $\text{FeS} - \text{Fe}_2\text{SiO}_4 - \text{SiO}_2$, the liquid is consumed before all the tridymite is resorbed, and the final solid is an aggregate of iron, fayalite, tridymite and pyrrhotite.

The liquid d, on the FeO side of the $\text{Fe}_2\text{SiO}_4 - \text{FeS}$ join, is used to illustrate a crystallization sequence in which the two-liquid field is encountered prior to the separation of tridymite. The liquid at d precipitates iron and fayalite and moves to d' on the boundary of the two-liquid field. The conjugate line JK forms a trough at the base of the two-liquid field whose sides slope inward from X and YZ. Conjugate silicate and sulfide liquids lie on isothermal lines on the sides of the trough. Thus the silicate liquid at d' is in equilibrium with a sulfide liquid at x. The silicate liquid now moves along XJ to d'' where, separating iron, fayalite and the sulfide liquid x', it finally disappears.

The position of x' is fixed by the relation that the line $\text{Fe}_2\text{SiO}_4 - x'$ must pass through d as the last of the liquid at d'' disappears. The sulfide liquid at x' then continues to precipitate iron and fayalite while moving across the iron-fayalite divariant surface to x'' on the univariant line OR , where pyrrhotite first appears. The liquid then moves to the eutectic at R , and the final product is an assemblage of iron, fayalite, pyrrhotite and wustite.

Liquids slightly more silica-rich than d will reach J , and when the silicate liquid is consumed the conjugate sulfide liquid will move to O . If the original liquid lies within the composition triangle $\text{FeO} - \text{Fe}_2\text{SiO}_4 - \text{FeS}$, all the silica at O is resorbed and the final liquid moves to R . Otherwise, crystallization ends at O .

Liquids whose bulk compositions lie within the two-liquid field have crystallization histories similar to those whose residual liquids penetrate this field. Liquids in the silica fields precipitate tridymite, move to the points J and K and finish crystallizing at O . At extremely high temperatures, in the vicinity of 1675°C , a three-liquid field was encountered in SiO_2 -rich compositions by Ol'shanski (1951); presumably, all such liquids finish crystallizing at O .

FeS - Fe₃O₄ - SiO₂: Much of the liquidus on this face of the tetrahedron was beyond the range of the experimental techniques used here. It was possible to get information only in the vicinity of the eutectic P (Fig. 11). The miscibility gap outside the projected boundary of the tridymite field is still present though it does not extend as far towards the FeS corner as on the FeS - FeO - SiO₂ face. Consequently, the sulfide liquid M, in equilibrium with magnetite and tridymite, contains a higher proportion of iron oxides. This is probably caused by the large shift of the tridymite field towards the Fe₃O₄ - FeS boundary of the diagram. Crystallizing liquids in all parts of this system will migrate to P to form an aggregate of magnetite, tridymite and pyrrhotite.

It appears from the few liquidus runs made around the miscibility gap that the FeS - Fe₃O₄ - SiO₂ join deviates considerably from ternary conditions. Conjugate liquids would lie on the join if it were ternary. Since magnetite is in equilibrium with pyrrhotite at the liquidus, the iron lost by the original FeS would lower the liquidus temperatures of the iron silicate liquid.

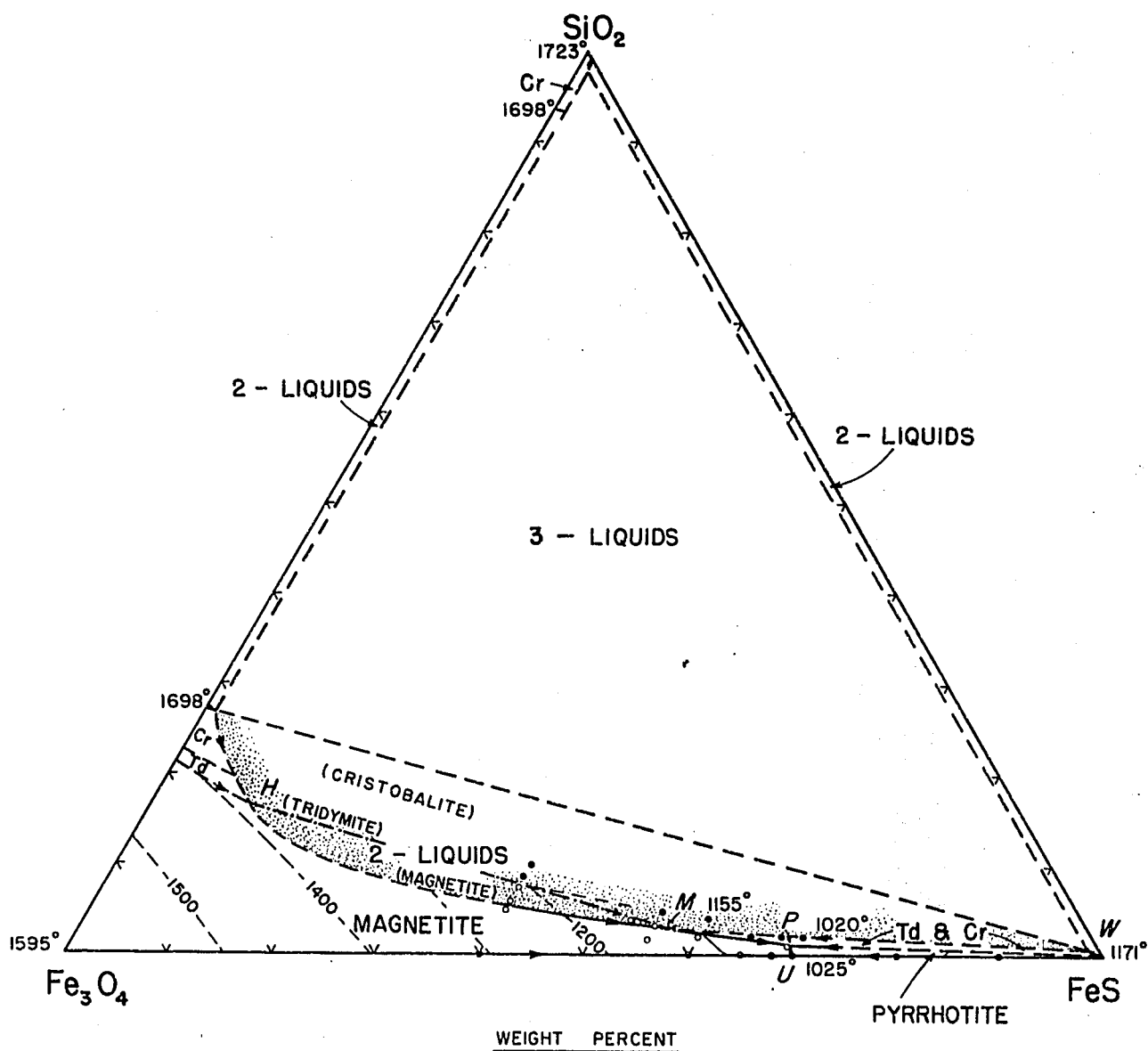


Fig. 11 The $\text{FeS} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system is not ternary due to the variability of the composition of pyrrhotite. Dashed lines are inferred. The outer edge of the 2-liquid field is stippled and phases below this field are in parenthesis.

Td = tridymite, Cr = cristobalite; open circles = liquidus, closed circles = liquid + tridymite.

Crystallization in the Quaternary System

The phase relations for the condensed system $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ are illustrated in the tetrahedron of Figure 12. No quaternary compounds are formed nor were stability fields of other new compounds encountered within the system. The previously described phase relations for the faces of the tetrahedron are drawn in with light lines, while those that penetrate the tetrahedron are shown as heavy lines. The lines within the tetrahedron are univariant, formed by the intersection of three divariant surfaces. Phase relations within the silica phase volume were not studied, and have thus been omitted from the quaternary diagrams.

The change in the system from the $\text{FeS} - \text{FeO} - \text{SiO}_2$ to the $\text{FeS} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ face is equivalent to the straight addition of oxygen to the system. That is to say, as oxygen is added, ferrous iron is converted to the ferric state to accommodate the increased negative charge. Ferrous oxide has the ability to combine with silica to form fayalite (Fe_2SiO_4) and liquids that can have a somewhat higher silica content (see Fig. 9). On the other hand, ferric oxide does not form stable compounds with silica alone and in the liquid state can dissolve a much smaller quantity of silica.

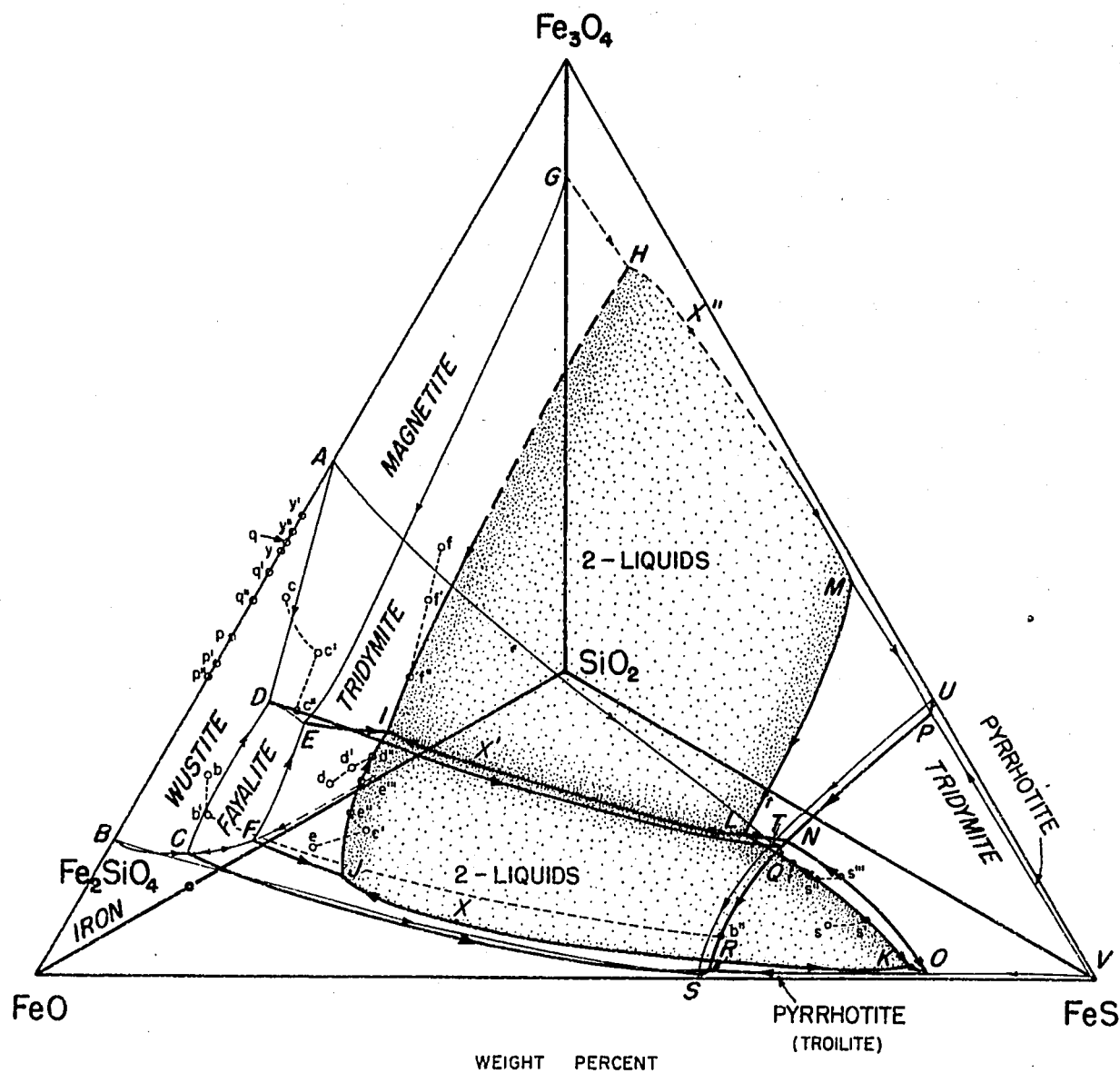


Fig. 12 Diagram of liquidus phase relations in the FeS - FeO - Fe₃O₄ - SiO₂ system. The SiO₂ apex is to the rear of the tetrahedron; the front surface of the 2-liquid phase volume is stippled. Light lines on the faces of the tetrahedron are phase boundaries; heavy lines are quaternary univariant lines. Phase relations are shown only in front of the 2-liquid and tridymite phase volumes. Quaternary invariant points are: J and K, 1140°, (iron, fa, td, 2-L, v); I and L, 1095°, (mt, fa, td, 2-L, v); N, 955°, (mt, fa, td, po, l, v); Q, 945°, (ws, mt, fa, po, l, v); R, 917°, (iron, ws, fa, po, l, v); other data are given in Table 4. Liquids b and c are in the wustite phase volume, d and e in the fayalite, and f in the magnetite phase volume. s, s' and s'' are the conjugate sulfide liquids of silicate liquids e', e'', and e'''; similarly, r and d' are conjugate liquids. The FeO - Fe₃O₄ - SiO₂ ternary is after Muan (1955). The FeS - FeO - SiO₂ system is revised after Ol'shanskii (1951) and Yazawa and Kameda (1953). mt = magnetite, ws = wustite, fa = fayalite, td = tridymite, po = pyrrhotite, l = liquid, 2-L = two liquids, v = vapor.

The miscibility gap separating silicate-rich and sulfide-rich liquids extends unbroken from the $\text{FeS} - \text{FeO} - \text{SiO}_2$ to the $\text{FeS} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ face (Fig. 12). The silicate liquid at the invariant point I is in equilibrium with magnetite, fayalite, tridymite and the sulfide liquid L. Similarly, silicate liquids along the univariant lines HI and JI have their conjugate sulfide liquids at points having the same temperature along ML and KL respectively.

The points X, X' and X'' are at maximum temperatures on the lines JXK, IX'L and HX''M. Temperatures on the curved divariant surface JIX'LKX, between the two-liquid and the fayalite phase volumes, decrease very little toward the univariant line IX'L. On the other side of this line, however, where magnetite is in contact with the two-liquid phase volume along surface HIX'LX'', the liquidus temperature increases rapidly away from IX'L.

The pyrrhotite phase volume is extremely thin, extending a very short distance from the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4$ face into the tetrahedron. It never contains more than about one percent SiO_2 . However, the lowest liquidus temperatures of the system are associated with this phase volume, and consequently pyrrhotite is strongly concentrated in the last liquids to solidify.

Tracing the paths of crystallization of liquids in the quaternary system is mainly an extension of the phenomena encountered on the faces of the tetrahedron. Liquids of the compositions b, c, d, e and f are used to typify some paths of crystallization in this system.

Wustite phase volume: The liquid b is used to illustrate the crystallization paths followed by liquids with a low oxygen content in the wustite phase volume. As heat is withdrawn from the liquid b, wustite of composition p crystallizes and the liquid moves along a curved path to b' on the wustite-fayalite divariant surface CDQR. As the liquid is moving to b' the wustite composition changes to p', such that the tie line between b' and p' passes through b. The points b, b', FeO and Fe_3O_4 all lie in one plane. Fayalite precipitates with wustite as the liquid moves down the temperature gradient on the divariant surface to b'' on the univariant line QR, where pyrrhotite joins the precipitating phases. The liquid disappears between b'' and R, the final crystal assemblage being pyrrhotite, fayalite and wustite of composition p''. The points FeS, Fe_2SiO_4 and p'' form a plane that passes through b.

A liquid with a higher oxygen content, c, separates wustite of composition q and moves to c' on the divariant surface ADQT while the wustite composition changes to q'.

Magnetite separates as the liquid moves from c' to c'' on the univariant line DQ ; c , c' , c'' , FeO and Fe_3O_4 all lie in one plane. As the liquid reaches c'' the mean composition of the iron oxides crystallized is at y , the point of intersection of the extended line $c'' - c$ and the $FeO - Fe_3O_4$ join. From c'' the liquid moves down the univariant curve DQ , separating fayalite, magnetite and wustite. Just as the liquid reaches the invariant point Q , fayalite, iron oxides and liquid form a plane that includes c , thus fixing the bulk composition of the iron oxides at y' . At Q , pyrrhotite separates with fayalite and wustite as the liquid dissolves magnetite. The final crystalline assemblage is wustite of composition q'' (24.5 wt.%O), magnetite, fayalite and pyrrhotite, with the bulk composition of the iron oxides moving to y'' .

Fayalite phase volume: Liquids crystallizing in the fayalite phase volume can also take diverse paths. Let us first examine the path taken by the SiO_2 -rich liquid d near the $FeO - Fe_3O_4 - SiO_2$ face. With a drop in temperature fayalite precipitates and the liquid moves along the line $Fe_2SiO_4 - d$ to d' on the divariant surface $EFJI$, where tridymite makes its appearance. From d' the liquid moves across the divariant surface to d'' on the univariant line JI . At this point a sulfide liquid, r , separates at the intersection of the isothermal surface through d'' and the univariant line

KL. With further cooling the liquids d'' and r move to I and L respectively. At invariant point I, fayalite, tridymite, magnetite and the sulfide liquid separate until the liquid at I is consumed. As soon as this happens the liquid L gains a degree of freedom and moves along the univariant line LN to N. Pyrrhotite precipitates at invariant point N and silica reacts with the FeO-enriched liquid. Since the original mixture was within the composition tetrahedron $FeS - Fe_3O_4 - Fe_2SiO_4 - SiO_2$, the liquid is consumed at N and fayalite, tridymite, magnetite and pyrrhotite are the final products.

A second liquid, e , having a much lower oxygen content, separates fayalite and moves to e' on the surface JTK of the two-liquid volume. A conjugate sulfide liquid s separates from e' . The liquids e' and s move to e'' and s' on the univariant lines JI and KL where tridymite begins to crystallize, then along these lines to e''' and s'' until the silicate liquid is consumed. The position of e''' can be computed since the position of s'' is known from the geometry of the relation: the plane containing the phases Fe_2SiO_4 , SiO_2 and liquid s'' must include the original bulk composition e at the moment the liquid at e''' disappears. The sulfide liquid has now gained another degree of freedom and, while continuing to precipitate fayalite and tridymite, moves across the divariant

surface KLNO to s''' on the univariant line ON. Pyrrhotite joins the separating phases at s''' , and the liquid moves to the invariant point N where magnetite, fayalite and pyrrhotite separate as the liquid reacts with tridymite. Since the original liquid e was in the composition tetrahedron $\text{Fe}_2\text{SiO}_4 - \text{Fe}_3\text{O}_4 - \text{FeS} - \text{SiO}_2$, the liquid is consumed at N and tridymite is present in the final crystal aggregate.

Crystallization paths of liquids that are very poor in silica in this phase volume may not intersect the two-liquids field. Instead they intersect the fayalite-pyrrhotite divariant surface RQNO, precipitate pyrrhotite, and move to one of the univariant lines NQ or QR. From these liquids, wustite or magnetite, or a mixture of the two, crystallizes with fayalite and pyrrhotite.

Other phase volumes: The crystallization of liquids of compositions within the magnetite volume is very similar to that just described for the fayalite volume, except that magnetite is the primary separating phase. As an example, the liquid f in the silicate-rich end of the magnetite phase volume precipitates magnetite and moves to f' , on the magnetite-tridymite divariant surface GHIE, along a straight line joining Fe_3O_4 to f. Tridymite separates with magnetite as the liquid moves down the temperature gradient on this surface

to f'' on the univariant line HI where the conjugate sulfide liquid t begins to separate on the univariant line ML. The point f'' is at the intersection of the plane $\text{Fe}_3\text{O}_4 - \text{SiO}_2 - f$ and the line HI. With further cooling the liquids move to the compositions I and L at the invariant point. When the liquid at I is consumed, the liquid at L moves to N. Since f is within the composition tetrahedron $\text{Fe}_3\text{O}_4 - \text{Fe}_2\text{SiO}_4 - \text{FeS} - \text{SiO}_2$, magnetite, faylite, tridymite and pyrrhotite are the final products. Liquids in the magnetite phase volume that lie outside this tetrahedron move from N to the invariant point Q and have wustite in place of silica in the final assemblage.

Liquids that lie in any of the other phase volumes crystallize in a similar manner. Crystallization of these liquids ends at the invariant points N, Q or R, or on the connecting univariant lines NQ and QR.

Fractional Crystallization

If melts in this system are cooled in such a manner that fractional crystallization can take place, the crystallization history is affected in two ways. (1) The reaction between magnetite and liquid to produce iron-poor wustite, and that of iron-poor wustite and liquid to yield an iron-

rich variety, are prevented from going to completion by the removal of the early-formed crystals from the system. As a result, the composition of liquids on the univariant lines DQ and QR change at a faster rate and the amount of reaction at the invariant point Q is lessened. The final liquids in all these cases are depleted in Fe_3O_4 with respect to those formed under equilibrium conditions.

(2) The second reaction is between tridymite and liquid at the invariant point N. Liquids reaching N from the univariant lines LN, PN and ON (Fig. 12) have precipitated tridymite along the way. Upon reaching N, the liquid reacts with tridymite while precipitating pyrrhotite, fayalite^{al} and magnetite. With the early removal of tridymite, or its incomplete conversion to fayalite, the liquid moves to N and on to Q where magnetite and wustite begin to crystallize, respectively.

The same result could be achieved by allowing the immiscible sulfide liquid to settle and collect below the silicate liquid. The silicate fraction would be completely solid before the underlying sulfide liquid would begin to crystallize. Under these conditions it is unlikely that FeO released from the sulfide liquid would be in a position to react with tridymite in the overlying crystalline aggregate. It is also conceivable that FeO in dispersed sulfide liquid droplets would

not react with tridymite in a surrounding crystalline mass. Since these sulfide liquids along the univariant lines between P and R contain only about one percent fayalite, their crystallization history is essentially that of crystallization in the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4$ system. Consequently, the crystalline phases that will be present depend on the composition of the sulfide liquid and will be either pyrrhotite and wustite, or pyrrhotite, wustite and magnetite. Below 560°C , wustite breaks down to the stable assemblage of magnetite and iron (see Fig. 3).

Fractional crystallization that would help to produce the immiscible sulfide liquid at an early stage does not occur in the system. The divariant surfaces concerned with the migration of the silicate liquid toward the immiscibility gap are formed at the intersection of the tridymite-magnetite (EGHI surface), tridymite-fayalite (CDEF surface) and magnetite-fayalite (DEIX'LNQ surface) phase volumes. Since there is no reaction between these compounds and the silicate liquid, their removal from the system has no effect on the composition of the remaining liquid.

Models for the Evolution of Sulfide Liquids

Sulfide liquids in this system can be generated in two ways: 1) by straight enrichment of sulfide in the liquid through the crystallization of other phases, and 2) by the

intersection of the crystallizing silicate liquid with the immiscibility gap. Generation of sulfide liquid by the second method can be influenced by a number of conditions, including

- a) maintenance of a constant composition of the system,
- b) maintenance of a constant fugacity of oxygen, and c) increase in the fugacity of oxygen.

The terms 'constant composition' and 'constant fugacity of oxygen' (constant f_{O_2}) are used here in the same sense as by Muan (1955) and Osborn (1959). The former term indicates that nothing is added to or subtracted from the system during crystallization. Constant f_{O_2} is used for the conditions when the f_{O_2} in the system remains the same during crystallization; that is, it must be buffered from an external source. Under this condition the phases may change in oxygen content as crystallization proceeds.

To illustrate the evolution of sulfide liquids we will consider mixtures near the $FeO - Fe_3O_4 - SiO_2$ face since liquids in many other parts of the system can be derived from them by crystallization processes. These sulfide-poor liquids can further be divided into silica-poor and silica-rich groups each having distinct paths to follow during crystallization.

Model A. Constant composition - silica poor: The silica-poor group of liquids originates in the composition tetrahedron $\text{FeO} - \text{Fe}_2\text{SiO}_4 - \text{Fe}_3\text{O}_4 - \text{FeS}$ of Figure 12. As crystallization proceeds the liquids move to the univariant line DQ and then gradually become enriched in FeS until they reach Q where pyrrhotite begins to crystallize. By this time about 99 percent of the silicate has crystallized. Thus, the sulfide liquid is the end product of the continuous crystallization of a very basic liquid.

Model B. Constant composition - silica saturated: The silica-rich group of liquids is in the $\text{Fe}_2\text{SiO}_4 - \text{Fe}_3\text{O}_4 - \text{FeS} - \text{SiO}_2$ composition tetrahedron of Figure 12. Crystallization of one or more phases ultimately moves the liquid towards the invariant point I where an immiscible sulfide liquid separates. It will separate continually with the oxide and silicate phases until the liquid at I is completely consumed. However, the sulfide liquid forms only a small portion (about 10 wt.%) of the material separating at I. In these cases a sulfide liquid is produced at a much earlier stage of crystallization than in the silica-poor group of liquids of Model A.

Model C. Constant fugacity of oxygen: Oxygen fugacities at the liquidus in this system have been measured only for the $\text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ face (Fig. 9). However, for purposes of illustration we will study the phase relations on a triangular join connecting FeS , SiO_2 and a point on the $\text{FeO} - \text{Fe}_3\text{O}_4$ join. Isobaric planes containing particular iron oxide mixtures would be curved surfaces and would not coincide altogether with the triangular joins. But the discrepancy would likely be small enough not to affect the general aspects of the phase relations discussed here.

Using the plane $\text{FeO}_x - \text{FeS} - \text{SiO}_2$ (Fig. 13) as an isobaric section, we can consider the effects of constant f_{O_2} on the crystallization of a liquid within the magnetite phase volume. The liquid m precipitates magnetite, but instead of moving directly away from the Fe_3O_4 corner of the tetrahedron, it must move on the oxygen isobaric plane. That is, it moves away from FeO_x while continuously absorbing oxygen from the buffered system. This has the effect of enriching the liquid in silica and sulfide and, depending on the original composition of the liquid, tridymite or sulfide liquid is the next phase to separate. The liquid moves from m to I' which is an invariant point under these conditions, and, separating magnetite, tridymite and a sulfide liquid at L' , is completely used up at this point. The sulfide liquid must now also crystallize under constant f_{O_2} . Consequently, it moves to N' , an invar-

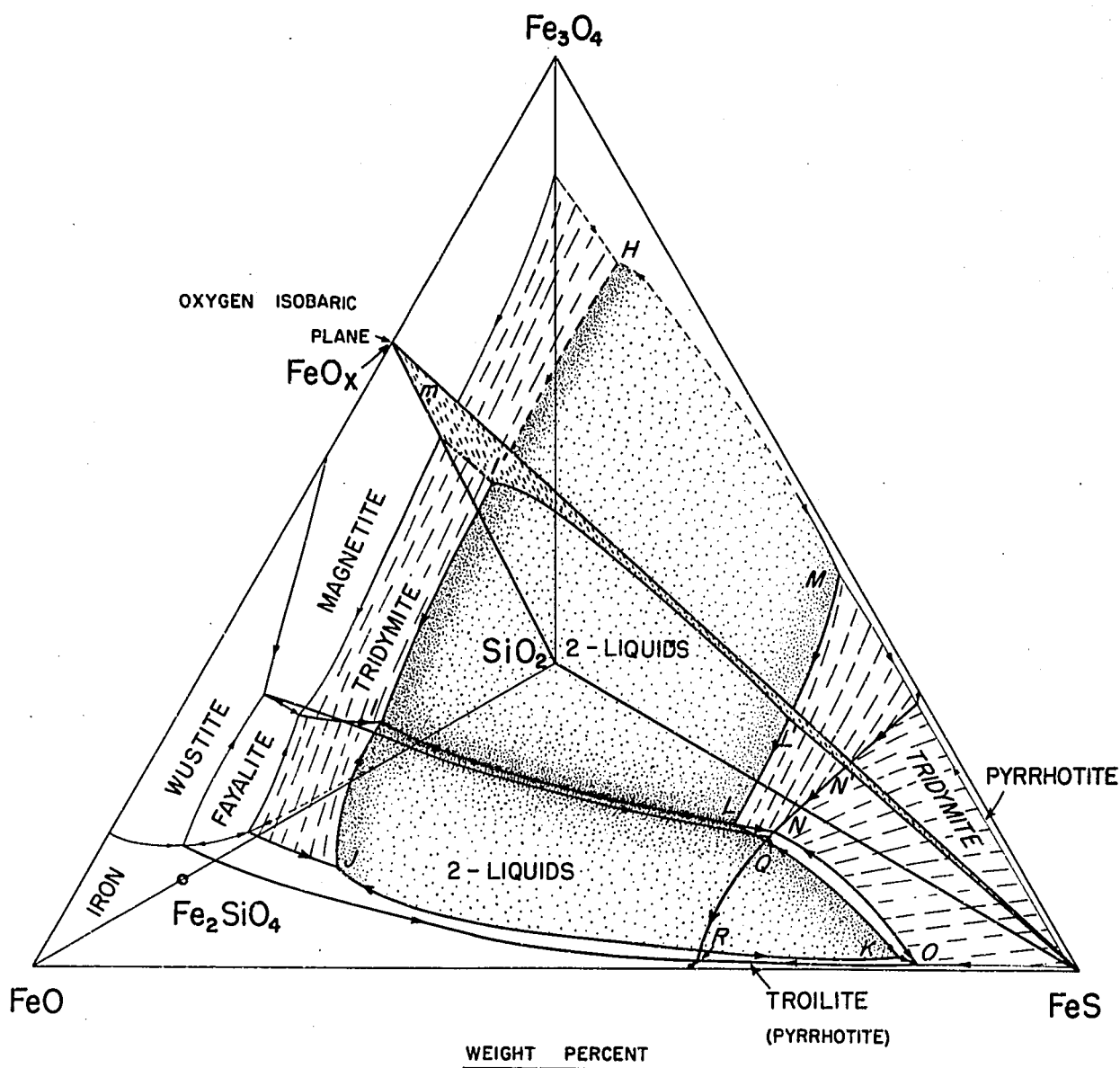


Fig. 13. Diagram of the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system showing the oxygen isobaric surface, discussed in the text for Model C, coinciding with the $\text{FeO}_x - \text{FeS} - \text{SiO}_2$ join. SiO_2 is to the rear of the tetrahedron. Surfaces of the tridymite and 2-liquid phase volumes are stippled to show their general shape and position within the tetrahedron. All crystallizing liquids move on the isobaric surface on which the points I' , L' , and N' are now invariant. Liquid m moves to I' and the sulfide liquid produced at L' moves to N' where crystallization is completed.

iant in this case, and crystallizes completely to magnetite, tridymite and pyrrhotite.

The significant points in this model are: (1) the rapid depletion of the liquid in ferrous oxide, (2) the production of a sulfide liquid at an early stage of crystallization, (3) the completion of crystallization of magnetite, tridymite and pyrrhotite at a higher temperature than would be the case if it crystallized at constant total composition, and (4) the final assemblage pyrrhotite-tridymite-magnetite can be formed at temperatures as much as 65 degrees lower than under constant composition conditions where it could only be formed from liquids originating on the $\text{FeS} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ face.

Model D. Increasing fugacity of oxygen: Silica is considerably more soluble in ferrous than in ferric oxide liquids (Fig. 9). Similarly FeS is more soluble in silica saturated FeO liquids than in those containing Fe_3O_4 (Figs. 10 and 11). Thus if the ferrous silicate liquid o (Fig. 14a) is oxidized, it is depleted in FeO, and the boundary of the silica field and 2-liquid field is moved across o toward the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4$ face of the tetrahedron. These relations are illustrated in Figure 14b which shows the change in liquidus temperatures at the outer edge of the 2-liquid field along the line A - A'. pp' and rr' are the 2-liquid field boundaries

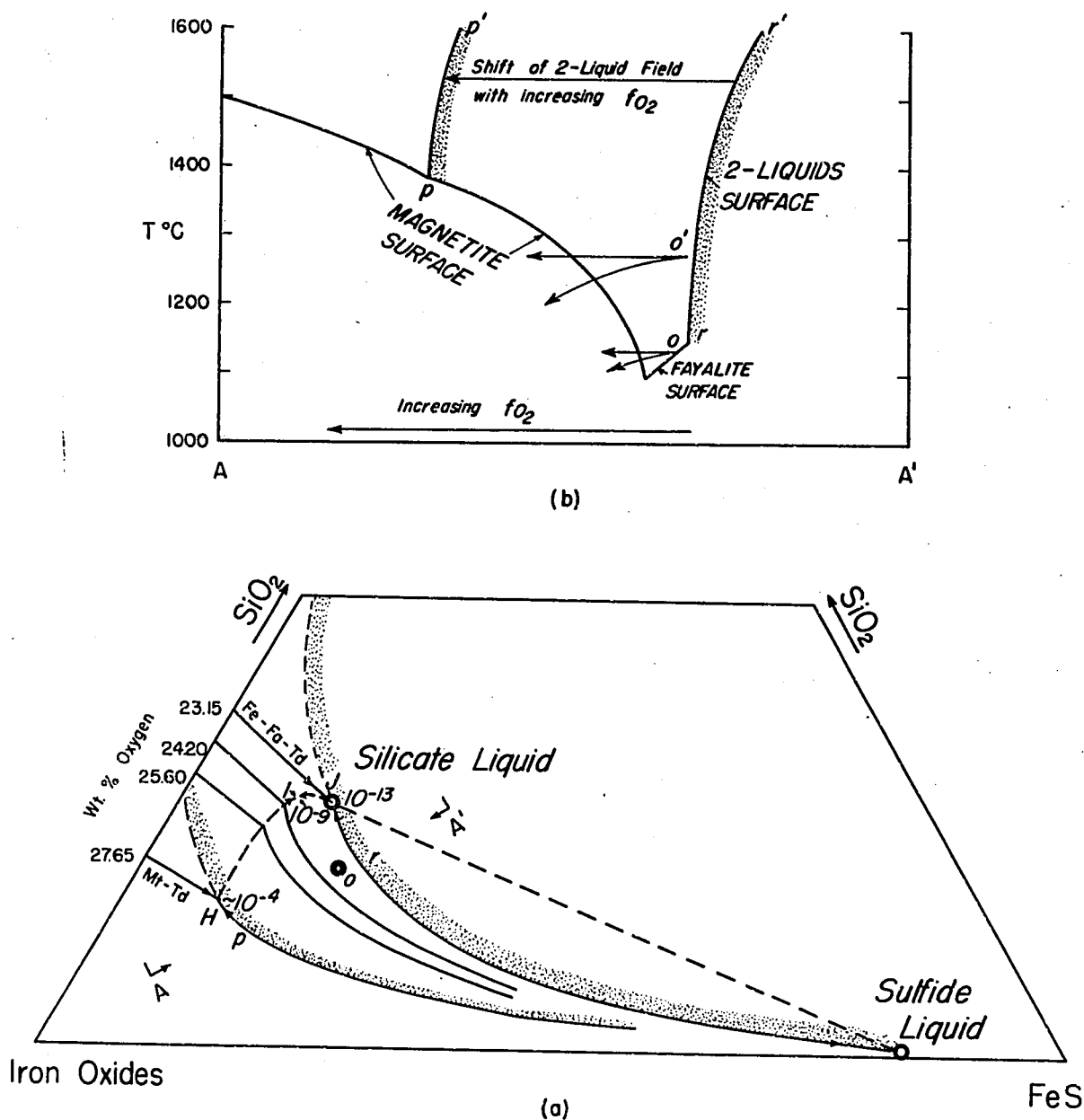


Fig. 14 (a) A diagram for Model D showing the 2-liquid surface in the quaternary system projected onto the FeS - FeO - SiO₂ face to illustrate its shift with increasing f_{O_2} . Fe-Fa-Td = iron-fayalite-tridymite; Mt-Td = magnetite-tridymite. H, I, and J are invariant points; associated f_{O_2} 's are in atmospheres. Point o represents a homogenous liquid at a low f_{O_2} , around 10⁻⁹ atm., which loses one-half its sulfide content on being oxidized to about 10⁻⁶ atm.

(b) A section along A - A' (expanded two times) illustrating the position of phase surfaces with respect to temperature. Liquid o is in equilibrium with fayalite, but when oxidized at constant or slowly falling temperature fayalite is resorbed, and only liquid is present until the magnetite surface is reached. o' represents a superheated liquid.

for mixtures made with FeO (23.1% oxygen) and Fe_3O_4 respectively. Oxidation of FeO moves the 2-liquid field to the left and depresses the liquidus temperature to the point where ferric oxide becomes so concentrated as to separate as magnetite. Homogeneous liquids could be partially oxidized and separated into immiscible sulfide and silicate liquids isothermally, or with falling temperature (shown by arrows on Fig. 14b), without the separation of magnetite; fayalite, if present, would be resorbed.

For example, a change in the oxidation state corresponding to a shift in the iron oxide composition from about 23.6 to 25.6 weight percent oxygen would cause one-half of the dissolved sulfides in liquid o to separate as an immiscible liquid. This is equivalent to a change in the fugacity of oxygen from about 10^{-9} to 10^{-6} atm. along the line HIJ (Fig. 14a). It will be noted that a decrease in oxygen fugacity would have the reverse effect; the liquid would then have a greater capacity to hold sulfides.

Chapter VI

Sulfides In Silicate Magmas

Introduction

The solubility of iron sulfide in iron silicate liquids has been shown to be limited by silica concentration and the oxidation state of the system. It has also been pointed out (Ch. II) that the activity of FeO probably governs the amount of sulfur that can be dissolved in many complex silicate liquids. Therefore, it should be feasible to assume that the solubility of sulfur in a natural magma is essentially governed by the activity of FeO and could be limited by the same factors as in the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system.

In this chapter the evolution and crystallization of certain magmas are considered and an attempt is made to predict the behavior of sulfur during these processes. Methods of formation of an immiscible sulfide liquid in magmas under different physico-chemical conditions are discussed, and

used to explain the occurrence of sulfides in basic igneous rocks and the genesis of certain types of ore deposits.

Solubility of sulfur in magma and in iron silicate liquids

The amount of sulfur that can be dissolved in basic magma appears to be in the order of 0.1 weight percent or less (see Table 5, p.87). This is small compared to the 4 percent sulfur (or 10% FeS) in iron silicate liquids at the invariant point J (Fig. 12). Considering the solubility of sulfur in silicate liquids to be essentially limited by its substitution for oxygen in Fe - O - Fe sites, as reasoned earlier (chapter II), two factors besides oxidation state are responsible for most of this change.

In the first place, basic magmas contain only about 10 percent iron oxides which is smaller by a factor of six than that in the most siliceous liquid in the experimental system. Secondly, ferrosillite (FeSiO_3) is not a stable phase in the system at confining pressures less than about 16 kb (Lindsley, 1967, p. 228), and below 1600°C iron oxides are not capable of forming liquids having this 1:1 mole ratio of FeO to SiO_2 (see Fig. 9). But in basic magmas where a large amount of MgO , CaO and Al_2O_3 are present, the liquid can become more siliceous and FeO will be tied up in pyroxene and other structures that greatly reduce its activity. These factors

would have the comparable effect of moving the invariant point J towards Y in Figure 10. At the same time and for the same reasons the sulfide liquid at K would move some distance towards Z.

Generation of Basic Magma

Since the ore deposits we are concerned with are associated with basic and ultrabasic igneous rocks, it is necessary first to consider the behavior of sulfur during the generation of their magmas in the mantle. The formation of large amounts of magma by partial melting of the mantle is widely accepted today. Bowen early (1928) advocated the hypothesis but the subject was more or less left dormant until Verhoogen (1954) and later Kuno (1960), Yoder and Tilley (1962), Kushiro and Kuno (1963), Ringwood (1966), Green et. al. (1967), Ito and Kennedy (1967) and others, reviewed and expanded on Bowen's hypothesis.

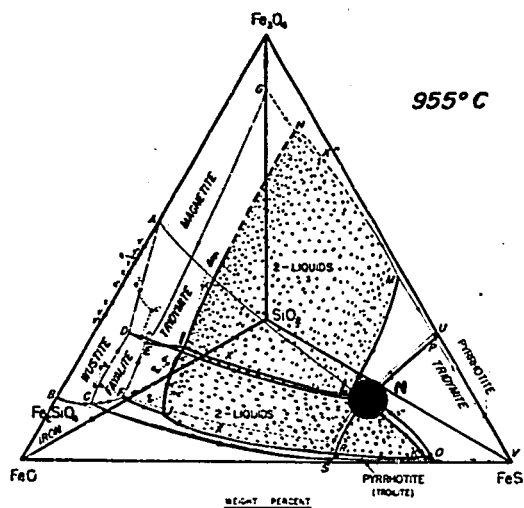
The partial melting of a rock is the reverse process of its crystallization from a melt. The last phases to crystallize are the first to melt, and as melting proceeds the liquid becomes more and more diluted with more refractory material. To illustrate this process where a sulfide phase is present, let us consider partial melting in the experimental system

FeS - FeO - Fe₃O₄ - SiO₂, assuming the system to be closed.

Partial melting in the FeS - FeO - Fe₃O₄ - SiO₂ system:

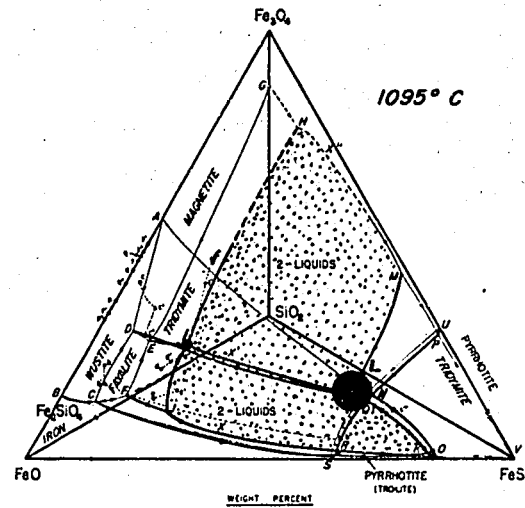
The first liquid to form from a solid of composition f in the magnetite phase volume of Figure 15a (see also Fig. 12 and page 65) would be the sulfide liquid at 955°C at the invariant point N. This liquid contains only about one percent silica, and with rising temperature a very small amount of tridymite, fayalite and magnetite would melt and be dissolved in the sulfide liquid^{until} the liquid had reached the invariant point L at 1095°C (Fig. 15b). As heat is added at 1095°C (Fig. 15c) fayalite, tridymite and magnetite melt in abundance and, being no longer soluble in the sulfide liquid, form a separate silicate liquid at I. This silicate liquid has about 10% FeS dissolved in it, and as it is being generated it constantly absorbs more and more of the sulfide liquid. When all fayalite is melted the temperature rises to that of f'' (Fig. 15d), at which point the last of the sulfide liquid is resorbed by the silicate liquid. Further melting of tridymite and magnetite undersaturates the silicate liquid with respect to FeS.

Iron silicate liquids generated under lower oxidizing conditions than above can become much more silica-rich (compare points F and G in Fig. 9), and at very low oxidation states



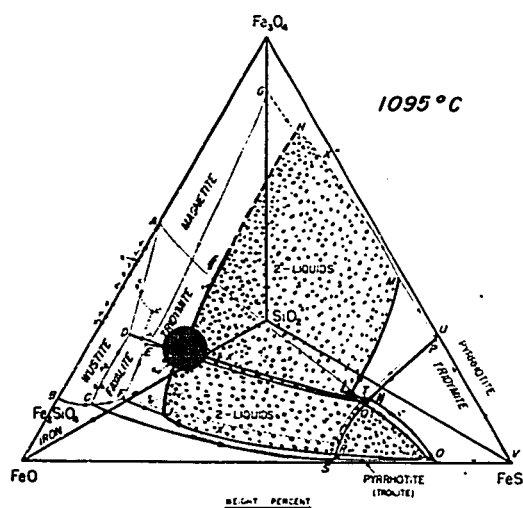
Mixture f begins melting at N, - 955°C

(a)



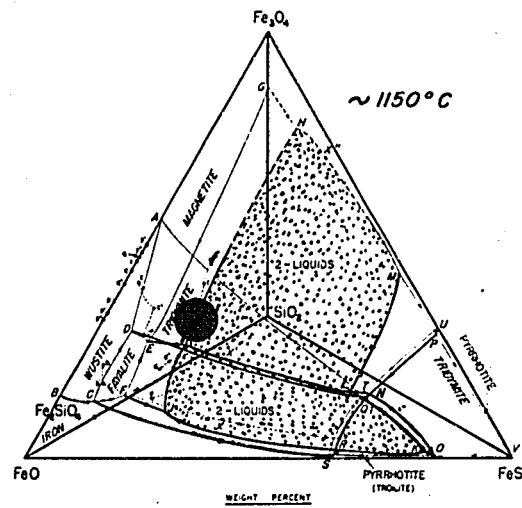
Start of heat being added at L

(b)



All fayalite melted

(c)



All sulfide liquid absorbed in silicate liquid

(d)

Fig. 15 Partial melting in the FeS - FeO - Fe_3O_4 - SiO_2 system.

they can dissolve larger amounts of FeS (16 percent FeS when in equilibrium with iron). Under these low oxidation conditions the sulfide liquid contains much less iron oxide. In all parts of the system liquids undersaturated with respect to silica can dissolve even larger quantities of FeS.

Some significant points emerge from this discussion of partial melting in the experimental system:

- 1) Sulfide liquids are generated first, the lowest temperatures being 945°C at the invariant point Q or 955°C at N.
- 2) Silicate liquids are generated at or close to invariant point I, 140° above N, at 1095°C , and then move to positions with higher or lower Fe_3O_4 contents depending on the bulk composition of the mixture.
- 3) The silicate liquid being generated absorbs the sulfide liquid gradually.
- 4) Under lower oxidation conditions the silicate liquid can dissolve larger amounts of SiO_2 and FeS, and the sulfide liquid dissolves much less iron oxide than under more oxidizing conditions.

Partial melting in the mantle: The composition of the upper mantle and the liquids that can be generated from it by partial melting have been reviewed by Green and Ringwood (1966). Many investigators consider the upper mantle to be ultrabasic material while others believe it to be eclogite. The ultrabasic rather than the eclogite model is used here for the same reasons as those outlined by Ringwood (1966a, p. 299). O'Hara and Yoder (1966) and Ito and Kennedy (1967) assume the mantle to be peridotite whereas Ringwood (1966a, p. 303) suggests a material comprised of 3 parts peridotite and one part basalt which he terms "pyrolite", or pyroxene-olivine rock.

The liquids that can be generated by partial melting in the mantle depend to a large extent on pressure and temperature. In contrast to this, the nature of the final liquid arriving at the surface depends mainly on the rate of its upward progress which governs the amount of fractional crystallization of the magma before extrusion (O'Hara and Yoder, 1966; Green, et al. 1967; Aumento, 1967; Ito and Kennedy, 1967). It is sufficient here to summarize what appear to be the important conclusions concerning the formation of basic magma, drawn from experimental data, as they relate to the present study:

- a) Basaltic liquids are generated by partial melting of various ultrabasic materials at depths ranging from 30 to 400 km. in the mantle (Green, et al. 1967).
- b) Different types of basaltic liquids may be formed under the following conditions:
 - i) different P - T regimes in the zone of melting.
 - ii) the proportion of the mantle melted.
 - iii) the degree of crystal fractionation of the liquid as it moves towards the surface.
- c) Basalt can be converted to eclogite under the pressure conditions of the upper mantle.
- d) The partial melting of eclogite can yield andesitic liquids under anhydrous conditions, and dacitic and rhyolitic liquids under hydrous conditions. (Green and Ringwood, 1966).

Sulfur in the mantle: We can now consider the role that sulfur plays in the partial melting of the mantle. Ringwood (1966a, p. 308) maintains that the mantle is homogeneous with respect to the mole ratio of $\text{FeO}/\text{FeO} + \text{MgO}$ at a value of 0.12 obtained from pyrolite. Similarly, he suggests sulfur is constant at about 0.03 weight percent. If these concentrations are constant, they essentially rule out variations in FeO and

sulfur contents of liquids due to depth of melting alone.

The ionic radius of sulfur (1.84 Å) is much larger than that of oxygen (1.40 Å) and therefore sulfur cannot readily substitute for oxygen in silicates. Under the high-confining pressure of the mantle sulfur would tend to form the dense sulfide phase rather than enter less dense silicate minerals. It is almost completely insoluble in silicate and oxide minerals at low pressures as attested by the occurrence of discrete sulfide grains in igneous rocks that contain only a fraction of a percent of sulfur. Nor will the melting point of iron sulfide be increased substantially by pressure since its liquid is only slightly less dense than the solid (Ubbelohde, 1965, p. 188). Naldrett (1967) found no measurable change in the melting temperature ($\pm 10^\circ$) of the assemblage magnetite plus pyrrhotite in the presence of water at 2 kb total pressure. Sulfides may, however, be more soluble in silicate liquids under pressure according to Skinner and Peck as reported by Naldrett and Kullerud (1967), but experimental results supporting this are not yet available. Consequently, oxidation state is assumed to be the principal factor controlling the temperature at which a sulfide liquid would be generated in the mantle.

Ringwood (1966c) suggests an oxidation state in the upper mantle at some value higher than that if iron were a stable phase. Sato and Wright (1966) measured oxygen fugacities in a lava lake in Hawaii and found them to be close to that of the quartz-fayalite-magnetite buffer (Fig. 16). Fudali (1965) measured the f_{O_2} produced by melting a number of basalts at 1200°C and obtained values ranging from $10^{-6.4}$ to $10^{-8.5}$ atm. (at this temperature the QFM buffer is 10^{-9} atm.). If we allow for a small amount of oxidation during the rise and extrusion of the magma, we see that the f_{O_2} at the point of magma generation in the mantle could be close to, or below that of, the quartz-fayalite-magnetite buffer and might be as low as the magnetite-wustite buffer.

Under these conditions a sulfide liquid would be formed in the mantle somewhere between points corresponding to the invariant points Q and N in the experimental system (Fig. 12). Therefore, considering pressure effects to be small, the first liquid would form slightly above 945°C . Sulfide liquid at N is in equilibrium with the tridymite-fayalite-magnetite-pyrrhotite assemblage. In the mantle this sulfide liquid would be widely dispersed and essentially the only liquid formed until silicates begin to melt around 1300°C (Ito and Kennedy, 1967, p. 532; Green and Ringwood, 1966). When silicates start

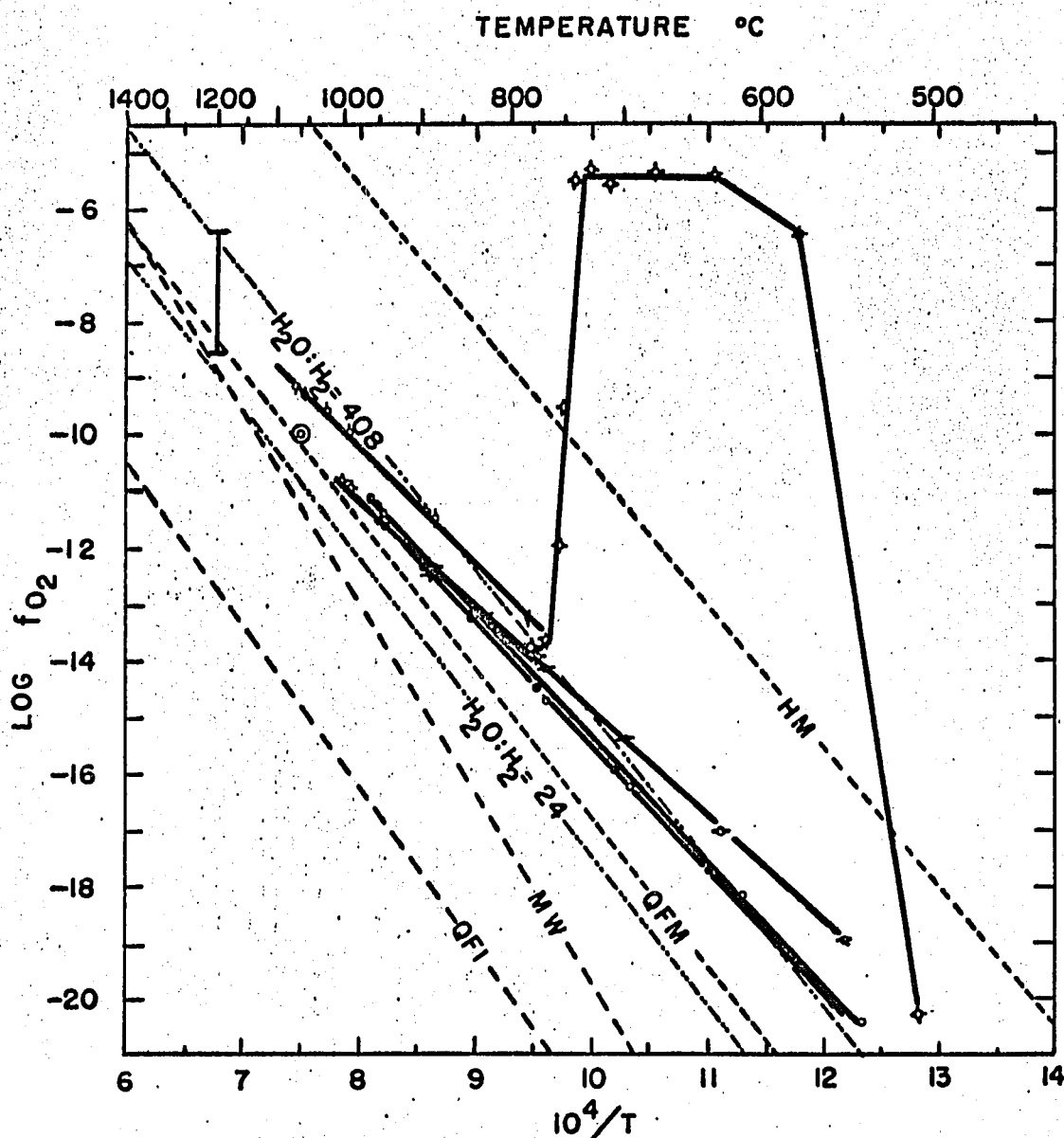


Fig. 16 Logarithms of oxygen fugacity (f_{O_2}) plotted against reciprocals of absolute temperature (T). Buffers shown are: HM = hematite-magnetite, QFM = quartz-fayalite-magnetite, MW = magnetite-wustite and QFI = quartz-fayalite-iron. Water-hydrogen mixtures are from Presnall (1966). The heavy lines are the oxygen fugacities measured in drill-holes in a basaltic lava lake in Hawaii by Sato and Wright (1966). The double circle is a plot of the values given for the sulfide liquid collected by Skinner and Peck (1966). The vertical bar denotes the range of oxygen fugacities measured by Fudali (1965). (Revised after Sato and Wright, 1966)

to melt in abundance they produce basaltic liquids which absorb only a small amount (0.15 wt. % or less) of the sulfide liquid. If we use Ringwood's (1966a, p. 322) value of 0.03% sulfur in the mantle and Riche's (1959) value of 0.027% sulfur in basalts (Table 5) we see that the basaltic liquid would always be saturated with sulfide. However, Riche also gives a value of 0.088% sulfur for gabbros which may indicate the greater loss of sulfur in surface flows.

Ringwood (1966a) proposes that liquids separate from the mantle when between 20 and 40 percent melting has occurred. Thus it can be seen that basaltic liquids may be saturated with sulfur regardless of whether they can dissolve only 0.027% or more than 0.10% sulfur. As the magma rises to a position high in the earth's crust, the degree of its oxidation will control the amount of sulfide liquid that separates. We now consider some methods of oxidation of the magma.

Sources of oxygen for oxidation of magma

Magma will tend towards equilibrium with the f_{O_2} of the rocks it intrudes if sufficient time is provided. In anhydrous environments the magma itself would control the f_{O_2} . However, highly oxidized rocks assimilated in the magma could raise its f_{O_2} . Carbonate rock might be effective in this respect.

Table 5. Sulfur content of basic rocks.

	wt.%S	Reference
Skaergaard Intrusion	0.005	Wager, et al. (1957)
Duluth Complex	0.03	Snyder (1959)
12 Gabbros	0.088	Riche (1959)
15 Basalts	0.027	Riche (1959)
24 Andesites	0.023	Riche (1959)
Mantle (estimated)	0.03	Ringwood (1966a)

The role of water as a source of oxygen in these environments has been stressed by Kennedy (1955), Osborn (1959), Hamilton, et al. (1964), Presnall (1966) and others. Hamilton, et al. determined the solubility of water in basalts and andesites and found it to be substantial (Fig. 17). The f_{O_2} exerted by mixtures of water and hydrogen are shown on Figure 16. Presnall (1966, p. 779) states, "Water in the amount of only 1.25 weight percent in a basaltic magma containing 10 weight percent FeO could provide sufficient oxygen for complete oxidation of this FeO to Fe_2O_3 ". However, he points out that the diffusion of hydrogen from the magma would not be rapid enough to acquire this degree of oxidation. That hydrogen can diffuse rapidly in media more or less impervious to water and oxygen is exemplified by the difficulty Eugster and Wones (1962) and Hamilton, et al. (1964) experienced in trying to contain hydrogen in buffered experiments involving water. The initial ratio of H_2O/H_2 in water being incorporated in the magma is important (Presnall 1966, p. 779). If the initial ratio is high the magma can become highly oxidized even without diffusion of hydrogen.

The water content of the mantle is probably very low even in the thin layer beneath the oceanic Mohorovicic discontinuity where amphibolite may be stable (Ringwood, 1966b,

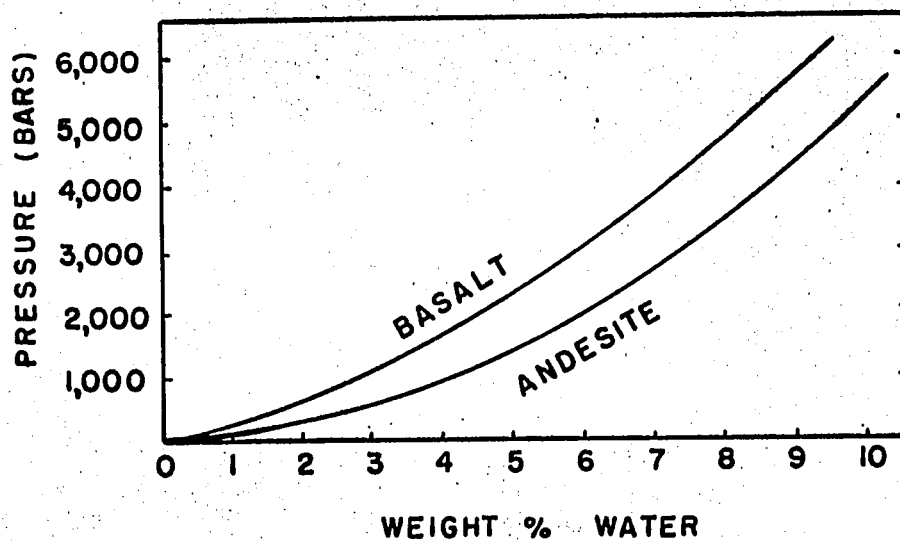


Fig. 17. The solubility of water in Columbia River basalt and Mount Hood andesite melts as a function of water pressure at 1100°C. (After Hamilton, et.al., 1964)

p. 361). Within the continental crust there could be a much different situation. A wet geosynclinal pile could provide a source of abundant water to an upward moving magma (Osborn, 1959, p. 664). Water in fractures in less porous rocks high in the continental crust could be incorporated quickly in the magma. Fractures and faults formed by the intrusion of magma could serve as channelways for the buffering gasses.

Separation of sulfide liquid from magma

We have seen that magma generated in the mantle would have a f_{O_2} close to the quartz-fayalite-magnetite buffer and would be saturated with sulfur. If this magma rises with little change in f_{O_2} and essentially as liquid the sulfur remains in solution except for a minor amount exsolved due to the reduction of confining pressure.

At the beginning of crystallization of phases that lower the amount of dissolved FeO, sulfide liquid begins to separate. If the f_{O_2} remains constant, increases slowly or decreases slowly during crystallization, the sulfide liquid continues to separate in this gradual manner until the amount of FeO is reduced to zero, or the temperature has fallen to the point where the sulfide liquid begins to crystallize. Beyond this point sulfur would separate from the magma in the form

of sulfide minerals. With a steady f_{O_2} the proportion of sulfide liquid to other phases separating at any time would be exceedingly small since the small amount of sulfur in the magma would essentially be separating during the entire crystallization history of the magma. Sulfide liquid would separate more rapidly during an increase in f_{O_2} and temporarily halt during a decrease in f_{O_2} , but would again become steady as the f_{O_2} became constant. A rapid rise in the f_{O_2} , would result in the immediate separation of a large proportion of the sulfur as sulfide liquid as was the case in Model D, page 73 (Fig. 14).

these

In geological terms, these phenomena could occur in the following manner.

- 1) Magma rises from the mantle with little oxidation and extrudes as flows; Most sulfur would separate as sulfide liquid during crystallization and disperse finely throughout the flows, while the remainder would dissolve in glass or escape as gas.
- 2) Magma from the mantle intrudes into a chamber in a low oxidation state: The sulfide liquid would separate gradually and settle together with other cumulate phases.

- 3) Intrusion of magma into a chamber with a rapid change to high f_{O_2} . A large amount of sulfide liquid would separate and be accompanied by an increased amount of magnetite, but there would be little change in the proportion of other phases separating. The dense sulfide liquid would quickly settle to the floor of the chamber.
- 4) Intrusion of magma with rapid oxidation taking place in the conduit below the chamber. A large amount of sulfide liquid separates and is intruded in a dispersed form in the magma if its upward movement were sufficiently rapid. There would be a certain lag in the arrival time of the more dense sulfide liquid due to differential settling (see Naldrett and Kullerud, 1967, p. 512). In slowly rising magma this factor might be important and result in the intrusion of an oxidized magma with a low sulfur content. A later intrusion of magma from the same conduit could contain a higher concentration of sulfide liquid.

Effect of f_{O_2} and f_{H_2O} on crystallization of magma

Kennedy (1955), Osborn (1959), Roeder and Osborn (1966) and Presnall (1966) have discussed the effects of the fugacity

of oxygen and water on the crystallization of basic magmas. Osborn showed that crystallization in a system closed to oxygen yielded iron-rich differentiates, the "Fenner trend", regardless of the initial oxygen fugacity, and suggested the Skaergaard intrusion as an example of this trend. Systems buffered with a relatively high f_{O_2} precipitate magnetite and become enriched in silica, the "Bowen trend".

Presnall (1966) considered hydrous magmas and pointed out the importance of the H_2O/H_2 ratio on the f_{O_2} . High ratios yield high f_{O_2} 's (see Fig. 16). Water entering the magma from the relatively cool environment of the upper crust would be likely to have a high H_2O/H_2 ratio. The crystallization trend of a magma containing water thus depends on the amount of water present, the initial H_2O/H_2 ratio, and the rate of diffusion of hydrogen from the magma. For a hydrous magma the effects can be summarized as follows:

- 1) If the system is open to the diffusion of hydrogen, the oxidation state is high, resulting in precipitation of magnetite and silica enrichment of the liquid.
- 2) If the system becomes sealed from its surroundings, the degree of oxidation depends on the initial amount of water and H_2O/H_2 ratio which according to Presnall produces such variants as:

- 1) initial low water content results in iron enrichment of residual liquids.
- ii) initial high water content with low H_2O/H_2 ratio (e.g., 24) similarly results in iron enrichment of the residual liquids.
- iii) initial high water content with high H_2O/H_2 ratio (e.g., 408) results in precipitation of magnetite and enrichment of liquids in silica, but not as strongly as in the case where f_{O_2} was buffered externally by water vapor with an H_2O/H_2 ratio of 408.

The effect of the suppression of iron-enrichment in the liquids is seen in the mafic minerals. Under the iron-enrichment trend olivine and pyroxene become increasingly enriched in the iron end members and little magnetite is formed. On the other hand, under a high fugacity of oxygen there is little change in the FeO content of these minerals and magnetite is precipitated continuously. If the amount of water dissolved in the magma is appreciable and the temperature is sufficiently low, hydrous mafic minerals, such as amphibole and mica, could form with two possible trends:

- a) Under initially low H_2O/H_2 ratios, hydrous mafic minerals could form with an iron-enrichment trend.
- b) Under initially high H_2O/H_2 ratios, hydrous mafic minerals could form with relatively constant FeO contents.

Partition of minor elements

During the cooling of a magma where a separate sulfide liquid is formed, metal cations are partitioned between silicate liquid, sulfide liquid and crystals. Cations having an $X - O : X - S$ bond energy ratio of about 1.85 or less in Table 1 (Ni^{2+} , Zn^{2+} , Fe^{2+} , Cu^+ , etc.) concentrate to a considerable degree in the sulfide liquid. Some of these base-metal cations may be removed from a magma in silicate and oxide crystals precipitated prior to the formation of the sulfide liquid (see Wager et al., 1957). Thus the amount of each base-metal entering the sulfide liquid is to a large degree proportional to the total amount of base-metals present in the magma and to the value of its $X - O : X - S$ bond energy ratio. In a general way, it is the primary type of magma, or the stage of differentiation at which an immiscible sulfide liquid is formed, that governs the type and amounts of base-metals it will contain.

Sulfide grains in basic igneous rocks

Sulfide liquid begins to separate when its saturation point in a magma has been exceeded. Since the activity of FeO in the magma is considered to be the main factor influencing sulfide solubility, oxidation of the melt or the precipitation of FeO-rich phases would cause sulfide liquid to separate.

From a magma in a low oxidation state and saturated with sulfur, an immiscible sulfide liquid would begin to separate soon after FeO-bearing phases begin to crystallize. The sulfide droplets thus formed would probably make up less than 0.1 percent of the separating material and would collect in the interstices of accumulated crystals on the floor of the intrusion. With further cooling interstitial silicate and sulfide liquids crystallize. The temperature of crystallization of the sulfide would be governed by the buffered f_{O_2} of the surroundings.

From the time the sulfide liquid separates and settles to the floor of the intrusion its crystallization history is affected very little by the silicate phases of the magma; the amount of silica dissolved in the sulfide liquid would be in the order of one or two percent. Hence it would crystallize in essentially the same manner as sulfide liquid in

the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system. Consequently, the sulfide liquid moves from the univariant line ML to the univariant line PN (Fig. 12) where pyrrhotite crystallizes. All phases in contact with the silicate liquid are buffered to the relatively constant f_{O_2} of the magma. Using the data from Figure 16 which places the f_{O_2} at a point just above the quartz-fayalite-magnetite buffer, pyrrhotite would begin to crystallize at some point just above 955°C . Since the amount of sulfide liquid is very small in proportion to the whole magma it will be buffered within a very narrow range of oxygen fugacity as it cools. That is, it will essentially be under a constant f_{O_2} and follow the course of crystallization of Model C, page 71, (and Fig. 13) with all the sulfide liquid crystallizing within a very narrow temperature range to an aggregate of pyrrhotite, magnetite and silicate.

If, however, the sulfide liquid becomes isolated in the interstices of accumulated silicate crystals it could conceivably be isolated from the oxygen buffer and crystallize in a closed system. In this environment, the sulfide liquid, while precipitating magnetite, would reach the univariant line PN, precipitate pyrrhotite, and move to the invariant point Q where wustite is a stable phase. If the system remained closed to oxygen wustite would invert to magnetite and iron as the assemblage cooled below 560°C .

The sulfide - magnetite - iron assemblage has been reported from a few localities (for instance, see Chamberlain, et al., 1965; and Chamberlain, 1967) but its environment has been such that circumstances other than those presented here have been advanced to explain its genesis.

An important relation emerges here. The mineral assemblages found in sulfide grains in igneous rocks are unlikely to yield the true composition of their parent sulfide liquid. In the majority of cases the liquid would be buffered at the oxygen fugacity of the magma which would result in all iron oxide being precipitated as magnetite. Only in exceptional cases would a sulfide liquid be isolated from an oxygen source and crystallize in a closed system where wustite could be stable. Thus melting experiments to find the temperature of crystallization could give erroneous results unless the f_{O_2} is known.

The formation of sulfide grains in volcanic rocks would be similar to that in the plutonic environment. Some sulfur would be dissolved in glass, but if the rocks are crystalline it would be distributed throughout as sulfide droplets. Basic magma coming through the oceanic crust has little chance to be oxidized, whereas magma coming through wet geosynclinal sediments could be in a highly oxidized state and lose much of its sulfur as sulfide liquid before extensive

crystallization of silicates occurred.

The formation of sulfide liquid in a magma need not be confined to ultrabasic and basic rocks. Magmas relating to the calc-alkaline suite of rocks are common in orogenic belts. Regardless of their origin, the solubility of sulfur in these liquids is probably controlled by the activity of FeO and oxidation could release much of this sulfur as sulfide. The base metals partitioning into the sulfide liquid would be in different proportions than those for basalts. In particular, nickel would be present in much smaller amounts and copper, zinc and the elements in the lower part of Table 1 would occur in greater proportions. The actual composition of the sulfide liquid would depend to a large extent on the composition of the silicate magma at the time it was being oxidized; that is, whether it was andesitic or even more siliceous.

Models for the genesis of magmatic sulfide ore deposits

Sulfide ores associated with basic and ultrabasic igneous rocks, the Sudbury-type, are generally accepted to have crystallized from sulfide liquid that co-existed immiscibly with the liquid silicate portion of a magma. The co-existence of these liquids implies that (a) they were generated simultaneously, (b) the sulfide liquid was dissolved in the silicate magma and under certain conditions became immiscible, or (c)

the magma incorporated sulfur which formed a sulfide liquid, the "sulfurization" process proposed by Kullerud (1963).

Simultaneous generation of sulfide and silicate liquids:

It was seen earlier that sulfide liquid would likely be an initial product of partial melting of the mantle. At these early stages of melting this small amount of sulfide liquid would be finely dispersed between silicate crystals. Partial melting of the silicate phases would allow the sulfide liquid to move and perhaps collect in larger masses. It can be argued that this sulfide liquid could be intruded into the upper crust in association with the silicate magma. Its higher density would cause it to lag and hence could form a later stage of intrusion. The source of sulfur is not a problem in this model.

There are, however, reservations about this hypothesis. In the first place magma rises from the mantle in a diapiric manner because of its instability in a surrounding of slightly higher density. Sulfide liquid, being much denser, would probably not rise under the same stress field. Secondly, all sulfide liquid generated in this manner would have essentially the same composition whereas magmatic sulfide orebodies reflect their host rock type by having high nickel:copper ratios in ultrabasic rocks and lower ratios in basic and intermediate rock types. This comparison of composition indicates at

least partial equilibrium between sulfide and silicate liquid which would be difficult to maintain if the sulfide liquid were always a large separate mass.

Lastly, if this process were operative there is no obvious reason why it should not occur in all environments receiving magma from the mantle. Magmatic sulfide ore deposits are found in only a very small number of igneous intrusions in continental crust environments. These points alone suggest that the formation of these ores must be due to very special events. These events are likely to be a combination of two or more geologic processes that have a low probability of overlapping.

The same type of reasoning can be used to evaluate the hypothesis that large amounts of sulfide liquid are released from magma by the change in confining pressure between the mantle and upper crust. Again, this is a process common to all magma, although depth of generation would be the important factor in controlling sulfide solubility in the original melt.

Separation of a sulfide liquid by oxidation: Knowing the solubility of sulfur in magmas to be very low, it may be difficult to visualize that certain large sulfide deposits were ever dissolved in the liquids that formed their host rocks. For example, a cubic mile of magma assaying

0.03% S contains 4 million tons of sulfur or an equivalent 11 million tons of FeS. The main problem is to get an appreciable portion of this sulfur out of solution as a sulfide liquid within a short period of the cooling history of the magma. The suggestions made here arise primarily from the phase work in the FeS - FeO - Fe₃O₄ - SiO₂ system.

In a previous section it was maintained that magma generated in the mantle would be saturated with sulfur since it would be in contact with an early-formed sulfide liquid comprising most of the sulfur in the zone of melting. A rise in the oxidation state would release a large proportion of this sulfur as immiscible sulfide liquid in a manner similar to Model D (page 58) in the FeS - FeO - Fe₃O₄ - SiO₂ system. Oxidation has been suggested by Emslie and Moore (1960) as the process for the separation of iron-nickel sulfide ores at Lynn Lake, Manitoba. The oxidizing process would have to be sufficiently rapid that the sulfide liquid would not be overly diluted with silicate minerals. Oxidation could take place while a magma is being emplaced in its subvolcanic chamber or in a conduit below. In this latter case the sulfide liquid would tend to lag and could conceivably form part of a later phase of the intrusive sequence. If the

fugacity of oxygen of the magma were above that of the quartz-fayalite-magnetite buffer, as would undoubtedly be the case, the sulfide liquid would crystallize to an assemblage of pyrrhotite (containing nickel, copper and other metals in solid solution) and magnetite. The composition of the ore might not truly reflect that of the sulfide liquid since during crystallization under the relatively constant f_{O_2} , all iron oxide would be precipitated as magnetite in the manner of Model C, page 71.

Petrologic evidence of the incorporation of water and the resulting oxidation of silicate magma may be revealed in the silicate and oxide assemblages of intrusions. These aspects have been dealt with by a number of investigators and have been summarized above (page 88). The magma could maintain contact with an external buffer and crystallize under a constant or slowly decreasing f_{O_2} , or it could become sealed from the buffer by the formation of a chill-zone and crystallize under a decreasing f_{O_2} , depending on the amount of water present and its initial $H_2O : H_2$ ratio. In either case some hydrous phase, amphibole, mica or serpentine, would form as their fields of stability were entered. Osborn's (1962) modification of Bowen's reaction series (Fig. 18) serves as a guide for the sequence of crystallization expected under the different conditions.

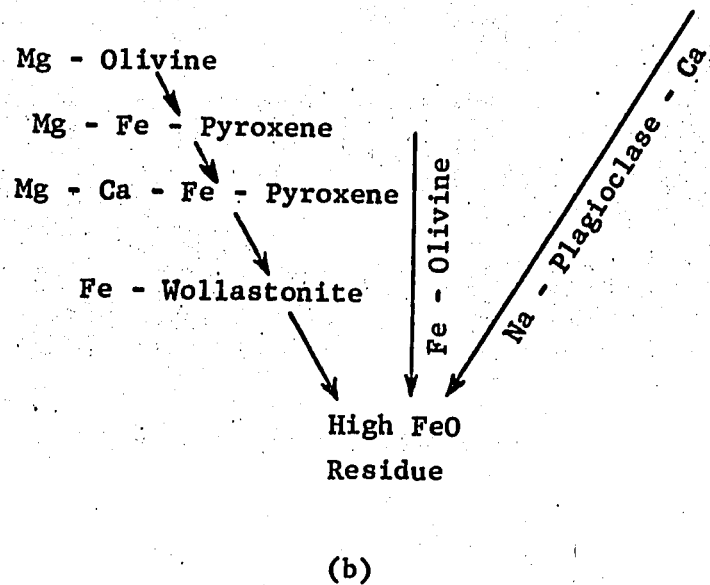
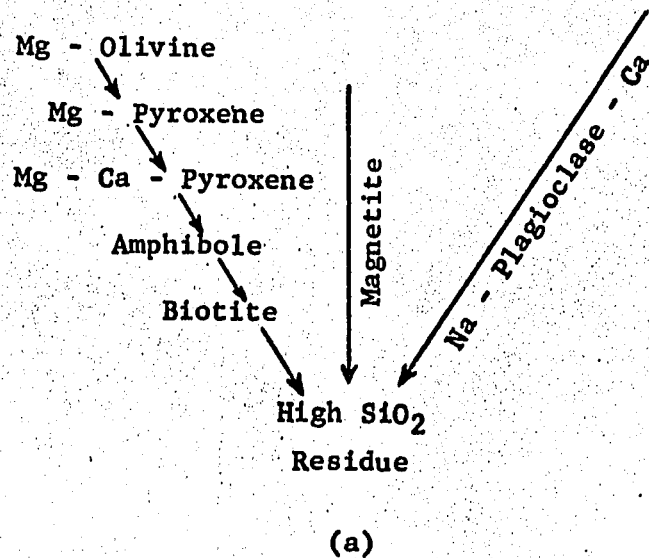


Fig. 18. Reaction series for subalkaline igneous rocks from magmas crystallizing under: a) hydrous conditions yielding a constant or steadily decreasing fugacity of oxygen, and b) anhydrous conditions in a system closed to oxygen. (After Osborn, 1962)

The high oxidation state required to separate a large amount of sulfide liquid need not necessarily remain high during subsequent crystallization of the magma. In a highly oxidized anhydrous system that became closed, magnetite precipitation would bring the f_{O_2} to a very low level which could result in iron enrichment of the silicate liquid. Where water was incorporated the f_{O_2} could be much higher while the magma was buffered by an external source but would drop slowly as it became sealed. These later changes in crystallization trends might obscure an earlier highly oxidized state of the magma.

Sulfurization process: Kullerud (1963) has shown that if sulfur is incorporated in a magma it can extract iron and other transition elements to form an immiscible sulfide liquid. He suggested that this process may have been operative in the formation of some Sudbury-type ore deposits. A study of the phase diagrams in Figures 4 and 12 shows this process to be compatible with the present work. The addition of sulfur would have an effect similar to that of oxygen. It would oxidize the magma, thus lowering its capacity to dissolve sulfur, while at the same time providing sulfur to the sulfide liquid. The main limitation of this mechanism is the scarcity

of sulfur in the crust. In the case of the ores at Sudbury, Thode, et al. (1962) have shown that the isotopic composition of sulfur indicates it had its origin in the mantle. This is also true of a number of other magmatic sulfide deposits, though still other deposits appear to have a mixture of mantle and crustal sulfur (see the compilation by Cheney and Lange, 1967, p. 86).

Summary: The oxidation model is preferred for a number of reasons.

- 1) It was shown in the experimental system that an iron sulfide liquid can be separated from an iron silicate liquid by oxidation alone.
- 2) The oxygen fugacities necessary to make this separation in the experimental system are well within the range of those found in magmas and occurring in upper continental crust environments.
- 3) Water as a source of oxygen is present in many upper continental crustal environments. It is soluble in magmas and the f_{O_2} it can produce is sufficiently high, and can be much higher than that required for the sulfide liquid separation process.
- 4) Kennedy (1955), Osborn (1959, 1962), Roeder and Osborn (1966) and Presnall (1966) have shown that

f_{O_2} probably plays an important role in the crystallization of magmas and that some magmas have indeed been subjected to wide ranges of f_{O_2} .

- 5) It is thus possible for a magma rising in the upper crust to be oxidized rapidly and intruded in such a manner that the sulfide liquid has time to settle into coherent masses. The probability of these events coinciding may be low, but so is the proportion of basic and ultrabasic intrusions having associated magmatic sulfide ore deposits.
- 6) Isotope studies indicate that the sulfur in at least a large proportion of the deposits studied had its origin in the mantle.

In many instances it may be difficult to determine if a magma has been subjected to such a rapid and intense oxidation process. For instance, the ultrabasic rock at the Marbridge mine (Clark, 1965) is now almost completely serpentized. But a study of unaltered intrusions containing magmatic sulfide ores might very well yield evidence of these influences, especially on its early history of crystallization.

Sulfide ores associated with volcanic rocks

Sulfides dissolved in acidic as well as basic magmas can be separated by oxidation and silica-enrichment. Calc-alkaline

magmas show a silica-enrichment trend and are most commonly formed in geosynclinal areas where water is abundant and can act as a source of oxygen. Hence, there is the possibility that volcanogenic sulfide deposits may be genetically related to a magma in which an immiscible sulfide liquid formed. However, sulfide droplets are dense and would tend to move downwards whereas the volcanogenic deposits are formed above the magma chamber.

An interesting phenomenon bearing on this problem was noted while working within the two-liquid phase volume of the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system. In a few runs that had high f_{S_2} and f_{O_2} (the f_{S_2} was probably greater than 1 atm.) the quenched sulfide liquid formed a layer up to 0.5 millimeters thick on top of the silicate glass. The silicate glass contained myriads of small spherical holes which undoubtedly were bubbles of gas formed during the quench. The significance of the bubbles is that they invariably had one or more small droplets of sulfide attached to them in the manner shown on Plate 6. The gas bubbles gave the appearance of "floating" the sulfide droplets, similar to the flotation of solids in mineral beneficiation processes. The surface energy relations between the sulfide liquid and sulfur vapor would be ideal for flotation according to Professor T. Salman (1967, personal communication).

Two explanations are advanced to account for this phenomenon. During the quench the temperature fell more rapidly in the portion of the silica glass capsule occupied by vapor than in the liquid which was held in an alumina container. Bubbles formed quickly in the liquid due mainly to the high f_{S_2} and rose to the surface with their attached sulfide droplets. In another run the neck of the silica tube broke during the quench. The subsequent loss of pressure, causing vapor to bubble from the liquid, very likely floated the sulfide liquid to the surface.

The idea that sulfides in magmas could be concentrated by flotation is now new. Goodchild, as reported by Lindgren (1928, p. 127), has suggested that gas bubbles could attach themselves to minute crystals and to drops of sulfide liquid and serve as agents of flotation. In a magma sulfide droplets would form a vapor if the fugacity of the volatile sulfur species, such as S_2 , H_2S and SO_2 , becomes greater than the external pressure. In a near-surface environment the external pressure on a vapor could be less than the load pressure if the enclosing rocks were permeable to vapor while being impermeable to the magma. Pressure on the magma would also be released periodically by the onset of volcanic activity and fracturing in the enclosing rock.

There is a readily available source of water in the sediments and volcanics of a geosynclinal pile. Upward movement of the magma would tend to keep it in constant contact with this water. In deeper parts of the geosyncline the f_{H_2} in the magma is controlled by water in the surrounding rocks. In a near-surface environment, however, some hydrogen could escape due to pressure release. This escape of hydrogen would permit more water to dissociate to further the oxidation of the magma.

This rapid change in oxidation state, accompanied by the precipitation of magnetite, would allow a large amount of sulfide liquid to separate in a fashion similar to that illustrated in Figure 14 (page 73a). Magmas containing appreciable water are probably capable of dissolving more sulfides than anhydrous ones, hence a higher f_{O_2} might be required to separate a sulfide liquid. Periodic releases of pressure would allow vapor to form around the sulfide droplets which would then rise by the flotation process. These rising sulfide droplets could escape through a volcanic orifice or collect in a cupola-type structure under low pressure. They may also become mixed and dissolved in aqueous solutions escaping from the magma and those present in fractures in the surrounding rock. Therefore it is possible to have a direct magmatic sulfide emanation or sulfide-

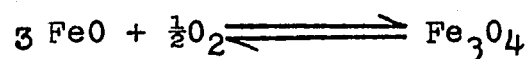
bearing hydrothermal solutions. The solutions could be released at the surface by fumarolic activity or they could precipitate their load in a suitable subsurface environment. The base metals found in the sulfide ore deposits would depend on whether the magma was basaltic, andesitic, dacitic or rhyolitic at the time of the formation of the sulfide liquid. Metals with low $X - O : X - S$ ratios, at the bottom of Table 1, page 8, (Fe, Zn, Cu, Pb, Ag, etc.) concentrate in increasingly acidic magmas.

This cyclic process proposed for the release and concentration of base-metal sulfides in near-surface volcanic environments would include the following stages:

1) the absorption of water by the magma (See Fig.17).

2) dissociation of water, $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$.

3) oxidation of the magma, mainly by the reaction



4) escape of hydrogen by (a) diffusion into the surrounding rocks, and (b) the more rapid method of streaming off during a pressure release.

- 5) the consequent further dissociation of water and oxidation of FeO.
- 6) immiscibility of sulfides and their upward movement by flotation.
- 7) deposition of the sulfides directly, or their incorporation into aqueous solutions.

In the light of these points it is suggested that the sulfide of many deposits, formed at or near the surface in a volcanic environment, originated by a process that would be self-perpetuating as long as water is available, the confining pressure is periodically released to stream off hydrogen and sulfides, and oxidizable materials are present.

Sulfides in oceanic and continental flood basalts:

Oceanic and continental flood basalts probably undergo very little change in composition during their migration through the crust, and sulfide ore deposits apparently do not exist in them. Their low fugacities of oxygen (Fudali, 1965; Sato 1966) indicate a lack of oxidation, and the thick monotonous piles of lava show clearly that little differentiation towards silica-rich members has taken place. Because there have been no changes that would lower the activity of FeO or effect

silica-enrichment in the magma, there is no reason to expect the dissolved sulfides to form a separate phase except under normal crystallization conditions.

Iron formations associated with sulfide ores: The oxidation of a magma considered necessary to produce a separate sulfide liquid also causes extra amounts of magnetite and possibly hematite to form. These minerals would tend to be concentrated in lavas associated with sulfide ores formed by this process. However, the iron oxides in the sulfide liquid and some of those in the magma could be dissolved in hydrothermal solutions and be a source of iron for the small, discontinuous iron formations so often found associated with sulfide ore deposits in volcanic environments.

Summary and Conclusions

- A. 1) Silicates melt to ionic liquids, and sulfur, as sulfide, is dissolved in these liquids essentially by replacing weakly bonded oxygen ions.
- 2) Of the geologically common metal cations, Fe^{++} forms the weakest bond to oxygen; hence oxygen bonded with Fe^{++} alone is most easily displaced by sulfur. The number of these $\text{Fe}^{++} - \text{O} - \text{Fe}^{++}$ groups in the liquid is a measure of the activity of FeO .
- 3) FeO has a high activity in comparison to CaO , MgO etc. in silicate liquids containing equal mole proportions of these oxides.
- 4) Sulfides can be extracted from FeO -bearing silicate liquids by reducing the activity of FeO :
- a) by the addition of silica and other oxides to form stable compounds with FeO .
 - b) by oxidation of FeO to Fe_2O_3 , and
 - c) by precipitation of FeO -rich phases.

- B. 1) Phase relations for the $\text{FeS} - \text{FeO} - \text{SiO}_2$ join, determined by Yazawa and Kameda (1953) in equilibrium with iron, were confirmed and extended through the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system.
- 2) The immiscibility gap between silicate liquid and sulfide liquid, present for liquids in equilibrium with iron, was found to extend throughout the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system.
- 3) A quaternary invariant point is present ($I = 10 \text{ FeS}$, 40FeO , $21\text{Fe}_3\text{O}_4$, 29SiO_2 ; $L = 57\text{FeS}$, 26FeO , $15\text{Fe}_3\text{O}_4$, 2SiO_2 ; 1095°C (Fig. 12) involving fayalite, tridymite, magnetite, silicate liquid (I), sulfide liquid (L), and vapor. This invariant point represents the lowest temperature at which silicate and sulfide liquids coexist in the system.
- 4) When a crystallizing silicate liquid disappears at the invariant point I (Fig. 13), the conjugate sulfide liquid at L moves to another invariant point ($N = 63\text{FeS}$, 20FeO , $16\text{Fe}_3\text{O}_4$, 1SiO_2 ; 955°C) where pyrrhotite separates with magnetite, fayalite and tridymite. If the original liquid has a high $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio, and is low in silica, the sulfide liquid moves to a lower invariant point ($Q = 62\text{FeS}$, 22FeO , $15\text{Fe}_3\text{O}_4$, 1SiO_2 ; 945°C) where the crystallizing assemblage is wustite, magnetite, fayalite and pyrrhotite.

5) If the f_{O_2} is held at a value above the quartz - fayalite - magnetite buffer, corresponding to invariant point N, all liquids crystallize to assemblages of tridymite, magnetite and pyrrhotite.

6) An homogenous liquid in the quaternary system can be separated into immiscible silicate and sulfide liquids by oxidation alone (Model D, Fig. 14). A change in the f_{O_2} from about 10^{-9} to 10^{-6} atm. at 1100°C is sufficient to separate one-half of the FeS in the liquid o (Fig. 14) as a sulfide liquid.

C. 1) The solubility of sulfur in silicate magmas is assumed to be essentially governed by the activity of FeO and limited by the same factors as in the FeS - FeO - Fe_3O_4 - SiO_2 system.

2) Basic magma is generated by partial melting of the mantle buffered by a f_{O_2} close to the quartz - fayalite - magnetite assemblage.

3) Under these conditions a sulfide liquid would form at a temperature close to 955°C , and a silicate liquid at approximately 1300°C , if we neglect the effect of pressure.

4) From the amount of sulfur assumed for the mantle (0.03 wt. percent) and that found in basic igneous rocks, (0.027 - 0.088 wt. percent) the silicate magma produced by partial melting will not dissolve all of the originally formed sulfide liquid until at least 30 percent of the mantle has melted. This magma, arriving at or near the surface, would be saturated with sulfide liquid.

5) Sulfide liquid becomes immiscible in silicate magma by precipitation of FeO-bearing minerals and by increase of f_{O_2} .

6) During an increase in f_{O_2} sulfide liquid would separate more rapidly and temporarily halt during a decrease in f_{O_2} , but would again separate steadily as the f_{O_2} became constant.

7) The f_{O_2} imposed on the sulfide liquid as it cools determines the temperature at which crystallization ends.

8) Large quantities of sulfide liquid that could form magmatic sulfide ore deposits may be generated in a number of ways including:

- a) A direct intrusion of mixed sulfide and silicate liquids from the mantle.
- b) The rapid oxidation of magma, essentially by the incorporation of water, during or preceding its emplacement in the crust.
- c) The "sulfurization" process proposed by Kullerud (1963).

The rapid oxidation method is considered to be the most probable one operative in the formation of magmatic sulfide ore deposits.

9) Volcanogenic sulfide ore deposits may be formed by collecting sulfide liquid droplets in a magma by a flotation process in which sulfur gases form the flotation bubbles.

Claims to Original Work

In the experimental part of the FeS - FeO - Fe₃O₄ - SiO₂ system the work was original with the exceptions outlined in Chapter III, "Previous Phase Equilibrium Work". The original phase studies and significant results of this work are listed below.

A. Experimental work

- 1) Determination of liquidus phase relations in the FeS - FeO - Fe₃O₄, FeS - Fe₃O₄ - SiO₂ and FeS - FeO - Fe₃O₄ - SiO₂ systems.
- 2) Demonstration of a mechanism by which sulfide liquid may be formed by oxidation of iron silicate liquid containing FeS.
- 3) Demonstration of the lowering of the magnetite - pyrrhotite - tridymite solidus temperature as much as 65 degrees by buffering the fo₂.

B. Geological implications

Mechanisms were proposed and supporting data cited for:

- 1) the generation of coexisting sulfide and silicate liquids by partial melting of the mantle;

- 2) the generation of basaltic magma saturated with sulfide;
- 3) the formation of magmatic sulfide deposits by intrusion of sulfide liquid generated by partial melting of the mantle; and
- 4) the formation of volcanogenic sulfide deposits by oxidation of magma and flotation of sulfide liquid droplets.

Suggestions for Further Work

There is much experimental work that could be done to clarify problems that exist in the liquidus phase relations between silicate, oxide and sulfide assemblages. Magma components, such as MgO , CaO and Al_2O_3 , added to the $FeS - FeO - Fe_3O_4 - SiO_2$ system would make the phase relations complicated and difficult to present. However, the effects of adding these components could be evaluated individually for specific fugacities of oxygen after the method used by Roeder and Osborn (1966) and Presnall (1966). A greater knowledge of the oxygen and sulfur fugacities in synthetic and natural immiscible silicate and sulfide liquids would be of much value. These and other suggestions are listed below.

- 1) Addition of such oxides as MgO , CaO , Na_2O , and Al_2O_3 and H_2O to the present system to determine their individual or combined effect on (a) the solubility of sulfur in silicate liquids and (b) the composition of the sulfide liquid.
- 2) Extension of the study of the phase relations in the Fe - S - O system to higher ^{oxygen}~~system~~ and sulfur contents.
- 3) A study of ways and means to measure the oxygen and sulfur fugacities in these systems at high temperatures.
- 4) A study of the effect of the addition of other transition elements on sulfur solubility in silicate liquids and on the composition of the sulfide liquid.
- 5) Determination of the effect/^{of}confining pressure on the phase relations in the system.
- 6) Determination of the extent of the solubility of sulfur in magmas.
- 7) The design of experiments to evaluate the factors involved in the flotation of sulfide liquid droplets in silicate liquids.

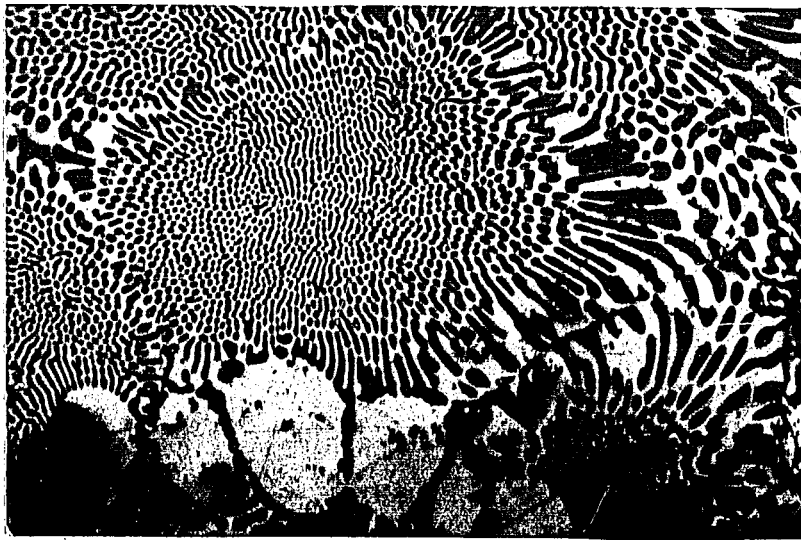
Acknowledgements

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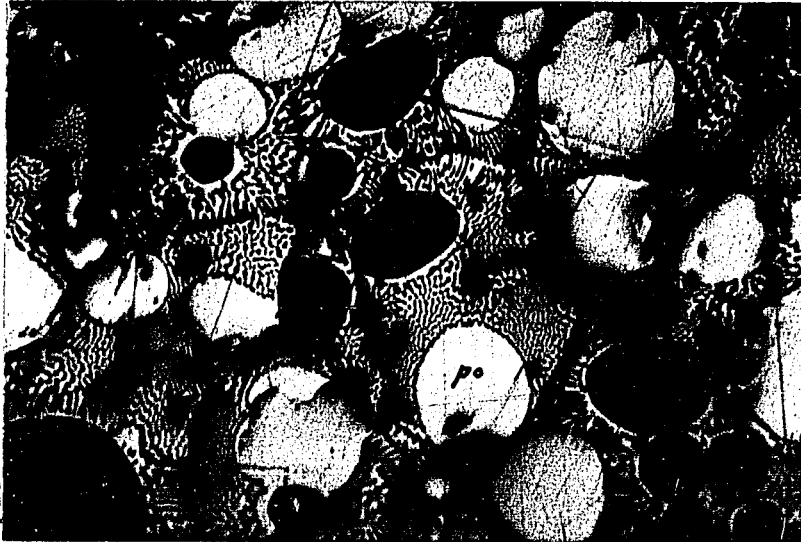
The equipment used was provided by Dr. L.A. Clark through N.R.C. grant No. A.-1111. Other financial assistance was supplied by a Shell Canada Fellowship, an A.S. Hill Bursary, and through N.R.C. grant No. A.-1111. Dr. A.J. Frueh and Dr. G.R. Webber allowed free use of X-ray equipment in their laboratories.

Plate 1

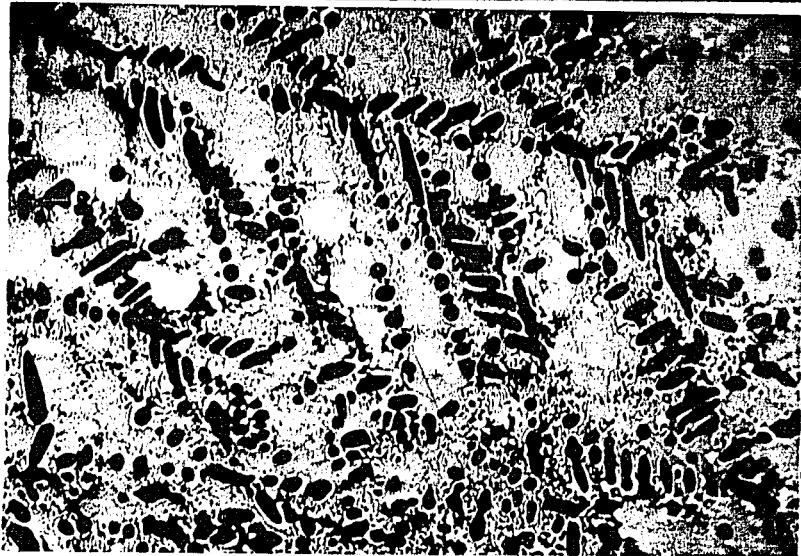
Photomicrographs



(a) X 400



(b) X 160



(c) X 160

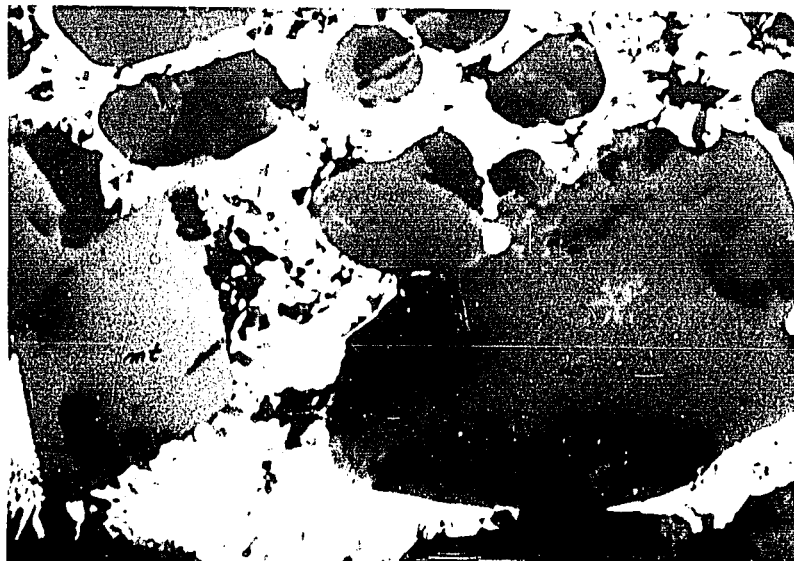
(a) Pyrrhotite crystals in an eutectic intergrowth of pyrrhotite and iron oxides that formed from liquid during the quench.

(b) Wustite and pyrrhotite crystals in liquid (eutectic intergrowth)

(c) Dendritic crystals of wustite formed during the quench, in an eutectic intergrowth of pyrrhotite and iron oxides.

Plate 2

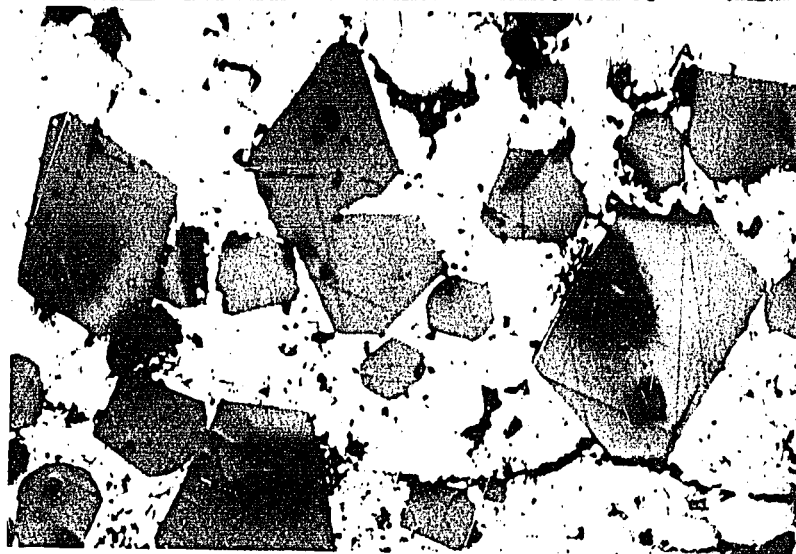
Photomicrographs



(a) X 200



(b) X 160



(c) X 160

(a) Wustite and magnetite crystals in liquid (eutectic intergrowth of pyrrhotite and iron oxide).

(b) Wustite crystals exsolving magnetite, surrounded by liquid as in (a).

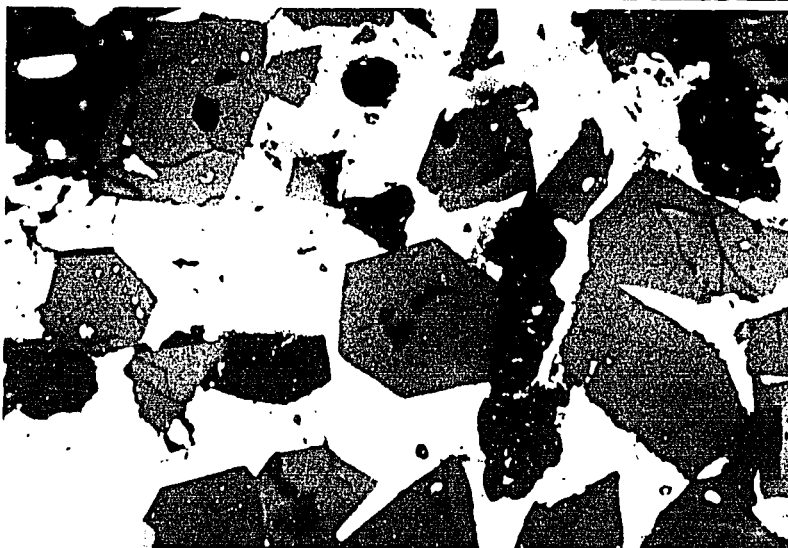
(c) Magnetite crystals surrounded by liquid (eutectic intergrowth containing dendritic pyrrhotite crystals).

Plate 3

Photomicrographs



(a) X 160



(b) X 160



(c) X 64

(a) Dendritic crystals of magnetite formed during the quench, surrounded by an eutectic intergrowth of pyrrhotite and iron oxides.

(b) Primary crystals of fayalite in sulfide liquid.

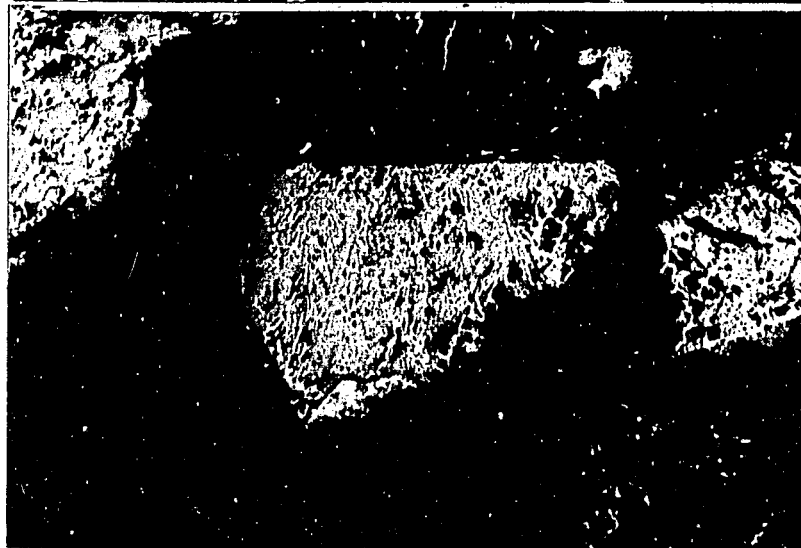
(c) Quench fayalite crystals in sulfide liquid.

Plate 4

Photomicrographs



(a) X 160



(b) X 160



(c) X 160

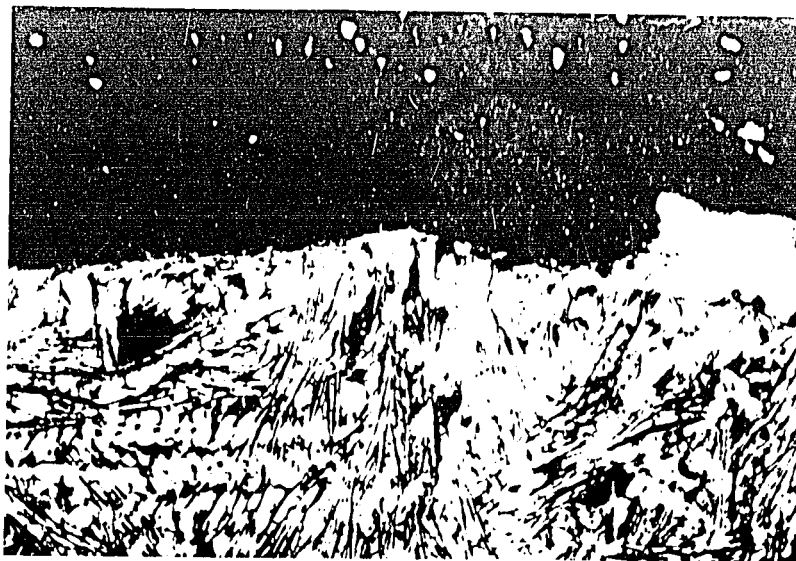
(a) Fayalite, magnetite and tridymite crystals in sulfide liquid (eutectic intergrowth).

(b) Immiscible silicate (dark glass) and sulfide (light eutectic intergrowth) liquids.

(c) Sulfide liquid below a silicate liquid containing small immiscible sulfide liquid droplets.

Plate 5

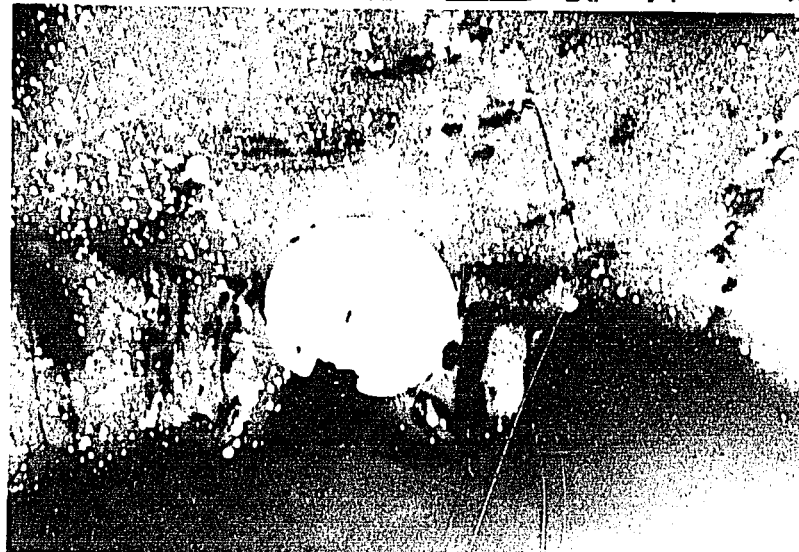
Photomicrographs



(a) X 160



(b) X 200



(c) X 160

(a) Silicate liquid above sulfide liquid containing dendritic wustite crystals.

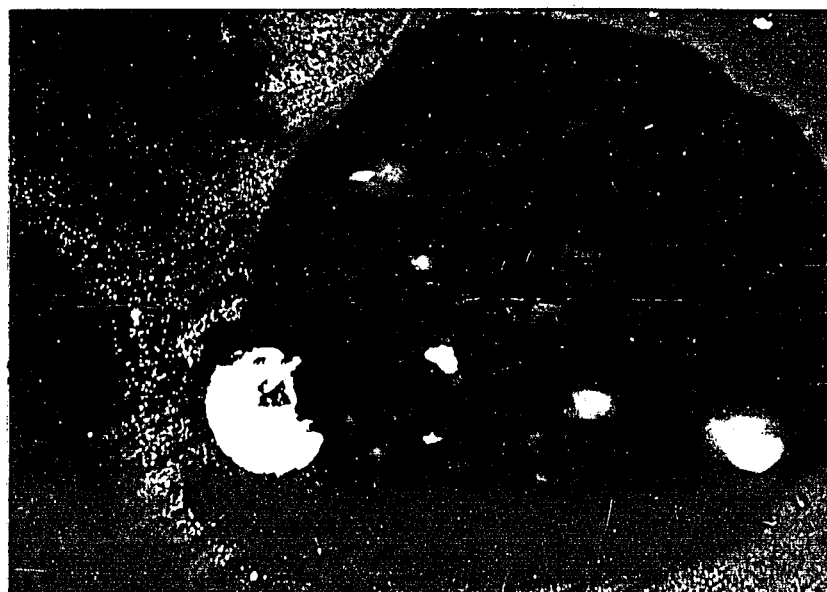
(b) Sulfide liquid (white) with quench fayalite (chain-like) and large dendritic wustite crystals.

(c) Round droplets of sulfide liquid in silicate liquid (dark glass).

Photomicrographs



(a) X 64



(b) X 160

(a) Silicate liquid (grey glass) containing sulfide liquid droplets (white) attached to gas bubbles. The bladed crystals are tridymite.

(b) Silicate liquid surrounding a sulfide liquid droplet attached to a gas bubble.

Bibliography

- Allen, W.C., and Snow, R. B., 1955, The Orthosilicate-iron oxide portion of the system $\text{CaO} - \text{'FeO'} - \text{SiO}_2$: Jour. Am. Ceram. Soc., v. 38, p. 264-280.
- Asanti, Von P., and Kohlmeier, E. J., 1951, Ueber die thermischen eigenschaften der verbindungen von kobalt mit sauerstoff und schwefel: Z. Anorg. allg. chem., v. 165, p. 90-98.
- Aumento, F., 1967, Magmatic evolution of the Mid-Atlantic Ridge: Earth Planet. Sci. Letters, v. 2, p. 225-230.
- Belov, N. V. , 1959, The structure of glass in light of the crystal chemistry of the silicates: The Structure of Glass, v. 2, p. 74-79, Consultants Bureau, New York. (Proceedings of the third All- union Conference on the Glassy State, Leningrad, Nov. 1959. Acad. Sci. USSR Press).
- Bloom, H., and Bockris, J. O'M., 1964, Structural aspects of ionic liquids; in "Fused Salts", Ed. B. R. Sundheim, p. 1-62, McGraw-Hill, New York.
- Bockris, J. O'M., Kitchener, J.A., Ignatowicz, S., and Tomlinson, J.W., 1952, Electric conductance in liquid silicates: Trans. Faraday Soc., v. 48, p. 75-91.

- Bockris, J. O'M., and Lowe, D. C., 1954, Viscosity and the structure of molten silicates: Proc. Roy. Soc. (London), v. A226, p. 423-435.
- Bockris, J. O'M., MacKenzie, J. D., and Kitchener, J. A., 1955, Viscous flow in silica and binary liquid silicates: Trans Faraday Soc., v. 51, p. 1734-1748.
- Bowen, N. L., 1928, The evolution of the igneous rocks: Princeton University Press, Princeton, N. J., 334p.
- Bowen, N. L., and Schairer, J. F., 1932, The system FeO - SiO₂: Am. Jour. Sci., v. 24, p. 177-213.
- Chamberlain, J. A., 1967, Sulfides in the Muskox intrusion: Can. J. Earth Sci., v. 4, p. 105-153.
- Chamberlain, J. A., MacLeod, C. R., Traill, R. J., and Lachance, G. R., 1965, Native metals in the Muskox intrusion: Can. J. Earth Sci., v. 2, p. 188-215.
- Cheney, E. S., and Lange, I. M., 1967, Evidence for sulfuration and the origin of some Sudbury-type ores: Mineralium Deposita, v. 2, p. 80-94.
- Clark, L.A., 1965, Geology and geothermometry of the Marbridge nickel deposit, Malartic, Quebec: Econ. Geol., v. 60, p. 792-811.
- Darken, L. S. and Gurry, R. W., 1945, The system Fe - O: Pt. 1, The wustite field and related equilibria: Jour. Am. Chem. Soc., v. 67, p. 1398-1412.

- Emslie, R. F., and Moore, J. M. Jr., 1961, Geological studies of the area between Lynn Lake and Fraser Lake: Manitoba Dept. of Mines Nat. Resources, Mines Branch Publ. 59-4.
- Eugster, H. P., and Wones, D. R., 1962, Stability relations of the ferruginous biotite, annite: J. Petrol., v. 3, p. 82-125.
- Flood, H., and Knapp, W. J., 1963, Acid - base equilibria in the system $PbO - SiO_2$: Jour. Am. Ceram. Soc., v. 46, p. 61-65,
- Foster, P. K., and Welch, A. J. E., 1956, Metal oxide solid solutions. I. Lattice constants and phase relations in ferrous oxide (wustite) and in solid solutions of ferrous oxide and manganese oxide: Trans. Faraday Soc., v. 52, p. 1626-1635.
- Fudali, R. F., 1965, Oxygen fugacities of basaltic and andesitic magmas: Geochim. et Cosmochim. Acta, v. 29, p. 1063-1075.
- Green, T. H., Green, D. H., and Ringwood, A. E., 1967, The origin of high-alumina basalts and their relationships to quartz tholeiites and alkali basalts: Earth Planet. Sci. Letters, v. 2, p. 41-51.
- Green T. H., and Ringwood, A. E., 1966, Origin of the calc-alkaline igneous rock suite: Earth Planet. Sci. Letters: v. 1, p. 307-316.

- Hamilton, D. L., Burnham, C. W., and Osborn, E. F., 1964,
The solubility of water and effects of oxygen fugacity
and water content on crystallization in mafic magma:
J. Petrol., v. 5, p. 21-39.
- Hilty, D. C., and Crafts W., 1952, Liquidus surface of the
Fe - S - O system: J. Metals, v. 4, p. 1307-1312.
- Ito, K., and Kennedy, G. C., 1967, Melting and phase relations
in a natural periodotite at 40 kilobars: Am. Jour.
Sci., v. 265, p. 519-538.
- Jensen, E., 1942, Pyrrhotite; melting relations and composition;
Am. Jour. Sci., v. 240, p. 695-709.
- Kay, D. A. R., and Taylor, J., 1960, Activities of silica in
the lime-alumina-silica system: Trans. Faraday Soc.,
v. 56, p. 1372-1386.
- Kelly, K.K., 1962, Heats and free energies of formation of
anhydrous silicates: U.S. Dept. Interior, Bur. Mines
R. I. 5901, 32p.
- Kennedy, G. C., 1955, Some aspects of the roles of water
in rock melts: G. S. A. Special Paper 62, p. 489-533.
- Knapp, W. J., 1966, Structural aspects of liquid silicates:
in "Selected Topics in High-temperature Chemistry", Ed.
T. Forland, p. 91-96, Scandinavian Univ. Press.

- Kullerud, G., 1963, The Fe - Ni - S system: Carnegie Inst. Wash. Yb. 62, p. 175-189.
- Kushiro, I., and Kuno, H., 1963, Origin of primary basalt magmas and classification of basaltic rocks: J. Petrol., v. 4, p. 75-89.
- Kuno, H., 1960, High-Alumina basalt: J. Petrol., v. 1, p. 121-145.
- Lindsley, D. H., 1967, Pressure-temperature relations in the system FeO - SiO₂: Carnegie Inst. Wash., Yb. 65. p. 226-230.
- Muan, A., 1955, Phase equilibria in the system FeO - Fe₂O₃ - SiO₂: AIME Trans., v. 203, p. 965-967.
- , 1966, Equilibrium measurements involving oxide and alloy phases at high temperatures: in "Selected Topics in High-Temperature Chemistry", Ed. T. Forland, p. 125-140, Scandinavian Univ. Press.
- Muan, A., and Osborn, E. F., 1965, Phase equilibria among oxides in steelmaking: Addison-Wesley Publishing Co., Reading, Mass., 236p.
- Myuller, R. L., 1960, Chemical characteristics of polymeric glass-formed substances and the nature of glass formation: The Structure of Glass, v. 2, p. 50-57, Consultants Bureau, New York. (Proceedings of the third All-Union Conference on the Glassy State, Leningrad, Nov., 1959, Acad. Sci. USSR Press).

- Naldrett, A. J., 1967, Melting relationships in a portion of of the system Fe - S - O and the crystallization of sulfide-oxide ore magmas: Geol. Soc. Am. Annual Meeting, Abs., p. 160.
- Naldrett, A. J., and Kullerud, G., 1967, A study of the Strathcona mine and its bearing on the origin of nickel-copper ores of the Sudbury District, Ontario: J. Petrol., v. 8, p. 453-531.
- Nockolds, S. R., 1966, The behavior of some elements during fractional crystallization of magma: Geochim. et Cosmochim. Acta, v. 30, p. 267-278.
- O'Hara, M. J., and Yoder, H. S., 1967, Formation and fractionation of basic magmas at high pressures: Scottish Jour. Geol., v. 3, p. 67-117.
- Ol'shanskii, Ya. I., 1951, The system Fe - FeS - FeO - SiO₂ (in Russian): Izvest. Akad. Nauk, S. S. S. R., Geol. Ser., 6, p. 128-152.
- Osborn, E. F., 1959, Role of oxygen pressure in the crystallization and differentiation of basaltic magma: Am. Jour. Sci., v. 257, p. 609-647.
- , 1962, Reaction series for subalkaline igneous rocks based on different oxygen pressure conditions: Am. Mineralogist, v. 47, p. 211-226.

- Pauling, L., 1960, The nature of the chemical bond: 3rd Ed., Cornell University Press, Ithaca, N. Y., 644p.
- Phillips, B., and Muan, A., 1960, Stability relations of iron oxides: phase equilibria in the system Fe_3O_4 - Fe_2O_3 at oxygen pressures up to 45 atmospheres: Jour. Phy. Chem., v. 64, p. 1451-1453.
- Presnall, D. C., 1966, The join forsterite-diopside-iron oxide and its bearing on the crystallization of basaltic and ultramafic magmas: Am. Jour. Sci., v. 264, p. 753-809.
- Richardson, F. D., and Fincham, C. J. B., 1954, Sulfur in silicate and aluminate slags: J. Iron Steel Inst., v. 178, p. 4-14.
- Riche, W., 1960, Ein beitrag zur geochemie des Schwefels: Geochim. et Cosmochim. Acta, v. 21, p. 35-80.
- Ringwood, A. E., 1966a, The chemical composition and origin of the earth: in "Advances in Earth Science", Ed. P.M. Hurly, M. I. T. Press, Cambridge, Mass. p. 287-356.
- , 1966b, Mineralogy of the mantle: in "Advances in Earth Science," Ed. P.M. Hurley, M. I. T. Press, Cambridge, Mass.
- , 1966c, Chemical evolution of the terrestrial planets: Geochim. et Cosmochim. Acta, v. 30, p. 41-104.

- Roeder, P. L., and Osborn, E. F., 1966, Experimental data for the system $\text{MgO} - \text{FeO} - \text{Fe}_2\text{O}_3 - \text{CaAl}_2\text{Si}_2\text{O}_7 - \text{SiO}_2$ and their petrologic implications: *Am. Jour. Sci.*, v. 264, p. 428-480.
- Rosenqvist, T., 1951, A thermodynamic study of the reaction $\text{CaS} + \text{H}_2\text{O} = \text{CaO} + \text{H}_2\text{S}$ and the desulfurization of liquid metals with lime: *AIME Trans.*, v. 191, p. 535-540.
- Roth, W.L., 1960, Defects in the crystal and magnetic structures of ferrous oxide: *Acta. Cryst.*, v. 13, p. 140-149.
- Salman, T., 1967, Personal communication.
- Sato, M., and Wright, T.L., 1966, Oxygen fugacities directly measured in magmatic gases: *Science*, v. 153, p. 1103-1105.
- Schuhmann, R., Jr., and Ensio, P. J., 1951, Thermodynamics of iron-silicate slags: slags saturated with gamma iron: *J. Metals*, v. 3, p. 401-411.
- Seybolt, A. U., and Burke, J. E., 1953, *Procedures in Experimental Metallurgy*: John Wiley & Sons.
- Snyder, I. L., 1959, Distribution of certain elements in the Duluth Complex: *Geochim. et Cosmochim. Acta*, v. 16, p. 243-277.
- St. Pierre, G. R., and Chipman, J., 1956, Sulfur equilibria between gasses and slag containing FeO . *AIME Trans.*, v. 206, p. 1474-1483.

- Thode, H.G., Dunford, H. B., and Shima, M., 1962, Sulfur isotope abundances in rocks of the Sudbury district and their geological significance: *Econ. Geol.*, v. 57, p. 565-578.
- Toulmin, P., and Barton, P. B. Jr., 1964, A thermodynamic study of pyrite and pyrrhotite: *Geochim. et Cosmochim. Acta*, v. 28, p. 641-671.
- Ubbelohde, A. R., 1965, *Melting and crystal structure*: Oxford University Press, 325p.
- Verhoogen, J., 1954, Petrological evidence on temperature distributions in the mantle of the earth: *Trans. Am. Geophys. Union*, v. 35, p. 85-92.
- Vogel, R., and Fulling, W., 1948, Das system Eisen-eisensulfid (FeS) - Wustit (FeO): *Festskrift J. Arvid Hedvall, Gumperts AB, Gothenburg*, p. 597-610.
- Vogt, J. H. L., 1921, The physical chemistry of crystallization and magmatic differentiation of igneous rocks. *Jour. Geol.* v. 29, p. 627-649.
- Wager, L. R., Vincent, E. A., and Smales, A. A., 1957, Sulfides in the Skaergaard Intrusion, East Greenland: *Econ. Geol.*, v. 52, p. 855-895.

Winegard, W. C., 1964, An introduction to the solidification of metals: Institute of Metals, Monograph and Report Series, N. 29, 98p.

Yazawa, A., and Kameda, M., 1953, Fundamental studies on copper smelting (1) Partial liquidus diagram for FeS - FeO - SiO₂ system: Tech. Reps. Tohoku Univ., v. 18, p. 40-58.

Yoder, H. S. Jr., and Tilley, C. E., 1962, Origin of basalt magmas: an experimental study of natural and synthetic rock systems: J. Petrol. v. 3, p. 342-532.

Appendix Tables

Tables of composition, temperature and phases present in quenched runs in the $\text{FeS} - \text{FeO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ system.

Charge No.	Composition (wt.%)			Temp. °C	Phases present
	FeO	Fe_3O_4	FeS		
S-11	40	20	40	1120 1130	ws + l l
S-25	32	28	40	1130 1135	ws + l l
S-25a	32	28	40	1150	l
S-26a	30	30	40	1150	mt + l
b				1200	l
S-27	27	33	40	1200	mt + l
S-50		60	40	1305 1315	mt + l l
S-5	50		50	1022 1030 1060 1066	iron + ws + l iron + l iron + l l
S-35	47	3	50	1040 1051	ws + l l
S-40	48.5	1.5	50	1050	iron + l
W-281	41	9	50	1031 1040	ws + l l
X-10	31	19	50	1050 1057	ws + l l
S-36	29	21	50	1050 1058	ws + l l
c				1100	l
S-38	27	23	50	1100	mt + l
S-37	25	25	50	1100	mt + l

Charge No.	Composition (wt.%)			Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS		
Z-13	22.5	33.5	44	1200	mt + l
Z-15	21	32	47	1200	mt + l
Z-14	20.5	31	48.5	1200	l
Z-10	17	25	58	1125	l
Z-11	17.5	26.5	54	1125	l
Z-12	18.5	27.5	56	1125	mt + l
S-46	10	40	50	1200	mt + l
S-43	75.5	12.5	15	1270 1280	ws + l l
S-47	55	30	15	1300 1312	ws + l l
S-48	43	42	15	1315 1325	ws + l l
S-42a	40	45	15	1340	mt + l
b	41.5	43.5	15	1340	l
S-32	65	5	30	1200	iron + l
S-34a	63	7	30	1200	l
S-34	63	7	30	1180 1190	iron + ws + l iron + l
S-41	61.5	8.5	30	1190	ws + l
W-284	58	12	30	1195 1203	ws + l l
XA-4	43	27	30	1205 1215	ws + l l
S-39	37	33	30	1210 1220 1227	ws + mt + l mt + l l
S-33	35	35	30	1200 1220	ws + mt + l mt + l
S-49	20	50	30	1339 1350	mt + l l

Charge No.	Composition (wt.%)			Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS		
S-24	57	3	40	1110	iron + ws + l
S-22a	55	5	40	1110	ws + l
				1115	ws + l
				1120	l
S-29	37	23	40	1125	ws + l
				1132	l
W-287	50	10	40	1115	ws + l
				1125	l
M-5a		50	50	1200	mt + l
		45	55	1200	l
S-30	31	19	50	1058	ws + l
				1062	l
S-4	40		60	920	iron + ws + po + l
				930	iron + ws + l
				935	iron + ws + l
				940	iron + l
S-7	38		62	925	iron + ws + l
S-6	37		63	925	po + l
				930	l
S-19	38	2	60	940	ws + l
				945	l
S-15	35	5	60	935	ws + po + l
				941	ws + l
				945	l
S-44	37	1.5	61.5	931	ws + po + l
				936	l
S-45	35.5	1.5	63	925	ws + po + l
				931	po + l
				935	l
W-288	29	6	65	954	po + l
				961	l

Charge No	Composition (wt.%)			Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS		
W-290	30	7	63	930	ws + po + l
				936	po + l
				946	po + l
				951	l
W-163	31.5	7	61.5	926	ws + po + l
				930	po + l
S-10	33	7	60	928	ws + po + l
				938	ws + l
				945	l
W-289	33	7	60	940	ws + l
				946	l
S-8	30	10	60	940	ws + po + l
				945	l
S-12	26	14	60	945	ws + po + l
				950	ws + l
				953	l
S-20	25	15	60	945	ws + po + l
S-16	23	17	60	975	l
				975	mt + l
S-23	20	20	60	1040	mt + l
S-28	21.5	18.5	60	1040	l
X-11a	23	14	63	955	po + l
	b 23.5	14.5	62	955	l
	c 24	15	61	955	mt + l
X-3	25	15	60	950	ws + po + l
				960	ws + l
S-85	24	15	61	941	ws + mt + po + l
				946	ws + po + l
				950	ws + l
				956	l
S-86	22	16.5	61.5	946	ws + mt + po + l
				951	mt + l
				956	l
S-87	22	14	64	956	po + l
				961	l

Charge No.	Composition (wt.%)			Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS		
M-4		40	60	1130	mt + l
				1135	l
M-6		35	65	1050	mt + l
				1075	mt + l
				1100	l
M-7		32	68	1025	mt + l
				1050	mt + l
				1075	l
M-3		30	70	1025	po + l
				1030	l
Z-1	12	18	70	1020	po + l
				1025	l
Z-4	13	19	68	1010	po + l
Z-5	14	20	66	1000	l
Z-8	14	21	65	995	mt + l
Z-6a	15	21	64	985	mt + po + l
Z-7a	16	22	62	1000	mt + l
Z-7b				1050	mt + l
Z-6b	15	21	64	1050	l
S-31	15	15	70	1007	po + l
				1012	l
X-2	19	11	70	990	po + l
				1000	l
S-14	21	9	70	995	po + l
				1000	l
W-282	25	5	70	975	po + l
				986	po + l
				992	l
S-3	30		70	975	po + l
				980	l

Charge No.	Composition (wt.%)			Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS		
S-2	20		80	1040 1045	po + l l
W-286	3	17	80	1030 1040	po + l l
X-6	8	12	80	1052 1058	po + l l
Z-3	12	8	80	1075 1080	po + l l
M-2		20	80	1070 1075	po + l l
S-1	10		90	1100 1105	po + l l
W-283	8	2	90	1098 1104	po + l l
X-1	6	4	90	1106 1112	po + l l
Z-2	4	6	90	1115 1120	po + l l
M-1		10	90	1125 1130	po + l l

	FeO	FeS	SiO ₂		
S-69	59	10	31	1160 1170	iron + fa + td + l iron + td + l
S-75	58	12.5	29.5	1171	iron + td + l
S-80	61	12.5	26.5	1152	iron + fa + td + l

Charge No.	Composition (wt.%)			Temp. °C	Phases present
	FeO	FeS	SiO ₂		
S-83	59	15	26	1150	iron + td + l
S-67	57	15	28	1140	iron + fa + td + l
				1150	iron + td + l
S-82	56	17	27	1142	iron + fa + td + l
				1145	iron + td + 2-L
S-62	53	20	27	1140	iron + fa + td + l
				1150	iron + td + 2-L
S-66	56	20	24	1142	iron + fa + 2-L
S-68	54.5	20	25.5	1150	iron + td + 2-L
S-84	60	20	20	1145	iron + l
S-74	52	40	8	1165	iron + l
S-71	50	40	10	1145	iron + fa + l
				1150	iron + 2-L
S-64	32	60	8	1135	iron + fa + l
				1140	iron + 2-L
S-65	26	70	4	1140	iron + td + 2-L
S-79	20	75	5	1156	iron + td + 2-L
S-78	22	75	3	1166	iron + 2-L
S-70	23	75	2	1150	iron + 2-L
S-72	21.5	77.5	1	1163	iron + 2-L
S-73	19	80	1	1165	iron + 2-L
S-76	19.5	80	0.5	1140	iron + fa + l
				1150	iron + 2-L
S-77	17	82	1	1135	iron + fa + l
				1140	iron + 2-L
S-81	14	85	1	1135	iron + fa + td + l
				1145	iron + td + l

Charge No.	Composition (wt.%)			Temp. °C	Phases present
	Fe ₃ O ₄	FeS	SiO ₂		
M-12a	55	40	5	1235 1250	mt + l l
b	53.5	40	6.5	1235	2-L
M-13	52.5	40	7.5	1200 1215	mt + 2-L 2-L
M-11	50	40	10	1200 1215	mt + td + 2-L td + 2-L
M-22	42	55	3	1152 1160	mt + 2-L 2-L
M-23	44	52.5	3.5	1150 1160	mt + 2-L 2-L
M-24	40	57.5	2.5	1143 1150	mt + l l
M-25	40	55	5	1160	td + 2-L
M-26	43.5	55	1.5	1165 1175	mt + l l
M-16	38	60	2	1110 1120 1135	mt + l l l
M-15	36	60	4	1135	td + l
M-17	30	69	1	1020 1030	po + mt + l l
M-18	33	65	2	1100	td + l
M-19	30	68	2	1025	td + l
M-20	28	70	2	1025	po + td + l

Charge No.	Composition (wt.%)				Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS	SiO ₂		
W-360	54.5	10.5	5	30	1120 1130	fa + l l
W-361	50	10	5	35	1125 1135	fa + td + l td + l
W-349	58.5	11.5	10	20	1125 1129	fa + l l
W-350	54.5	10.5	10	25	1115 1120	fa + l l
W-353	52.5	10	10	27.5	1100 1105	fa + l l
W-351	50	10	10	30	1100 1105	fa + l l
W-354	48	9.5	10	32.5	1105 1109	fa + td + l td + l
W-352	46	9	10	35	1120 1125	fa + td + l td + l
W-297	63	12	20	5	1175 1188 1200	ws + l ws + l l
W-292	58.5	11.5	20	10	1105 1111	ws + l l
W-296	57	11	20	12	1100 1110	fa + l l
W-294	54.5	10.5	20	15	1111 1116	fa + l l
W-293	50	10	20	20	1080 1110 1115	fa + l fa + l l
W-298	48	9.5	20	22.5	1104 1112	fa + l 2-L

Charge No.	Composition (wt.%)				Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS	SiO ₂		
W-299	46	9	20	25	1109	fa + td + 2-L
					1115	2-L
c	44	9	20	27	1115	td + 2-L
W-313	42	8	20	30	1110	fa + td + l
					1119	td + 2-L
W-302	48	9.5	40	2.5	1060	ws + l
					1070	l
W-312	47	9.5	40	3.5	1050	ws + fa + l
					1060	fa + l
					1065	l
W-300	46	9	40	5	1066	fa + l
					1074	l
W-311	44	8.5	40	7.5	1095	fa + l
					1103	l
W-299	42	8	40	10	1104	fa + 2-L
					1110	2-L
W-303	40	8	40	12	1099	fa + 2-L
					1110	2-L
W-301	37.5	7.5	40	15	1095	fa + 2-L
					1105	2-L
c	35.5	7.5	40	15	1105	td + 2-L
W-304	33.5	6.5	40	20	1095	fa + td + 2-L
					1105	td + 2-L
W-305	25	5	60	10	1095	fa + td + 2-L
					1105	td + 2-L
W-307	27	5.5	60	7.5	1096	fa + td + 2-L
					1106	td + 2-L
W-306	29.5	5.5	60	5	1100	fa + 2-L
					1105	2-L
W-309	31.5	6	60	2.5	1050	fa + l
					1088	fa + l
					1095	l

Charge No.	Composition (wt.%)				Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS	SiO ₂		
W-310	32	7	60	1	950	fa + l
					1000	l
c	31.5	6.5	60	2	1000	fa + l
d	32.5	7	60	0.5	930	fa + po + l
					934	l
W-327	25	5	65	5	1095	fa + td + 2-L
					1105	td + 2-L
W-328	25	5	67.5	2.5	1090	fa + td + l
					1100	2-L
W-331a	25	5	68.5	1.5	1070	fa + l
b	25	5	69	1	1030	fa + l
c	25	5	69.5	0.5	990	po + l
W-325	21	4	70	5	1095	fa + td + 2-L
					1106	td + 2-L
W-326	21	4	72.5	2.5	1095	fa + td + 2-L
					1100	td + 2-L
W-332a	21	4	73.5	1.5	1050	fa + td + l
b	21	4	74	1	1030	fa + l
c	21	4	74.5	0.5	1020	po + l
W-316	14.5	3	80	2.5	1055	td + po + l
					1060	td + l
W-336	6.5	1	87.5	5	1100	td + po + l
					1105	td + l
X-45	43	24	30	3	1125	ws + l
X-42	41.5	23.5	30	5	1125	mt + l
					1140	l
X-44	40.5	22.5	30	7	1125	mt + l

Charge No.	Composition (wt.%)				Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS	SiO ₂		
X-39	38.5	21.5	30	7	1100 1105	mt + l l
X-43	36.5	20.5	30	13	1078 1093 1100 1120	mt + fa + l fa + l 2-L 2-L
X-46	37.5	21	30	11.5	1120	l
X-40	35	20	30	15	1075 1095 1100 1120	mt + fa + td + l fa + l 2-L 2-L
X-41	33.5	19	30	17.5	1100 1120	td + 2-L td + 2-L
X-28	35	20	40	5	1075 1088 1100 1125	mt + fa + l mt + l l l
X-32	33.5	19	40	10	1050 1065 1092 1100	mt + fa + l fa + l fa + l 2-L
X-34	31	18	40	11	1095	td + 2-L
X-33	30.5	17	40	12.5	1097	td + 2-L
X-38	24	13.5	60	2.5	960 970 1100 1110	fa + td + po + l fa + td + l fa + td + l td + l
X-58	42	23	5	30	1210 1218	mt + l l
X-63	51.5	28.5	10	10	1220 1230 1250 1260	ws + mt + l ws + l ws + l l

Charge No.	Composition (wt.%)				Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS	SiO ₂		
X-47	48	27	10	15	1210 1220	mt + l l
X-52	47	26	10	17	1180	mt + l
X-56	46	25.5	10	18.5	1180 1200 1210	mt + l mt + l l
X-48	45	25	10	20	1160 1190 1200	mt + l mt + l l
X-49	41.5	23.5	10	25	1180 1195	mt + l l
X-55	40.5	23	10	26.5	1160 1175	mt + l l
X-53	40	22	10	30	1200	l
X-50	38.5	21.5	10	30	1200	td + l
X-20	45	25	20	10	1170 1182	mt + l l
X-24	43.5	24	20	12.5	1150 1160	mt + l l
X-23	41.5	23.5	20	15	1120 1130 1140	mt + fa + l mt + l l
X-27	40	22.5	20	17.5	1125 1130	mt + l 2-L
X-21	42	18	20	20	1090 1110	mt + td + 2-L 2-L
X-25	37	21	20	22	1095 1110	mt + td + 2-L 2-L
X-26	36	20.5	20	25	1110	td + 2-L
X-22	35	20	20	25	1090 1095 1120	mt + fa + td + l mt + td + 2-L td + 2-L

Charge No.	Composition (wt.%)				Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS	SiO ₂		
Z-26	26.5	43.5	10	20	1237 1255	mt + 1 1
Z-25	25	40	10	25	1200 1215 1270	mt + 1 1 1
Z-27	24	38.5	10	27.5	1270	td + 1
Z-34	28	39	12.5	24.5	1200 1210	mt + 2-L 2-L
Z-33	25.5	41.5	20	13	1250 1262	mt + 1 1
Z-18	25	40	20	15	1220 1235	mt + 2-L 2-L
Z-29	24	38.5	20	17.5	1225	2-L
Z-16	23	37	20	20	1130 1170 1185	mt + td + 2-L mt + 2-L 2-L
Z-20	22	36	20	22	1175 1200	mt + td + 2-L td + 2-L
Z-21	21	34	40	5	1185 1203	mt + 1 1
Z-28	20	32.5	40	7.5	1185	2-L
Z-17	19	31	40	10	1120 1130	mt + 2-L 2-L
Z-23	18.5	30	40	11.5	1070 1080	mt + 1 1
Z-30	14.5	23.5	60	2	1070 1100 1120	mt + td + 1 td + 1 1
Z-31	15	24	60	1	1070 1080	mt + 1 1

Charge No.	Composition (wt.%)				Temp. °C	Phases present
	FeO	Fe ₃ O ₄	FeS	SiO ₂		
Z-32	13.5	22.5	60	4	1100	td + 2-L
					1120	td + 2-L
Z-35	13	22	62.5	2.5	1100	td + 2-L
					1130	td + 2-L
S-51	50	20	20	10	1080	ws + fa + l
					1100	ws + l
					1110	ws + l
					1125	l
S-55	47.5	20	20	12.5	1090	ws + fa + l
					1100	fa + l
					1110	l
S-52	37	20	20	23	1095	mt + fa + td + l
					1100	td + 2-L
S-63	34	24	20	22	1095	mt + fa + td + 2-L
					1100	mt + td + 2-L
					1105	td + 2-L
S-62	52	1	20	27	1140	iron + fa + td + l
					1150	iron + td + 2-L
S-53	38.5	18.5	40	3	1050	ws + fa + l
					1060	ws + l
					1065	l
S-57	37	18	40	5	1060	fa + l
					1070	l
S-54	28	22	40	10	1095	mt + td + 2-L
					1105	td + 2-L
S-61	42	11	40	17	1135	fa + td + l
					1140	td + 2-L
S-60	57	1	15	27	1135	fa + td + l
					1140	fa + td + l
					1150	td + l