MELTING RELATIONS AND ELEMENTAL DISTRIBUTION OF PORTION OF THE SYSTEM Fe-S-Si-O TO 32 KB WITH PLANETARY APPLICATION

N81-11154

(NASA-CR-163713) MELTING RELATIONS AND ELEMENTAL DISTRIBUTION OF PORTION OF THE SYSTEM Fe-S-Si-O TO 32 KB WITH PLANETARY APPLICATION (Lunar and Planetary Inst.) 23 p HC A02/MF A01 CSCL 07D G3/25

Unclas 38320

A Research Summary

by

Wuu-Liang Huang
Lunar and Planetary Institute
3303 Nasa Road One
Houston, Tx 77058

October 1980

ABSTRACT

The melting relations and distribution of K and Cs in portion of the system has been determined at high pressures. In contrast with the phase relations at 1 atm, ferrosilite is stable as a primary phase at high pressures, because of the incongruent melting of ferrosilite to quartz plus liquid, and the boundary between the one- and two- liquid fields on the join $Fe_{1-x}O$-FeS-SiO_2 shifts away from silica with increasing pressures. If the effect of pressure onthe composition of immiscible liquids can be extrapolated to the pressure at the mantle-core, a dense, immiscible Fe-S-O liquid sinking through a silicate mantle should not carry appreciable amounts of silicon with it. The significance of K to the thermal history of the outer core has been widely recognized. In the present study, K has been found to have limited solubility in metal sulfide liquids at pressures up to 45 kb. The speculation (Carmichael & Budowinski, 1979) that K may dissolve significantly in metal-metal sulfide liquids after undergoing first order isomorphic transition has been tested by determining the distribution of Cs between sulfide and silicate liquids as an analogy to K. At 45 kb, 1400°C and 27 kb, 1300°C only limited amount of Cs has been detected in quench sulfide liquids even at pressures beyond the isomorphic transition of Cs. If Cs is a good analogy to K and the high pressure element distribution are quenchable, then these results suggested that the isomorphic transition in K may not increase its solubility in metal sulfides.

INTRODUCTION

Recent models suggest an earth's core containing iron-nickel alloy with 9 to 13 wt.% light elements which are mostly sulfur, silicon or oxygen. The other planets may have similar core (Brett, 1976). The relative low Fe-FeS eutectic temperature observed in high pressure experiments has led to the suggestion that core segregation might be accomplished by the sinking of Fe-FeS liquid through silicate mantle (Murthy and Hall, 1970).

The melting reactions between silicates and sulfides in the system Fe-S-Si-O over a range of temperatures, pressures, oxygen and sulfur fugacities may be related to the nature of mantle-core boundary. Also, the investigation of partitioning of same trace elements between immiscible sulfur and silicate liquids may provide information about the composition of planetary core. Previous studies relevant to the system at 1 atm were reviewed by Maclean (1969), and a miscibility gap separating sulfur and silicate liquids was found. The present study extends the previous work of the system to mantle pressures in order to explore the effect of pressure on the melting relations and to determine the distribution of potassium, cesium and sodium between two immiscible liquids.

EXPERIMENTAL METHODS

The research was experimentally performed by using the facilities at the Johnson Space Center. High pressure experiments were conducted in piston-cylinder high pressure apparatus using glass-talc furnace assembly. A piston-out procedure was used, applied with a -3 kb pressure correction. For interlaboratory calibration, the corrected pressure for quartz-cocsite transition were delimited at 29.5 kb-800°C and 31.2 kb-1000°C, and the melting of NaCl was determined at 8.8 kb-930°C and 20 kb-1100°C, by using the same precedure and furnace assembly (figure 1 and 2). Temperature, measured by means of $Pt\text{-}Pt_{90}Rh_{10}$ thermocouple, was considered accurate to better than ±15°C. Run duration varied from 30 to 240 minutes. Synthetic troilite, wüstite (23 wt.% oxygen), high purity silica glass and synthetic ferrosilite glass were used as starting materials. Graphite capsules were used for most of runs, but results were occasionally tested by using iron capsules.

The elements distribution was measured by using ARL electron microprobe. Clinopyroxene (CP19), troilite, orthoclase, oligoclase and Cs-dopped synthetic glass were used as standards. The Albee-Bence program was used for reducing and correcting analytical data.

EXPERIMENTAL RESULTS

General Remarks

The effect of pressure on the melting relations in portion of the system was determined up to 32 kb. The effort was concentrated in the melting relations on the join $Fe_{1-x}O$-FeS-SiO_2 at 27 kb and on the melting relationship of ferrosilite from 7 to 32 kb. The miscibility gap between sulfide and silicate liquids found in low pressure study persists at high pressures. The delineation of the boundary was attempted by measuring the elements distribution in quenched glass. The results were not satisfactory due to the presence of quenched crystal in the glass. Therefore, the boundary was mainly determined by run products. The identification of two-liquids field was based on the presence of spherical sulfide liquid phase in the silicate liquid phase. The solid phase was mainly identified by the crystal shape and reflectivity of the polished section, and was occasionally checked by electron microanalyzer.

The melting reaction curve of ferrosilite was readily identified by the appearance of the stable assemblage fayalite plus quartz or ferrosilite by crystals at subsolidus and the presence of a significant amount of quench liquid above solidus. Trace amounts of quartz, liquid and possible fayalite were unexpectedly observed as inclusions in coarse-grained ferrosilite in the stability field of ferrosilite by using the stoichiometric $FeSiO_3$ as starting material. There are three possible explanations: (1) The bulk composition of starting ferrosilite glass is shifted away from the ferrosilite by reacting with graphite capsule to form metal iron and carbon oxide; a small amount of metal iron with vermicular texture present in quenched liquid supports this speculation. (2) The contamination of trace amount of water causes an incipient melting of ferrosilite; a small divariant melting interval detected at higher pressures supports this explanation. (3) Metastable assemblage of fayalite plus quartz in ferrosilite field melts at lower temperature following the reaction: fayalite + ferrosilite $\rightleftharpoons$ liquid. The present author labled the upper boundary of the divarient intervals which corresponds to the appearance of a large amount of liquid as the univariant curve in P-T projection.

Melting Relations of $Fe_{1-x}O$-FeS-SiO_2

Figure 3 shows the results on the section with 40 wt.% through the ternary join $Fe_{1-x}O$-FeS-SiO_2. In contrast with the phase relations at 1 atm. pressure, ferrosilite becomes stable as a primary phase at 27 kb. However, because of the incongruent melting of ferrosilite to quartz plus liquid, the primary field of ferrosilite is constrained in the lower silica portion of the join. The stability field of fayalite as a primary phase decreases considerably at high pressure. The pressure effect on the liquids temperature is about 5.1°C/kb. The temperature increases from 1140°C for the invariant reaction: fayalite-tridymite-sulfide-liquid-silicate liquid at 1 atm to 1280°C for the corresponding invariant reaction: ferrosilite-quartz-sulfide liquid-silicate liquid at 27 kb.

Table 1 and figure 4 summaried the experiemental run results on the join $Fe_{1-x}O$-FeS-SiO_2. In figure 4, the boundaries of primary fields were partially labelled because of the insufficiency of experimental data. However, based on the available data, the phase relations at 27 kb when compares with that at low pressure show several distinctive characteristics: (1) The boundary between one- and two- liquid fields shifts away from silica as pressure increases; (2) Ferrosilite becomes a primary phase on the join; (3) The primary field of fayalite decreases or disappears as composition move toward FeS; (4) The primary field of silica extends significantly toward the $Fe_{1-x}O$-FeS join with 20 wt.% FeS.

Melting of Ferrosilite ($FeSiO_3$)

Lindsley et al (1964) first reported the synthesis of ferrosilite at high pressure. They also found that ferrosilite melted incongruently to a Fe_2SiO_4-rich liquid plus quartz. The present investigation experimentally determines the melting relation of ferrosilite in the binary system Fe_2SiO_4-SiO_2.

The run results are shown in figure 5 and listed in table 2. The subsolidus reaction: Fa + Qz $\rightleftharpoons$ Fs were previously determined by Lindsley (1965) and Smith (1971). The invariant point (Fa + Qz + Fs + L) was delineated by intersecting the subsolidus univariant curve with the melting curve of the ferrosilite. At pressure below the invariant point, fayalite and quartz melts eutectically to a liquid with composition within the join Fa-Fs. At higher pressures ferrosilite becomes stable and melts incongruently to quartz and liquid with composition still within the join Fa-Fs. I sought a singular point on this reaction curve at which the melting of ferrosilite would change from incongruent to congruent. The point may exist at pressure greater than 32 kb.

Ferrosilite in the presence of fayalite starts to melt at slightly lower temperature according to the geometrical configuration of univariant curves around the invariant point. No attempt has been made to delimite this reaction.

K and Cs Partitioning in Two Liquids

The analytical results of the distribution of K and Cs between two immiscible liquids were summarized in table 3. The experiments were performed at 27 and 45 kb. The analysis of K and Cs was initially designed by using AAS. Because of the failure to separate these two quench liquids, the analysis was performed by using microprobe. The results were considered as semi-quantitative. The absolute concentration of these heavy alkali metals in sulfide liquid is in the order of 100 ppm, while in silicate liquid it is in the order of 1 %. These heavy alkali metals are preferentially dissolved in silicate liquid, even at pressure beyond the first order transition of Cs (table 3).

PLANETARY APPLICATION

Murthy and Hall (1972) suggested a Fe-FeS core segregated from the mantle. On the other hand, Ringwood (1966) preferred a Fe-Si core which was considered in chemical disequilibrium with the mantle. The nature of boundary between metal core and silicate mantle, therefore, may be constrained by the melting reactions in the system Fe-S-Si-O.

The melting relations in the system at low pressure have been investigated experimentally in detailed by many authors (e. g. Naldrett, 1969; Maclean, 1969; Shimazak and Clark, 1973). The extrapolation of these results to the conditions of mantle-core boundary is limited due to the paucity of experimental data at high pressure. The present study attempts to extend the portion of melting relation on the system to higher pressure. Although the pressures of core-mantle boundary can hardly reach in this laboratory, the investigation concentrates onthe pressure effects of the melting relation. The results may provide some basic information for extrapolation to higher pressure.

Based on the same motivation, Wendlandt and Huebner (1979) studied the melting relations in the system Fe-S-O at 30 kb and found that only negligible amounts of oxygen could be dissolved in first eutectic Fe-FeS liquid. By adding silicon to the system, the present study shows that the miscibility gap between silicate and sulfide liquid expands with pressure. If the effect of pressure on the composition of immiscible sulfide liquid can be extrapolated to mantle-core pressures, a dense, immiscible Fe-S-O liquid sinking through a silicate mantle should not carry appreciable aomounts of silicon with it. Therefore, on the basis of Murthy and Hall's model, a silicate mantle may be equilibrated with a Fe-FeS outer core containing only limited amounts of silicon and oxygen.

The significance of K to the thermal history of the outer core has been widely recognized (Hall and Murthy, 1971; Lewis, 1971). Many authors (e. g. Murthy& Hall, 1971) have proposed that potassium might be present in significant amount in Fe-FeS outer core. A few experiments up to 40 kb showed that only a very limited amount of K could be dissolved in Fe-FeS liquid (Ganguly & Kennedy, 1977), in metal-sulfide liquid immiscible with basaltic liquid (Overshy and Ringwood, 1972) and in sulfide liquid in partially melting carbonaceous chondrite (Seitz and Kushiro, 1974). The present study determines firstly the partitioning of K and Na between coexisting immiscible liquids in the system. The results show that K and Na preferentially enter silicate by factors of 200. However, The recent study of Carmichael and Budowinski (1979) has strengthened the proposal of Murthy and Hall. It showed that on the basis of the measurement of electron structure of heavy alkali metals at high pressure, K, Rb and Cs should behave as monovalent transition elements after undergoing a first order isomorphic transition. They found that the transition pressures for K and Cs, respectively were 290 and 42 kb. It is probable that the failure to detect significant amount of K in metal liquid is due to the insufficiency of the applied pressures. Because the pressure of the K transition is beyond obtainable with a piston-cylinder, the distribution of Cs between the two immiscible liquids has been studied at 45 kb as an analogy to K. The result shows that only limited amount of Cs has been detected in quench sulfide even at pressures beyond the isomorphic transition of Cs. If Cs is a good analogy to K and the high pressure elements distribution is quenchable, then the isomorphic transition in K may not increase its solubility in metal sulfides.

ACKNOWLEDGEMENTS

This report summarized the major research while the author was a visiting scientist at Lunar and Planetary Institute.

The experimental work was performed at NASA Johnson Space Center. Drs. R. J. Williams and G. E. Lofgren kindly provided access to their equipments. O. Mullins and S. P. Smith of Lockheed Electronics Company also assistanted in laboratory work. I would like to express my sincere appreciation to them, especially to R. J. Williams for his stimulating discussion.

FIGURE LEGENDS

Figure 1. P-T projection for the transition of quartz $\rightleftharpoons$ coesite. The experiments were conducted both with piston-in and piston-out procedure. The starting materials are 1:1 mixture of quartz and coesite. The half-filled symbols indicate no reaction detected. The results are used for pressure calibration.

Figure 2. P-T diagram showing the melting of halite determined by differential thermal analysis. The results are used for pressure calibration.

Figure 3. Isobaric diagram showing the melting relations of a section through the join $Fe_{1-x}O$-FeS-SiO_2 at 27 kb. Solid symbol indicates runs above liquidus. The half-filled circles are runs with liquid and crystals. Dash-dotted line separated the region of the liquid field from that of two immiscible liquids.

Figure 4. Isobaric diagram showing the miscibility gap in the join $Fe_{1-x}O$-FeS-SiO_2. The heavy solid line indicates that at 27 kb whereas the heavy dotted line indicates that at low pressure.

Figure 5. P-T projection showing the melting relations in binary system Fe_2SiO_4-SiO_2. Dash-dotted lines were estimated. All runs used $FeSiO_3$ glass as bulk composition. Open circles indicate subsolidus runs. The dash-dotted lines are schematic.

REFERENCES

Akalla, J., Vaidya, S. N. and Kennedy, G. C. The melting of sodium chloride at pressure to 65 kb: Phys. Rev.

Brett, R. (1976) The current status of speculation on the composition of the core of the earth: Reviews of Geophy. and Phys., 14, p. 375-382.

Boettcher, A. L. and Wyllie, P. J. (1968) The quartz-coesite transition measured in the presence of a silicate liquid and calibration of piston-cylinder apparatus: Contr. Mineral. and Petrol. 17, 224-232.

Carmichael, I and Bukowinski, M. S. T. (1979) Electronic structure of the heavy alkali metals and their apparent depletion in the earth: EOS 60, 964.

Ganguly, J. and Kennedy, G. C. (1977) Solubility of K in Fe-S liquid, silicate-K-$(Fe\text{-}S)^{liq}$ equilibria, and their planetary implications: Earth Planet. Sci. Lett. 35, 411-420.

Hall, H. T. and Murthy, V. R. (1971) The early chemical history of the earth: some critical elemental fractionations: Earth Planet. Sci. Letters 11, 239-244.

Lewis, J. S. (1971) Consequences of the presence of sulfur in the core of the earth: Earth Planet. Sci. Letters 11, 130-134.

Lindsley, D. H. (1965) Ferrosillite: Carnegie Inst. Wash. Year Bk. 64, 143-150.

Lindsley, D. H., Davis, B. T. C., and MacGregor, I. D. (1964) Ferrosillite synthesis at high pressures and temperatures: Science 144, 73-74.

Maclean, W. H. (1969) Liquidus phase relations in the FeS-FeO-Fe_3O_4-SiO_2 system, and their application in geology: Economic Geol. 64, 365-384.

Murthy, V. R. and Hall, H. T. (1970) The chemical composition of the earth core: possibility of sulfur in the core, Phys. Earth Planet. Interiors 2, 276-282.

Oversby, V. M. and Ringwood, A. E. (1972) Potassium distribution between metal and silicate and its bearing on the occurence of potassium in the earth's core: Earth Planet. Sci. Lett. 14, 345-347.

Naldrett, A. J. (1969) A portion of the system Fe-S-O between 900°C and 1080°C and its application to sulfide ore magmas: Jour. Petro. 10, 171-201.

Ringwood, A. E. (1966) Chemical evolution of the terrestrial planets: Geochim. Cosmochim. Acta 30, 41-104.

Shimazak, H. and Clark, L. A. (1973) Liquidus relations in the FeS-FeO-SiO_2-Na_2O system and geological implications: Economic Geology 68, 79-96.

Smith, D. (1971) Stability of the assemblage iron-rich orthopyroxene-olivine-quartz: Am. Jour. Sci. 271, 370-382.

Wendlandt, R. F. and Huebner, J. S. (1979) Melting relations of portions of the system Fe-S-O at high pressure and application to the composition of the earth's core: Abs. Lunar Planet. Sci. Conf. X. 1329-1331.

Table 1. Experimental Run Results for the Phase Relations on the Join FeS-$Fe_{1-x}O$-SiO_2

Run No.	Press. kb.	Temp. ^oC	Time hour	Composition Fes	wt.% $Fe_{1-x}0$	SiO_2	Run Products
		FeS40 $Fe_{1-x}0$60	-----	FeS40 $SiO_2$60			
341	27	1325	1	40	55.5	4.5	Ws+1L
344A	27	1350	1	40	55.5	4.5	Ws+1L
345	27	1400	1/2	40	55.5	4.5	1L
311	27	1250	1	40	53	7	Ws+Fs+1L
321	27	1300	1/2	40	53	7	two stage
	27	1275	3/4	40	53	7	Ws+Fs+1L
344B	27	1325	1	40	53	7	Ws+2L
343	27	1350	1	40	53	7	Ws(tr)+2L
323	27	1225	2	40	50.5	9.5	Fs+Fa+1L
313	27	1250	1	40	50.5	9.5	Fs+Fa(?)+2L
327	27	1275	1	40	50.5	9.5	Fs+Fa(?)+2L
346	27	1300	2	40	50.5	9.5	2L
308	27	1200	3	40	48.0	12	Fs+Fa(tr)+1L
307	27	1250	3 1/2	40	48	12	Fs+2L
320	27	1275	1	40	48	12	Fs+Fa(tr)+2L
309	27	1300	1/2	40	48	12	2L
322	27	1275	1	40	45.5	14.5	Fe+2L
312	27	1300	3/4	40	45.5	14.5	2L
310	27	1300	1	40	43	17	Qz+L
325	27	1350	1/2	40	43	17	2L

(To be continued)

FeS20 $Fe_{1-x}O$80 ----- FeS20 $SiO_2$80

358	27	1425	3/4	20	67.5	12.5	Ws+1L
352	27	1350	2	20	65	15	Ws+2L
354	27	1400	1	20	65	15	Fs+2L
342	27	1350	1	20	62.5	17.5	2L+quench silicat
339	27	1300	1 1/2	20	57.5	22.5	2L

FeS60 $Fe_{1-x}O$40 ----- FeS20 FeS40

340	27	1300	1 1/2	60	35.5	4.5	Fs+2L

$Fe_{1-x}SiO_4$ ------ FeS

361	27	1375	1	12.5	61.7	25.8	Qz+2L
360	27	1350	1	10.0	63.5	26.5	Qz+2L

$FeSiO_3$ ------ FeS

351	27	1350	1 1/2	5	51.8	43.2	Qz+2L
353	27	1350	2	2.5	53.1	44.4	Qz+2L

Abbreviations: Ws-Wustite: Fs-ferrosilite; Fa-fayalite; Qz-quartz; 2L-two immiscible sulfide and silicate liquids; 1L-one liquid; two stage-run first brings to certain T for some duration, then brings to the desired temperature; P-graphite capsule wraped by platinum capsule; (tr)-trace in amount.

ORIGINAL PAGE IS
OF POOR QUALITY

Table 2. Experimental Run Results for the Melting of ferrosilite

Run No.	Corrected Pressure kb	Temp. °C	Time hour	Run Products
328	12	1200	2	Fa+Qz
329	12	1125	3	two stages
	12	1225	2	Fa+Qz
330	12	1125	2	two stages
	12	1150	2	Qz+L
363p	17	1200	17	Fs+Fa+Qz
333	17	1260	2	Fs+Qz+Fa(tr)+L(tr)
326	17	1275	1	Fs+Qz+Fa+L
367	22	1200	26	Fs+Fe+Qz
334	22	1200	4	two stages
	22	1300	1	Fs+Qz+L
324	22	1325	1	Qz+L
316	27	1200	2	two stages
	27	1300	1 1/2	Fs+Qz+L
317I	27	1200	2 1/2	two stages
	27	1325	1	Qz+Fe+L
315	27	1200	3	two stages
	27	1350	3/4	Fs+L+Qz
368p	27	1350	2	Qz+L
362p	27	1375	2	Qz+L
314	27	1200	3 1/2	two stages
	27	1200	3 1/2	Qz+L

364p	27	1550	4	Qz+L
336	32	1200	4	two stages
	32	1350	1	Fs+L(tr)
319	32	1375	1	Fs+L
318	32	1200	5	two stages
	32	1400	1/2	Qz+L
347I	32	1400	1/2	Fs+Qz+L

Abbreviations are used the same a those in table 1.

Additional abbreviations: Fe-iron metal; I-iron capsule was used.

Table 3. Partitioning of K, Cs and Na between immiscible sulfide and silicate liquids.

$$Kd \doteq \frac{C\ (\text{SILICATE LIQUID})}{C\ (\text{SULFIDE LIQUID})}$$

	K	Cs	Na
27 KB 1235°C	194	—	257
27 KB 1300°C	167	73	—
45 KB 1400°C	182	68	—

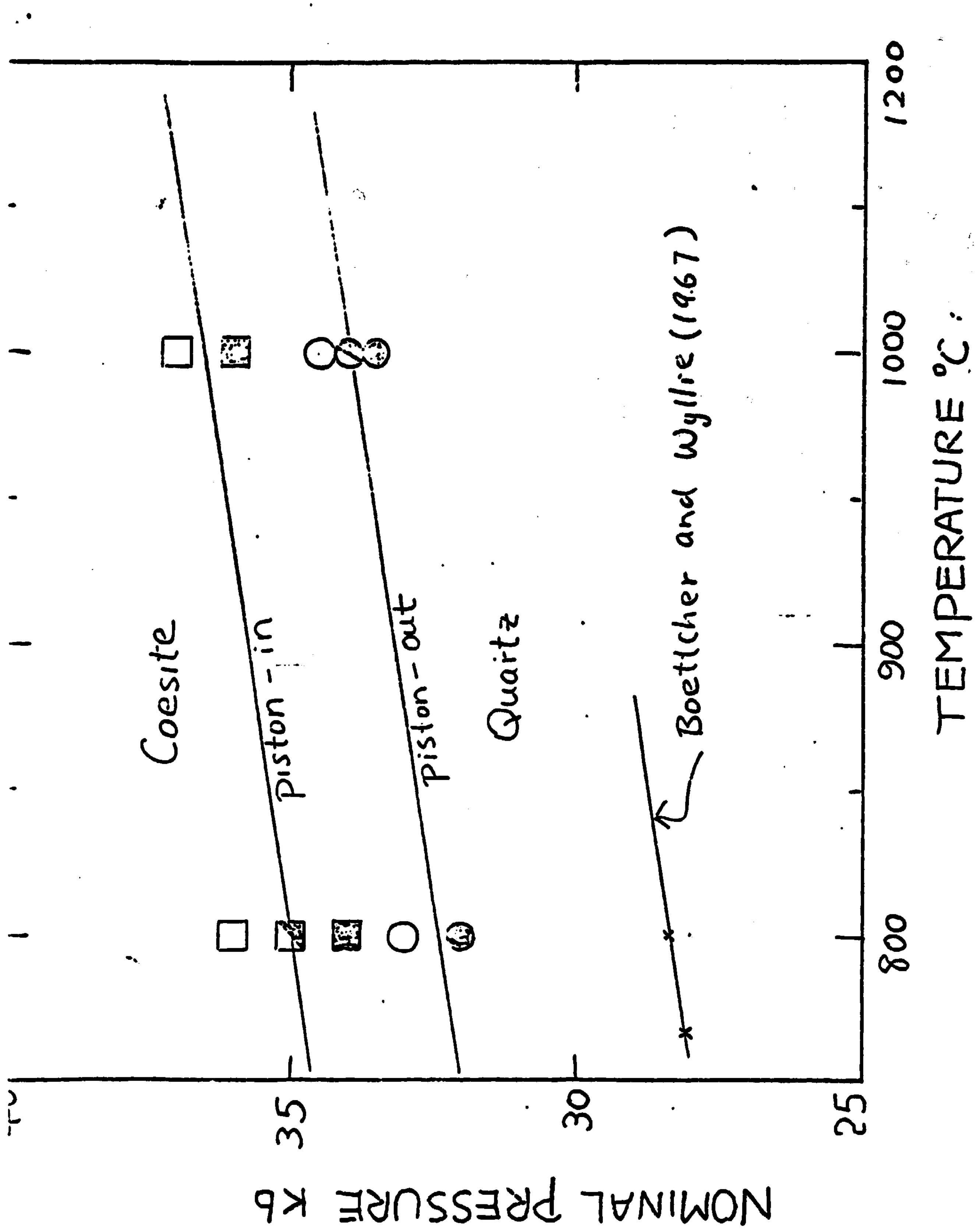
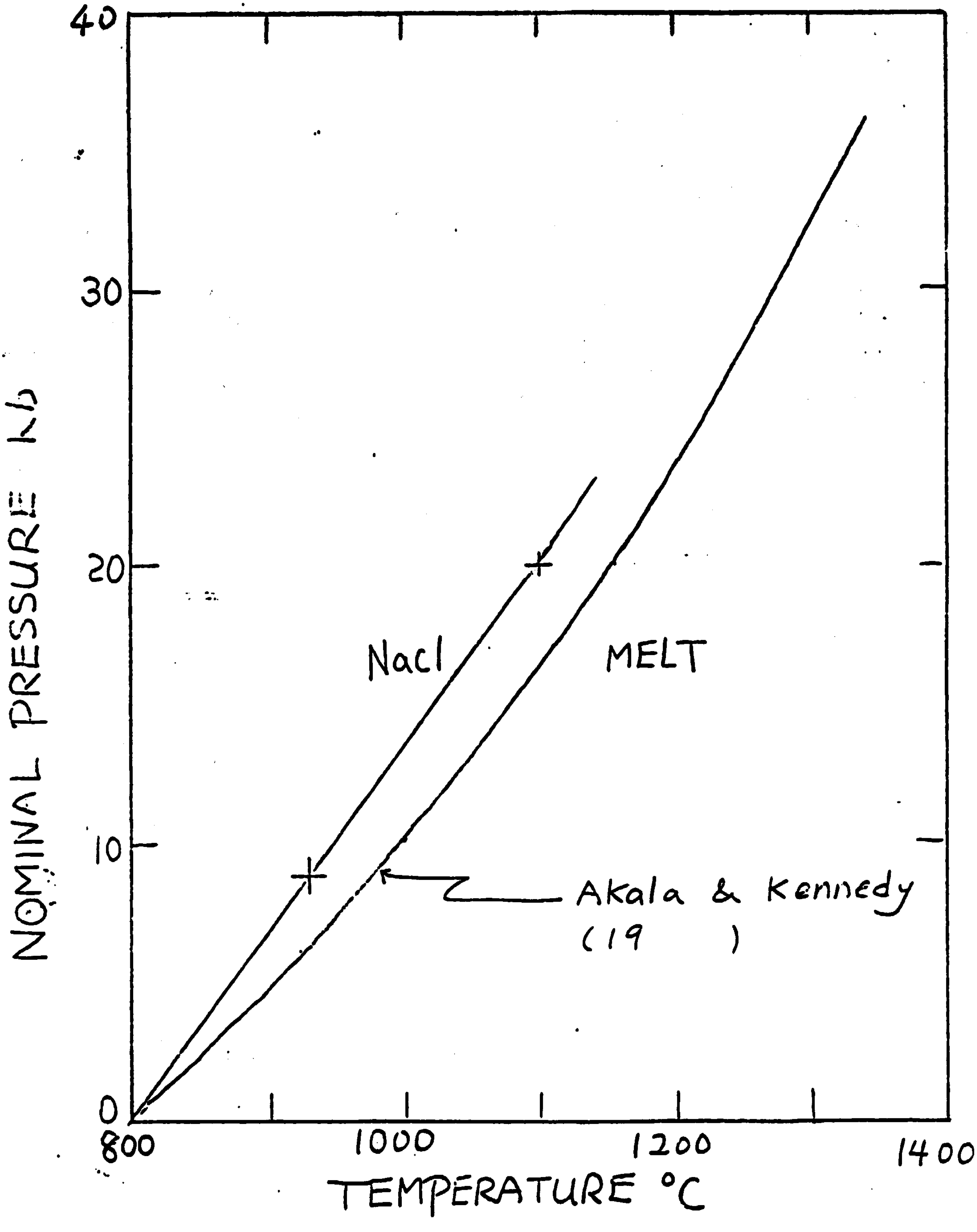
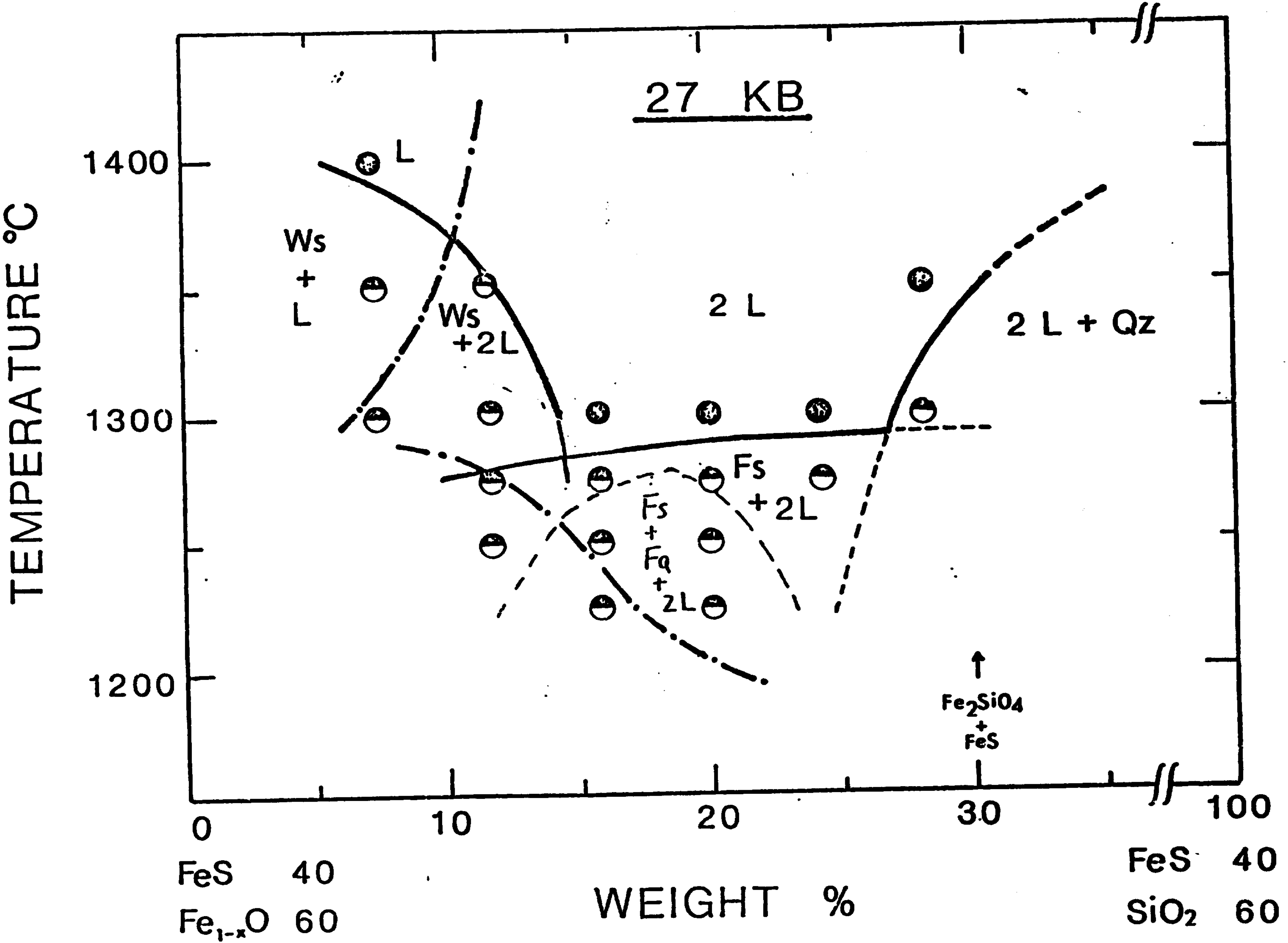


Fig. 1

ORIGINAL PAGE IS
OF POOR QUALITY

Fig 2


NOMINAL PRESSURE kb
40
30
20
10
0
800
1000
1200
1400
TEMPERATURE °C
Nacl
MELT
Akala & Kennedy
(19)


27 KB
TEMPERATURE °C
1400
1300
1200
L
Ws + L
Ws +2L
2 L
2 L + Qz
Fs +2L
Fs + Fa + 2L
Fe2SiO4 + FeS
0
10
20
30
100
FeS 40
Fe1-xO 60
WEIGHT %
FeS 40
SiO2 60

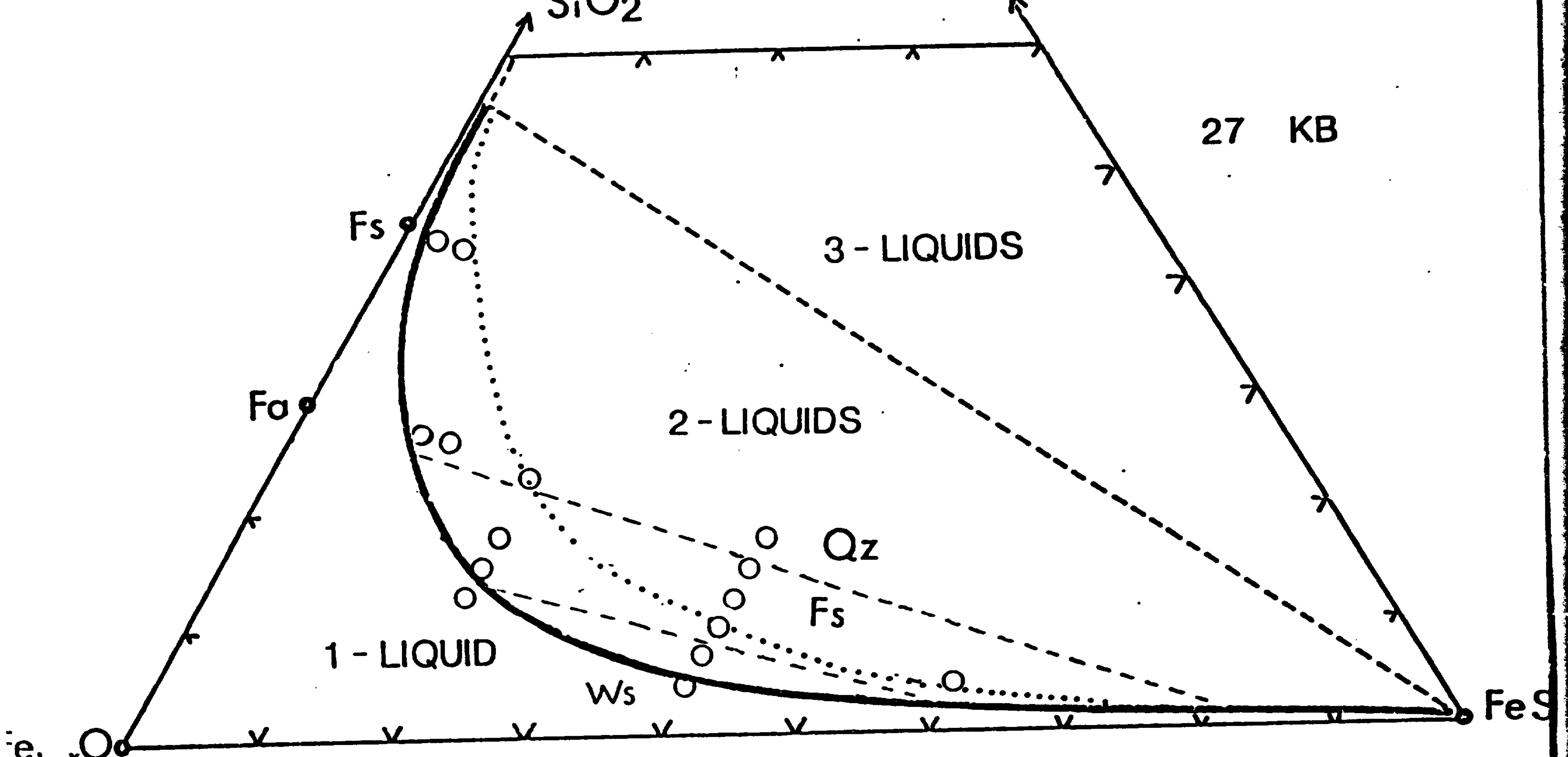


Fig. 11

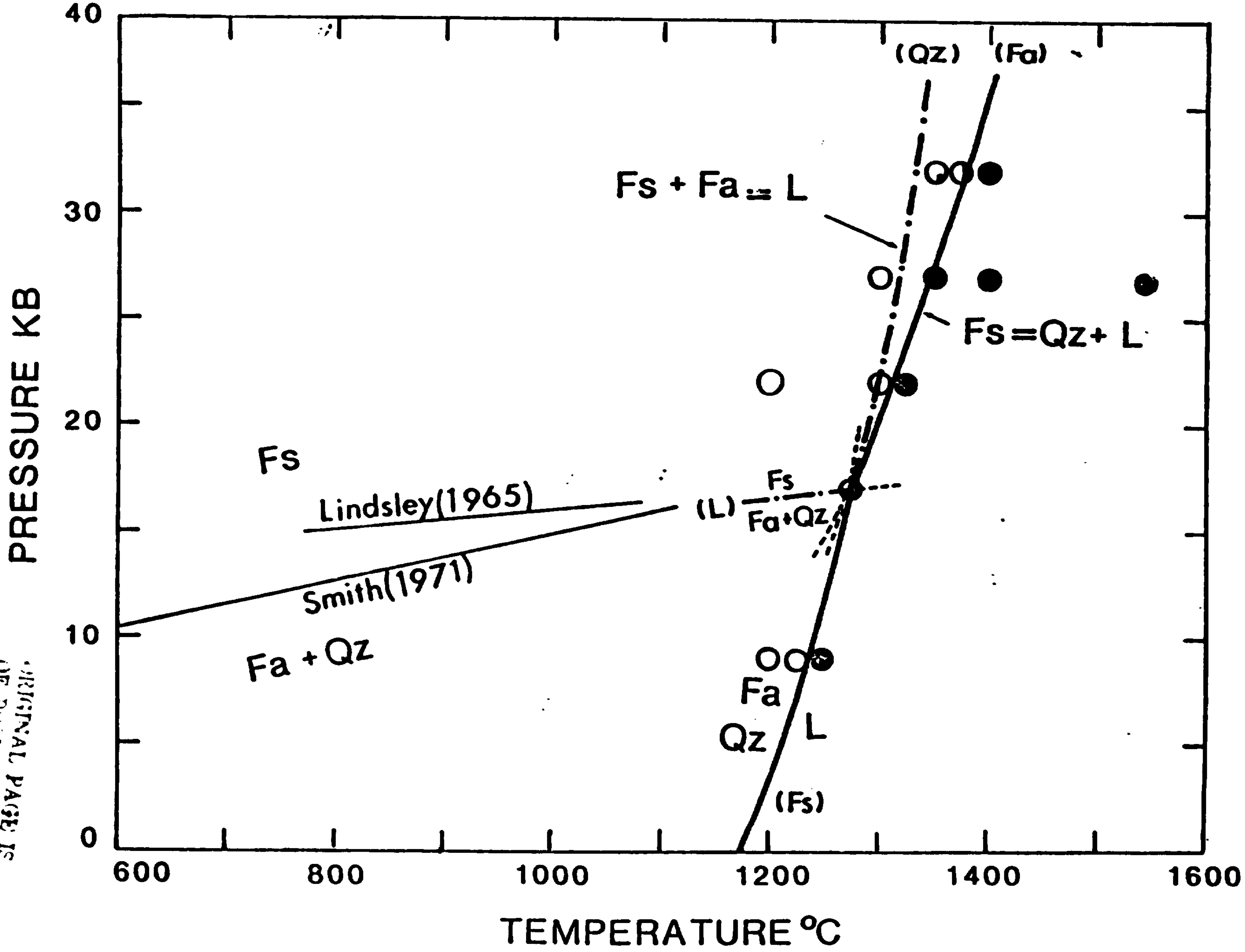

40
30
20
10
0
PRESSURE KB
600
800
1000
1200
1400
1600
TEMPERATURE °C
(Qz)
(Fa)
Fs + Fa = L
Fs = Qz + L
Fs
Lindsley(1965)
Smith(1971)
(L)
Fs
Fa+Qz
Fa + Qz
Fa
Qz
L
(Fs)

Fig. 5