SOLID SOLUTIONS OF THE TYPE (Ca,Mg,Mn,Fe)S AND THEIR USE AS GEOTHERMOMETERS FOR THE ENSTATITE CHONDRITES

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ABSTRACT

Determination of the phase relations in the system MgS-MnS-CaS-FeS shows that niningerite (MgS) and alabandite (MnS) have extensive and strongly temperature dependent solid solutions towards FeS. The CaS-contents of niningerites and alabandites, and the MgS- and MnS-contents of oldhamites (CaS) in the assemblage oldhamite plus troilite plus niningerite or alabandite respectively, are also strongly temperature dependent. Interpretation of sulfide compositions in enstatite chondrites after Keil (1968) shows that type I, intermediate, and type II enstatite chondrites all have minimum temperatures of formation in the range 600°C to 800°C. Type II's cannot have been derived from type I's by metamorphism.

Quenching rate studies of niningerites and alabandites coexisting with troilite at 800°C show that type I and intermediate type enstatite chondrites must have cooled at rates at least as fast as 0.1°C/minute, and are presumably debris resulting from one or more impact events. Type II enstatite chondrites cooled much more slowly and in support of Keil's (1968) contention, must have a completely separate origin from type I's.

INTRODUCTION

An Fe-saturated pyrrhotite (FeS), commonly called troilite, is a nearly ubiquitous phase in meteorites. Indeed troilite is so common that with the exception of rare carbonaceous chondrites a major proportion of all the sulfur in meteorites is found either in troilite or in secondary sulfide phases that have exsolved from it during the meteorite cooling history. In the stony meteorites, and particularly the enstatite chondrites, a number of other primary sulfides have also been observed. One, the monosulfide oldhamite (CaS), occurs in all known enstatite chondrites, though its abundance is considerably less than that of troilite with which it invariably coexists. Oldhamite, which is a cubic monosulfide isostructural with NaCl, is unknown in terrestrial rocks.

Recent studies by Keil (1968) and others of the mineralogy of enstatite chondrites showed that in all the samples examined a second monosulfide isostructural with NaCl also occurred as a primary phase. Electron microprobe analyses by Keil revealed a bimodal distribution of compositions; in the class of enstatite chondrites classified as type I by Anders (1964), the second cubic monosulfide is essentially MgS and for this new mineral Keil and Snetsinger (1967) proposed the name niningerite. In the type II enstatite chondrites the second cubic monosulfide is essentially MnS, and is therefore alabandite.

Keil's (1968) detailed mineralogical analyses of all available enstatite

chondrites have therefore revealed a trimodal distribution of composi-
tions among the cubic monosulfides, which may be either Ca-, Mg-, or
Mn-rich. His work has also revealed a ubiquitous assemblage in which
troilite coexists with two cubic monosulfides, one of which is always
oldhamite, with the second being either alabandite or niningerite, but not
both.

Examination of the compositions of the cubic monosulfides shows that
each is really a complex solid solution in which the major substituting
cations are Ca, Mg, Mn, and Fe. Niningerite, for example, always con-
tains several percent of Ca and Mn in solid solution, and alabandite
several percent of both Ca and Mg. The most abundant component in
solution, however, is Fe, which is observed to replace up to half of the Mg
and Mn in niningerite and alabandite respectively. Although Keil re-
ported other elements such as Cr, Zn, and Ti in the cubic monosulfides,
they are minor and with the exception of Cr, present in amounts con-
siderably less than 1 percent. The essential compositions of the three
monosulfides found in enstatite chondrites can be written:

niningerite	$(Mg,Fe,Mn,Ca)S$
alabandite	$(Mn,Fe,Mg,Ca)S$
oldhamite	$(Ca,Mg,Mn,Fe)S$

Keil's (1968) careful analyses showed, furthermore, a considerable
range in the FeS contents of alabandites and niningerites. As both phases
coexist with troilite and might presumably be, or have been, saturated
with FeS at some time in their history, it seems possible that some aspects
of the thermal history of the enstatite chondrites might be deciphered if
the phase relations in the system FeS-MnS-MgS-CaS are known. It is the
purpose of this paper to report on the relevant phase relations and draw
some conclusions regarding the meteorites.

METHODS OF STUDY

Compounds and charges of differing compositions were prepared by reactions in sealed
evacuated silica glass tubes. Stoichiometric charges of MgS, MnS, and FeS were first
prepared from their elements using spectrographically pure starting materials, and of CaS
from Fisher reagent by reducing any sulfate present with excess sulfur. They were then
mixed in suitable proportions to prepare more complex compositions. Charges were heated
in muffle furnaces designed to have essentially isothermal volumes and automatic tempera-
ture regulation of $\pm 2°C$ up to 1100°C. Reaction times varied from 1 to 100 days, depend-
ing on the temperature of the experiment and the number of times the sample was homog-
enized by grinding.

Once a compound had been prepared it was examined by one or more of three X-ray
diffraction techniques; X-ray diffractometer, Straumannis-mount powder camera or
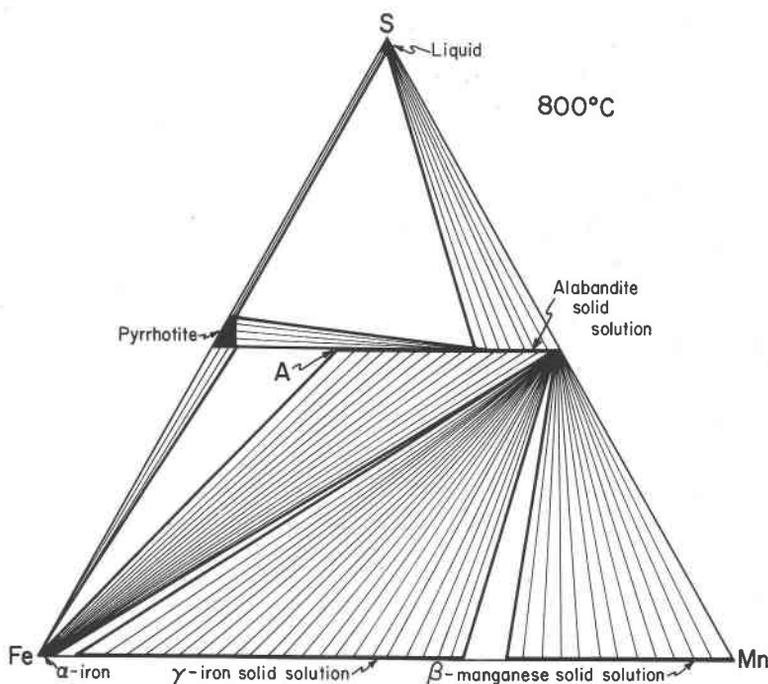Guinier-deWolff focussing camera. For purposes of determining unit cell edges of the cubic

FIG. 1. Phase diagram for the system Fe-Mn-S at 800°C. The extensive alabandite solid solution coexists with α-iron, reaching a maximum at point A where it coexists with manganiferous troilite and α-iron.

sulfides, NaF was added as an internal standard to the X-ray mounts. The cell edge of the NaF had previously been determined as 4.6327 ± 0.0002 Å by comparison with the cell edge of a gem diamond, for which a value of $a_0 = 3.56703$ Å was selected (Parrish, 1960). A portion of the charge from each experiment was mounted in a cold-setting, clear epoxy resin and polished both for examination under reflected light microscopy and for analysis of individual grains by a four-channel electron micro-probe analyser (Acton Labs). The microprobe analyser was also invaluable in providing information on the homogeneity both of individual grains and between grains in a given charge.

Within the quinary system Ca-Mg-Mn-Fe-S there are several phases in addition to the cubic monosulfides of interest in this study. A complete examination of the phase relations in so large a system would be very time consuming, but fortunately there are some factors which lead to useful simplifications.

The first and most important simplifying feature is that the only stable sulfide phases throughout the temperature and pressure range of interest are binary compounds and their solid solutions. Neither ternary nor quaternary phases have been discovered. The second simplifying feature is that the three important ternary systems, Fe-Mn-S, Fe-Mg-S, and Fe-Ca-S, all have the same form (Figure 1) in which the stoichiometric cubic monosulfides and their solid solutions coexist with metallic Fe. The ternary phase diagrams are thus very similar to that presented for Fe-Zn-S by Barton and Toulmin (1966) and the same reasoning used by them to establish that the maximum solubility of FeS in ZnS occurs in the

three-phase field $Fe+FeS+(Zn,Fe)S$ applies in the present case and can be extended directly to the ternary and quaternary solid solutions. Inasmuch as Keil (1968) showed that a metallic (Fe,Ni) phase was always present in enstatite chondrites, we need only study the composition of cubic monosulfides for which the activity of sulfur (a_{S_2}) is buffered by the assemblage $Fe+FeS$, in order to approximate the meteorite systems. A small button of pure iron was therefore inserted in the silica glass reaction vessel so that it could serve as an a_{S_2} control, but was positioned so that it could not directly enter the reaction under investigation. The Fe-rich limits of cubic monosulfide solid solutions presented in the subsequent diagrams, therefore, correspond to point A in Figure 1, and are those in which the cubic monosulfides coexist with both metallic Fe and troilite.

Properties of the Phases Encountered

Cubic monosulfide. The three end-member cubic monosulfides, oldhamite (CaS), niningerite (MgS), and alabandite (MnS), have identical structures and symmetries (space group, *Fm3m*). The structure is a simple one in which sulfur atoms occupy the nodes of a face centered cubic lattice and the Ca, Mg, or Mn atoms occupy the octahedral sites.

Table 1. Comparisons Between the Present Study and Previous Work for the Unit Cell Edges of CaS, MgS, and MnS. Where the Temperature of Measurement is Known it is Given in Parentheses. Values Originally Stated in kX Units Have Been Converted to Å by the Conversion Factor 1.00202

| Investigator	Unit Cell Edge, a_o
CaS	
Primak, Kaufman, and Ward (1948)	5.6951
Guntert and Faessler (1956)	5.6905 (21°C)
Swanson, Gilfrich, and Cook (1957)	5.6948 (25°C)
Present Study	5.6953 (24°C)
	± 0.0008
MgS	
Primak, Kaufman, and Ward (1948)	5.2018
Guntert and Faessler (1956)	5.2034 (21°C)
Swanson, Gilfrich, and Cook (1957)	5.200 (25°C)
Present Study	5.2020 (25°C)
	± 0.0008
MnS	
Schnaase (1933)	5.223
Mehmed and Haraldsen (1938)	5.222
Kroger (1939)	5.219
Swanson, Fuyat, and Ugrinic (1955)	5.2236 (26°C)
Present Study	5.2234 (25°C)
	± 0.0008
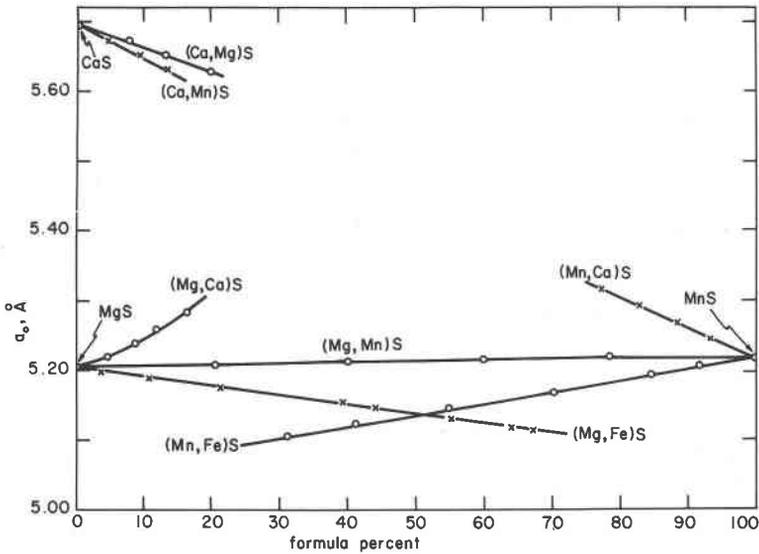
FIG. 2. Effect of binary cation substitutions on the unit cell edges of
cubic monosulfide solid solutions. Data are given in Table 2.

There is no evidence to suggest that the cubic monosulfides have large
variations in stoichiometry. To the contrary, within our weighing limits
stoichiometric variations from a metal/sulfur ratio of 1:1 could not be
detected. Extensive cation substitutions occur in the octahedral sites,
however, and lead to marked changes in the unit cell edges of the cubic
monosulfides. In the binary solid solutions the cell edges vary linearly
with composition except for (Mg, Ca)S which is markedly curved (Figure
2, Table 2). In the extensive ternary solid solutions all the cell edge
variations become non-linear however (Figure 3, Table 3), and while the
effect in the quaternary volume FeS-MgS-MnS-CaS has not been ex-
plored, it is probable that the non-linear behavior will also hold there.

Previous work on the cell edges of the cubic monosulfides has been es-
sentially limited to the pure compounds. In each case, the cell edge de-
termined in the present work is in good agreement with earlier studies
(Table 1). Primak *et al.* (1948) reported a cell edge of 5.2616 Å for an
(Mg, Ca)S solid solution containing 13.5 formula percent CaS, which is
also in agreement with the present work. The only other work reporting a
cell edge on a comparable monosulfide solid solution is that by Lee
(1955), who found that a natural alabandite from the Kusugi Mine in
Japan contained 6.17 formula percent FeS in solid solution and had a cell
edge of 5.212 ± 0.004 Å, again in agreement with the present study.

TABLE 2. EFFECT OF BINARY CATION SUBSTITUTIONS ON THE UNIT CELL EDGES OF CUBIC MONOSULFIDE SOLID SOLUTIONS

| formula percent				$\underline{a}$, Å	formula percent				$\underline{a}$, Å
CaS	MnS	MgS	FeS	±0.0008	CaS	MnS	MgS	FeS	±0.0008
–	–	100	–	5.2020	90.65	9.35	–	–	5.6506
–	–	96.34	3.66	5.1972	86.46	13.54	–	–	5.6313
–	–	89.38	10.62	5.1903	6.85	93.15	–	–	5.2504
–	–	78.65	21.35	5.1774	12.02	87.98	–	–	5.2732
–	–	61.68	39.22	5.1567	17.14	82.86	–	–	5.3014
–	–	55.76	44.24	5.1511	22.78	77.22	–	–	5.3206
–	–	44.90	55.10	5.1307	92.09	–	7.90	–	5.6745
–	–	35.92	64.08	5.1175	87.05	–	12.95	–	5.6526
–	–	32.66	67.34	5.1161	80.27	–	19.73	–	5.6288
–	100	–	–	5.2234	4.60	–	95.40	–	5.2188
–	91.59	–	8.41	5.2100	8.70	–	91.30	–	5.2370
–	84.55	–	15.45	5.1996	11.97	–	88.03	–	5.2622
–	70.36	–	29.64	5.1764	16.35	–	83.65	–	5.2862
–	55.09	–	44.91	5.1504	–	78.33	21.67	–	5.2225
–	41.07	–	58.93	5.1289	–	59.90	40.10	–	5.2187
–	31.15	–	68.85	5.1082	–	39.82	60.18	–	5.2142
100	–	–	–	5.6953	–	20.44	79.56	–	5.2086
95.29	4.71	–	–	5.6726					
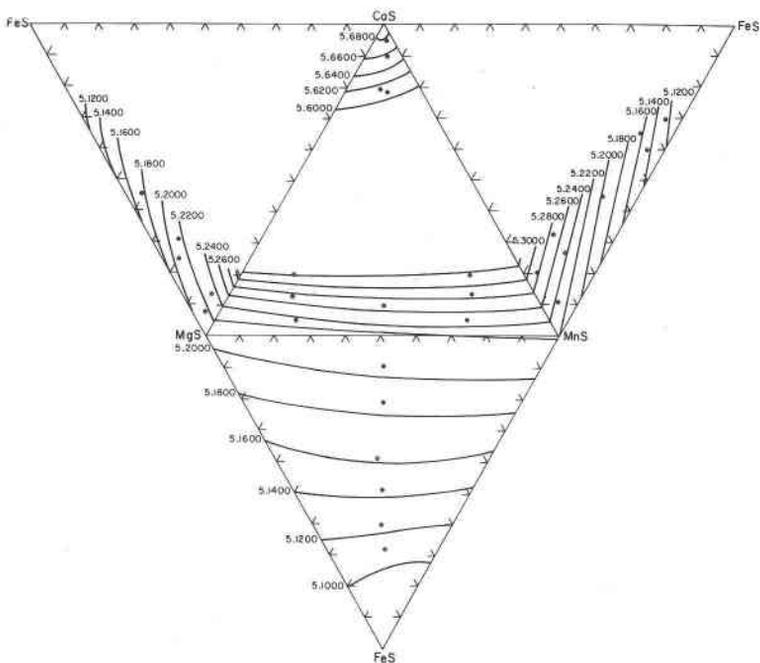
FIG. 3. Effect of ternary cation substitutions on the unit cell edges of cubic monosulfide solid solutions. Data are given in Table 3.

TABLE 3. EFFECT OF TERNARY CATION SUBSTITUTIONS ON THE UNIT CELL
OF CUBIC MONOSULFIDE SOLID SOLUTIONS

Formula percent				$\underline{a}$, Å
CaS	MgS	MnS	FeS	± 0.0008
5.19	71.78	23.03	–	5.2345
12.72	69.07	18.21	–	5.2733
19.90	65.05	15.05	–	5.3201
9.90	44.83	45.27	–	5.2659
5.17	23.23	71.60	–	5.2481
13.28	17.97	68.75	–	5.2902
19.69	15.30	65.01	–	5.3191
94.95	1.96	3.09		5.6754
89.97	3.99	6.04		5.6576
79.13	11.34	9.53		5.6160
78.25	9.75	11.99		5.6042
3.63	92.62	–	3.74	5.2128
4.99	75.78	–	19.23	5.2015
4.84	54.92	–	40.24	5.1783
6.26	40.32	–	53.42	5.1616
8.24	86.82	–	4.94	5.2354
7.95	69.30	–	22.75	5.2156
11.69	–	73.31	15.00	5.2484
17.97	–	67.29	14.74	5.2724
9.82	–	55.20	34.98	5.1986
4.92	–	40.15	54.93	5.1511
9.79	–	34.92	55.29	5.1638
4.80	–	30.20	65.00	5.1285
5.24	–	89.51	5.25	5.2344
15.30	–	79.71	4.99	5.2820
–	15.08	16.69	68.23	5.1102
–	20.08	19.34	60.58	5.1258
–	25.21	25.57	49.22	5.1435
–	31.65	29.24	39.11	5.1619
–	38.93	40.02	21.05	5.1865
–	44.24	45.85	9.91	5.2045

Troilite. Because all experiments containing iron sulfide as a phase were carried out in the presence of a metallic Fe phase, and because iron sulfides cannot be shown to form more Fe-rich compositions than FeS, (Toulmin and Barton, 1964), troilite or stoichiometric FeS, was the only iron sulfide encountered.

The troilite, X-rayed at room temperature, showed the diffraction pattern typical of stoichiometric FeS as reported by Berry and Thompson (1962). While the room temperature X-ray patterns all indicate a superlattice on the basic NiAs-type structure, it is well established that in pure FeS the superlattice is not stable above 138°C. (See Barton and Skinner, 1967). Though not specifically checked, therefore, it is assumed that the

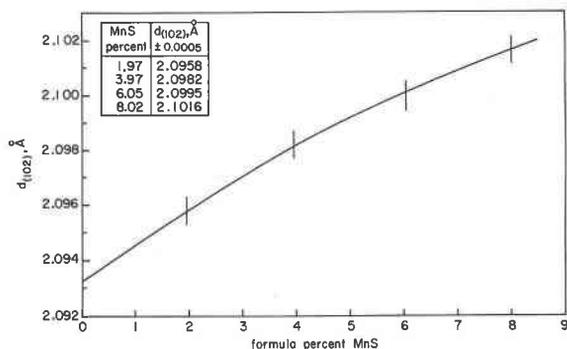| MnS percent	$d_{(102)}$, Å ± 0.0005
1.97	2.0958
3.97	2.0982
6.05	2.0995
8.02	2.1016

Fig. 4. The effect of Mn replacing Fe in troilite, shown by an increase in the spacing of the (102) reflection of the troilite sub-cell.

stoichiometric FeS phase in all of the present work had the basic NiAs-type structure under the conditions of the high temperature experiments.

Troilite does not tolerate detectable amounts of either Ca or Mg replacing the Fe in solid solution, but it does accept significant amounts of Mn. In a series of experiments at 1000°C, the solubility limit was found to be 7.5 ± 0.5 formula percent MnS in FeS. Substitution of Mn for Fe causes an expansion in the unit cell of troilite and this is shown in Figure 4, where the spacing of the (102) plane of the basic troilite sub-cell is plotted against composition.

PHASE RELATIONS

Compositional relations between coexisting phases are most conveniently presented geometrically. The relations are straightforward and unambiguous, but it must be remembered that in all diagrams in which FeS appears as a component, metallic Fe, which does not appear on the plot as a phase, was nevertheless present as a buffer for a_{S_2}.

The figure contains an embedded data table:

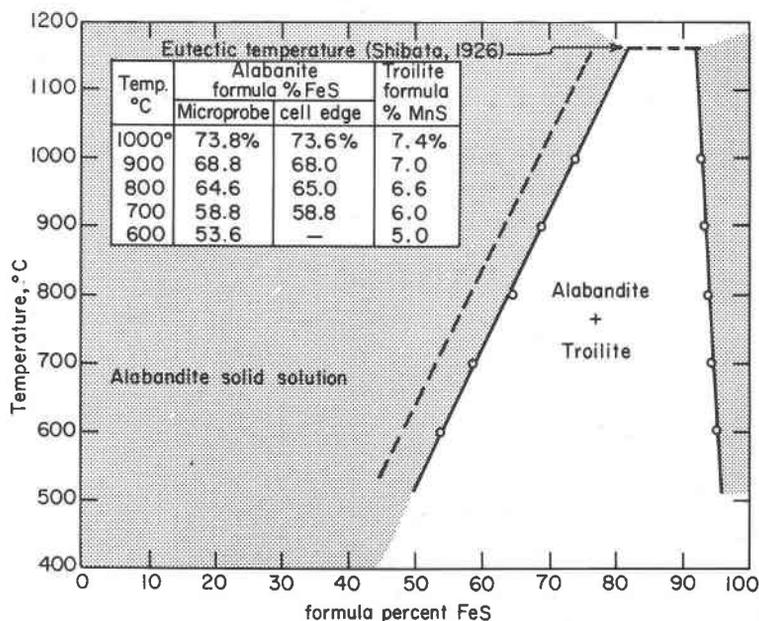| Temp. °C	Alabanite formula % FeS		Troilite formula % MnS
	Microprobe	cell edge	
1000°	73.8%	73.6%	7.4%
900	68.8	68.0	7.0
800	64.6	65.0	6.6
700	58.8	58.8	6.0
600	53.6	—	5.0

FIG. 5. The solvus between alabandite and troilite. The dashed line is the solvus determined by Shibata (1926) using "appearance of phase" runs. There is a question regarding the accuracy of Shibata's temperature measurements (see text).

Binary phase relations
1) MnS-FeS

The only binary join on which previous work has been published is the important metallurgical one, MnS-FeS. Shibata (1926) used appearance of phase runs to demonstrate the remarkable capacity of MnS to accommodate FeS in solid solution, and to determine a eutectic temperature of 1162°C. Although melting relations were not specifically checked in the present study some information was obtained. Changes held at 1125°C for four days were found to contain a small amount of quenched liquid, thus casting considerable doubt on the eutectic temperature proposed by Shibata. The composition limits of the solvus, however, have been carefully checked over a 400°C range (Figure 5). The iron-rich limits for alabandites were determined both by microprobe analysis and be cell edge determinations of coexisting alabandites+troilites. The two are in close agreement. The composition of the troilites in equilibrium with ferroan alabandites were measured directly by microprobe analysis.

The ferroan alabandite solvus is linear within limits of measurement from 600°C to 1000°C, and is exceedingly asymmetric with respect to

the manganoan troilite solvus. The position of the solvus was determined both by solution and exsolution runs, with identical results. There can be little doubt, therefore, that the asymmetry of the solvus is correct.[1]

Although the position of the solvus determined in the present work is offset by 6 formula percent FeS from that determined by Shibata (1926), the two are sensibly parallel. To eliminate any possibility of incorrect analytical techniques, the solvus position was further checked by appearance of phase runs at 850°C. Month-long runs, ground three times to assure homogeneity, gave a solvus position of 66.5 ± 0.5 formula percent FeS, in exact agreement with the X-ray and microprobe determinations. The reasons for the disagreement are not obvious. Though Shibata's experiments were not conducted under a controlled a_{S_2}, it is unlikely that departures in the troilite compositions from FeS to $Fe_{1-x}S$ would produce such a uniform solvus shift at all temperatures. It seems more reasonable to suspect the differences might have arisen by a systematic offset of approximately 100°C in Shibata's temperature measurements, an error which would also account for the lack of agreement with his eutectic temperature.

After completion of the present study, the results of an unpublished doctoral thesis of 1960 at the Ruprecht-Karl University, Heidelberg by W. G. Schück were brought to our attention. Schück determined a eutectic at 11 mol. percent FeS and 1120°C, in agreement with our suggested reduction for Shibata's eutectic value. He also estimated the solvus, using unbuffered runs and X-ray diffraction measurements to determine compositions. His solvus is highly assymetric but is considerably less FeS-rich than ours. We have not had access to Schück's data, but suggest that because the displacement is in the correct direction for pyrrhotite departing from FeS in composition, his diagram is only a pseudo-binary and cannot be directly compared with ours.

2) *MgS-FeS*

The solubility of MgS in troilite is below the detection limit of the present study, there being neither a significant shift produced in $d_{(102)}$ of troilite, nor a detectable response on the microprobe. The limit of MgS in FeS is therefore below 0.1 formula percent MgS up to 1000°C.

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[1] Polished surfaces of quenched alabandites in the approximate range 65 to 80 percent FeS are anomalously anisotropic in reflected light. X-ray powder diffraction patterns do not show any line splitting, super-structure lines or symmetry changes, nor are there breaks in the smooth curve of cell edge versus composition. The intensity of anisotropism appears to be related to both the Fe-content and the rapidity of quenching. No suitable explanation for the phenomenon was found, and as it is a quenching problem, apparently not related to the phase relations, it was not further investigated.

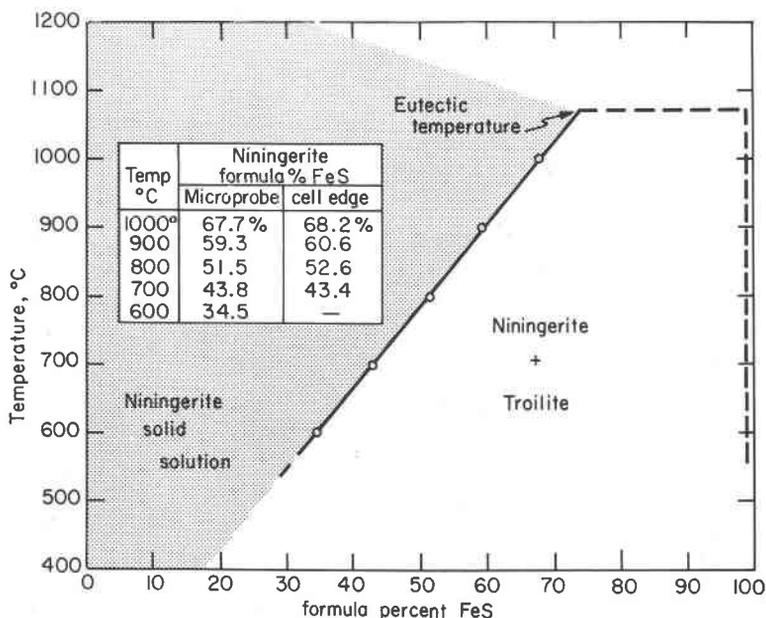| Temp °C	Niningerite formula % FeS	
	Microprobe	cell edge
1000°	67.7%	68.2%
900	59.3	60.6
800	51.5	52.6
700	43.8	43.4
600	34.5	—

FIG. 6. The solvus between niningerite and troilite.

The solubility of FeS in niningerite, however, is very extensive (Figure 6). The solvus is very similar to the alabandite solvus in that it is essentially linear and remarkably asymmetric. The solvus position was again measured by X-ray cell edge and by microprobe analysis, and was closely checked by comparison of both solution and exsolution runs.

Melting relations were encountered by the appearance of a troilite +niningerite eutectic at $1070° \pm 20°C$.

3) CaS-MnS

The solvus between oldhamite and alabandite narrows rapidly at high temperatures (Figure 7). While the point was not specifically checked, it is probable that a closure occurs and a complete solid solution exists below the liquidus because of the high melting temperatures of both oldhamite and alabandite. The solvus positions were determined only by unit cell edge measurements.

4) CaS-MgS

The solvus between oldhamite and niningerite (Figure 8) is very similar to that with alabandite. The probability of a closure and the existence of a complete solid solution between CaS and MgS is even greater than for

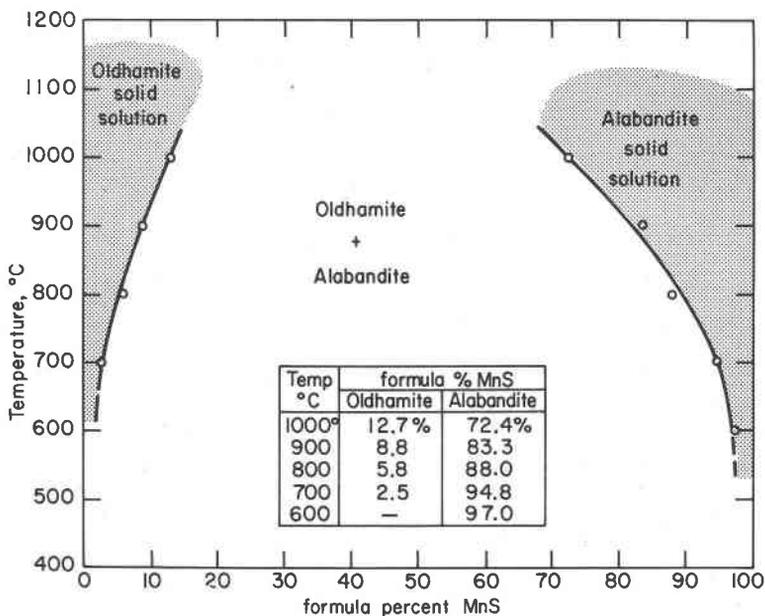| Temp	formula % MnS	
°C	Oldhamite	Alabandite
1000°	12.7%	72.4%
900	8.8	83.3
800	5.8	88.0
700	2.5	94.8
600	—	97.0

FIG. 7. The solvus between oldhamite and alabandite.
Phase compositions were determined from unit cell edge measurements.

CaS and MnS, because the solvus is nearer closure at 1000°C, and because the melting temperature of MgS is even higher than that of MnS.

5) *CaS-FeS*

No detectable solubility was found for CaS in FeS, and the solubility of FeS in CaS is so small up to 1000°C that we could not determine it accurately. At 1000°C we found that less than 1 formula percent FeS dissolved in CaS, but we also found it so difficult to obtain a homogeneous distribution of the Fe that we could not make meaningful microprobe analyses.

6) *MnS-MgS*

At all temperatures between 600°C and 1000°C, we found that MnS and MgS form a completely miscible solid solution. Melting relations were not detected up to 1100°C and the homogeneous compound ($Mg_{0.5}$, $Mn_{0.5}$)S, did not show any sign of unmixing when held at 500°C for 2 months. The temperature range of the complete solid solution can thus be accepted as extending down to 500°C.
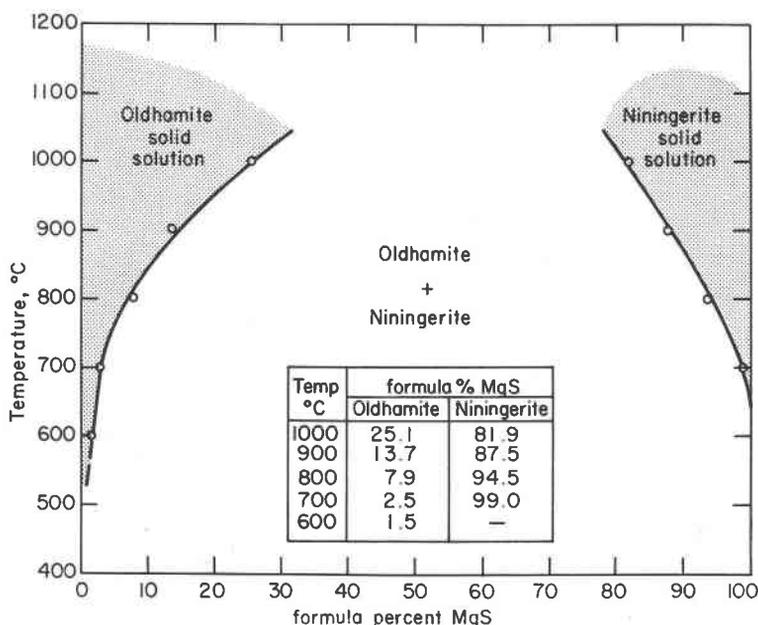
Fig. 8. The solvus between oldhamite and niningerite.
Phase compositions were determined from unit cell edge measurements.

Ternary Phase Relations. The ternary phase relations between the four end members FeS, MnS, MgS, and CaS are simple extensions of the binaries.

1) *FeS-MnS-MgS*

The shape of the ternary solvus (Figure 9) was determined at 5 temperatures by microprobe analyses of coexisting troilites and alabandite-niningerite solid solutions. Two different assemblages were measured at each temperature.

The troilites have the same MnS contents as their binary counterparts at the same temperatures, and in no case was a detectable solubility for MgS in FeS found. The ternary solvus departs from linearity, being slightly convex towards FeS.

2) *FeS-MgS-CaS*

The phase relations were determined solely by microprobe analyses. Coexisting niningerite, oldhamite, and troilite gave a unique solution for the three phase field (Fig. 10, Table 4), because the assemblage is in-
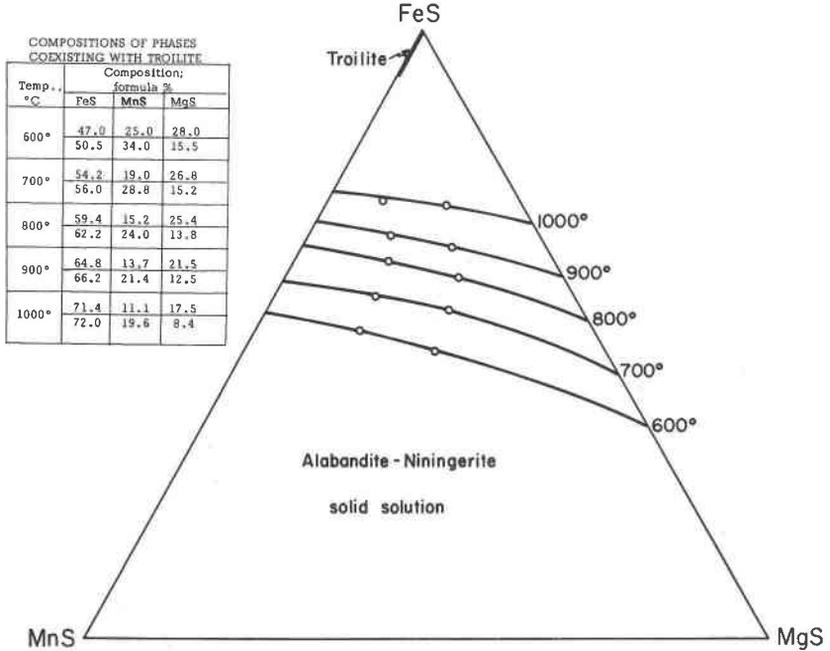
COMPOSITIONS OF PHASES COEXISTING WITH TROILITE

Temp., °C	Composition; formula %		
	FeS	MnS	MgS
600°	47.0	25.0	28.0
	50.5	34.0	15.5
700°	54.2	19.0	26.8
	56.0	28.8	15.2
800°	59.4	15.2	25.4
	62.2	24.0	13.8
900°	64.8	13.7	21.5
	66.2	21.4	12.5
1000°	71.4	11.1	17.5
	72.0	19.6	8.4

Fig. 9. The ternary solvus in the system FeS-MnS-MgS.
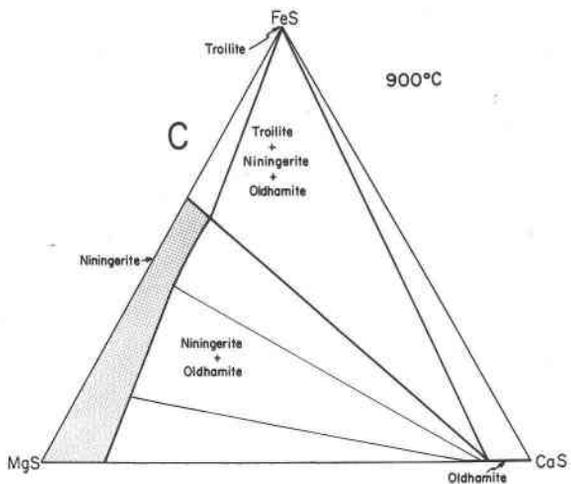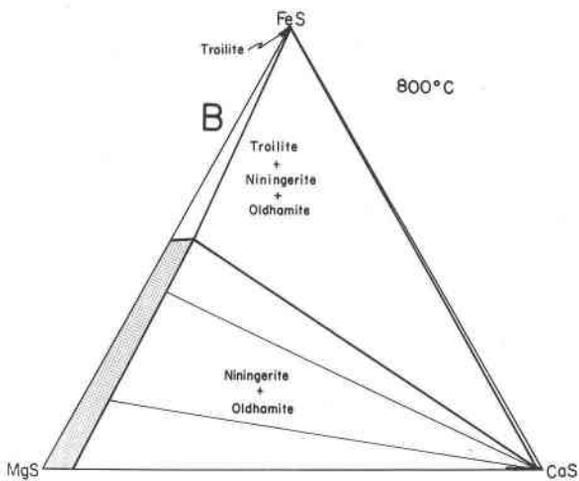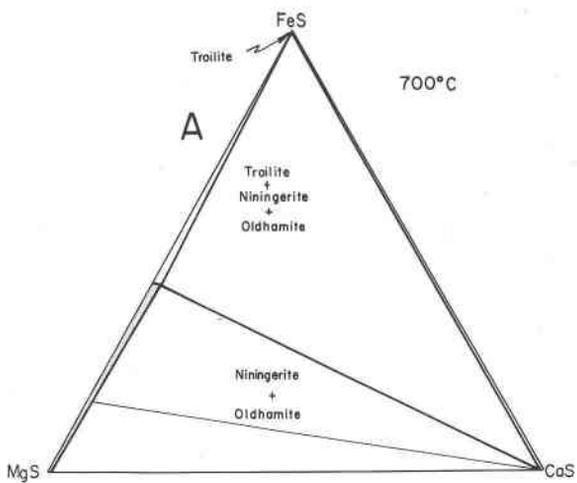Phase compositions were determined by microprobe analysis.

variant at a fixed temperature and a_{S_2}. Similarly, the two phase assemblage niningerite+oldhamite is isothermally univariant so that analyses of the two coexisting phases define the composition limits of the solid solutions.

Oldhamite does not dissolve a significant amount of FeS, so the oldhamite solid solution remains essentially binary towards MgS. The soild solution field for niningerite, however, is sensibly ternary.

A question of some importance to the application of the present studies to meteorite sulfides is the effect that CaS has on the solubility limit of FeS in niningerite. If CaS had no effect—that is, if Ca could be considered to substitute for Mg alone—the FeS content of the niningerite coexisting

≫→

Fig. 10. Phase relations in the system FeS-MgS-CaS. A, 700°C. B, 800°C. C, 900°C. Compositions of coexisting phases were determined by microprobe analysis. Data are given in Table 4.

A — 700°C

FeS
Troilite
Troilite + Niningerite + Oldhamite
Niningerite + Oldhamite
MgS — CaS

B — 800°C

FeS
Troilite
Troilite + Niningerite + Oldhamite
Niningerite + Oldhamite
MgS — CaS

C — 900°C

FeS
Troilite
Troilite + Niningerite + Oldhamite
Niningerite
Niningerite + Oldhamite
MgS — CaS
Oldhamite

with troilite + oldhamite should be the same as that of niningerite on the binary solvus at the same temperature. It is clear from Figure 10 that at 700°C and 800°C this is almost exactly the case. At 900°C, however, there is an apparent decrease of approximately 3 formula percent FeS from the equivalent binary composition. The effect may well become more pronounced at higher temperatures, but as it is with lower temperature results that we are concerned here, it is a reasonable assumption that CaS does not significantly change the solubility of FeS in niningerite.

3) *FeS-MnS-CaS*

The phase relations are very similar to those for FeS-MgS-CaS (Figure 11, Table 5). The oldhamite solid solution field is an exception in that up to 1 formula percent FeS was found in solid solution at 900°C. Troilite also has a measurable solid solution field, but it is sensibly binary, along the FeS-MnS join. Troilite compositions in the field alabandite + oldhamite + troilite were found to be identical with those in the FeS-MnS binary at the same temperature.

The effect of CaS on the solubility of FeS in alabandite is apparently small or zero at both 700°C and 800°C, but, as in niningerite, a detectible reduction occurs at 900°C.
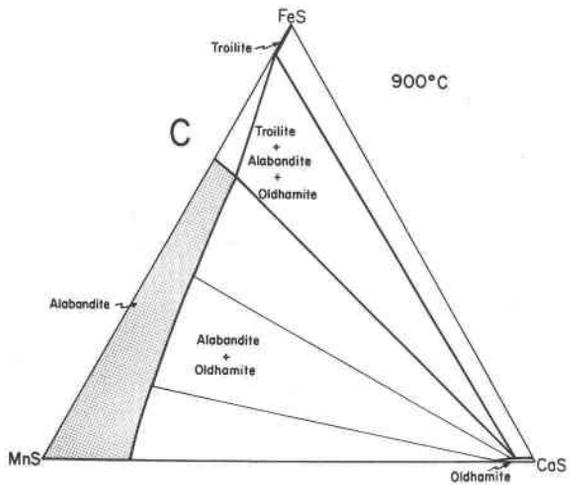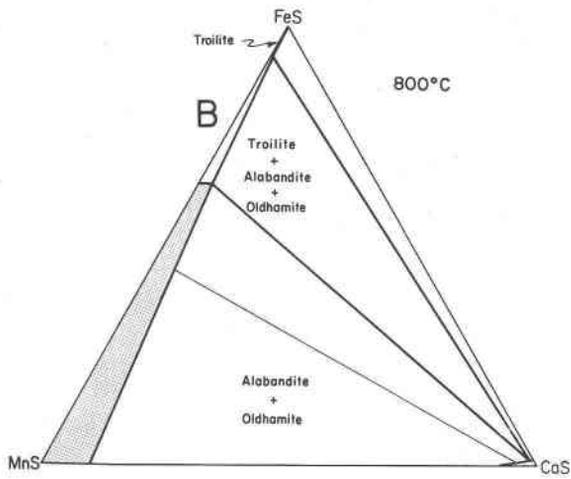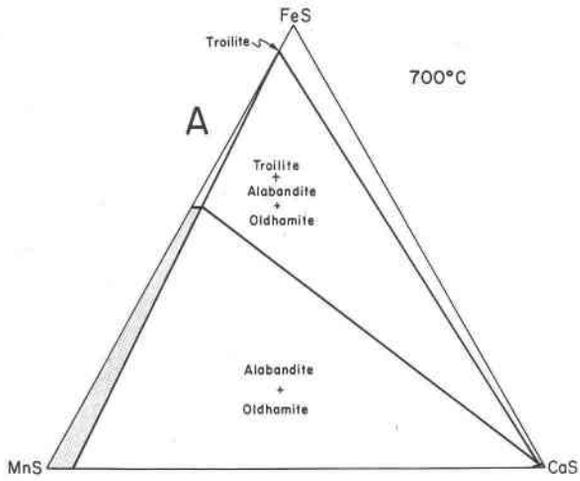
4) *MnS-MgS-CaS*

The ternary phase relations are very similar to both of the binaries MnS-CaS and MgS-CaS (Figure 12). Microprobe analyses of coexisting oldhamite and niningerite–alabandite solid solutions at three temperatures established that both sides of the ternary solvus were slightly convex towards each other.

Quaternary Phase Relations. The simplicity of the quaternary phase relations does not warrant the complexity of a three dimensional plot. The ternary composition fields project into the quaternary volume without distortion and as closely as could be measured, the quaternary field boundaries so generated are linear. The ternary phase compositions therefore serve as adequate measures for their quaternary equivalents. To check this point in the important assemblage troilite+oldhamite+niningerite—alabandite solid solution, a charge containing the three phases was equilibrated at 800°C and the niningerite-alabandite solid solution analyzed. The composition, expressed in formula percent, was CaS, 4.1 percent; MgS, 32.9 percent; MnS, 7.0 percent; and FeS, 56.0 percent. The equivalent FeS content for a ternary compound, in which the CaS is computed as MgS, can be read directly from Figure 9 as being an identical 56.0 formula percent FeS. While departures from linearity must

TABLE 4. COMPOSITIONS OF COEXISTING PHASES IN THE SYSTEM FeS-MgS-CaS DETERMINED BY MICROPROBE ANALYSIS. THE THREE-PHASE ASSEMBLAGES CONTAIN TROILITE, COMPOSITION FeS, IN ADDITION TO THE OLDHAMITE AND NININGERITE LISTED

THREE-PHASE ASSEMBLAGES

Temp. °C	Phase	Composition; formula %		
		MgS	CaS	FeS
700°	Niningerite	55.1	2.3	42.6
	Oldhamite	1.4	98.5	0.1
800°	Niningerite	43.7	4.3	52.0
	Oldhamite	3.2	96.6	0.2
900°	Niningerite	36.8	6.7	56.5
	Oldhamite	8.1	91.6	0.3

TWO-PHASE ASSEMBLAGES

Temp. °C	Phase	Composition; formula %		
		MgS	CaS	FeS
700°	Niningerite	82.5	2.0	15.5
	Oldhamite	0.5	99.4	0.1
800°	Niningerite	51.0	4.5	44.5
	Oldhamite	0.6	99.2	0.2
800°	Niningerite	78.8	5.6	15.6
	Oldhamite	1.0	99.8	0.2
900°	Niningerite	52.2	7.3	40.5
	Oldhamite	9.8	89.9	0.3
900°	Niningerite	73.6	11.0	15.4
	Oldhamite	12.5	87.2	0.3

A — 700°C. FeS (Troilite); Troilite + Alabandite + Oldhamite; Alabandite + Oldhamite; MnS; CaS

B — 800°C. FeS (Troilite); Troilite + Alabandite + Oldhamite; Alabandite + Oldhamite; MnS; CaS

C — 900°C. FeS (Troilite); Troilite + Alabandite + Oldhamite; Alabandite (Alabandite + Oldhamite); MnS; CaS (Oldhamite)

certainly occur in the quaternary volume, they are apparently small and it is clearly adequate for the present case to assume that they do not.

COMPARISON WITH METEORITE SULFIDES

Keil (1968) analyzed coexisting troilites, oldhamites, niningerites, and/or alabandites from 14 of the 15 known enstatite chondrites. There is no absolute test to establish that the phases are, or were, an equilibrium assemblage. To the contrary, Keil showed that while individual grains of niningerite are homogeneous, considerable differences can be found between distant grains, a situation suggestive of an approach to equilibrium between adjacent grains but not between distant grains.

The troilites all contain minor amounts of Ti, Cr, Zn, and Mn, with Cr and Ti, in that order, being the most abundant. Together these two exceed the contents of Mn and Zn by a factor of ten. There is therefore little that can be deciphered from the troilite compositions in terms of the present work.

The only significant solid solution elements detected in the oldhamites were Mg, Mn, and Fe and accordingly the oldhamite compositions normalized to the components CaS, MgS, MnS, and FeS are presented in Table 6. The analyses of both niningerite and alabandite show Cr to be present in solid solution in addition to Ca, Mg, Mn, and Fe. Though not a major element in any case, Cr is present in the same or lesser amounts than Ca. Without any direct evidence, it has been assumed that small amounts of Cr follow the same pattern as Ca, and do not change the observed phase relations nor significantly alter the solubilies of the major components. In recasting Keil's analyses, therefore, Cr has been deleted and the compositions normalized in terms of the components MgS, MnS, CaS, and FeS (Table 6). The errors introduced in such a treatment are probably too small to significantly affect the conclusions to be drawn.

Temperatures of Formation (Temperatures of last equilibration). We have already seen that small amounts of CaS do not significantly alter the solubility of FeS in niningerite and alabandite up to 800°C. The FeS contents of niningerites and alabandites should therefore indicate the last temperatures at which the phases were in equilibrium and thereby the *minimum* temperatures of formation. The estimates can only be min-

FIG. 11. Phase relations in the system FeS-MnS-CaS. A, 700°C. B, 800°C. C, 900°C. Compositions of coexisting phases were determined by microprobe analysis. Data are given in Table 5.

TABLE 5. COMPOSITIONS OF COEXISTING PHASES IN THE SYSTEM FeS-MnS-CaS DETERMINED BY MICROPROBE ANALYSIS

THREE-PHASE ASSEMBLAGE

Temp. °C	Phase	Composition; formula %		
		MnS	CaS	FeS
700°	Alabandite	39.0	2.0	59.0
	Troilite	5.8	0.0	94.2
	Oldhamite	0.8	99.0	0.2
800°	Alabandite	33.6	2.9	63.5
	Troilite	6.3	0.0	93.7
	Oldhamite	1.8	97.5	0.7
900°	Alabandite	28.7	6.9	64.4
	Troilite	6.8	0.0	93.2
	Oldhamite	3.2	95.8	1.0

TWO-PHASE ASSEMBLAGE

Temp. °C	Phase	Composition; formula %		
		MnS	CaS	FeS
800°	Alabandite	51.4	4.4	44.2
	Oldhamite	4.0	95.7	0.3
900°	Alabandite	68.9	14.2	16.9
	Oldhamite	6.8	92.8	0.4
900°	Alabandite	48.8	9.2	42.0
	Oldhamite	4.2	95.1	0.7

Temp., °C	composition; formula %		
	CaS	MgS	MnS
800°	92.3	6.1	1.7
	7.5	67.9	24.6
800°	94.2	1.4	4.4
	15.1	20.9	74.0
900°	86.9	9.6	3.5
	14.6	64.8	20.6
900°	89.4	2.4	8.2
	18.8	18.6	62.6
900°	87.4	6.2	6.4
	16.4	41.2	42.4
1000°	76.2	18.1	5.7
	22.0	58.1	19.9
1000°	81.3	10.2	8.5
	24.9	37.6	37.5

FIG. 12. The ternary solvus in the system CaS-MgS-MnS.
Compositions of coexisting phases were determined by microprobe analysis.

imums, because there is no sure way of saying how much FeS may have exsolved during a meteorite cooling history. By combining MgS and CaS as a single component, the 14 niningerite and alabandite compositions can be plotted on the FeS-MgS-MnS ternary (Figure 13). As pointed out by Keil, they fall into two very distinct groupings—the niningerites, found only in type I and intermediate enstatite chondrites fall near the MgS-FeS line, while the alabandites, found only in type II enstatite chondrites, fall in a small cluster near the MnS-FeS side line.

The niningerites, as a group, all have compositions indicative of much higher temperatures than the alabandites. Indeed, *Abee* and *Saint Sauveur* have *minimum* temperatures of formation between 700° and 800°C, Adhi-Kot between 600° and 700°C, and Indarch between 500° and 600°C. Because it is unsafe to use a linear extrapolation below 500°C for the FeS-MnS and FeS-MgS binary solvi, it is misleading to assign specific minimum formation temperatures below 500°C on the basis of the present data. It is clear, nevertheless, that the alabandites as a group not only give minimum formation temperatures that are much below those for the niningerites, but that they may possibly be as low as 200°C.

The errors involved in plotting CaS with MgS are small. If it were all plotted as MnS, the indicated temperatures for the niningerites would drop about 20°C and for the alabandites about 8°C—hardly significant in view of the other uncertainties.

The CaS contents of the niningerites and alabandites can also be used to indicate minimum temperatures of formation. The CaS contents of the synthetic niningerites and alabandites in the assemblage troilite+old-hamite+alabandite or niningerite (Figures 10 and 11) have been plotted
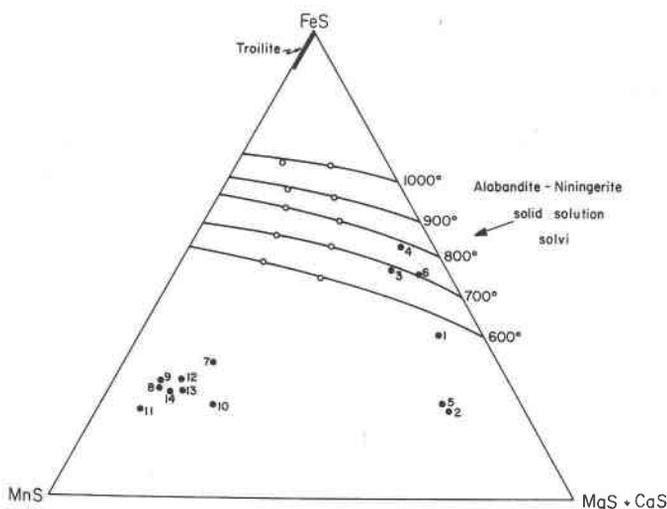

Fig. 13. Compositions of niningerites and alabandites from enstatite chondrites (after Keil, 1968), normalized to MgS, MnS, CaS, FeS, and with CaS plotted as MgS, plotted on the ternary solvus in the system FeS-MgS-MnS. Minimum temperatures of formation can be read directly from the diagram. Specimen numbers refer to samples listed in Table 2.

against temperature in Figure 14, and the CaS contents of the natural samples indicated. As with the FeS contents, the extrapolation necessary for the alabandites is too long to be meaningful, but the indicated temperatures are again low. Much higher temperatures are again indicated for niningerites than for alabandites, though the actual minimum temperatures suggested are even higher than they were for the FeS contents, reaching 880°C for *Abee!*

Finally, the MgS and MnS contents of oldhamites coexisting with troilite and niningerite or alabandite should also indicate minimum temperatures of formation (Figure 15). The MgS contents of oldhamites in type I and intermediate enstatite chondrites exceed the MnS contents
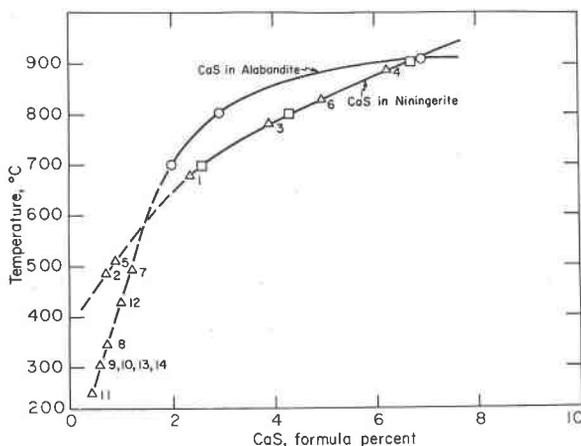
FIG. 14. The CaS-contents of alabandites and niningerites coexisting with oldhamite and troilite. Numbered points refer to meteorite samples (after Keil, 1968), listed in Table 6.

by a factor of ten (see Table 6), and the indicated high temperatures which are in accord with the high temperatures suggested by niningerite composition from the same meteorites, can be accepted with assurance. The oldhamites in the type II meteorites, with the exception of Khairpur, contain about equal amounts of both MnS and MgS, and neither the MgS nor MnS curves in Figure 15 can be safely used. However, it is highly likely that the actual minimum equilibrium temperatures would fall between the MgS and MnS curves. In-as-much as the MnS curve lies above the MgS curve, the temperatures indicated for the oldhamites of
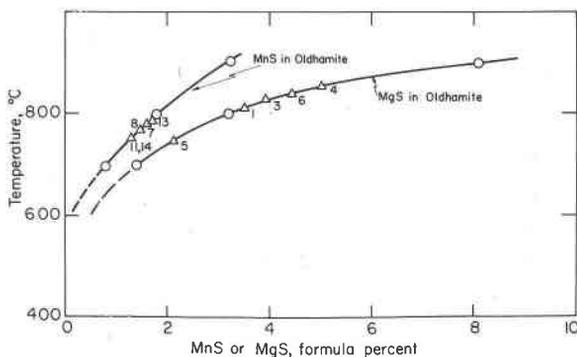

FIG. 15. The MnS-, and MgS-contents of oldhamite coexisting with troilite and alabandite or niningerite respectively. Numbered points refer to meteorite samples (after Keil, 1968), listed in Table 6.

TABLE 6. NORMALIZED COMPOSITIONS OF OLDHAMITES, ALABANDITES, AND NININGERITES
FROM ENSTATITE CHONDRITES, FROM ANALYSES BY KEIL (1968). WHERE OLDHAMITE
DATA ARE MISSING, THE SPECIMEN AVAILABLE TO KEIL DID NOT
CONTAIN GRAINS SUITABLE FOR ANALYSIS

No.	Meteorite	Type (after Keil)	Mineral	Composition, formula %			
				MgS	CaS	MnS	FeS
1	Indarch	I	niningerite	54.3	2.3	8.5	34.9
			oldhamite	3.5	95.3	0.3	0.9
2	Kota-Kota	I	niningerite	65.9	0.7	14.4	19.0
3	Adhi-Kot	I	niningerite	37.0	3.9	10.3	48.8
			oldhamite	3.9	94.3	0.5	1.3
4	Abee	I	niningerite	33.8	6.2	6.0	54.0
			oldhamite	5.0	94.4	0.5	0.1
5	St. Mark's	intermediate	niningerite	64.0	0.9	14.7	20.4
			oldhamite	2.1	97.0	0.3	0.6
6	Saint Sauveur	intermediate	niningerite	41.5	4.9	5.5	48.1
			oldhamite	4.4	93.1	0.5	2.0
7	Daniel's Kuil	II	alabandite	15.8	1.2	54.1	28.8
			oldhamite	1.7	96.4	1.6	0.3
8	Hvittis	II	alabandite	8.7	0.7	67.2	23.4
			oldhamite	1.3	96.8	1.5	0.4
9	Atlanta	II	alabandite	8.2	0.6	66.1	25.1
10	Blithfield	II	alabandite	20.8	0.6	58.8	19.8
11	Jajh deh Kot Lalu	II	alabandite	7.8	0.4	73.3	18.5
			oldhamite	1.5	96.6	1.3	0.6
12	Khairpur	II	alabandite	11.9	1.0	62.0	25.1
			oldhamite	1.7	97.8	0.1	0.4
13	Pillistfer	II	alabandite	13.5	0.6	63.0	22.9
			oldhamite	1.7	96.2	1.7	0.4
14	Ufana	II	alabandite	11.2	0.6	65.6	22.6
			oldhamite	1.4	97.0	1.3	0.3

type II chondrites are high, an observation that is not in accord with the compositions of associated alabandites, but is in accord with Larimer's (1968) conclusions concerning *Jajh deh Kot Lalu*.

In summary, the evidence to be drawn from the compositions of both the niningerites and oldhamites from type I and intermediate enstatite chondrites indicates high temperatures of formation. If the evidence is to be denied and lower temperatures proposed, then some mechanism must be found for forming and maintaining super-saturated solid solutions. The compositions of alabandites in type II enstatite chondrites indicate low temperatures of equilibration, while the oldhamites from the same samples indicate high temperatures.

Cooling Rates. Sulfide compounds in general have much higher reaction rates than those observed in silicates and it is rare for high temperature compositions and assemblages to remain unreacted during cooling. Natural processes so commonly involve slow cooling rates that sulfide mineral compositions indicative of temperatures above 400°C are rarely preserved (Barton and Skinner, 1967). It is a pertinent question to ask,

therefore, what the cooling rates must have been to quench the high FeS-contents observed in some niningerites. In an attempt to answer the question simple quenching rate studies were carried out with binary, ternary, and quaternary solid solutions.

Compositions were selected so that equilibration at 800°C would yield a coexisting cubic monosulfide solid solution and troilite. Samples were equilibrated for three months to insure that all grains were homogeneous and at least 0.1 mm in diameter. They were then carefully split into a number of samples, each in its own capsule and each with an iron button to buffer a_{S_2}, then reheated for a further two weeks at 800°C to reduce chances of heterogeneous nucleation by accidental strains introduced during handling. The binary and ternary charges finished as two coexisting phases, while the quaternary charge finished as a three-phase assemblage consisting of troilite plus oldhamite plus a niningerite solid solution.

The charges were cooled at constant rates and a sample withdrawn and quenched in ice water at fixed temperature intervals. Compositions of the cubic monosulfide solid solutions were determined from their X-ray cell edges.

Results of the quenching tests are summarized in Figure 16. If a sample remained unreacted on cooling from 800°C—that is, if it quenched perfectly—the cell edge and hence the composition of the cubic monosulfide would remain unchanged and would follow path X in Figure 16a. If a sample re-equilibrated perfectly as the temperature fell, the composition would follow path Y along the solvus in Figure 16a. The binary solid solutions (Figures 16b and c) both showed an approach to re-equilibration, even at quenching rates as fast as 0.1°C/min. down to 600°C. The MgS-rich ternary solid solution (Figure 16d) reacted very similarly to the binary solutions. In the case of the quaternary solid solution, interpretation of the data raises a question. Because there is no optical evidence that oldhamite has exsolved during quenching, we have made the assumption that the change in cell edge is due solely to the exsolution of troilite. The composition path shown in Figure 16e is plotted on this assumption. If the assumption is incorrect, it is nevertheless true that the quaternary solid solution shows a continuing cell-edge change, and therefore some approach to re-equilibration, down to 550°C with a cooling rate of 0.01°C/min. The presence of Ca in solid solution apparently does not significantly change the rate of equilibration therefore.

The conclusions to be drawn from the quenching experiments are obvious. The alabandites found in type II enstatite chondrites must have cooled at rates less than 0.01°C/min., but niningerites found in type I and intermediate enstatite chondrites must have been quenched very
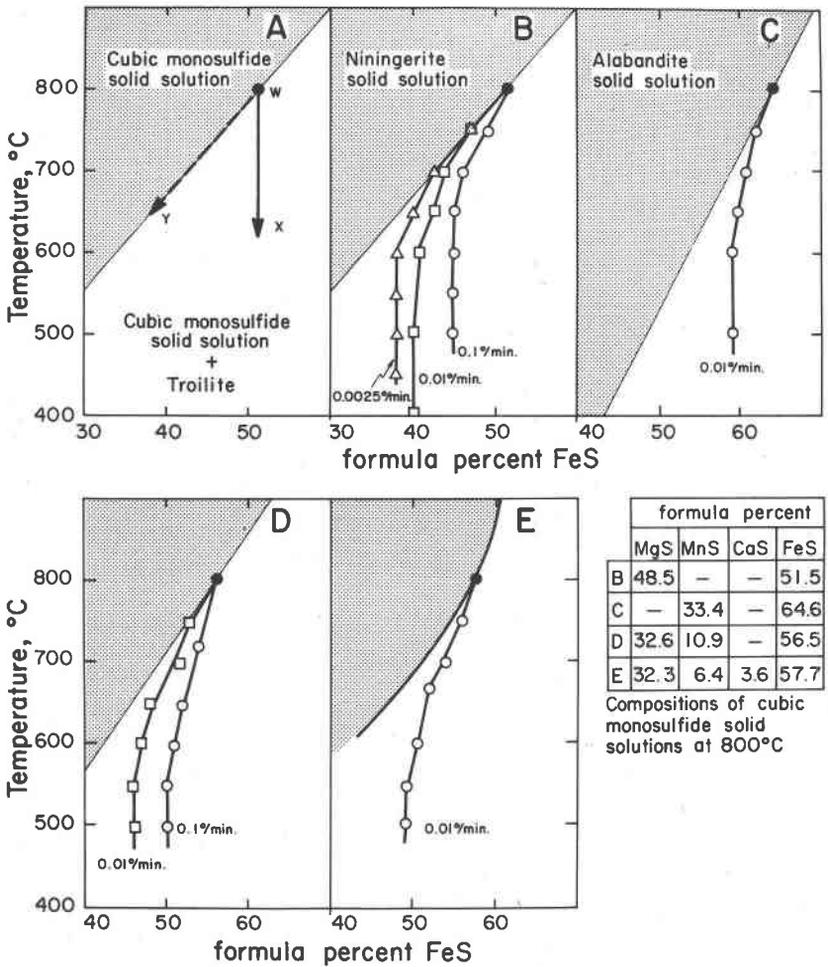
FIG. 16. Composition changes in cubic monosulfide solid solutions cooled at different rates. Solid solutions were equilibrated with troilite for three months, cooled at fixed rates and samples withdrawn at specific temperature intervals. Compositions were determined by unit cell measurements.

   A. A solid solution formed at 800°C has composition W on the solvus. With perfect quenching, compositions of quenched phases follow path X. With perfect equilibration, compositions will follow the solvus along path Y.
   B. Niningerite solid solutions cooled at three different rates.
   C. Alabandite solid solution. The quenching properties are similar to those of niningerite.
   D. Manganiferous niningerite has quenching properties similar to those of niningerite (B).
   E. A manganiferous niningerite coexisting with oldhamite and troilite.

much more rapidly through the temperature range 500°–800°C. Indeed, *Abee* and *Saint Sauveur* must have cooled at rates exceeding 0.1°C/min. In the event that the presence of small amounts of Cr, Zn, or other trace elements slowed the rate of re-equilibration by several orders of magnitude, the quenching rates remain exceedingly fast for most natural processes. As the enstatite chondrites do not have features suggesting they are volcanic in origin, the most likely explanation is that type I and intermediate chondrites are small fragments resulting from meteorite impacts. The high temperatures needed to cause the observed cubic monosulfide compositions may have arisen from the impact event itself, or possibly may record high surface temperatures on the impacted body.

CONCLUSIONS

The compositions of the cubic monosulfides found in all types of enstatite chondrites shows they must have formed at high temperatures. Although the actual formation temperatures cannot be specified, the compositions of both niningerites and oldhamites in type I and intermediate enstatite chondrites indicate minimum formation temperatures in the range 600°C to 800°C. Alabandites in type II enstatite chondrites have minimum formation temperatures about 200°C, while the associated oldhamite compositions indicate temperatures nearer 800°C.

Inasmuch as the minimum formation temperatures of type I and intermediate enstatite chondrites are above 600°C, it is difficult to see how type II samples can be derived by metamorphism from type I samples, as suggested by a number of writers. The present evidence thus supports Keil's (1960) contention of separate origins for type I and type II enstatite chondrites.

Quenching rate studies show that type I and intermediate enstatite chondrites must have cooled at exceedingly fast rates—in excess of 0.1°C/min. through the range 500°–800°C in some cases—to have preserved the cubic mono-sulfide compositions observed by Keil (1968). Type II enstatite chondrites, however, must have cooled at very much slower rates. Because of Larimer's (1968) compelling evidence on the same point, we have accepted the 800°C minimum formation temperature evidence of the oldhamites from type II specimens as being correct. The observed alabandite compositions in the assemblage troilite plus oldhamite must reflect cooling rates many orders of magnitude slower than those for type I and intermediate specimens. These cooling rate differences thus further enhance the chemical arguments on which are based the separation of enstatite chondrites into two different classes. There is no support in the present data for separating intermediate from type I enstatite chondrites.

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