THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

THE MICROSTRUCTURE OF SILICA IN THE PRESENCE OF IRON OXIDE

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I. INTRODUCTION

This paper is concerned with the microstructures that are developed when iron oxide is present with silica at elevated temperatures. It is a consequence of earlier observations of the microstructures of silica and basic refractories which have undergone service alterations.

Silica brick maintain their strength under high temperature service even when large quantities of fluxing oxides are present. This observation, which is general, is illustrated by the data in Table 1.[1] The 19% of fluxing oxides also dissolved additional silica so that the total liquid content was more than 25%. Even so, the hot surface of the brick maintained its strength during service at 3000°F.

This situation is more noteworthy when it is compared with magnesia refractories. A few percent silica with the periclase makes the magnesia brick quite weak at elevated temperatures. This weakness is observed as cracks and failure in the sub-surface zones of the brick during service.[2] The liquid content was only 4%, markedly less than in the silica brick.

A microscopic examination revealed a definite difference in the microstructure of the two. The liquid in magnesia brick formed a nearly complete film around the periclase grains. The liquid in the silica

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1 Wells, R. G., and Van Vlack, L. H., "Alteration of Silica Brick During Open Hearth Service," Unpublished report, South Works, U. S. Steel Corp. (1950).
2 Wells, R. G., and Van Vlack, L. H., "Mineral and Chemical Changes in Periclase Brick under Conditions of Steel Plant Operation," J. Am. Ceram. Soc., V. 34, pp. 64-70, (1951).

brick did not penetrate the grain interfaces; rather, there was still considerable solid-to-solid contact. The larger amount of liquid was located at the grain edges. These observations led to this study in which (1) time, (2) temperature and (3) atmosphere were considered as possible variables affecting the microstructure, and hence the strength characteristics of silica refractories.

II. PREVIOUS WORK

Three areas of literature review are necessary for this work: (1) temperature studies, (2) oxidation studies, and (3) factors controlling microstructure.

(1) Temperature Studies.

The phase relationships for the ferrous oxide-silica system are well established. In the presence of excess silica, the SiO_2 content increases from 38% in the eutectic liquid at 2150°F to 55% in the monotectic liquid at 3090°F[3]. Fayalite (Fe_2SiO_4) is the secondary solid phase in the presence of excess silica.

A review of the temperature stability of the silica phase is desirable since metastable cristobalite is developed in the tridymite range. Normally, cristobalite is the primary phase between 1470°C (2678°F) and the melting temperature at 1710°C (3110°F). Tridymite's range is between 1470°C and 875°C (1607°F). It is not unusual to find cristobalite below 1470°C. Two conditions can lead to this situation. The first arises from the fact that the cristobalite-to-tridymite inversion is very sluggish. A high activation energy is required and very little transformation energy is released. Therefore, cristobalite remains in a metastable condition after being formed at higher temperatures. The second method of obtaining cristobalite below 1470°C is as an intermediate, or transition phase in the quartz-to-tridymite reaction. Ferguson

3 Bowen, N. L. and Schairer, J. F., "System Ferrous Oxide-Silica," Am. J. Sci., 5th Series, 24, pp. 177-213 (1932).

and Merwin[4] observed this situation and used it as an example of Ostwald's rule which states "In all reactions the most stable state is not straight way reached, but the next less stable or that state which is the least stable of the possible states."

Sosman[5] suggests that the metastable inversion temperature of quartz-to-cristobalite must lie below 1250°C since the transformation is quite rapid at that temperature. However, he states that if flux is used, the tridymite is formed directly and not cristobalite. The thermodynamic relationship of the quartz-to-cristobalite inversion was examined by Mosesman and Pitzer[6]. They assigned temperature of 1300°K (1880°F) as the meta-equilibrium temperature on the basis of volume changes and the equation $dP/dT = \Delta S/\Delta V$.

4 Ferguson, J. B. and Merwin, H. E., "The Melting Points of Cristobalite and Tridymite," Am. J. Sci., V. 46, pp. 417-26 (1918).
5 Sosman, R. B., The Properties of Silica, New York: The Chemical Catalog Co., pp. 65 (1927).
6 Mosesman, M. A., and Pitzer, K. S., "Thermodynamic Properties of the Crystalline Forms of Silica," J. Am. Chem. Soc., V. 63, pp. 2348-56 (1941).

(2) Oxidation Studies.

The siliceous liquids investigated by Bowen and Schairer[3] contained ferrous oxide. More oxidizing conditions alter the phase relationship somewhat. Darken's[7] results are summarized in Figure 1. This presentation is, in reality, a plot of the binary eutectic troughs of the ternary system, $FeO-Fe_2O_3-SiO_2$, as a function of the oxidation level (Figure 2) shown by Muan[8]. For purposes of this paper, which is always concerned with excess silica, the important features of the combined data of Darken's and Muan's works include: (a) the lowest melting liquid is at 1150°C (2100°F) with an iron oxide to silica ratio close to the ratio which exists for the binary eutectic, (b) magnetite (Fe_3O_4) forms as a secondary solid phase when the CO_2/CO ratio is greater than 10/1, (c) fayalite (Fe_2SiO_4) forms as the secondary phase in more reducing environments and (d) the silica molar composition of the liquid melt is quite insensitive to both temperature and oxidation level. This latter fact is summarized in Table 2.

7 Darken, L. S., "Melting Points of Iron Oxides and Silica: Phase Equilibrium in the System Fe-Si-O as a Function of Gas Composition and Temperature," J. Am. Chem. Soc., V. 70, p. 2046 (1948).
8 Muan, Arnulf, "Phase Equilibrium in the System $FeO-Fe_2O_3-SiO_2$," J. Metals, V. 7, Sept. 1957, Trans. Am. Inst. Min. Met. Engr., V. 303, pp. 965-76 (1955).

(3) Microstructural Studies.

Smith[9] has shown that the microstructures of many materials may be related to the relative interfacial energies as shown in Figure 3. The dihedral angle, which penetrates between two grains, approaches zero as the ratio of the phase boundary energy to the grain boundary energy approaches one-half. With lower energy ratios, solid-to-solid grain boundary contacts disappear.

The actual dihedral angles, which are a function of the relative interfacial energies, can not be measured directly. Rather, a two dimensional cut is observed in which the angle may appear to be greater or smaller. However, a statistical sample[9,10] has a mode which is within $5°$ of the true angle[10], or a median which is within $1°$ of the true angle[11].

Previous microstructural studies of iron oxide-silica mixtures are limited to phase identifications in the altered zones of silica refractories during service. These data are reported most completely by Harvey[12]. In general there is (1) a gray, hot face zone composed of cristobalite and magnetite. (2) The next lower temperature zone contains magnetite and tridymite instead of cristobalite. (3) The following zone has tridymite, less iron oxide and a large amount of flux rich in CaO, and Al_2O_3. The flux may or may not be crystallized. When it does

9 Smith, C. S., "Grains, Phases and Interfaces: An Interpretation of Microstructure," Trans. Am. Inst. Min. Met. Engrs., V. 175, pp. 15-51 (1948).
10 Harker, D. and Parker, E., "Grain Shape and Grain Growth," Trans. Am. Soc. Met., V. 34, pp. 156-195 (1945).
11 Reigger, O. and Van Vlack, L. H., Unpublished (1958).
12 Harvey, F. A., "Comparison of Used Silica Brick from Insulated and Uninsulated Basic Open-Hearth Roofs Compared," J. Am. Ceram. Soc., V. 18, pp. 86-94 (1935).

crystallize, calcium and iron metasilicates form from the siliceous glass. (4) A series of colored bands are usually present between the altered zones and the unaltered brick. This is a staining by vapor deposition and is independent of microstructure.

III. EXPERIMENTAL PROCEDURE

All samples were made from reagent grade SiO_2 and Fe_2O_3. The former was quartz. Compacts were formed from powders and bonded with ethyl silicate which was hydrolyzed with isopropanol to produce an amorphous silicic acid. The initial stages of heating decomposed and volatilized the resulting products except for SiO_2.

Compacts were examined in which 5, 10, 25 and 40% FeO (added as Fe_2O_3) were present. Each combination would have the same phase compositions (Figure 2). The resulting geometry of the microstructures were identical except for the relative amounts of silica and silicates. However, the 40% mixture permitted easier micro-examination because there was more liquid. Therefore, most of the quantitative comparisons for different heat treatments were made on the higher iron oxide mixtures.

The samples were heated in a combustion tube furnace under CO_2/CO atmospheres. The times, atmospheres and temperatures are presented in Figure 4. Three general oxidation levels were chosen: (1) "reducing", $CO_2/CO = 1$, (2) "neutral", or $CO_2/CO = 10$, and (3) "oxidizing", or air. (See Figure 1). These oxidation levels may be converted to equivalent, but experimentally indirect oxygen pressures, P_{O_2}, by the relationship

$$\log P_{O_2}^{1/2} = \log \frac{P_{CO_2}}{P_{CO}} - \frac{66,560}{4.575T} + \frac{20.15}{4.575} .$$

The cooling rate was accentuated by removing the sample from the high temperature zone of the furnace. About one minute was required to decrease the temperature below "red heat". This cooling rate did not produce any evidence of additional silica precipitation. Fayalite or

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magnetite crystallization was initiated in some but not all of the samples. When this occurred, the original silica-liquid interface was not changed. Thus, the high temperature geometry was preserved. Water quenching was not feasible since it induced cracking, and it promoted surface oxidation.

Micrographic techniques were standard for mounting, polishing, and the initial examination of reflected light samples. Quantitative micrographic procedures utilized an ocular micrometer for size measurements and intersection grids for phase volume measurements by point analysis[13].

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13 Van Vlack, L. H., To be published, 1958.

IV. RESULTS AND DISCUSSION

General observations include the facts that the grain growth of tridymite is greater than the grain growth of cristobalite at the same temperature. Tridymite was never found above 1470°C. However, cristobalite could be formed below 1470°C. When cristobalite was formed below 1470°C, it was eventually replaced by tridymite. The cristobalite grains were approximately equi-axed. The tridymite grains were tabular, presumably basal plates. Crystal-to-crystal contact was maintained in all samples, even when 40% iron oxide (70% liquid) was present. As a result the sample retained its shape during heat treating. These observations are illustrated in Figures 5, 6, and 7.

(1) Geometric Relationships.

Closer examination seemed to be warranted for the interfacial energy relationships which governed the shape of the silica grains in a siliceious liquid. The average tridymite-liquid interfacial energy (Figure 8) was 0.57 of the tridymite grain boundary energy at 2200°F (1200°C). This figure dropped to 0.53 at 2625°F (1440°C). The 7 % drop is most readily explained on the basis of a somewhat greater solubility of SiO_2 in the liquid at the higher temperature. As such the solid and liquid are more nearly alike at the higher temperature.while the grain boundary is essentially constant in character.

The cristobalite-liquid mixture behaved similarily except that the ratios were about 10% higher for comparable temperatures (Figure 8).

An explanation for this difference is somewhat speculative, either, (1) the energy of the cristobalite-liquid interface is higher than the energy of the tridymite-liquid interface, or (2) the cristobalite grain boundary energy is less than the tridymite-grain boundary energy, or (3) both. The second alternative seems the most plausible since cristobalite has a higher crystal symmetry than tridymite. Therefore, the crystal disorder at the boundary of the cristobalite would be less.

The tridymite grains did not spheroidize as did cristobalite to minimize their external surface and energy. Therefore, some initial doubt existed as to whether the tridymite developed geometric equilibrium as readily at the grain boundaries. Closer examination revealed that the grain boundary angles did approach equilibrium (Figure 4). The lack of spheroidization of the tridymite crystals could be attributed to their larger grain size and anisotropic, euhedral growth.

(2) Oxidation Effects.

Higher oxidizing atmospheres introduced magnetite as a secondary solid phase and reduced the liquid content. This agrees with phase diagram expectations. These atmospheres did not affect the liquid-silica boundary energies. The observations indicate that the sudden failure of silica refractories in metallurgical furnaces by the impingement of reducing flame arises from the resultant increase in liquid content and not from a liquid penetration between the silica grains (Figure 7c). Thus, this service phenomena has a different mechanism than silicate fluxing of magnesium refractories in which a small amount of liquid penetrates the grain boundaries.

Since the energy of the silica-liquid interface does not change when ferric ions are added to the liquid, it must be concluded that the form of the iron ion does not affect the interface structure. Rather the interface structure is controlled by the silica network. Figure 2 and Table 2 indicate that the SiO_2 molar composition is close to 0.45 for all of these liquids which are in equilibrium with solid silica regardless of the oxidation level.

(3) Silica Phases.

Cristobalite was observed to form most readily by solution of quartz into the $FeO-SiO_2$ liquid and subsequent crystallization. The new cristobalite crystals were sub-hedral within the liquid (Figure 7). No evidence of direct quartz-to-cristobalite inversion were observed when a flux was present. When it was not present, extended heating showed cristobalite as a less reflective phase at the quartz surfaces.

Thus for silica-iron oxide mixtures, the following reaction sequence appears to be appropriate:

$$\text{quartz} \rightarrow \text{liquid} \rightarrow \text{cristobalite} \ .$$
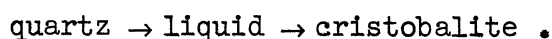
The prior reactions also occurred below 1470°C in the tridymite range. This differs from previous observations[5] which reported that tridymite formed directly in the presence of mineralizing fluxes.

The cristobalite which does form below 1470°C is altered to tridymite during extended heating periods. This is shown in Figure 6. The change involves simultaneous resolution of the cristobalite and a crystallization of the tridymite from the liquid. Immediately below 1470°C, the over-all quartz-to-tridymite change in the presence of iron oxide is:

$$\text{quartz} \rightarrow \text{liquid} \rightarrow \text{cristobalite} \rightarrow \text{liquid} \rightarrow \text{tridymite.}$$
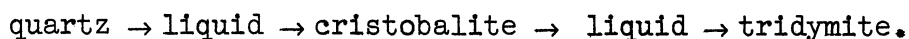
The intermediate development of cristobalite at 2200°F (1200°C) was not observed microscopically nor by x-ray diffraction. At these and lower temperatures, the tridymite formed by the reaction sequence,

quartz → liquid → tridymite.
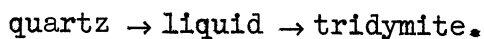
The above solution and crystallization steps to effect phase inversions in the presence of flux are not unexpected because the required activation energy would undoubtedly be less through the liquid phase. As such, the liquid, rather than the iron oxide, would be the mineralizer which accelerates the inversion.

The metastable quartz-to-cristobalite inversion temperature has never been ascertained accurately. Sosman[5] had considered that it was below 1250°C. Mosesman and Pitzer[6] calculated it at 1300°K (1027°C) on the basis of volume changes and the equation $dP/dT = \Delta S/\Delta V$. If the inversion temperature were that low, cristobalite should have been present in all of the short time tests above the eutectic at 1180°C (2156°F). This was not the case in this study, thus suggesting that this transition temperature is not as low as calculations showed.

The advisability of generalizing with Ostwald's rule is questioned. The observations of this study indicate that cristobalite does not have to form prior to tridymite. It appears more logical to consider that it is possible to form a metastable phase if this phase has less free energy than the original one. Thus in Figure 9, cristobalite is more stable than quartz and will form from quartz at 1400°C. At some lower temperature, cristobalite has more free energy than quartz under any condition. Hence, the high temperature polymorph can only exist by undercooling that which was formed at higher temperatures and not by metastable crystallization.

V. CONCLUSIONS

The microstructures of silica-iron oxide mixtures are by no means stereotyped. The phases, their size, and their geometry will vary with temperature. The oxidizing character of the atmosphere did not have a noticeable effect in this particular system. Since the silica molar fraction of the liquid in this system does not vary from approximately 0.45 for various oxidation levels, it may be unwise to generalize that there is an absence of oxidation effects in other systems.

The microstructures of iron oxide-silica mixtures always possess a skeleton of crystals with solid-to-solid contact. This provides coherency until unusually large amounts of liquid are present. It permits the conclusion that silica brick maintain their strength in service because of their microstructure.

Miscroscopic examinations suggest that the quartz-to-cristobalite inversion temperature is higher than previously calculated. A definite temperature was not ascertained, but lies between 1200°C and 1400°C.

VI. ACKNOWLEDGEMENTS

TABLE 1

FLUX CONTENT OF SILICA BRICK[1]

| | Oxide content - % | | |
	Surface Zone	2 inches behind surface	4 inches behind surface
Iron Oxide	11.	13.	5.
CaO	1.	5.	7.
Al_2O_3	.2	1.	1.
Total Flux* (Volume %)	15	26	18

* The total contained the above oxides. In addition, it was saturated with SiO_2.

TABLE 2

SILICA SATURATED LIQUIDS (CALCULATED FROM DATA BY MUAN[8])

Temperature °C	Atmosphere CO_2/CO ratio	SiO_2 Mol Fraction
1200	1	0.43
1200	10	0.42
1400	1	0.46
1400	10	0.45
1500	1	0.48
1500	10	0.47
1600	10	0.5
1600	air	0.4

TABLE 3

GRAIN BOUNDARY ANGLES (LIQUID BETWEEN SILICA GRAINS)

Temperature, °F	Time, Hour	Atmosphere, CO_2/CO	Silica Phase	Angle, degrees
2780	1	10	Crist.	55
2780	2	10	Crist.	55
2700	2	10	Crist.	51
2700	2	air	Crist.	61
2700	2	air	Crist.	59
2625	48	10	Trid.	35
2550	2.25	1	Crist.	64
2550	7	1	Crist.	59
2550	22	1	Trid.	47
2550	22	10	Trid.	45
2400	2.25	1	Trid.	*
2400	48	10	Trid.	42
2300	2.25	1	Trid.	*
2300	72	10	Trid.	55
2200	2	1	Trid.	*
2200	7	1	Trid.	*
2200	72	10	Trid.	55
2125	191	10	Trid.	*
2100	3	10	Trid.	*

* Insufficient time for geometric equilibrium
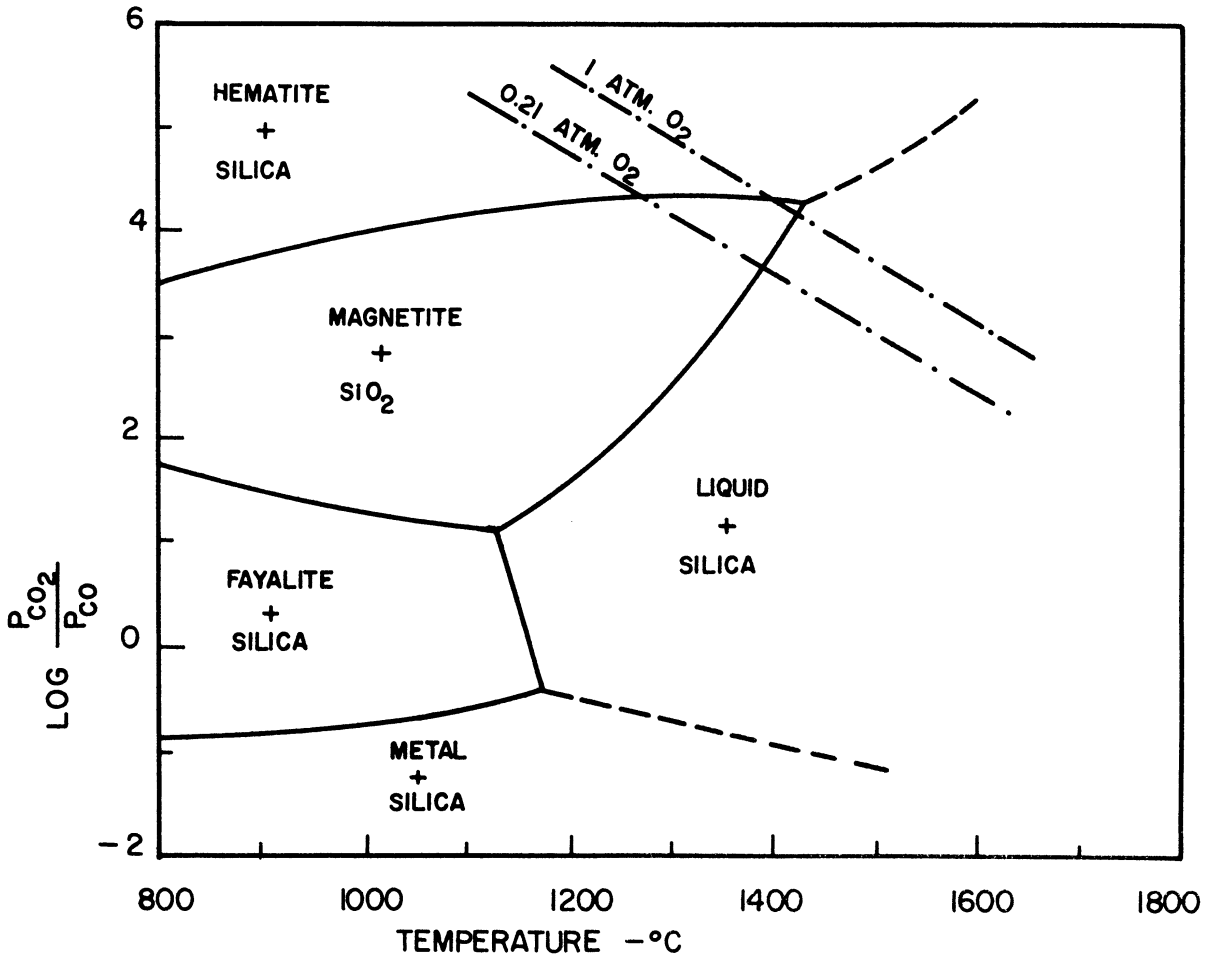
Figure 1.   Iron Oxide-Silica Phases vs. Oxidation
Level. (After Darken[7]). The Oxygen
Curves are Calculated with $OH° = +66,560$
and $\Delta S° = +20.15$ for the Reaction,
$CO_2 \rightarrow 1/2\ O_2 + CO$.
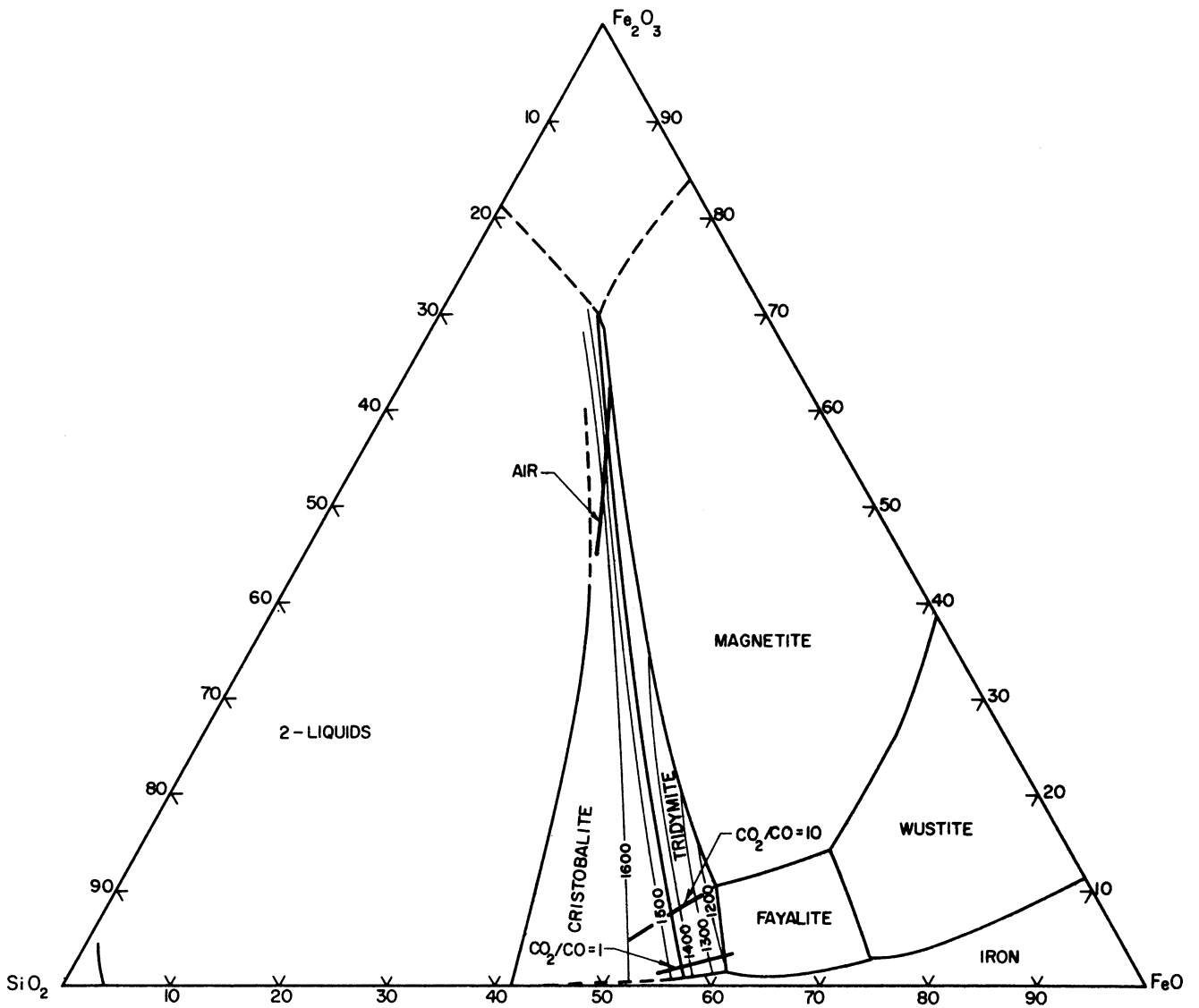
Figure 2. FeO-Fe₂O₃-SiO₂ System. The Oxidation Levels are
Calculated from Muan.(8)
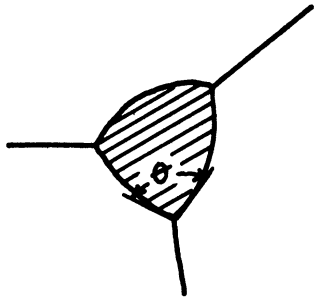
(a) $\dfrac{\text{Grain Boundary Energy}}{\text{Phase Boundary Energy}} = 1$

$\Theta = 120°$
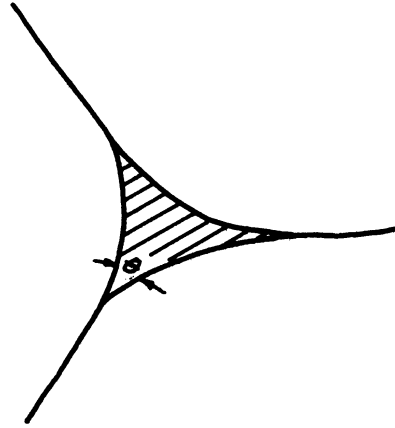
(b) $1 > \dfrac{\text{Grain Boundary Energy}}{\text{Phase Boundary Energy}} > 0.5$
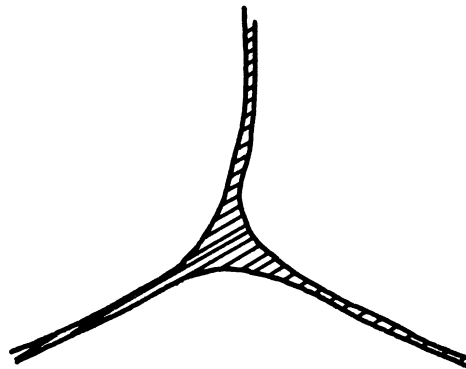
(c) $\dfrac{\text{Grain Boundary Energy}}{\text{Phase Boundary Energy}} \leq 0.5$

$\Theta = 0°$

Figure 3. Phase Geometry vs. Energy Ratios. The Liquids in
Silica Brick Approximate the Relationships Shown
in (b). The Liquids in Magnesia Brick Approximate
Those Shown in (c).
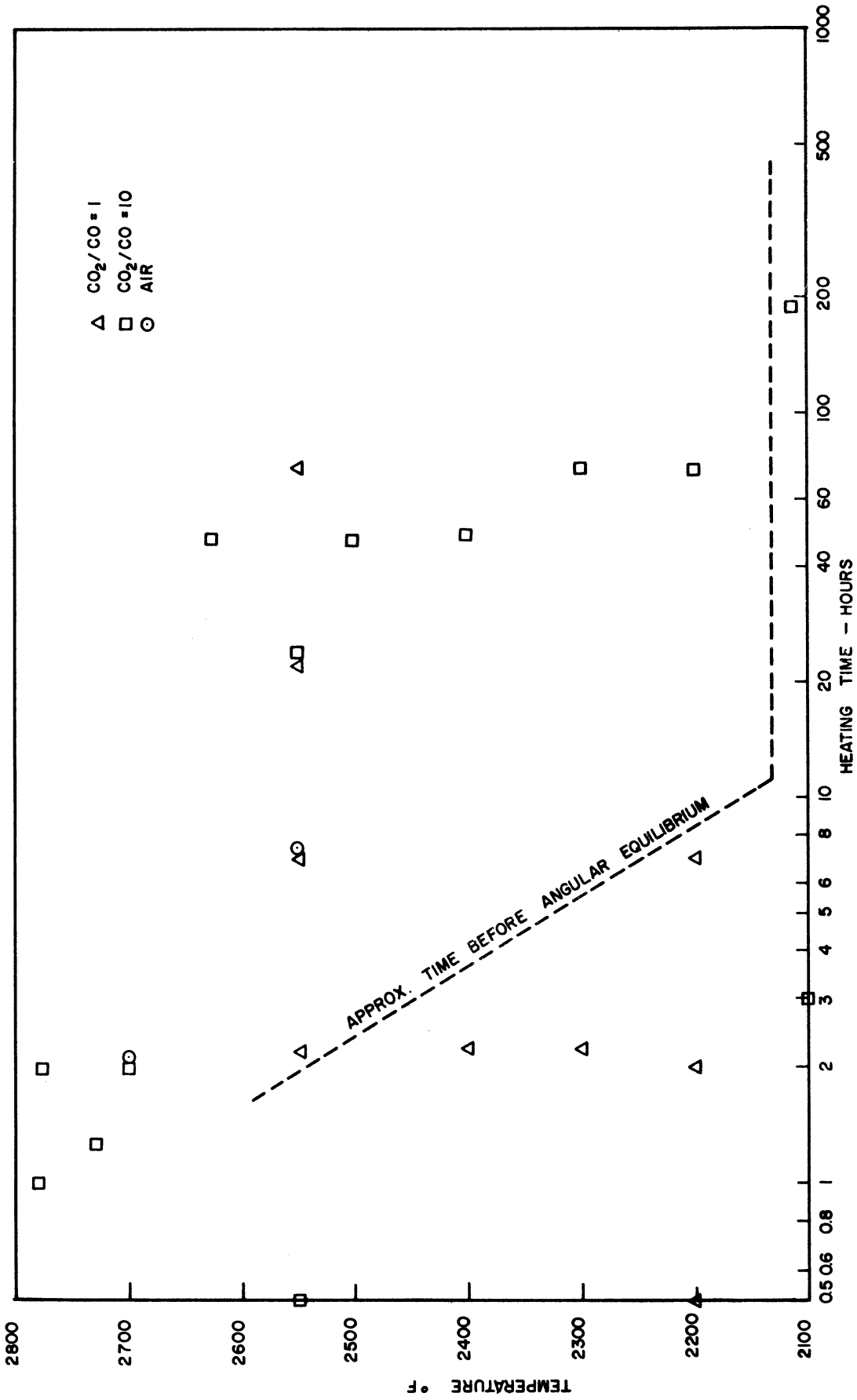
Figure 4. Heat Treatments.

(a) 2 hours;
$CO_2/CO=1$.

(b) 7 hours;
$CO_2/CO=1$.
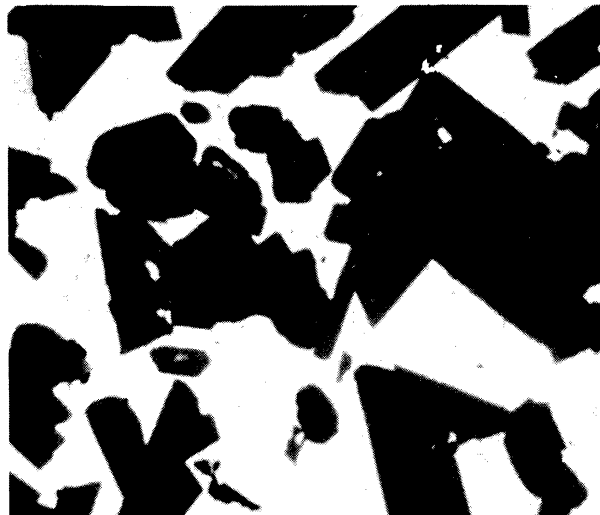
(c) 70 hours;
$CO_2/CO=10$.

Figure 5. Tridymite growth in an iron oxide-silica liquid at 2200°F
(1200°C). X300.
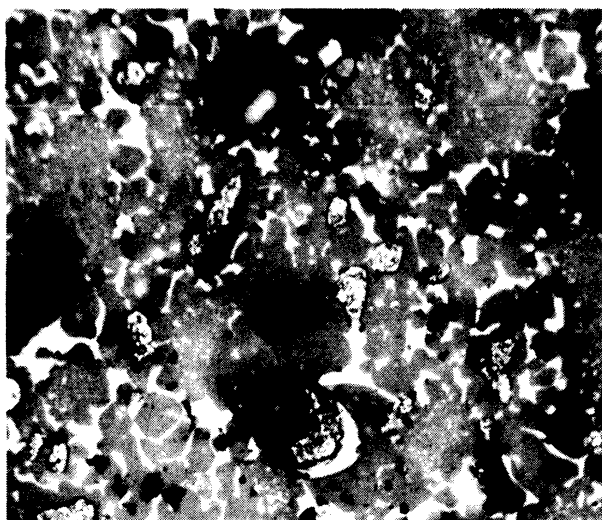
(a)
30 minutes;
$CO_2/CO=10$.
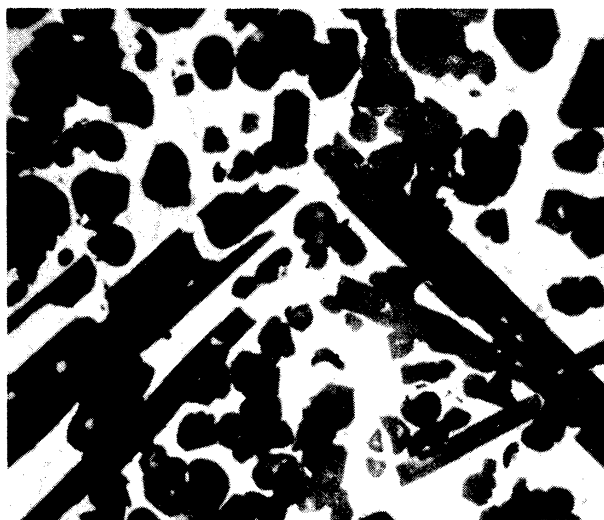
(b)
2.25 hours;
$CO_2/CO=1$.

(c)
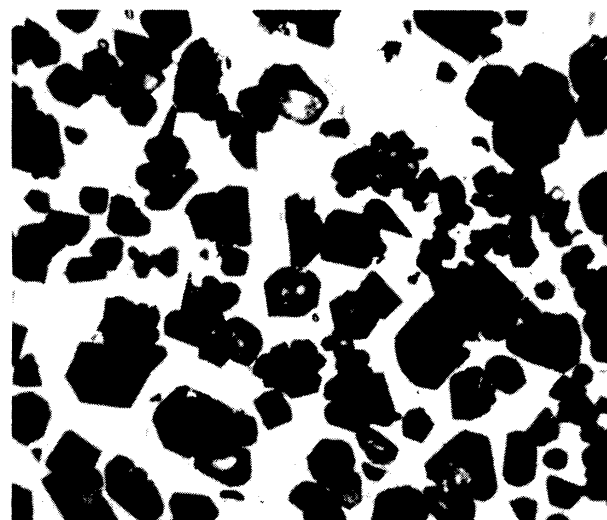7 hours;
$CO_2/CO=1$.

(d)
22 hours;
$CO_2/CO=1$.

Figure 6.   Silica phase changes in an iron oxide-silica liquid at 2550°F (1400°C). X300. Remnants of the original quartz may be seen in (a). However, most of the solid silica phase already is equiaxed cristobalite. Tridymite is not evident. It grows as basal plates after longer heating times, eventually replacing the cristobalite completely.
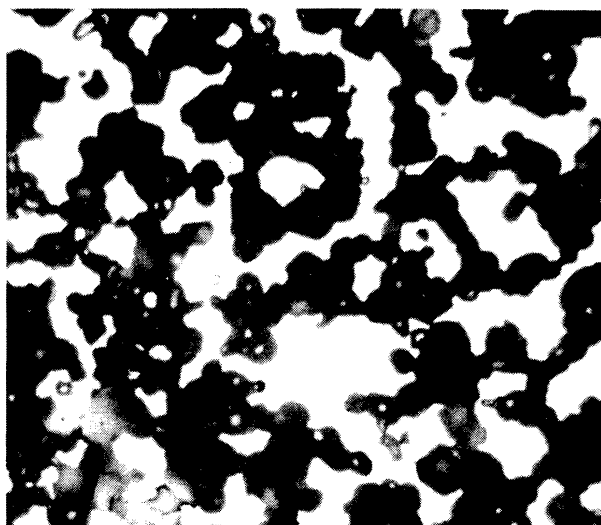
(a)
2 hours;
air

(b)
Preheated 18 hours
at 2600°F, then 2 hours
at 2700°F in air.

(c)
2 hours;
$CO_2/CO=10$.

Figure 7. Cristobalite formation in an iron oxide-silica liquid at
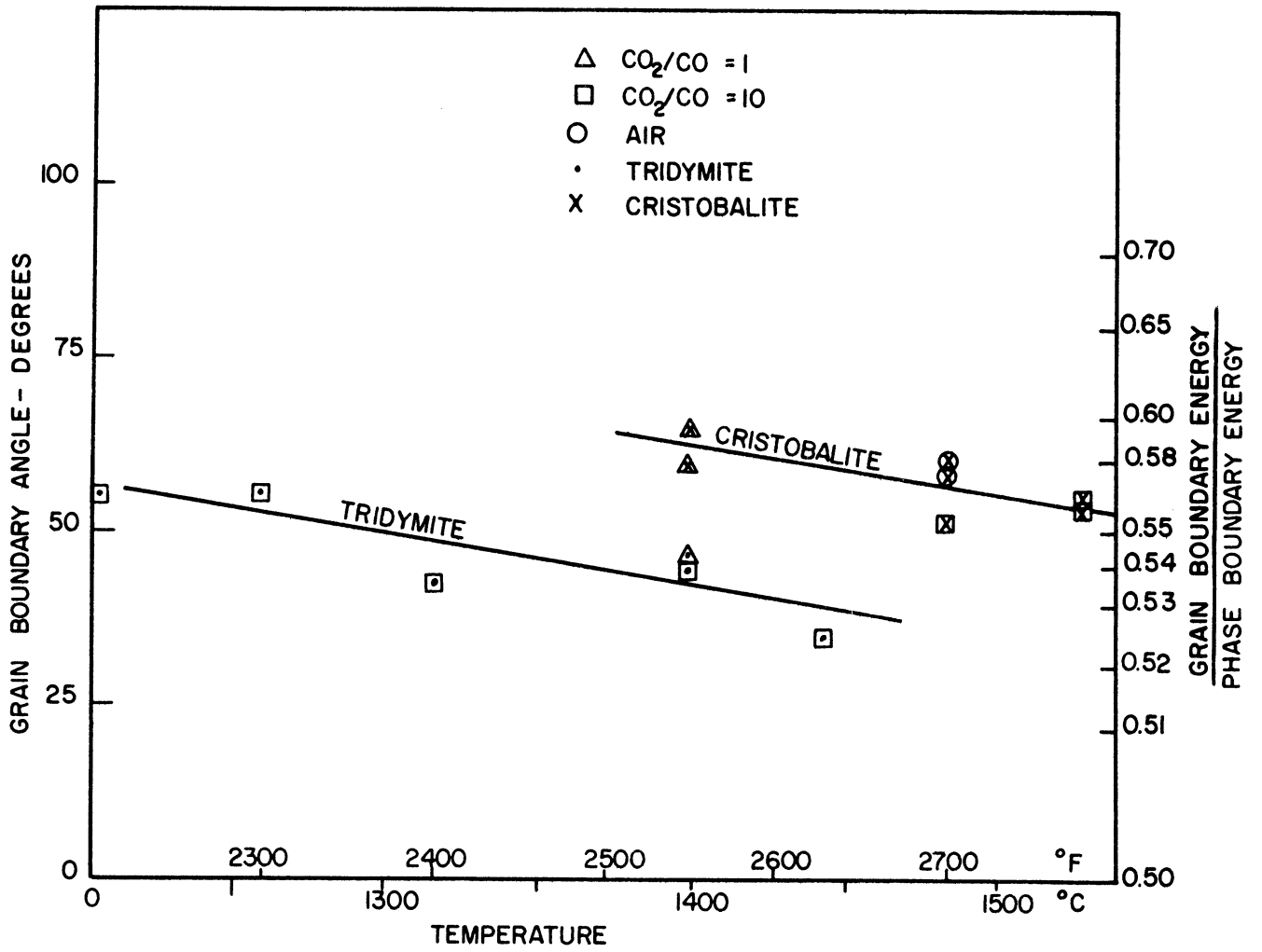2700°F (1480°C). X300.

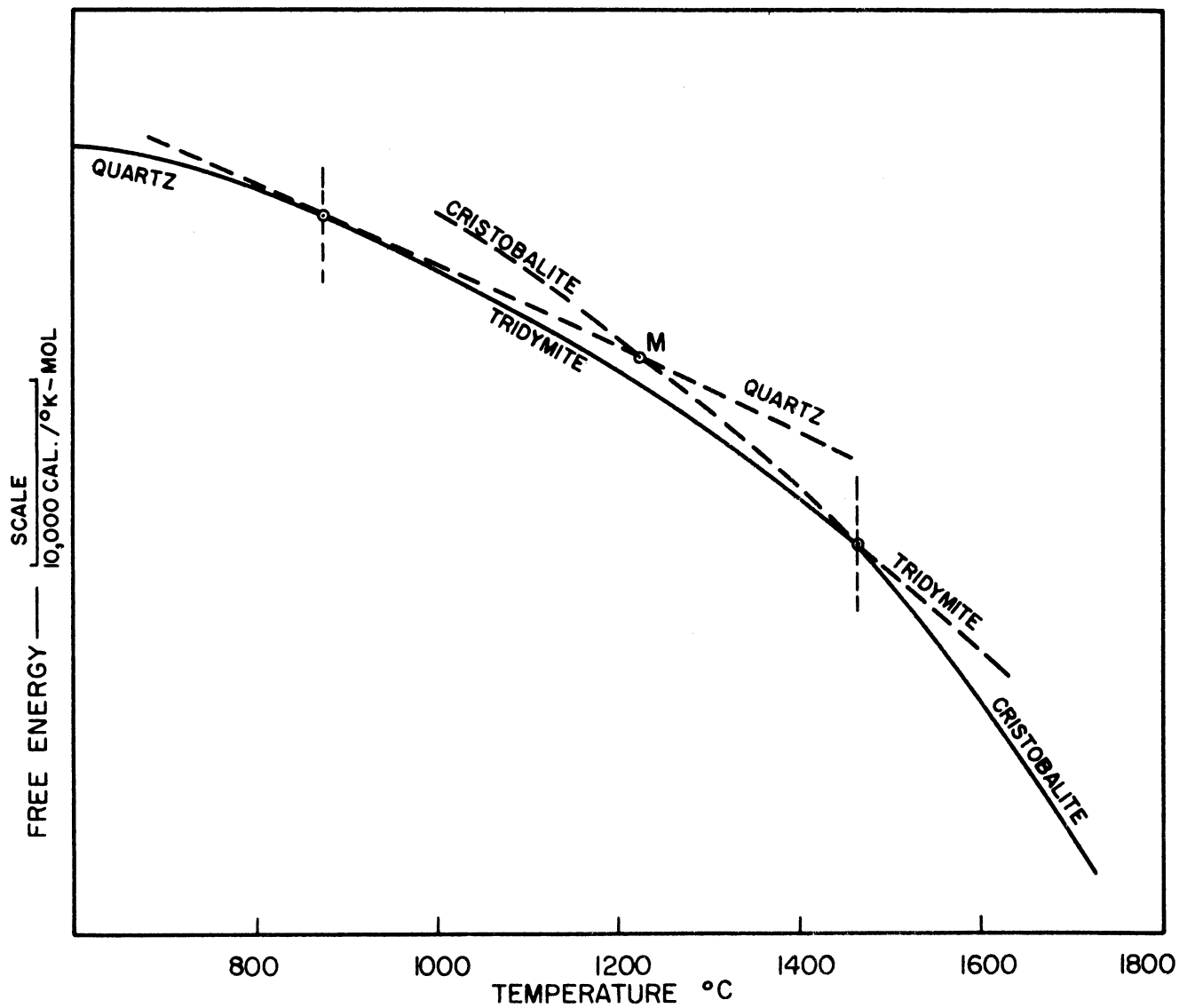Figure 8. Grain Boundary Angle vs. Temperature. (See Table 3 for Data)

Figure 9. Free Energy of Silica Minerals. Ostwalds rule
Providing for the Metastable Formation of Cristo-
balite would Apply only Above Temperature, M.
This Temperature is Between 1200°C and 1400°C.