

5.0 SAMPLE PREPARATION

5.1 Equipment

5.1.1 Furnace

A Deltech Model DT/28/VT/OC/C vertical tube furnace (figure 15) was acquired and modified to provide a controlled atmosphere for sample preparation. Adding a gas-tight top cap with sample support, gas supply and exhaust fittings and a gas-tight bottom cap with a quick-opening mechanism was sufficient. Additional modifications were made to improve operability and performance. See Appendix F for details.

The Deltech furnace came equipped with two thermocouples in the furnace chamber. One of these was connected to a programmable temperature controller, which in turn directed an SCR controller to control power to the heater elements. The second thermocouple was connected to a protection module that trips the furnace if the heater chamber temperature exceeds a user-specified value. The maximum safe operating temperature of the heater chamber is 1500 °C. This is based on the refractories used. I recommend setting the protection thermocouple set point at 1470 °C. This provides adequate operating margin for heating samples to 1200 °C, while maintaining 30 °C margin to the furnace design temperature.

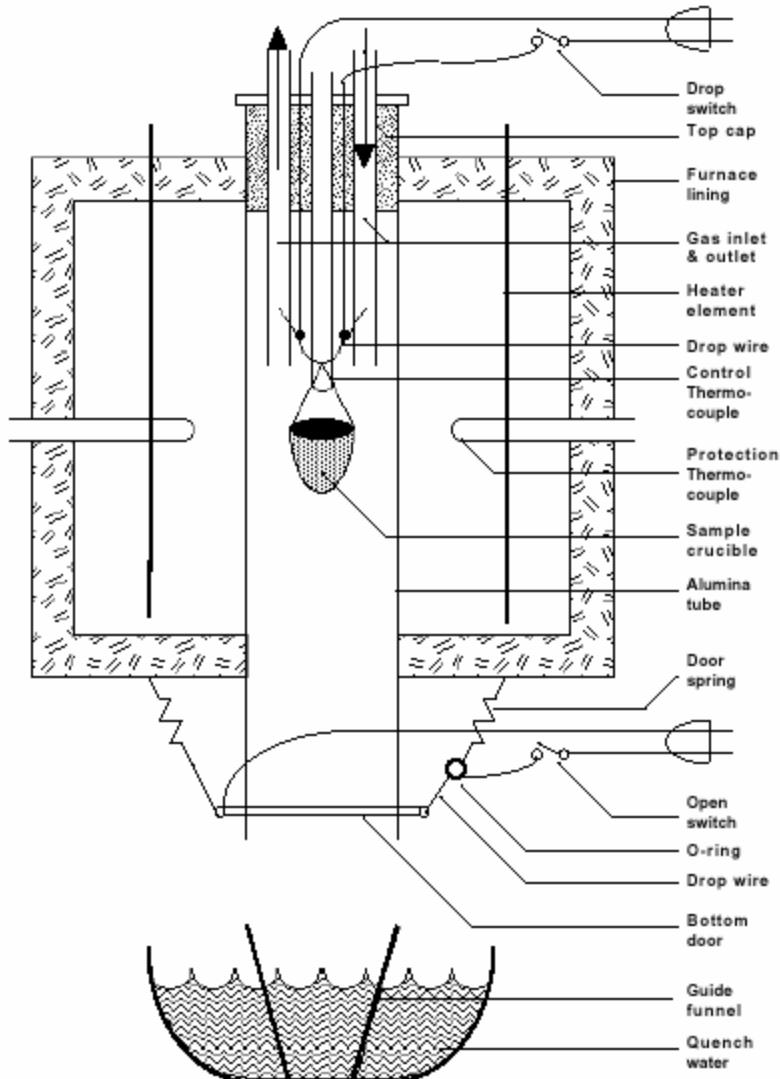


Figure 15 Sample preparation furnace.

The thermocouple arrangement on the Deltech furnace did not measure temperature at the sample location. I had Deltech furnish an additional, longer thermocouple, and mounted it in a second top cap so that the temperature-sensitive portion of the thermocouple was approximately 25 mm from the sample crucible. This thermocouple was used for controlling furnace temperature for all runs starting with Sample 009. Experience with this arrangement indicates that a large difference in temperature exists between the heater chamber and the sample location, reaching 250 °C for a 1200 °C sample temperature. The temperature difference is attributed to heat removal by the gas mixture flowing in the sample chamber. It was suggested that a portion of the difference might be due to differences between the thermocouples. To test this, the sample and protection thermocouples were both placed to measure heater chamber temperature. The furnace was operated at numerous temperatures (see Appendix C), and the indicated temperatures from the two thermocouples were compared. There were no significant differences that would indicate that the indicated difference between the heater chamber and the sample chamber were due to differences in thermocouple characteristics. Since the difference appeared to be real, it was measured for a number of temperatures during the sample 009 runs (see Appendix C). The following relationship between heater chamber temperature and sample temperature was obtained:

$$T_{\text{sample chamber}} = 0.873 T_{\text{heater chamber}} - 63.8 \quad [\text{°C}] \quad (5.1.1-1)$$

This relationship was used to recalibrate the sample preparation temperatures for Samples 001 through 008. This recalibration is considered approximate, mainly because changes in gas flow between runs causes variations in the heat removal from the sample chamber.

Placing the control thermocouple in the sample chamber rather than in the heater chamber increases temperature control accuracy, but introduces a significant lag in the controller response. This tends to destabilize the temperature control, so the controller PID set points needed to be adjusted. The final values chosen are given in the detailed operating procedures in Appendix

B. The overshoot in heater chamber temperature is important during glass-forming runs, where the heater chamber temperature exceeds 1400 °C in steady-state (the furnace insulation may be damaged above 1500 °C). The overshoot can be eliminated by changing the PID set points (specifically, by decreasing the proportional gain and derivative control, and increasing the integral time constant), but only by sacrificing rapid response at all temperatures. A more practical approach is to limit the maximum heater output by setting “Hi” in the temperature controller to 70 percent.

Deltech recommends connecting the furnace to a 60 A, 208 Vac, 60 Hz, 1Ø supply. The university electricians refused to connect the furnace to more than a 40 A source, so there is some risk of the furnace feeder breaker tripping during full-power operation. For this reason, the maximum power set point “Hi” in the furnace temperature controller should be set to a reduced value. The value of 70 percent suggested in the previous paragraph has proven adequate to avoid this problem.

Detailed operating procedures for the Deltech furnace are given in the instruction manuals supplied with the furnace.

5.1.2 Gas mixing apparatus

H₂ and CO₂ were used to control the oxygen fugacity in the sample preparation furnace. These gases were mixed together in a gas-mixing apparatus built and described by Clauter [1979] and based on a design by Nafziger, et al [1971] (figure 16). This gas mixer has the ability to provide high accuracy at mixing ratios varying from 1:1 to over 100:1.

Clauter describes the operational considerations for using the gas-mixer. These will not be repeated here, except to note deviations arising from modifications that I made to the apparatus and from differences in our application. Step-by-step operating instructions based on his discussion are included in Appendix B. Appendix F discusses a perplexing operational problem that I encountered, and its solution.

I used a mixture of H₂ and CO₂ to control the oxygen fugacity in the sample preparation furnace. To substantially reduce the possibility of a hydrogen explosion, the hydrogen is obtained as 10%H₂+90%N₂. This mixture cannot explode when mixed with pure CO₂ in any proportion; whereas a mixture of more than 50% H₂ in CO₂ can, even in the absence of oxygen [Clauter, 1979]. The 10%H₂+90%N₂ is also relatively (but not perfectly) safe, since the worst-case mixture with air is barely inside the flammability limits (figure 17), but caution is still essential. Note that Clauter's 0.05% explosion limit for H₂ in air is incorrect by two orders of magnitude. When 10%H₂+90%N₂ is mixed with CO₂ in the ratios used in this study, the mixture cannot form a flammable mixture with air.

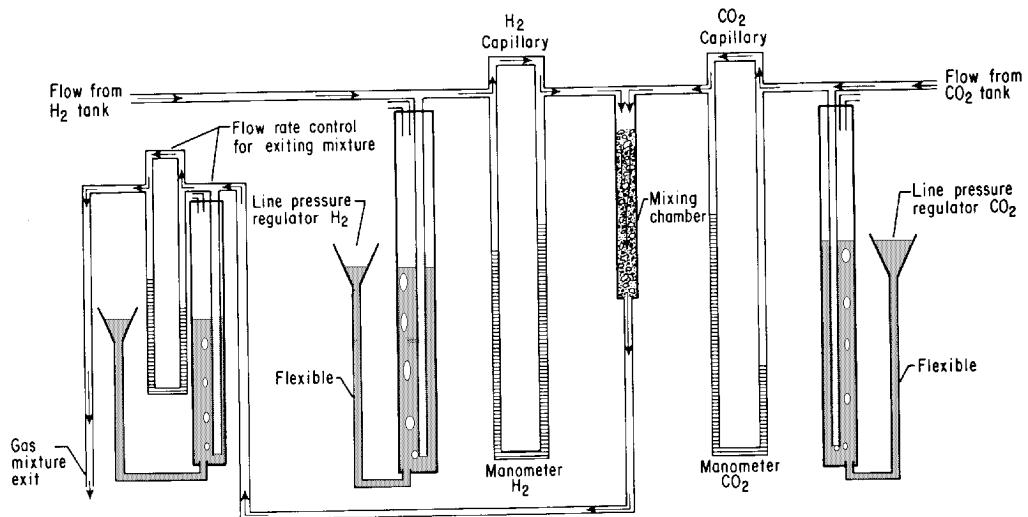


Figure 16 Gas-mixing apparatus. Gas flows are adjusted by changing the elevation of the corresponding line pressure regulator reservoir. [Nafziger, et al, 1971]

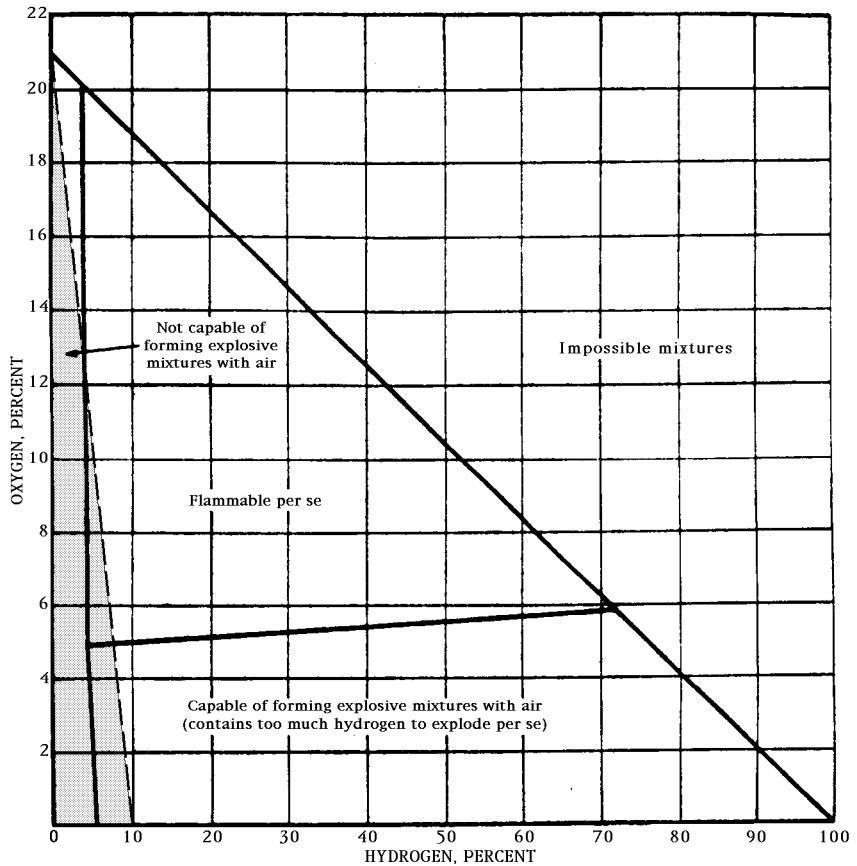


Figure 17 Flammability limits of H₂-N₂-O₂ mixtures, adapted from Coward and Jones [1952]. The dashed line shows the mixtures attainable by mixing 10%H₂+90%N₂ with air. The shaded areas show the hydrogen/oxygen mixtures attainable as CO₂ is added to the mixture. CO₂ has a greater inhibiting effect on flammability than N₂, so any mixture of CO₂ with equal parts of 10%H₂+90%N₂ cannot form an explosive mixture with air under the test conditions used.

The proper mixing ratios were determined from the tables by Deines, et al [1974] and the magnetite stability diagram of Spencer and Lindsley [1981] (figure 9). Clauter elected to measure oxygen fugacity during his experiments, and built a zirconia probe for this purpose. Dr. Schmidt discouraged using a probe, if possible, because of Clauter's difficulties in keeping it operational. Worm [personal communication] did not use a fugacity probe in any of his studies. Precise oxygen fugacity control is not necessary when preparing magnetite because of the wide stability field (about 3 to 4 orders of magnitude) at the temperatures used in the glass-ceramic process. Fugacity control is more important when preparing titanomagnetites, because oxygen fugacity is the dominant factor controlling the ulvöspinel content of the resulting titanomagnetite.

My choice of mixing H₂ and CO₂ differs from Worm's procedure. Worm [1986] uses a mixture of CO and CO₂ to control oxygen fugacity. Examination of the fugacity tables and magnetite stability diagram mentioned previously shows no clear advantage to using one mixture versus another. The explosion hazard presented by hydrogen on one hand is offset by the toxicity of carbon monoxide on the other. My decision was based on personal preference, augmented by Dr. Schmidt's past experience with H₂/CO₂ mixes and the availability of an explosive gas detector in Materials Engineering.

Clauter recommends using Darken and Gurry's [1945] ideal linear gas flow rate of 0.9 cm/s for vertically-mounted furnaces. The sample-preparation furnace has a cross-sectional area that is nine times that of the TRM furnace, and I felt that the corresponding increase in gas consumption was undesirable. I arbitrarily reduced the gas flow by about an order of magnitude in the initial sample preparation run (#001). That run was successful, as were later runs with similar gas flows. Based on this purely empirical approach, I recommend using total mixed gas flows of about 4 cm³/s for sample preparation.

Clauter calibrated the gas-mixer flow control orifices using a mercury-seal piston displacement device. This device could not be located; therefore, the flow

orifices were calibrated by trapping a volume of gas over water, and determining the flow from the volume trapped and the elapsed time. Worm used the same procedure in his work [personal communication]. Detailed procedures are given in Appendix B, and the resulting calibration curves are given in Appendix C.

I mounted a manometer on the gas mixer for measuring the pressure in the sample-preparation furnace exhaust tube. A positive pressure here indicates that the furnace is gas-tight or, at worst, leaking gas outwards. In either case, there will be no oxygen entering the furnace to upset the fugacity control.

5.2 Glass-ceramic procedure

The glass-ceramic procedure used to produce the samples for this study was originally described by Worm [1986] and appeared in English in Worm and Markert [1987b]. The procedure is to melt a mixture of oxides of Fe, Ti, Si, Ca, and others in an atmosphere that can control oxygen fugacity to within the titanomagnetite stability field. The melt is rapidly quenched to form a glass. The glass is subsequently heat-treated to nucleate and grow titanomagnetite and other crystals. The heat-treatment is terminated by a second quench, yielding the desired samples. Details are provided in the following subsections.

5.2.1 Ingredients and initial glass formation

The initial step is to mix a suitable collection of oxides in the desired proportion. Dr. Worm [personal communication] recommended using the following mixtures as a starting point:

$\text{SiO}_2 \cdot \text{H}_2\text{O}$	4.0 g
CaO	2.5 g
$\text{Fe}(\text{CO}_2)_2 \cdot 2(\text{H}_2\text{O})$	3.0 g for SD, 7.0 g for MD
TiO ₂	0.0 g for magnetite, as needed to maintain desired FeO/TiO ₂ ratio for titanomagnetites.
K ₂ CO ₃	0.7 g
Na ₂ CO ₃	0.7 g

Dr. Worm determined these values empirically by starting with a typical calc-alkaline basalt composition, then eliminating oxides of Al, Mg, and Mn, all of which are readily incorporated in the spinel structure of magnetite. Silicic acid ($\text{SiO}_2 \cdot \text{H}_2\text{O}$) is preferred over silica (SiO_2) because it is more readily available in a pure form. Oxalic acid ($\text{Fe}(\text{CO}_2)_2 \cdot 2(\text{H}_2\text{O})$) is used instead of iron oxides because it is nonmagnetic and easier to mix. Potassium and Sodium carbonates are used as a source of the corresponding oxides, with the CO₂ in the carbonates driven off during heating.. These oxides significantly lower the melting temperature of the mixture. Experience (e.g., Sample 020) indicates that melting takes place at less than 1150 °C and that 1200 °C is acceptable for sample preparation. This is well within the capabilities of the Deltech furnace. In contrast, phase diagrams for the CaO - FeO - SiO₂ system without K₂O or Na₂O (figures 18 and 19) show melting temperatures that are several hundred degrees higher. These diagrams also suggest keeping the Ca:Si ratio between 5:4 and 2:3 in order to avoid dramatic increases in the melting point.

Both silicic and oxalic acids vary in hydration, and should be written as $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ and $\text{Fe}(\text{CO}_2)_2 \cdot n(\text{H}_2\text{O})$, respectively. This causes some uncertainty in the melt composition, but this does not cause any problems in producing magnetite samples.

There is some evidence in some of the SEM photographs and electron microprobe analyses that there may be two distinct liquid phases in some of the

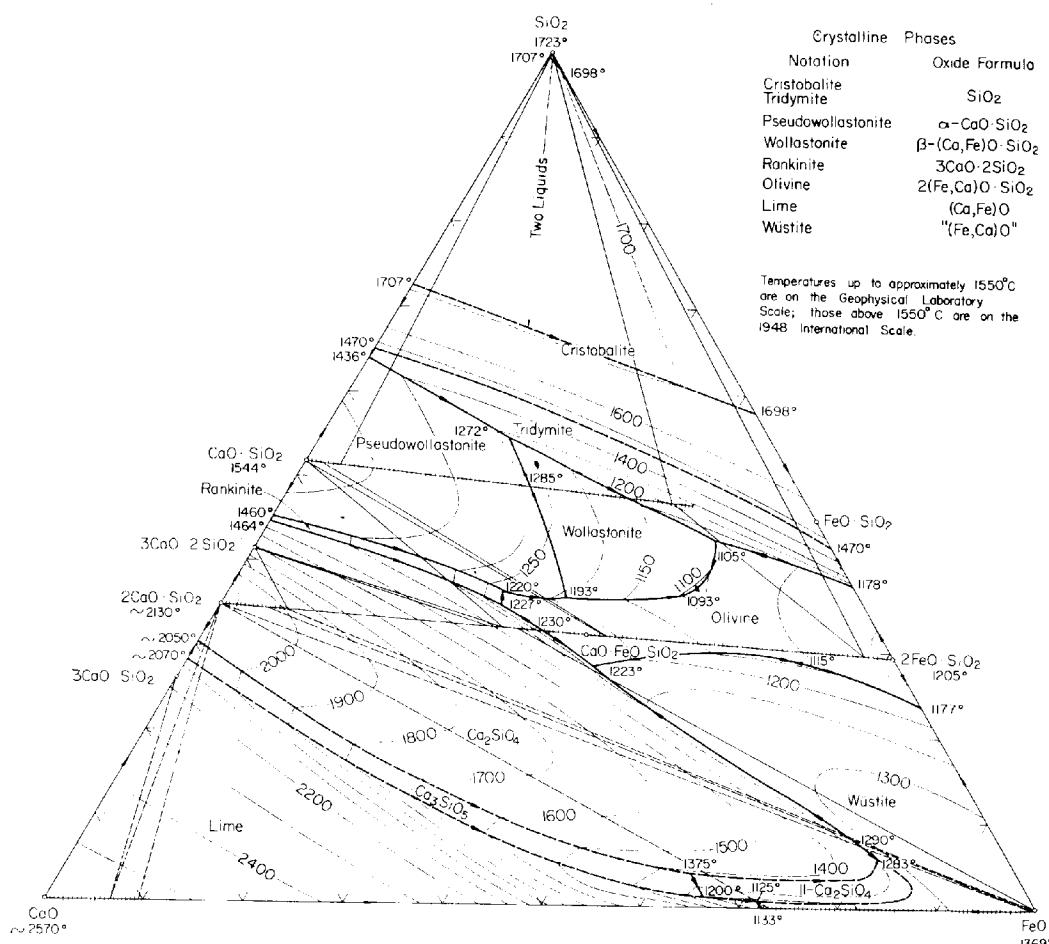
melts. This has been observed previously in the CaO - FeO - SiO₂ system [Levin, et al, 1964]. One of the liquids appeared to be richer in Fe and K than the other. Most, if not all, of the magnetite was formed in the glass formed from this phase. This is not a problem in the current study provided one recognizes the possibility that two pieces of the same sample might have different magnetite concentrations. Normalizing the results obtained from different pieces of the same sample eliminates this concern. Increasing the furnace temperature might cause the two liquids to mix, but this would require pre-heating the gas mixture if furnace temperature limits are not to be exceeded. Since this adds substantial complexity to a process that is already working acceptably, and since figures 18 and 19 suggest that the necessary temperatures could not be achieved, this was not pursued.

It would seem desirable to lower the Fe content of the mixture in order to spread the magnetite grains apart, thus reducing the potential for magnetic interactions between the grains. Samples 013, 014, and 015 were prepared with this in mind. No magnetite was found in any of these by either x-ray diffraction or SEM examination, nor did any of these samples show a measurable IRM (using the spinner magnetometer) when exposed to fields up to 1 T (10,000 Gs). It is tentatively concluded that a minimum Fe₂O₃ concentration of 10 to 15 wt% is needed to produce magnetite-bearing samples.

Fig. 586

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Metal Oxide Systems

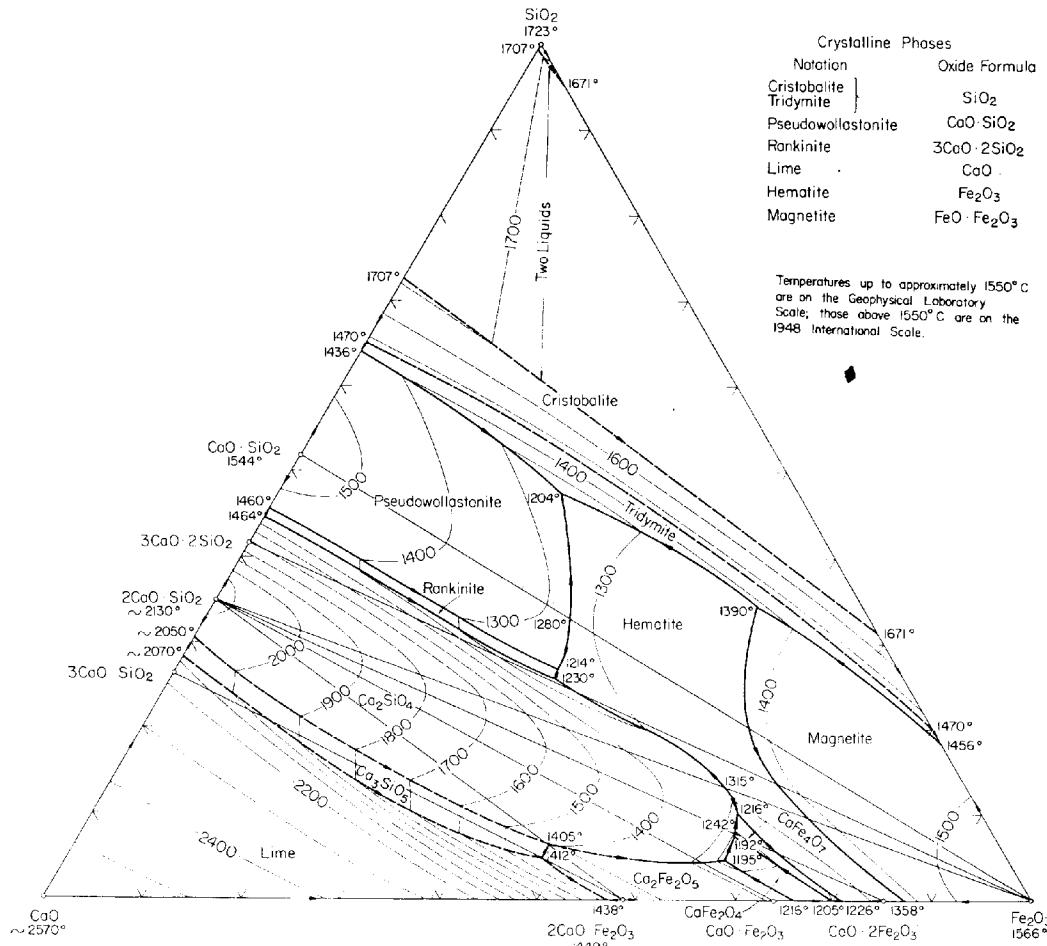
CaO-FeO-SiO₂FIG. 586. - System CaO-“FeO”-SiO₂; composite. (Oxide Phases in Equilibrium with Metallic Iron)

E. F. Oshorn and Arnulf Muan, revised and redrawn “Phase Equilibrium Diagrams of Oxide Systems,” Plate 7, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

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Figure 18 The system CaO-FeO-SiO₂ in equilibrium with metallic iron. From Levin, et al [1964].

CaO-Fe₂O₃-SiO₂FIG. 656.—System CaO-“Fe₂O₃”—SiO₂; composite. (Condensed Phases in Equilibrium with Air).

E. F. Osborn and Arnulf Muan, revised and redrawn “Phase Equilibrium Diagrams of Oxide Systems,” Plate 10, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

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Figure 19 The system CaO-FeO-SiO₂ in equilibrium with air. From Levin, et al [1964].

5.2.2 Heat-treatment process

Once the components have been melted and quenched, the resulting glass must be heat-treated to nucleate and grow titanomagnetite crystals. Ideally, the optimal temperatures for crystal nucleation should be lower than that for crystal growth (figure 20) [McMillan, 1979]. If so, it should be possible to heat the glass to a temperature that promotes crystal nucleation, but only allows negligible crystal growth. After holding the sample at the nucleation temperature for a period of time, the temperature could then be increased to one where crystal growth proceeds rapidly, but nucleation is inhibited. Figure 21 shows the ideal profile. Since significant nucleation and growth are not allowed to occur simultaneously, this kind of profile would be expected to yield a relatively uniformly-sized assemblage of titanomagnetite crystals.

Unfortunately, the glass compositions used in this study are not typical of those used in commercial glass-ceramics, so there is no adequate information on the precise shapes of the nucleation and growth curves in figure 20. As a result, the holding temperatures shown in figure 21 are not known. Worm and Markert [1984] suggested that both temperatures lie within the interval between 600 and 1000 °C. My experience tends to support this recommendation, but further study is needed. This was outside the scope of this project, and was not pursued.

Despite the theoretical advantages of the two-step process, good results can be obtained by other temperature versus time profiles. Several of my early runs were made by heat-treating at a single temperature, with good results. For example, sample 006 was heat-treated for 16 hours at 634 °C, and produced an assemblage of $1.18 \pm 0.35 \mu\text{m}$ crystals. As we shall see, this sample yielded some of the better magnetic data obtained during this study.

Another approach is to omit quenching the melt, and slowly cool the melt until it crystallized. Several samples were prepared this way. In general, this yielded samples with larger crystals and a broader size distribution. Worm [1984] relied on this technique to produce his coarse-grained samples as well.

In principal, the grain size can be controlled by varying the length of the crystal growth step. I was not able to demonstrate this. For example, samples 002 and 005 were each held at 722 °C for 8 and 70 hours, respectively, yet their grain sizes and distributions were nearly identical. This may indicate that these holding times were too long to effectively limit crystal growth. I had more success in controlling crystal size by varying the Fe content of the melt, with larger crystals resulting from higher Fe concentrations.

There is still too little experience with the glass-ceramic method to be able to produce magnetite grains of a specified size without resorting to trial-and-error tactics. The results summarized in Appendix A and the tables in Worm [1984] can provide some guidance. There is a need for a systematic study to determine the proper nucleation and growth characteristics of the melts used here. This was outside the scope of the present study, and left for the future.

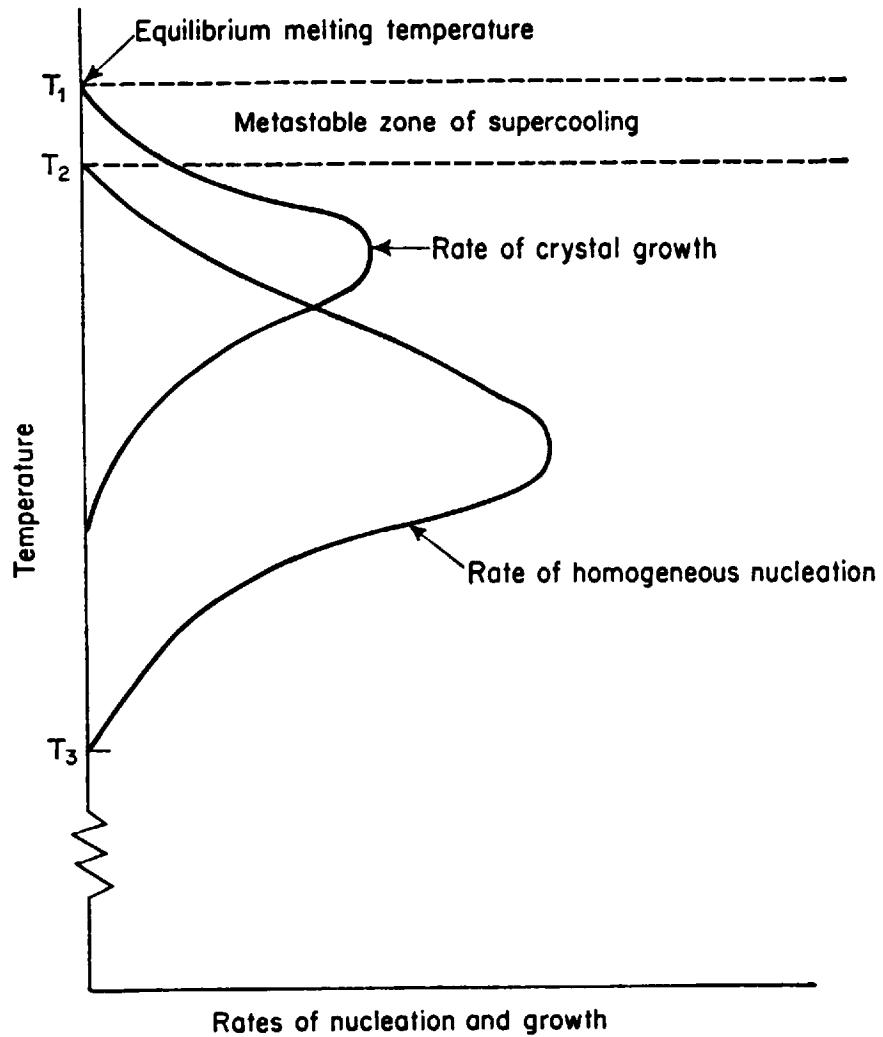


Figure 20 Theoretical effect of temperature on the rate of homogeneous nucleation and crystal growth in a viscous liquid. [McMillan, 1979].

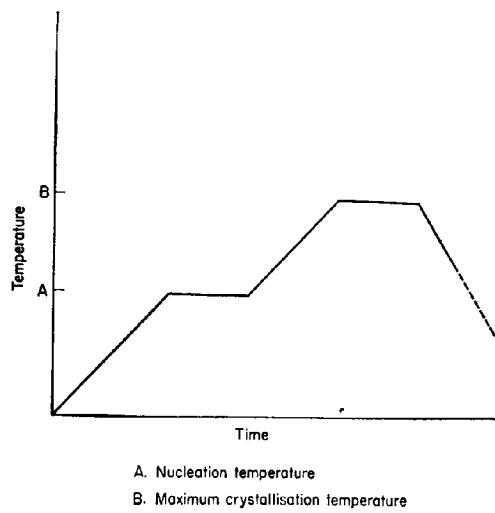


FIG. 30. Idealised heat-treatment schedule for a glass-ceramic.

Figure 21 Ideal heat-treating profile. [McMillan, 1979].

5.3 Discussion of procedure

The glass-ceramic procedure allows one to produce an assemblage of (titano-)magnetite grains in a silicate matrix. This procedure has several advantages over other methods.

1. Stoichiometry: The glass-ceramic method is amenable to crystal growth in a controlled atmosphere, and hence stoichiometry can be controlled.
2. Dispersion: The (titano-)magnetite crystals are usually well-distributed throughout the matrix. Since the crystals are grown in place and not free to move, the problems associated with trying to keep magnetic particles from clustering after formation are eliminated. Even when the melt separates into immiscible liquids, the (titano-)magnetite crystals are often well-distributed in the phase in which they form.
3. Barrier to oxidation: The (titano-)magnetite crystals form inside a glassy or crystalline matrix, where they are protected from oxidation. This protection is not complete, and some oxygen can diffuse through the matrix, but certainly with greater difficulty than through the powdered matrix typically used to disperse crystals produced by other techniques.
4. Grain size: Crystals are easily produced in the grain sizes corresponding to the SD through MD transition, which is of great interest in theoretical rock magnetism.
5. Size distribution: The heat treatment process allows one to maintain relatively close control over the (titano-)magnetite size distribution for a wide range of crystal sizes.
6. Crystal shape: The glass-ceramic method often produces euhedral magnetite octahedra. Other methods, such as grinding, often fail to do so.

7. Low internal stresses: Stresses in the resulting crystals are less than those introduced by methods involving sample grinding. The effect of residual internal stresses can be reduced by annealing the sample prior to the magnetic experiments.

The glass-ceramic method is not without disadvantages. The major problem with the method is that it is still a “hit or miss” approach. There has not been enough experience with the method to be able to accurately predict the melt composition and heat-treatment needed to produce (titano-) magnetite crystals of a pre-specified size.

The second disadvantage is that it appears to be difficult to produce samples with very low (titano-)magnetite concentrations. This may only reflect the particular melt compositions used to date, or it may be a fundamental difficulty of all practical melts. This is another area that deserves further investigation.

The third disadvantage is that the magnetite nucleation temperature appears to be around 600 to 700 °C, which is not much higher than the magnetite Curie temperature (~ 586 °C). If the crystallization process is not carried through to completion in the sample preparation stage, it may continue during any TRM experiments. The change in sample characteristics would then invalidate the TRM experimental results. The sample can be thermally cycled prior to any TRM experiments, causing the sample to reach an equilibrium state, but this negates using time as a controlling parameter during the sample preparation process. It is essential to characterize the sample after completing all magnetic measurements to confirm that there were no significant changes to the sample characteristics (e.g., grain size) during the experiments. This final characterization is performed on the same fragment used for the magnetic measurements, and eliminates the effect of differences between the fragment used for the initial characterization and the magnetic experiments.