An Investigation of the Thermal Equilibrium Diagrams of the Systems FeO-MnO and MnO-SiO_2.

By

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Until a comparatively short time ago steel making was regarded more as an art than as a science; but the greatly increased rate of production which became necessary during the war, and the cut-throat competition which has been a feature of the industry since, brought about very marked changes both in the engineering and metallurgical aspects of steel production. The progress made on the engineering side has been steady and continuous. Dr. M'Cance said in his presidential address to the West of Scotland Iron and Steel Institute in October of last year (1933):- "On the engineering side, the principles governing the production of steel can be said to be clearly perceived in a manner which renders their application along universally accepted lines a simple matter".

In recent years there has also been an extensive attack along physico-chemical lines, on some of the perplexing metallurgical problems which confront the steel manufacturer, but, to quote Dr. M'Cance again, "it cannot be said that progress on the metallurgical side has reached such an advanced stage. It is not that marked progress has not been made, but the chemical behaviour of iron is peculiarly involved and the proper understanding of its complications awaits the solution of problems in pure science which yield to the inspiration of the individual rather than to the organised attack".

Without a doubt, one of the most, if not the most, interesting and yet puzzling aspects of the whole question of steel manufacture is the slag-metal relationship. That the slag does play an enormous part in the refining of the metal and is responsible for the presence or absence of many of those qualities which differentiate good from bad steel, has been recognised for a long time by all practical steel melters. But in what way the composition and physical properties of the slag should be controlled to ensure the production of the best steel is a question on which few are agreed.

The widely varying methods of working down a charge which are to be observed in practice furnish ample proof of this statement.

Another factor which has become increasingly important in late years is the presence in the finished steel of non-metallic inclusions. The study of the mode of occurrence and nature of these inclusions has been rendered more imperative by the modern demand for high-tensile alloy steels. In this connection it has been pointed out that the presence of an inclusion, which in a mild steel may be of little or no importance may be the cause of a fatigue failure in a high-tensile steel.

Any attempt to shed further light on the nature and physical properties of slags will be very valuable in the solution of these varied problems. The properties which must receive particular attention in the investigation are the melting temperatures, the viscosities and the optical data.

The slags met with in practice are very complex, often containing four, five, six or more constituents, and any advance in the real understanding of such materials can only be made by the acquisition of fundamental knowledge of the equilibria existing between each pair of constituents and the application of such knowledge to the study, and construction of, ternary and more complex systems. An examination of the literature will show that comparatively little real knowledge is available regarding even simple binary non-metallic systems. A book published in 1930 by Benedicks and Löfquist on "Non-metallic inclusions in iron and steel" contains practically all the information available on the subject up to that date, and a study of this most interesting and valuable book will reveal the fragmentary and incomplete character of the evidence collected. In this book the authors rightly point out that:- "Complete solution of the problem of slag in iron and steel implies a full knowledge of the equilibrium diagrams of the systems containing on the one hand metallic iron; and on the other non-metallic compounds of iron and metalloids, including oxides, sulphides and silicates".

The work outlined in this paper was undertaken with the object of establishing and making available some of this fundamental knowledge. It is concerned with the thermal and optical properties of the two very important systems:- FeO-MnO and MnO-SiO_2.

The problems inherent in the investigation of such systems are many and varied. They are concerned principally with the manufacture of furnaces capable of very high temperatures, with the provision of suitable refractory materials, and accurate methods of thermal measurement.

The record shows a continuous development in the technique required for investigations of this type. At the start, the molybdenum-wound furnaces employed had a useful range up to about 1550°C, and a short life period. In the later stages temperatures of nearly 1900°C were recorded and the furnaces had a much longer life. The experiments with the various refractory materials showed that molybdenum crucibles were much more satisfactory for this type of work than any of the substances previously employed. The greatest advance made, however, was in the application of the principle of the differential thermocouple to the study of thermal arrests in these mixtures of non-metallic substances. It has been shown that the great advantage of the differential thermocouple over the ordinary thermocouple is in the investigation of small and long-continued thermal arrests, which cannot be detected by ordinary means. It is rather interesting to compare the results obtained for the two systems; first by the ordinary thermal methods set out in Sections 1 and 11; and second by the use of the differential thermocouple set out in Sections 111 and 1V. A comparison which will clearly bring out the advantage stated above to be obtained by the employment of the differential thermocouple.

The optical properties of the constituents have also been investigated as detailed later.

Section 1. The Investigation of the System FeO-MnO by direct thermal methods.

The molybdenum furnace. All the thermal determinations were carried out in a molybdenum-wound furnace. The general design of the furnace is indicated in fig. 1. It consists of a cylindrical steel casing (15 in. diam. and 16 in. high) closed at the top and bottom by steel plates ($\frac{1}{2}$ in. thick). The furnace tube is made of alundum and is 3 in. internal diam. and 18 in. long. The tube is made in the following way. A cylindrical steel core is covered with three or four thicknesses of wet brown paper. Alundum cement is made up into a paste with water and applied evenly on top of the paper. The paste is allowed to dry and is then rubbed down to size with coarse emery cloth. Care is taken to ensure that the tube is of equal thickness all round. String is then wound round the tube over a length of about 11 ins. Five turns of string are applied on each inch of length. A thin coating of alundum is then put on top of the string. The whole is again dried and burned at 500°C. The tube is slipped off the core. The string has been burned away and winding channels may be easily cut on the outside of the alundum with an old hack-saw blade. The bottom of the tube is closed with a plug of alundum. The completed tube is then baked at 1000°C.

Molybdenum wire, 0.04 in. diam., is wound round the outside of the tube, about 40 ft. of this wire are required. The winding is covered with a coating of alundum. The tube, when inserted into the furnace rests on a distributor block. This is simply a short cylinder of alundum closed at one end. Below the open end of the cylinder is the orifice by which a mixture of inert gases enters the furnace; holes are bored in the wall of the cylinder at regular intervals to ensure an even flow of gases over the whole outer surface of the winding. The top of the furnace tube projects about $1\frac{1}{2}$ in. above the top plate of the casing. There is a circular hole 4 in. diam in the top plate and the annular space between the plate and the tube is packed with asbestos wool and a coating of alundum applied on top.

The furnace is lagged with asbestos wool and this is prevented from coming into contact with the winding by an outer alundum tube (4½ in. diam. and 14½ in. high) which is completely contained within the casing.

The terminals of the winding are taken out through two holes in the top and bottom plates respectively. The wires are insulated from the casing by inserting short lengths of silica tubing in the holes and threading the wire through these tubes. The open ends are plugged with asbestos wool and alundum.

To maintain an inert atmosphere around the molybdenum winding, which will oxidise on the slightest provocation, a mixture of nitrogen and hydrogen gases is kept continually passing through the furnace. The mixture of gases is obtained by cracking ammonia. Ammonia (0.88 sp. gr.) is boiled in a large flask, the stream of gas is passed over a mercury pressure valve and then into the cracking furnace. This consists of a large diameter tube wound with nichrome wire. Seven Morganite tubes, connected in series, are contained within this large tube. The Morganite tubes are filled with iron turnings and the temperature of the furnace is maintained about 800°C. By passing ammonia gas over these heated turnings a large proportion of it is broken down into nitrogen and hydrogen. The gases issuing from the cracking furnace are washed free from ammonia in a special washer and dried in sulphuric acid bubblers and calcium chloride tubes and then delivered to the furnace.

The gases when delivered to the furnace are relatively cool and must absorb an appreciable amount of heat during their passage through the furnace. It has been found, however, that if the alundum coating over the furnace winding is made thick, e.g. ½ - ¾ in. that the efficiency of the furnace is greatly increased. It would appear that the fine pores in the alundum act as preheating chambers for the cool gases, which are thus raised to a very considerable temperature before actually coming into contact with the winding. Later experience with a vacuum furnace has shown that the gases are the main conductors of heat from the furnace winding to

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the charge. The result of this preheating of the gases is to render possible the attainment of much higher temperatures.

The thermocouple. The molybdenum-tungsten thermocouple was used in the measurement of higher temperatures in all the subsequent experiments. A considerable length of wire (usually 15-30 yds.) of each metal was obtained. The molybdenum wire used was 0.65 m.m. in diam. and the tungsten wire 0.4 m.m. The hot junction was formed by simply twisting the molybdenum wire tightly round the tungsten wire for a distance about $\frac{3}{8}$ in.

The thermocouple was standardised from room temperature up to about 1100°C against a carefully calibrated chromel-alumel thermocouple, specially kept for this purpose. It is found that within this region the E.M.F.-temperature curve takes the general form shown in fig. 2. The curve is parabolic in form and the general equation for it is:- $y = ax^n$, where $n = 2$. The maximum E.M.F. in this region occurs about 700°C, and the reversal about 1000-1100°C.

If, by means of the equation, the curve is extrapolated up to 1600°C it is almost invariably found that when the thermocouple is standardised against commercially pure iron the values obtained for the delta change point at 1400°C and for the melting point, 1537°C, fall on this extrapolated portion of the curve. One other interesting fact is the remarkable similarity which may be observed in the calibration curves obtained for different batches of wire, and it is generally found that the calibration curve changes very little on changing over to a new couple. For these reasons a high degree of confidence in the standardisation is possible, but it must be stated that there is a disconcerting lack of reliable data for standardisation purposes at temperatures above 1200°C.

Owing to the occurrence of this maximum in the calibration curve the useful range of the thermocouple is from 800°C up to the highest temperature at which it has been used in these experiments viz. 1860°C.

There are two disadvantages in the use of this couple:-

(a) The necessity for maintaining an inert atmosphere, since both metals are very easily oxidised.

(b) The extreme brittleness of the tungsten wire after use. About 9 to 12 ins. will break off before a new junction can be made.

It is found that at high temperatures the thermocouple gives erratic readings, this effect being probably due to the electromagnetic field set up by the large current flowing in the furnace winding. This defect can be remedied by binding a piece of thin molybdenum sheet right round the outside of the "pythagoras" tube. The action of the "grid" may be explained on the well-known electrical principle that if a closed conductor is placed within an electromagnetic field no lines of force can penetrate into the space within the conductor.

The Refractory Materials Used.

In this first series of experiments the crucible was contained within a "pythagoras" tube (90 cms. long, 60 m.m. external diam. and 50 m.m. bore). The material of which these tubes are constructed is a non-porous refractory with a softening temperature of about 1600 to 1650°C. During the preliminary experiments a vacuum was maintained within the tube: but it was found that at temperatures somewhat below 1600°C the tube collapsed inwards over the heated zone and cracked in a very short time. This trouble was overcome by evacuating the tube at ordinary temperatures and then allowing purified nitrogen to enter until a pressure of about half-an-atmosphere was recorded within the tube. At the maximum temperatures employed this volume of gas was just about enough to give one atmosphere of pressure and collapsing and buckling of the tubes at temperatures below 1600°C was greatly minimised. The arrangement of the manometer and the connections to the exhausting pump and to the nitrogen supply are shown in the diagram in fig. 1.

The question of a refractory for the manufacture of crucibles to contain the melts was the next problem. The use of carbon was ruled out due to interaction with the melt. Fireclay would contaminate the materials and melts at a comparatively low temperature. Magnesia would probably be the best material but crucibles of this material of the size required could not be bought and several attempts were made to prepare suitable ones in the laboratory. Magnesium carbonate was calcined at red-heat and then heated in alundum pots in a large molybdenum-wound furnace to ensure that the shrinkage of the material would be as complete as possible.

The magnesia was heated over considerable periods at the highest temperature which could be attained in the furnace. It was found, however, that when the burned material was moulded into crucibles, slowly dried and burned the crucibles produced contained large cracks and were of no use.

Various bonding materials; calcined but unshrunk magnesia, magnesium chloride, nitrate, etc., were all tried, the materials were crushed very finely and intimately mixed, but crucibles which did not contain cracks could not be produced and the hope of using magnesia crucibles was finally abandoned.

An iron crucible was next tried but seemed to interfere seriously with the behaviour of the thermocouple and its use was also discontinued.

Alundum crucibles were then tried. These crucibles were prepared by ramming in a wooden mould and when rubbed down to size were $\frac{3}{4}$ in. internal diam. $1\frac{1}{2}$ in. external diam. and about 3 in. in height. They were dried carefully in air and then baked at about 1100°C. **After** this treatment they are hard and compact. After a mixture had been melted it was found that serious corrosion had taken place in the crucible. The alundum thermocouple sheath in particular was very seriously affected. It was suggested at the time that this was mainly an absorption effect, and that very little chemical action was taking place. In the light of later work, however, it would appear that chemical action does take place between FeO, MnO and Al_2O_3 (Herty, Fitterer and Byrns. Mining and Met. Investigations, 1930, Co-operative Bull. No. 46). In order to counteract this supposed absorption of the charge by the crucible, alundum crucibles, prepared as above, were treated in the following way. The crucibles were soaked in a concentrated solution of magnesium nitrate, and the space above the surface of the solution exhausted, by this means most of the air in the pore spaces of the crucibles was expelled. The crucibles were then dried and burned at about 1450°C in the molybdenum-wound furnace. During the burning the magnesium nitrate

nitrate/
is converted to magnesium oxide, and at the high temperature the magnesium oxide reacts with alundum and the surface of the crucible becomes covered with a sort of glaze. These treated crucibles resisted the action of the charge better than the ordinary alundum crucibles but considerable corrosion still took place and the crucibles tended to soften appreciably when heated above 1550°C, but were used with a fair degree of success for the rich FeO melts. For the rich MnO melts these crucibles could not be used but it was found that the corrosive action of these melts on pure alundum crucibles was much less and untreated crucibles were used. Later work by Fritterer, Herty and McCaughey (Mining and Met. Investigations, 1927, Bull. No. 34, p. 65 and "Progress Report on the system MnO, Al_2O_3 and SiO_2" by Herty and Fritterer Oct. 16 1931) has shown that FeO and MnO form a series of liquid solutions with MgO. It would appear, then, that contamination of the melts is possible both by Al_2O_3 and MgO.

It is also stated that commercial alundum contains small percentages of silica to serve as a bonding material. The presence of this silica must also play a part in the contamination of the melts.

The refractories prepared as shown were the best then available for the work and since all the crucibles were fired at very high temperatures it is probable that contamination of the melts was kept to a minimum.

Analysis of the melts was made whenever sufficient material was available and the following results seem to show that there has been a distinct measure of contamination:-

Mixtures made up.		Analysis after melting.	
FeO.	MnO.	FeO.	MnO.
80%	20%	74.9%	21.4%
70%	30%	65.2%	32.9%
60%	40%	57.9%	40.5%
40%	60%	37.6%	59.9%
30%	70%	29.9%	67.5%.

Just how far this contamination affected the results cannot be known with certainty, but a comparison of the results obtained by the use of these refractories with those obtained by the use of molybdenum crucibles will show some considerable differences particularly in the melting points of the rich MnO melts.

Thermocouple Sheaths.

These were also made of alundum and were formed in a wooden mould. A piece of wire about 3/32 in. in diam. was used as a core. While the alundum was still plastic the wire was carefully removed and the sheath dried and burned and then rubbed down to size with coarse emery cloth. One end was plugged with alundum. They were fired at a high temperature. In the finished state the sheaths were usually about 4 in. long, $\frac{3}{8}$ in. external diam. and 3/32 in. internal diam. Those which were to be used for the richer FeO melts were treated with magnesium nitrate in exactly the same way as the crucibles.

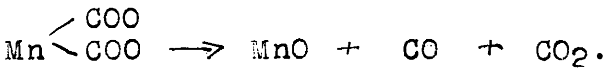
The preparation of the FeO and MnO.

It was considered desirable to obtain the substances in the purest form. Neither substance can be obtained commercially in a very high state of purity. It was decided to prepare both substances in the laboratory.

The preparation of MnO.

Quite a number of references are to be found in chemical literature for methods of preparing MnO. Scheele obtained it by heating manganous carbonate to redness out of contact with air, Arfvedson by heating manganous carbonate to redness in a current of hydrogen, and Moissan by the reduction of manganese dioxide by hydrogen at about 300°C.

A number of attempts to prepare the compound in these ways were made. MnO_2xH_2O was precipitated from an aqueous solution of a manganese salt by the action of bromine and ammonia, this compound was dried and heated in a stream of hydrogen at a bright red heat but the pure oxide was not obtained in this way. Further attempts were made to reduce pure MnO_2 and $MnCO_3$ respectively in a stream of hydrogen at a bright red heat, but an oxide of the typical bright green colour could not be obtained and the chemical composition never agreed with the formula MnO. A final attempt was made by decomposing manganous oxalate which can be obtained in a very pure state commercially. The decomposition was carried out in an exhausted tube at a temperature of about 800°C. About 250 gms. of the oxalate were contained in an alundum tube. The oxalate had to be very tightly packed in the tube and the stopper of the tube wedged firmly in with asbestos wool. Otherwise the entire contents were liable to blow out whenever the decomposition started. The reaction may be expressed as follows:-



$$Mn\begin{matrix}\diagup COO\\ \diagdown COO\end{matrix} \longrightarrow MnO + CO + CO_2.$$

If the tube is kept exhausted the reaction goes to completion at temperatures above 600°C.

It was found that the MnO produced at this temperature was not stable and oxidised on standing in air. In extreme cases spontaneous oxidation took place if the tube containing the oxide was given a sharp knock. This difficulty was overcome by decomposing the oxalate at about 700°C and when decomposition was complete the temperature was raised to about 1000-1100°C. There was considerable shrinkage in the volume of the oxide and after this treatment it appeared to be in a more granular form which is quite stable in air at ordinary temperatures.

When pure the oxide is a bright olive green colour. No references to the reduction by carbon can be found and reduction by hydrogen is stated not to begin till 1300°C.

Preparation of FeO.

Three methods of preparing this oxide are mentioned in chemical literature. It is stated to be produced by the reduction of ferric oxide in hydrogen at about 300°C. But when prepared in this way oxidises in air with incandescence. Sabatier and Sendrens (Compt. Rend. 1892, 114, 1429) obtained it by the action of nitrous oxide on metallic iron at 200°C. It is stated to be produced by the addition of ferrous oxalate to boiling potassium hydroxide solution, in this way it is obtained as a black velvet powder. Neither of the two latter methods seemed to be very satisfactory and other methods were tried.

Magnetic oxide, prepared by heating pure iron to bright redness in a current of air (Pfeil, J.I.S.I. 1931, 1. 237) was heated to 1000°C and maintained at that temperature for six hours. There was quite an appreciable increase in the amount of ferrous iron present, but the product was not pure FeO. Magnetic oxide was reduced by hydrogen at 500°C, again a fair percentage of FeO was produced but the purity was not considered sufficiently high.

Ferrous oxalate can be obtained in a high state of purity commercially and it was found that if the oxalate was decomposed in an exhausted tube, FeO together with varying amounts of

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magnetic oxide of iron, free iron and carbon was obtained.

Probably in the main the decomposition follows the simple equation:-

$$Fe\langle^{COO}_{COO} \longrightarrow FeO + CO + CO_2.$$

But a number of side reactions may quite possibly take place even in the very short time before the gaseous products of decomposition are removed from the furnace. These possible side reactions are as follows:-

$$3FeO + CO_2 \rightleftharpoons Fe_3O_4 + CO \quad \text{------------(2)}$$

$$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2 \quad \text{------------(3)}$$

$$Fe_3O_4 + C \rightleftharpoons 3FeO + CO \quad \text{------------(4)}$$

$$FeO + CO \rightleftharpoons Fe + CO_2 \quad \text{------------(5)}$$

$$FeO + C \rightleftharpoons Fe + CO_2 \quad \text{------------(6)}$$

$$CO_2 + C \rightleftharpoons 2CO \quad \text{-----------(7).}$$

The presence of small amounts of iron, magnetic oxide and carbon can all be accounted for by these reactions. The furnace tube was kept exhausted by an Edwards "Hyvac" pump during the period of the decomposition. These pumps are capable of attaining a vacuum of 0.01 m.m. of mercury but the gases are evidently long enough in the furnace before removal by the pump to permit some of the reactions mentioned above to proceed to some extent at least.

A series of experiments was carried out in order to find the most suitable temperature for the decomposition of the oxalate and the purest product was obtained when the temperature of the furnace was about 700°C. The product obtained at this temperature analysed about 99% FeO.

It may be mentioned that in all the analyses carried out on these samples, the total iron was estimated by the ordinary method of reduction with stannous chloride and oxidation with a standard solution of potassium dichromate. Quite a number of methods for the estimation of ferrous iron were experimented with but concordant results could not be obtained with any of these. The usual procedure was to remove any iron and magnetic oxide with a magnet and

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then estimate the total iron in the remainder of the sample. The more nearly this value approached to 77.7%, which is the percentage of iron in FeO, the purer was the product assumed to be. The procedure is undoubtedly open to question, but as the method was easily standardised, and is capable of giving a high degree of accuracy, it probably furnished as true a guide to the composition of the oxide as would have been obtained by the use of some of the more elaborate but probably less accurate methods for the estimation of ferrous iron.

When making the larger quantities required for the melts, the furnace was exhausted, heated to 700°C and maintained at that temperature for two to three hours. The "Hyvac" pump was kept continuously working. About 200 gms. of oxalate were decomposed at one time. 100 gms. of CO and CO_2 are liberated during the decomposition of the 200 gms. of oxalate. At 700°C this weight of gas will occupy a very considerable volume and a certain period of time must elapse before it will all be removed by the pump and thus opportunity is afforded for some of the gas-solid reactions mentioned to take place. Magnetic oxide and carbon are produced in varying proportions, but at 700°C the carbon seems to react with the CO_2 giving CO~~2~~ as in eqn. (7) and the magnetic oxide is reduced by CO and carbon as in eqns. (3) and (4). The resulting product has a composition corresponding to about 99% FeO.

The Procedure Adopted for the determinations in the System FeO-MnO.

A charge of about 50 gms. was made up for each determination. The FeO and MnO were weighed out in the required proportions, intimately mixed together and ground into a powder. The charge was then introduced into a crucible. For the richer FeO melts, an alundum crucible treated with magnesia was used, for the richer MnO melts a plain alundum crucible was satisfactory. In every case the couple was inserted into an alundum sheath, which had been treated in exactly the same way as the crucible. The couple was wedged into the sheath by packing it in with asbestos wool, and the sheath was bound in position in the crucible with iron wire. The whole was then lowered into the "Pythagoras" tube. The thermocouple leads are threaded through two glass tubes in the rubber bung as shown in the diagram. The bung was then pushed well home; a solution of collodion in amyl acetate being used to seal up the junctions of bung and tube in order to ensure that the apparatus was gas-tight. The Pythagoras tube was then lowered carefully into the furnace, and when in position was exhausted by the "Hyvac" pump. A stream of nitrogen was passed through the apparatus for a few minutes, the supply was cut off and by means of the pump the pressure in the tube reduced to about half-an-atmosphere. The pressure is recorded on the manometer shown in fig. 1. The furnace was then gradually heated up till a current of about 26-27 amps. was passing through the winding.

The thermal curves were taken in the usual way, the time required for each 0.02 m.v. rise in temperature being observed on a stop-clock and recorded.

Two heating and cooling curves were taken on each occasion, but in many cases no thermal arrests of any magnitude were found on the second heating and cooling curves.

A series of typical heating and cooling curves obtained during the investigation are shown in figs. 3 to 14.

The Thermal Changes in FeO.

Many attempts to determine the melting and freezing points of FeO were made in the early stages of this work. A few of the thermal curves obtained are shown in figs. 3 and 4.

It will be noted that in none of these are there any thermal arrests corresponding to a definite melting or freezing point. Arrests of varying magnitude are found in the heating curves at about 1350°C, 1410°C and 1460-1480°C, this top point being usually the most pronounced. The full significance of these points was not realised at first.

Benedicks and Lofquist (Non-Metallic Inclusions in Iron and Steel, 1930, p. 56) and Hanson and Tritton (J.I.S.I. 1924, 11. p. 90) indicate that FeO undergoes a peritectic dissociation at a temperature around 1370°C. It would appear to be a reasonable assumption, then, that, on heating up an alloy of the composition FeO (77.7% Fe and 22.3% O) a peritectic dissociation will take place resulting in the formation of two phases -a solid phase, consisting of free iron containing a very small amount of oxygen in solid solution; and a liquid phase consisting of a rich iron-oxygen solution. The mixture melts completely and becomes homogeneous at some higher temperature.

The occurrence of three arrests on the heating curves of FeO, as shown in figs. 3 and 4, may be quite easily explained on this assumption. The lower arrest at 1350°C will mark the temperature of the peritectic dissociation. The second, and very small arrest at 1410°C will almost certainly mark the γ to δ transformation in iron, the small increase in the usual value for the temperature of this transformation being due to the presence of the oxygen in solid solution. The upper arrest at 1460°C will indicate the temperature at which the mixture becomes completely melted.

Under normal conditions the arrest at 1460°C, which marks the temperature at which the material becomes completely molten, should be very small. It will be noted, however, from the curves in figs. 3 and 4 that this arrest is quite pronounced. As was indicated earlier there is a possibility of reaction between FeO, alumina and magnesia, these reactions will proceed most rapidly just as the material becomes melted, and it is to this fact that the pronounced arrest at 1460°C, is undoubtedly due.

When the thermal curves of FeO were investigated by means of the differential thermocouple method, arrests corresponding approximately to those obtained in this earlier work were again observed. The arrests on the heating curves were found to occur at 1355°C, 1410°C and 1480°C.

In these later curves, figs. 49 and 50 the arrest at 1355°C is found to be the most marked and will almost certainly indicate a dissociation of the peritectic type.

In the experiments just referred to the FeO was melted in molybdenum crucibles, in which practically no contamination of the material has been found. In the curves obtained when the FeO was melted in these crucibles, it will be noted that the upper arrest at 1480°C is very small. A fact much more in keeping with what would be expected.

From the thermal curves, shown in figs. 49 and 50 it would appear that these changes are reversible, and arrests are to be observed on the cooling curves, which correspond very closely in temperature and magnitude, with those on the heating curves.

In addition there is quite a promounced arrest at about 1350°C on several of the cooling curves determined by the direct thermal method, as shown in figs. 3 and 4. A fact which would still further emphasise the importance of this phase change which the material is undergoing at this temperature.

A microphotograph of a sample of FeO, melted in an alundum crucible is shown in fig. 15 (a). It will be observed that some material in the form of needles has crystallised out of the melt during cooling. This material will, almost certainly, be magnetite and would substantiate the idea, put forward by several investigators, that at lower temperatures, probably 550-600°C, FeO breaks down into iron and magnetite.

Discussion of the results obtained in the FeO-MnO determinations.

It has been pointed out that diagrams like FeO-MnO are not true binary diagrams, but are actually sections through a ternary diagram, in this case the Fe-Mn-O system. The complexities in the behaviour of FeO make it still more difficult to construct a reasonable binary diagram from the data obtained.

Benedicks and Lofquist in their provisional diagram assume 1350°C as the melting point of FeO, and draw in a dotted line from about 1470°C to meet the liquidus. Following this idea, and in accordance with what has just been stated regarding the thermal changes in FeO, the melting point of the oxide, for the purpose of the diagram has been assumed at 1350°C. An attempt has been made to incorporate all the data in a simple quasi-binary diagram. SHOWN IN FIG. 16. It was found that the addition of MnO to FeO raises the melting point of the mixture, and that up to about 10-12% MnO the resulting product is a homogeneous phase. The microphotograph shown in fig. 15 (b) seems to bear out the idea that up to this composition the material is homogeneous.

The thermal curves for mixtures with compositions varying from 12% to about 55% MnO, figs. 5-9, all show an arrest at about 1415°C. A constant arrest of this type will, in all probability mark the occurrence of a peritectic reaction, so that the existence of two separate solutions between FeO and MnO must be assumed. This assumption is strongly supported by a study of the microphotographs. In the microphotographs for the 50/50 and 35/65

35/65/ FeO/MnO melts as shown in fig. 15 (c) and (d) there seems to be unmistakable evidence of the existence of two separate phases.

This is rather unexpected, as both oxides crystallise in the cubic system and X-ray analysis has shown that they have a unit cube of the NaCl pattern; the figures given for the parameter of FeO being 4.29 and that of MnO 4.4 A°. Complete solubility of the two oxides might quite well be expected but the evidence of both the thermal curves and micro-examination all goes to show that this complete solubility does not exist and that there is a break in the liquidus at B.

In fixing the upper part of the liquidus, a rather curious fact emerges. The upper arrests on the thermal curves for mixtures from 15% up to 100% MnO are indicated below

Mixture.		Temperature of upper arrest in °C.
FeO %.	MnO %.	
85	15	1425
80	20	1450
75	25	1450
70	30	1475
65	35	1500
60	40	1485
55	45	1495
50	50	1505
45	55	1510
40	60	1510
35	65	1513
30	70	1525
20	80	1547
10	90	1580
	100	1585.

It will be noted that if the value for the 75/25 FeO/MnO melt is not taken into account and a smooth curve drawn through the remaining four points; up to the composition 65/35 FeO/MnO, the slope of the curve obtained is much steeper than that of the curve joining the remaining upper arrest points and if extrapolated up to 100% MnO, would cut the temperature axis at above 1700°C.

It will be shown in Section lV that this system was reinvestigated using the differential thermocouple and molybdenum crucibles. On this subsequent examination this upper part of the liquidus was found to be a curve with a much steeper slope,

slope,/ and the melting point of MnO was found to be about 1780°C.

The only reason that can be put forward for the marked break in the slope of the curve and the marked flattening out of that portion between 40% and 100% MnO is that in this region contamination of the melt by alumina and magnesia from the crucible is most intense, resulting in this lowering of the melting points of the various mixtures. The magnitude of these upper arrest points also strongly suggests that quite pronounced reaction has taken place. For, under normal circumstances, the arrest marking the liquidus in a series of solutions would be very small; a fact which may be appreciated by a study of the thermal curves for these same mixtures as obtained in Section IV.

Meantime the liquidus has been fixed by the line DB which falls along the majority of the upper arrest points.

The determination of the solidus lines is a matter of some difficulty owing to the unsatisfactory nature of the evidence furnished by the thermal curves. The position of the first solidus line between FeO and the peritectic composition at P is very tentative. On the heating curve for the 85/15 FeO/MnO mixture, fig. 5, it will be noted that there are three arrests:- 1375°C, 1415°C and 1425°C. The middle point indicates the peritectic reaction, the upper the temperature at which the charge becomes completely molten, but the lower arrest can be taken as a guide in fixing the solidus for the α-solution range, and the line is tentatively indicated as AP.

When the position of the solidus line for the β-solution is considered, a little more definite evidence is furnished by the heating curves for the following compositions, lower arrests occuring at the temperatures indicated:-

Mixture.		Lower arrest temperature in °C.
FeO %.	MnO %.	
10	90	1530
20	80	1495
30	70	1475
45	55	1455.

The last point is rather doubtful.

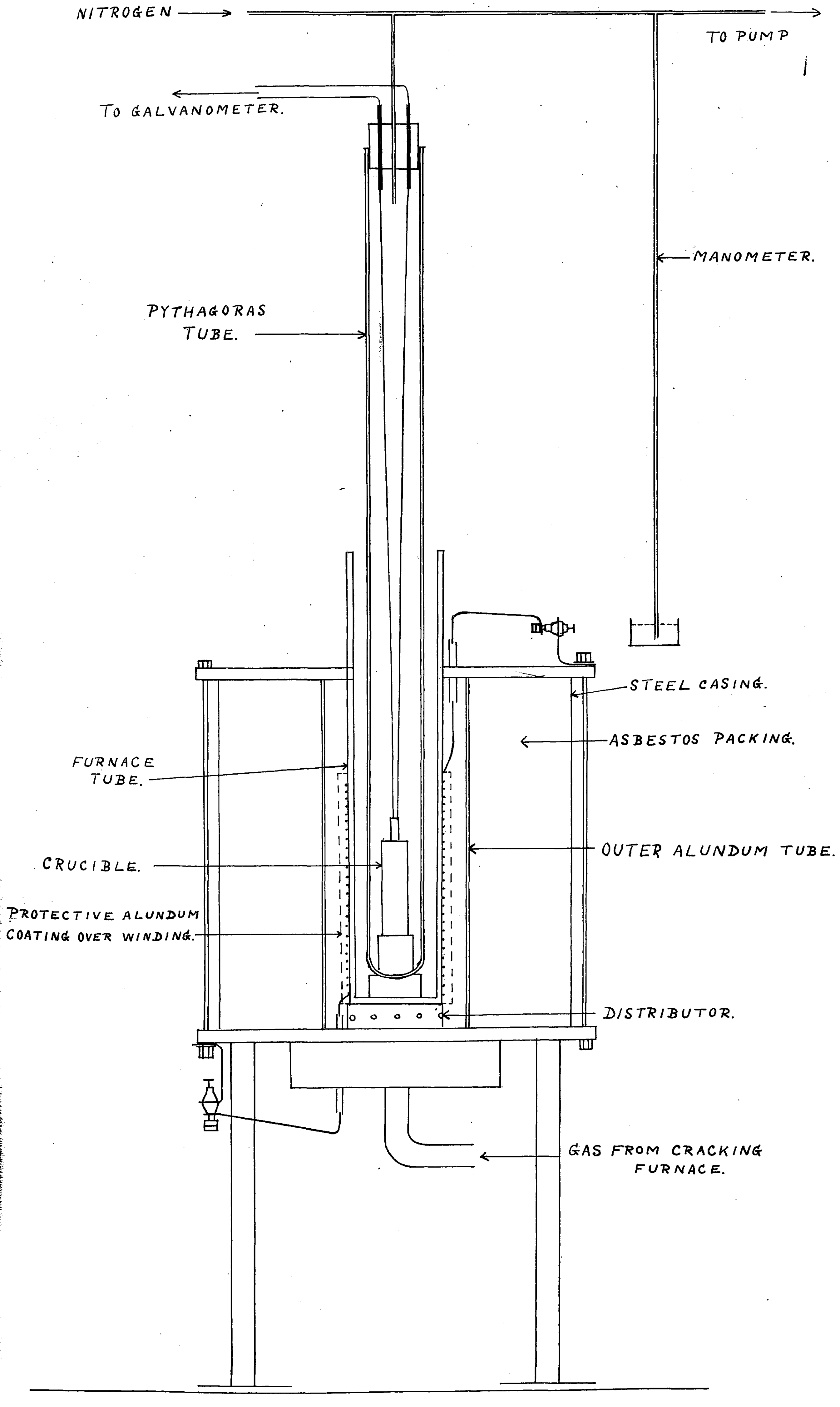
Using these arrests the position of the solidus line for the solution has been indicated as shown by DC.

It was very difficult to obtain pieces of the melt for microscopic examination, and in general all that could be used was a small piece at the end of the thermocouple sheath, which was ground flat, polished and examined.

Those microphotographs which furnish evidence of the two separate phases have already been referred to. Traces of the two separate phases can be observed in the microphotographs for the 35/65 and 20/80 FeO/MnO mixtures, fig. 15 (d) and (e). These compositions actually occur outside the range over which the two constituents exist, as indicated on the diagram. The presence of small amounts of the two constituents can be looked for even at these compositions, owing to the wide gap which exists between the liquidus and solidus. Considerable variations in the composition of liquid and solid during freezing of the melt may be expected and the composition of the residual liquid may quite easily extend into the region of the two constituents.

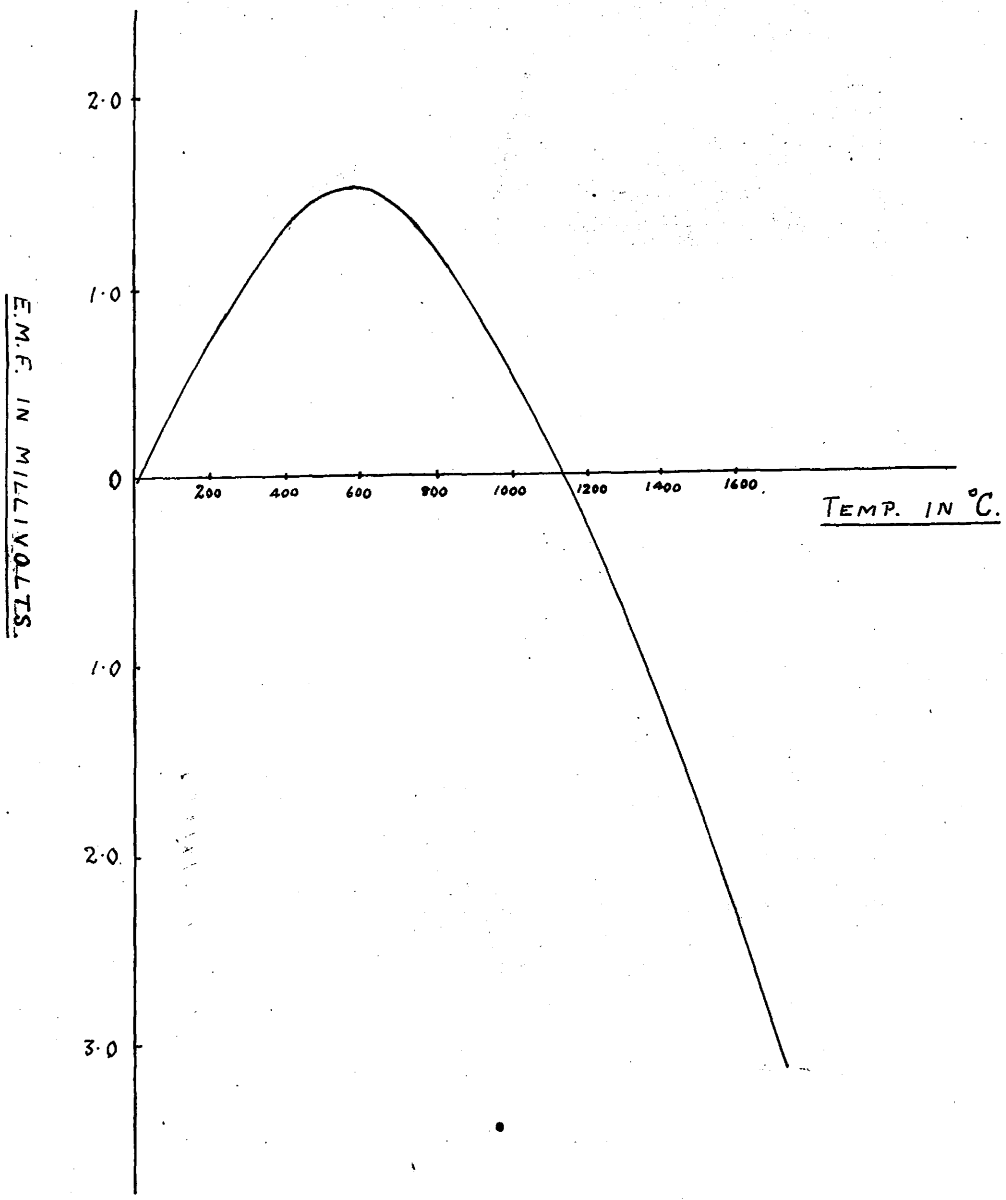
Another feature of interest in the microscopic examination of the higher MnO melts is the occurrence of considerable amounts of a grey glassy material, which may be observed surrounding the grains. Examples of this can be seen in fig. 15 (d) and (e). The amount of this material increases very rapidly in the higher MnO melts and may be correlated with the fact that the arrest points on the cooling curves for these mixtures are very small or non-existent. It may then be easily surmised that crystallisation in these melts does not proceed rapidly and in some cases may be entirely suppressed so giving rise to the presence of this glassy material.

FIG. 1.



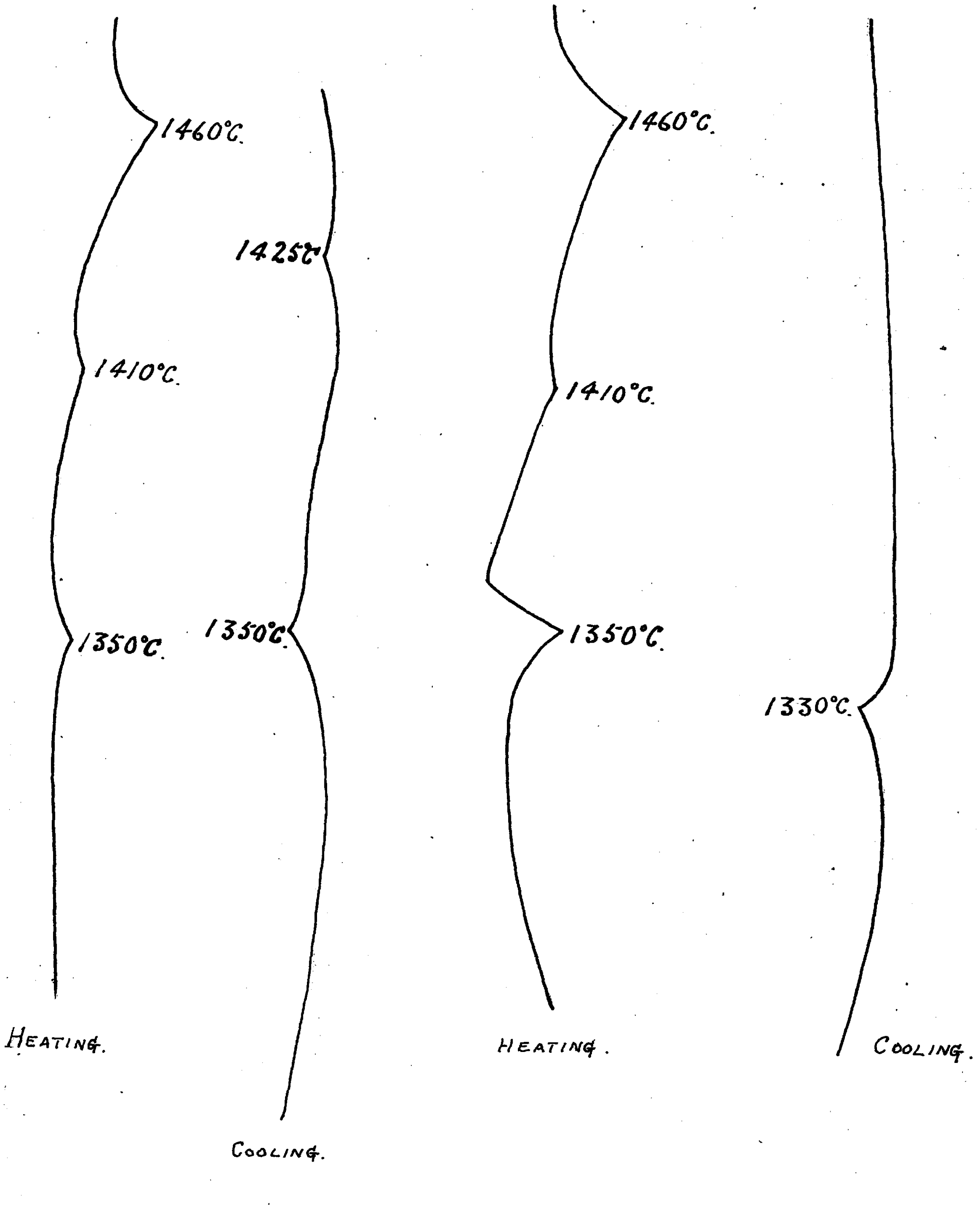
THE MOLYBDENUM-WOUND FURNACE.

Fig. 2



TYPICAL CALIBRATION CURVE FOR A MOLYBDENUM-TUNGSTEN THERMOCOUPLE.

FIG. 3.

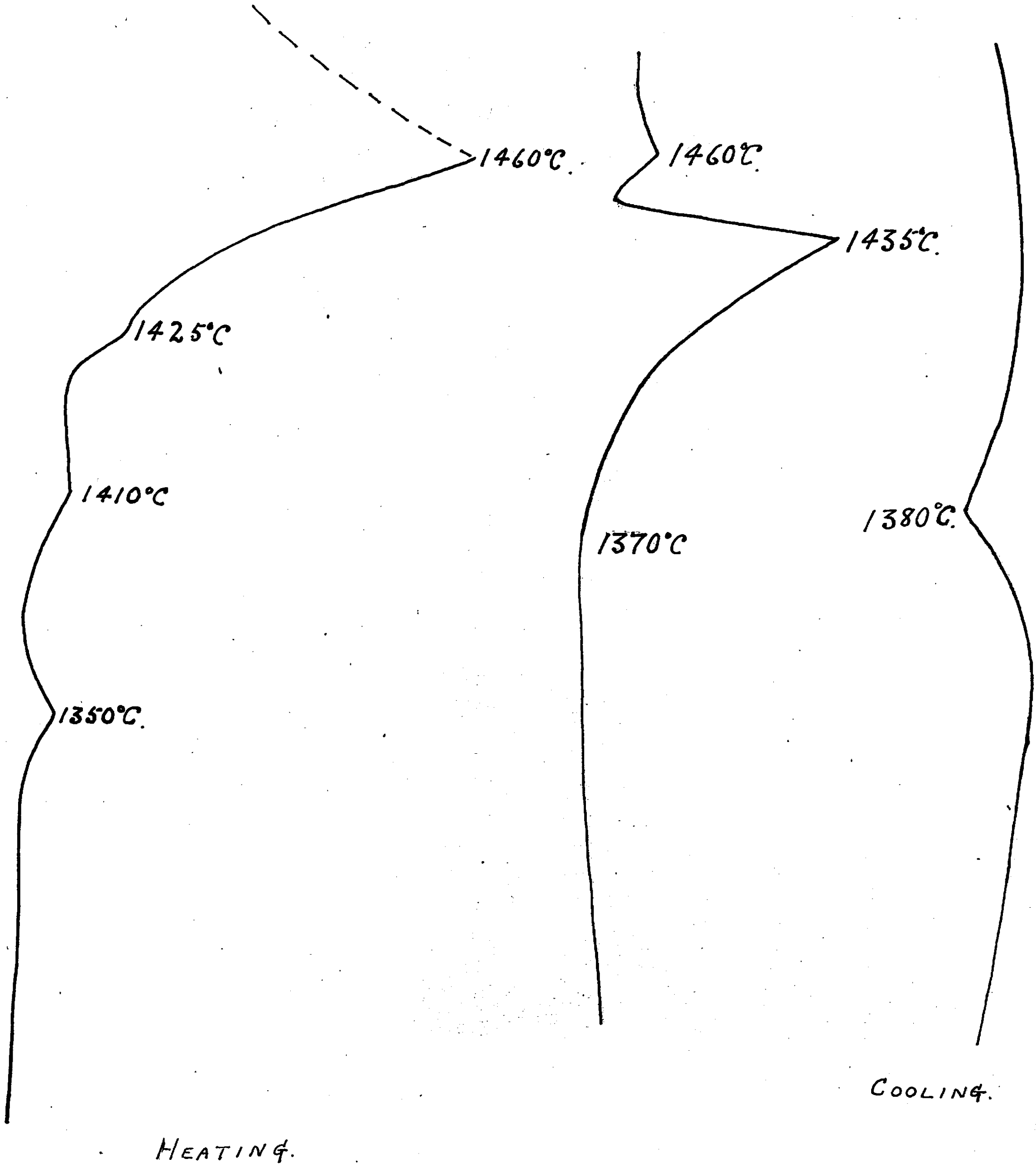


FeO. 100%.

THERMAL CURVES FOR VARIOUS SAMPLES.

ALL CURVES TRACED FROM ORIGINALS BY AN EIDOGRAPH AND REDUCED BY ½.

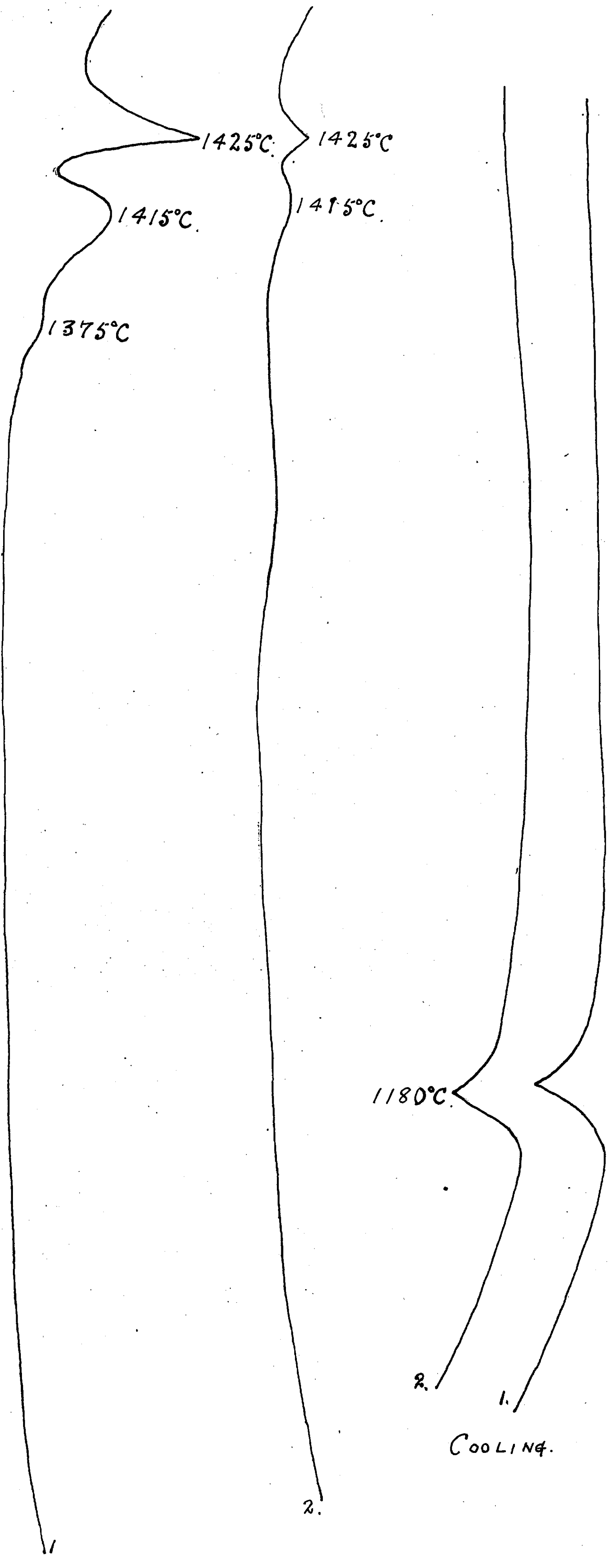
<u>FIG. 4.</u>



FeO. 100%.

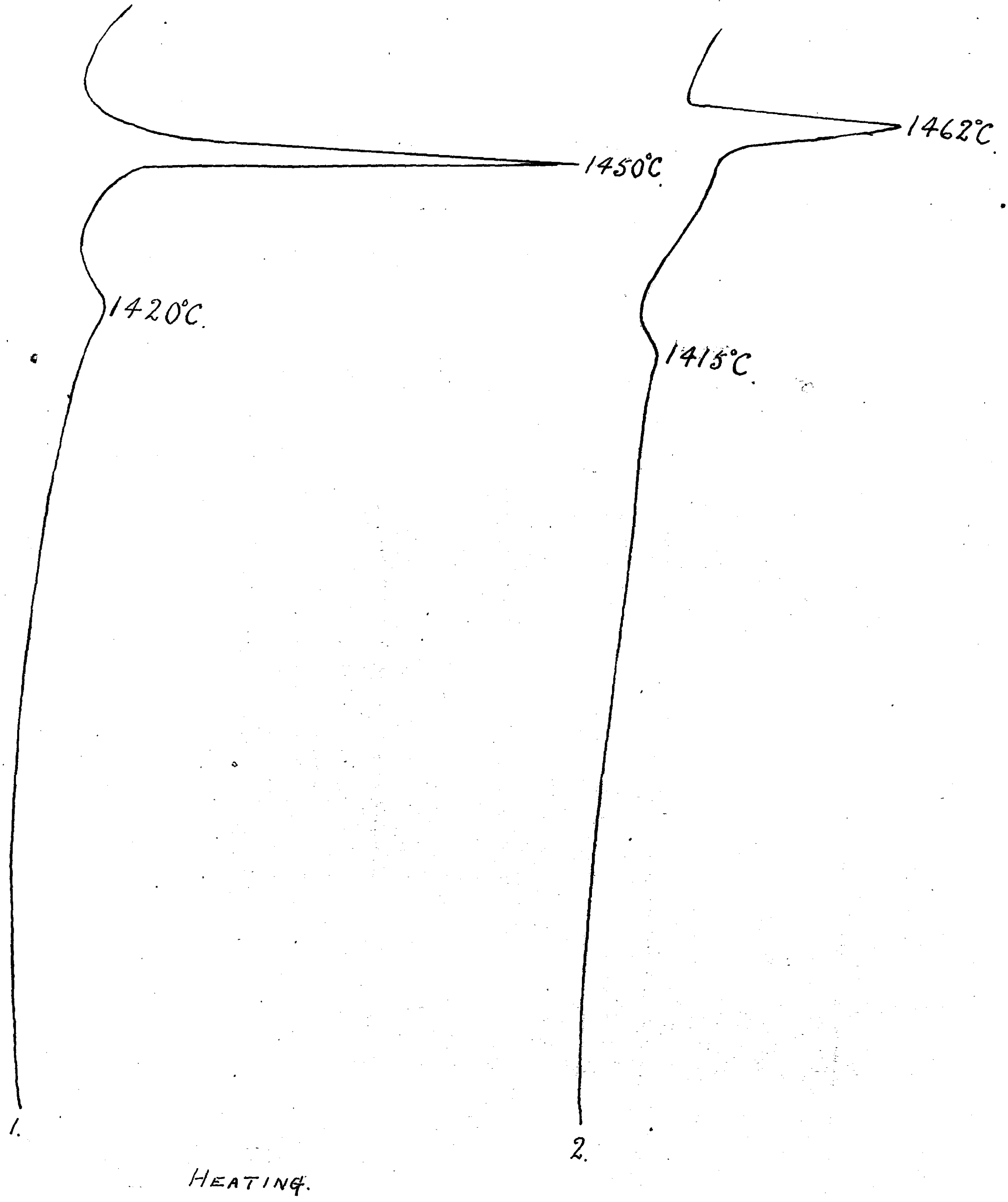
THERMAL CURVES FOR VARIOUS SAMPLES.

Fig. 5



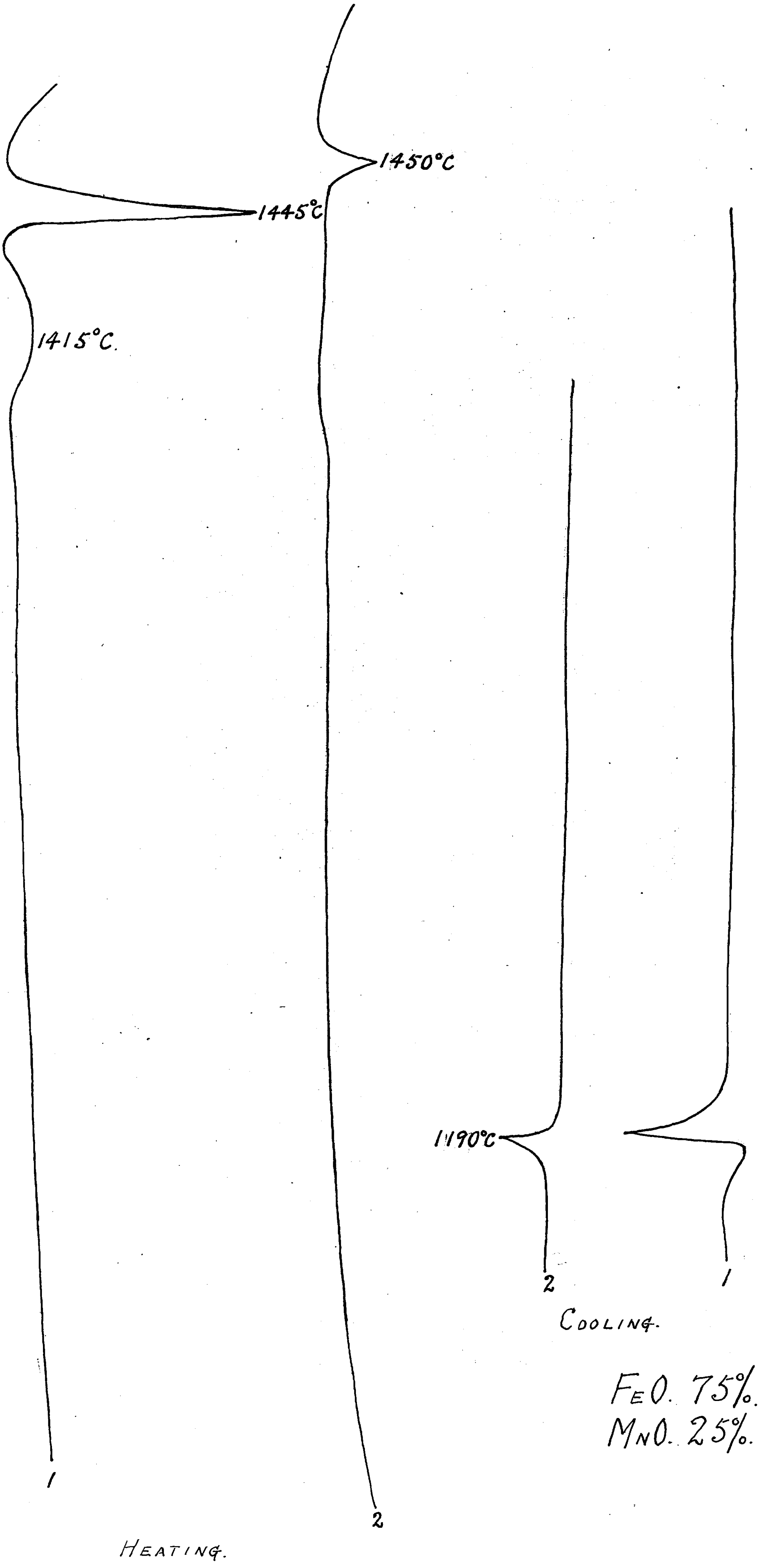
FeO. 85%.
MnO. 15%.

FIG. 6.



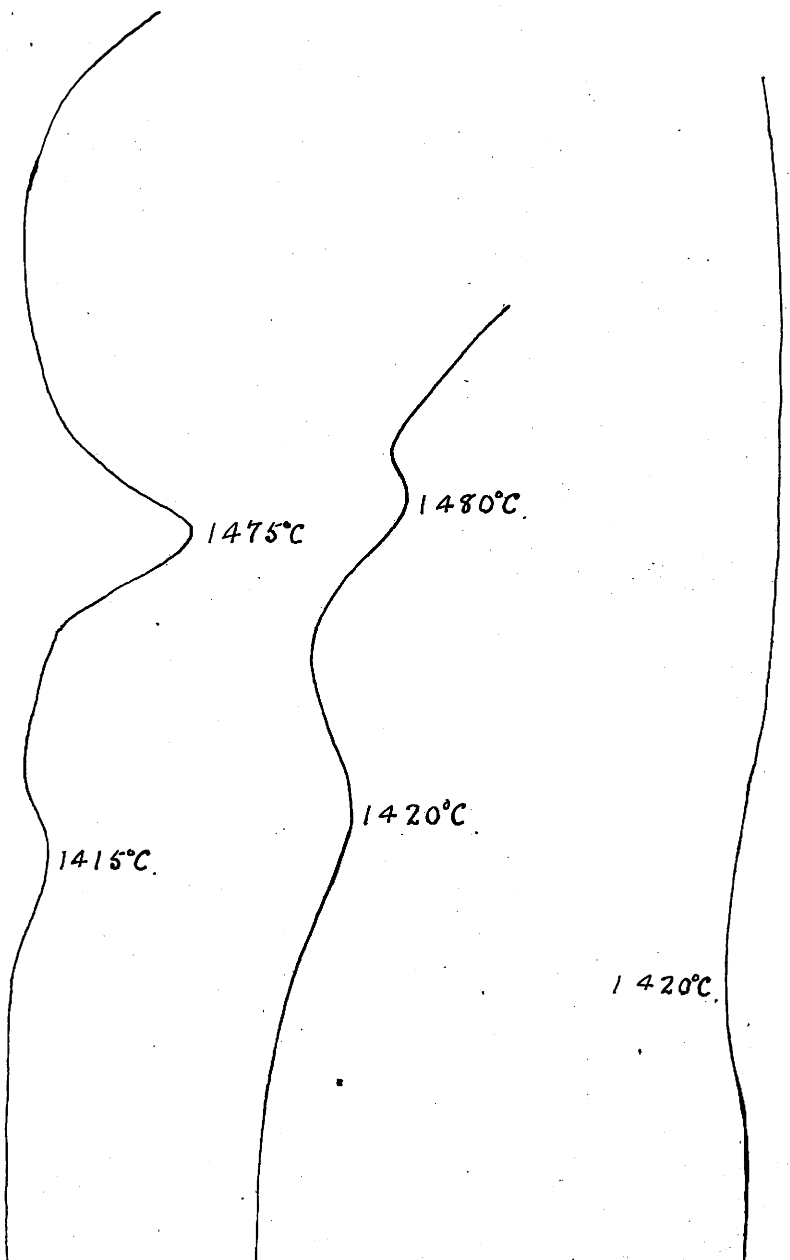
FeO. 80%.
MnO. 20%.

Fig. 4.



FeO. 75%.
MnO. 25%.

Fig. 8.



FeO.. 70%..
MnO.. 30%.

Fig. 9.

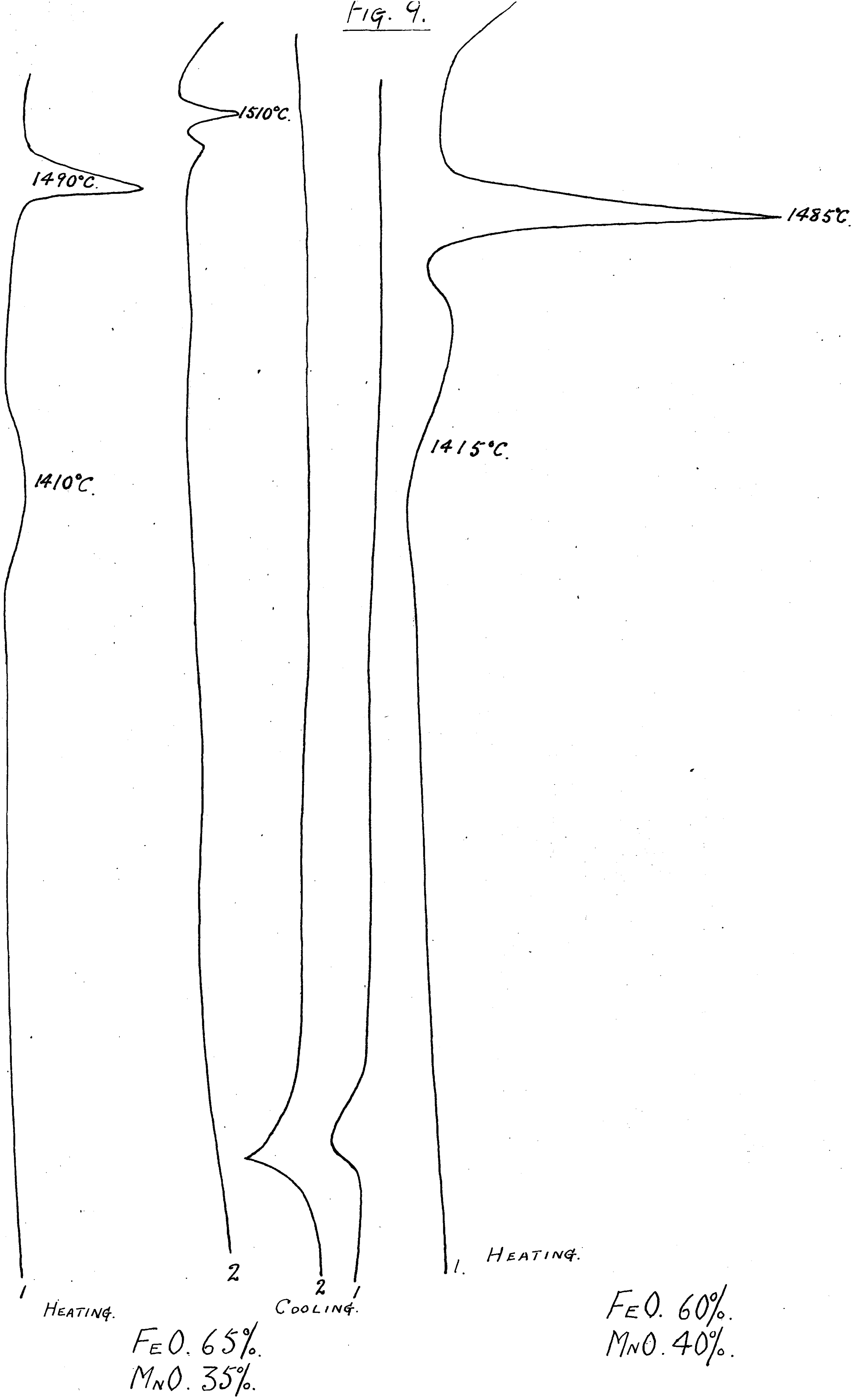
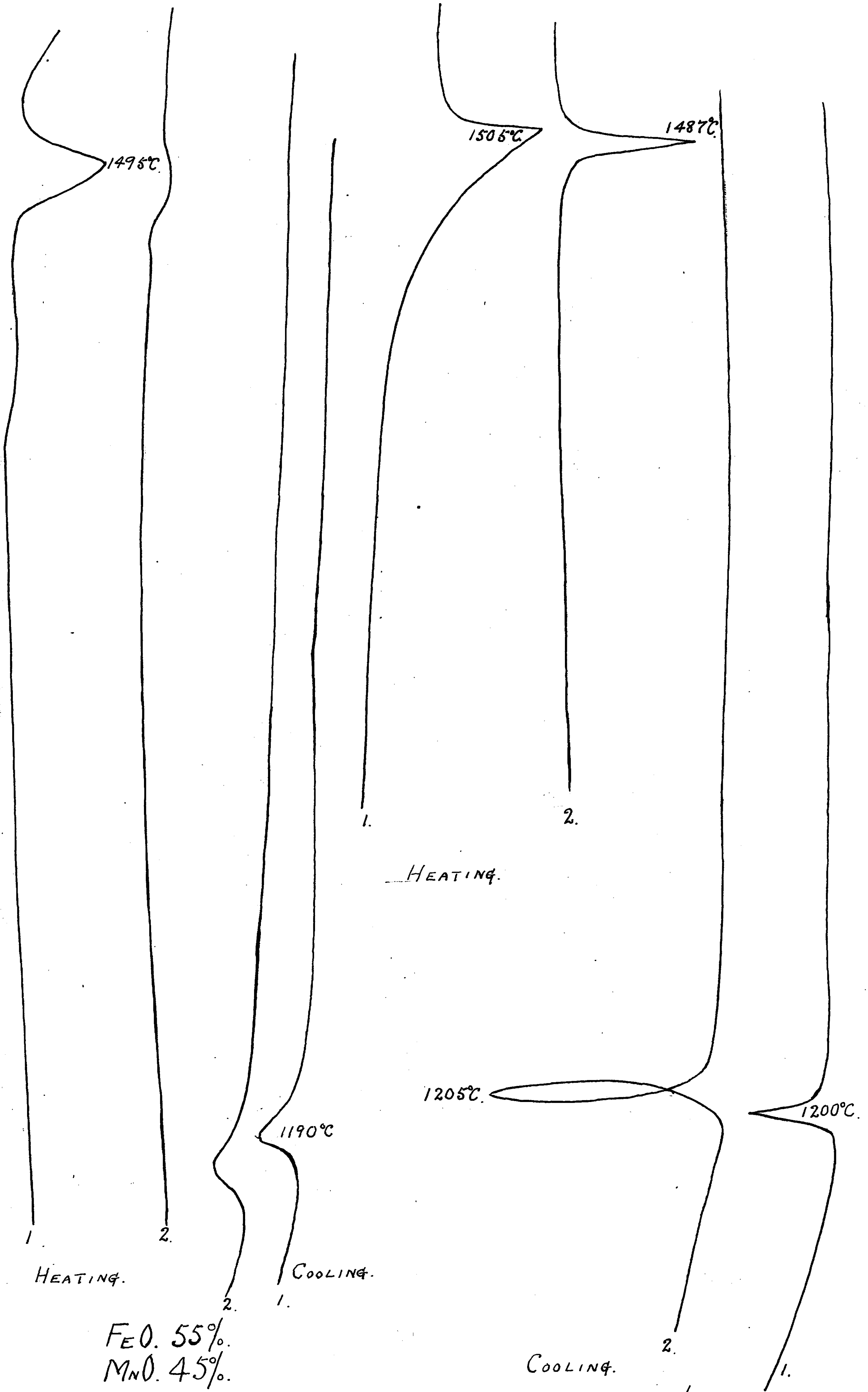

1490°C.
1510°C.
1485°C.
1410°C.
1415°C.
1
2
2
1
1.
Heating.
Cooling.
Heating.
FeO. 65%.
MnO. 35%.
FeO. 60%.
MnO. 40%.

FIG. 10.



FeO. 55%.
MnO. 45%.

FeO. 50%.
MnO. 50%.

FIG. 11.

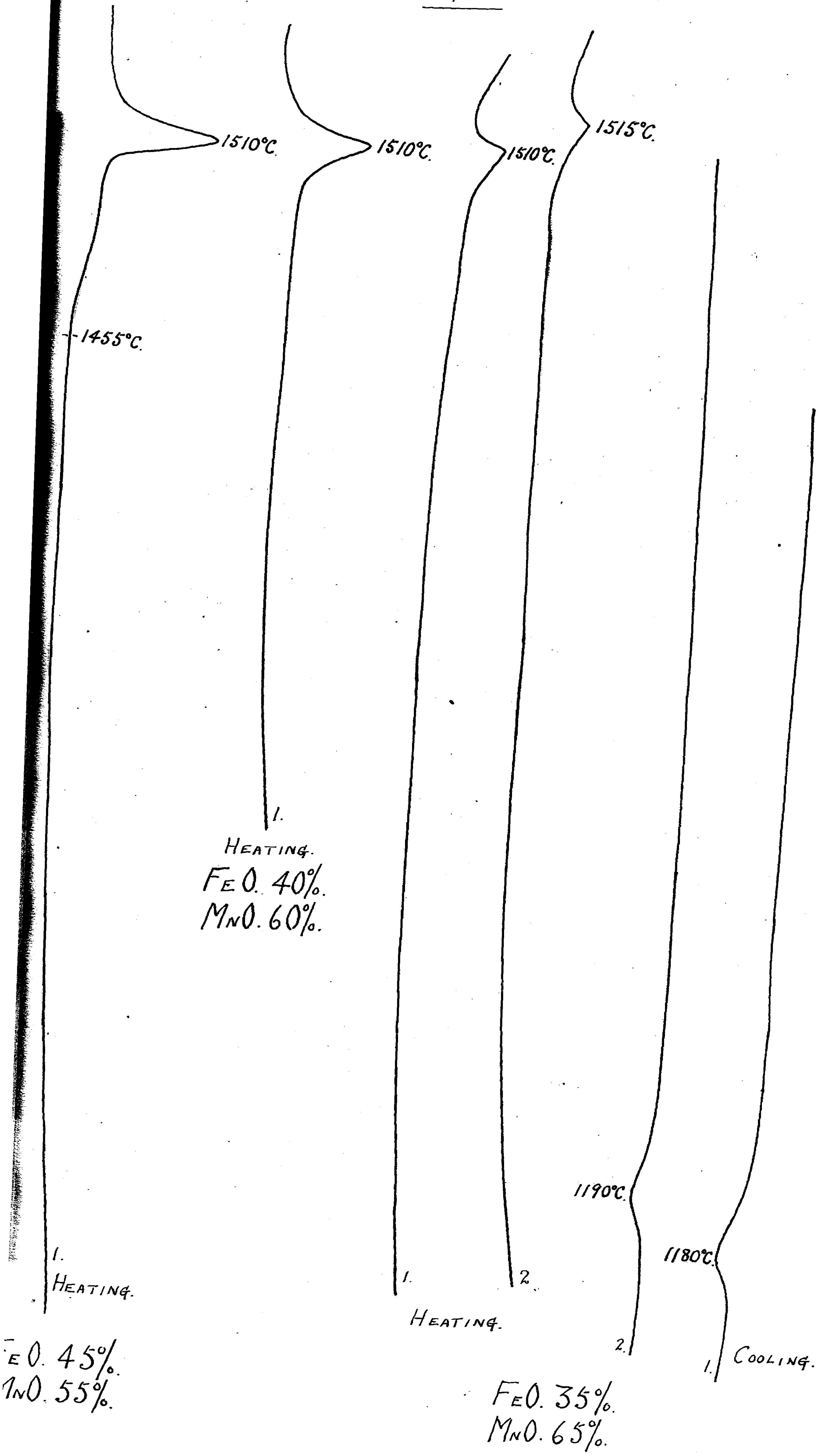

1510°C.
1455°C.
1.
Heating.
eO. 45%.
nO. 55%.
1510°C.
1.
Heating.
FeO. 40%.
MnO. 60%.
1510°C.
1515°C.
1.
2.
Heating.
1190°C.
1180°C.
2.
1.
Cooling.
FeO. 35%.
MnO. 65%.

Fig. 12.

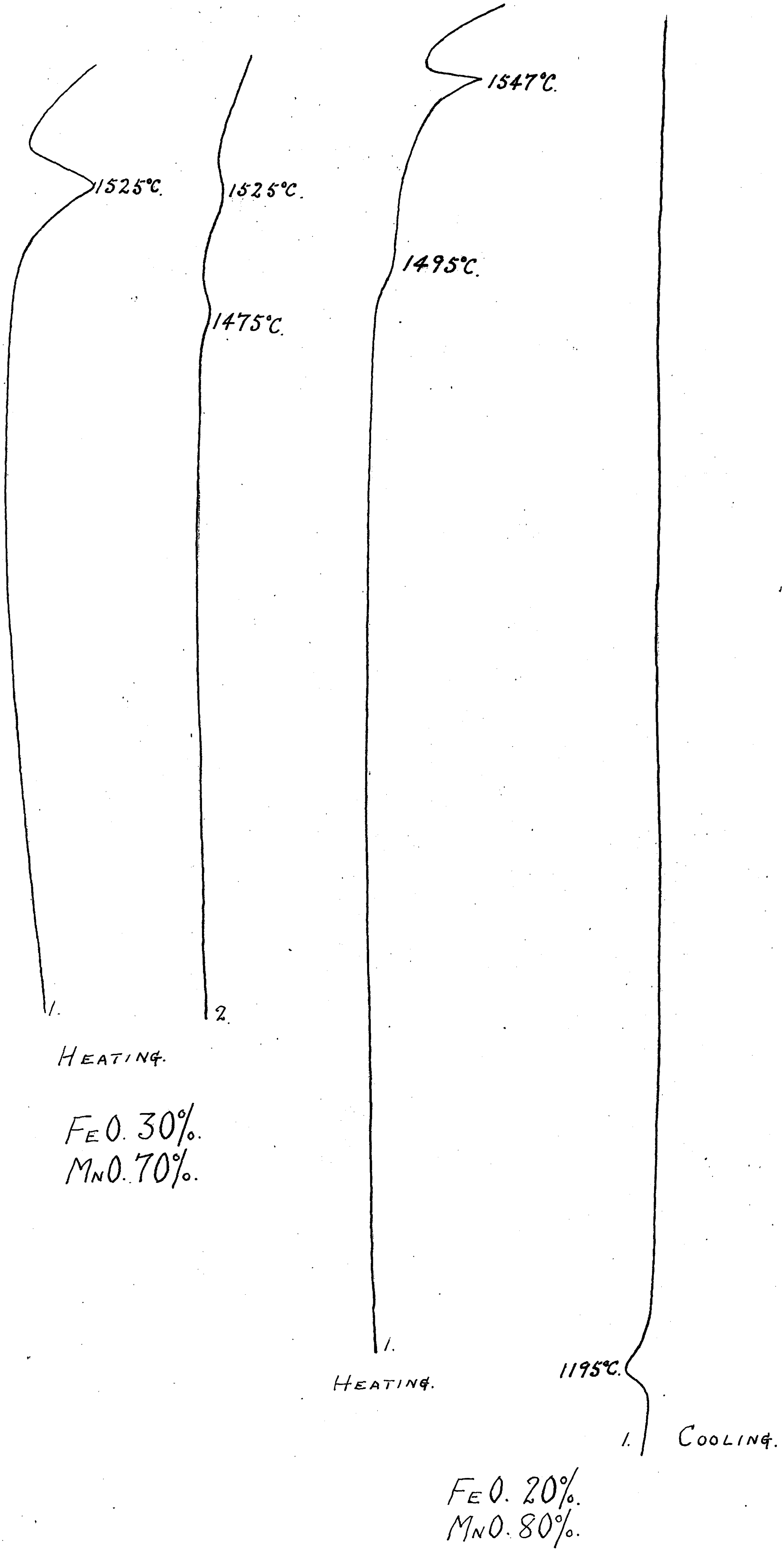
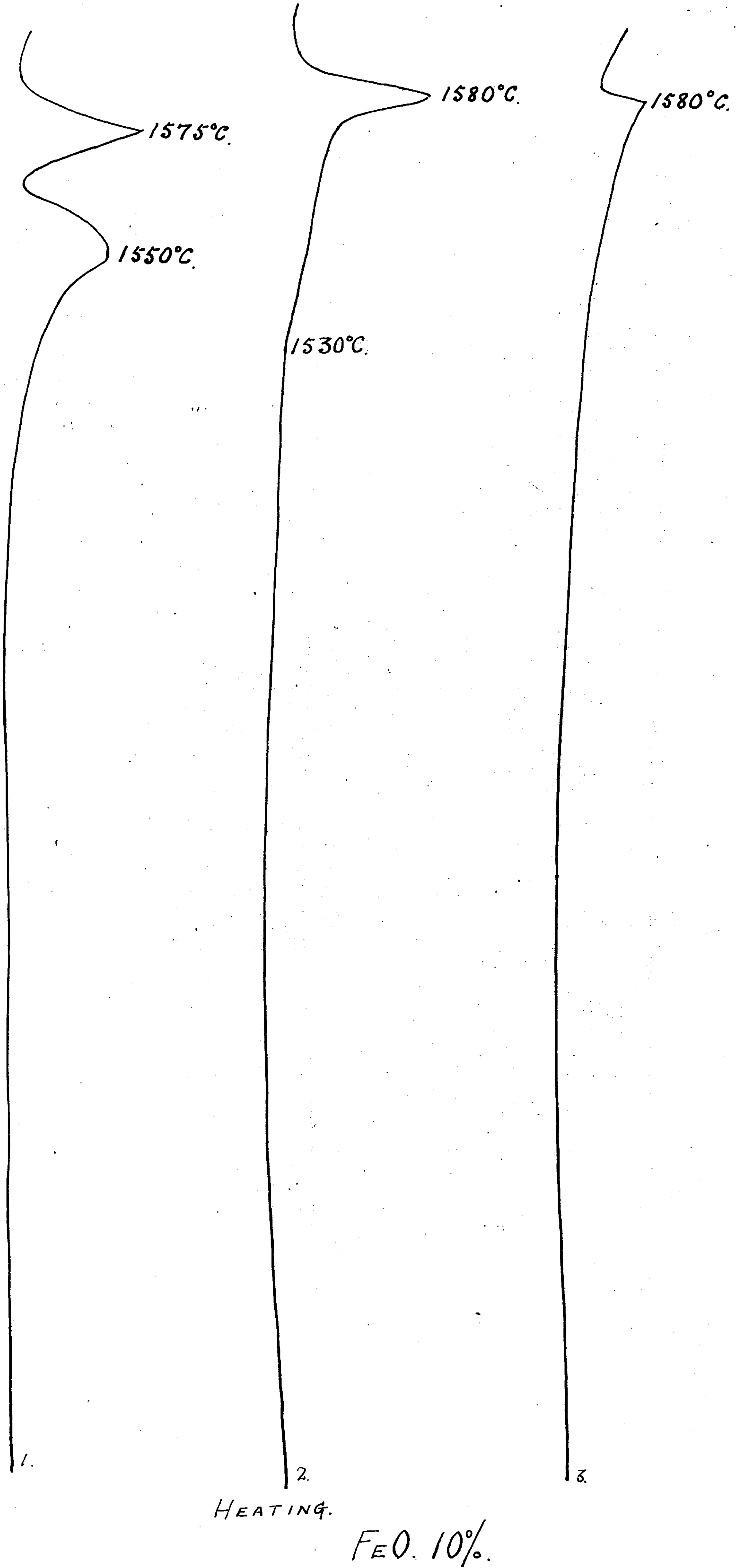

1525°C.
1525°C.
1475°C.
1.
2.
Heating.
FeO. 30%.
MnO. 70%.
1547°C.
1495°C.
1.
Heating.
1195°C.
1.
Cooling.
FeO. 20%.
MnO. 80%.

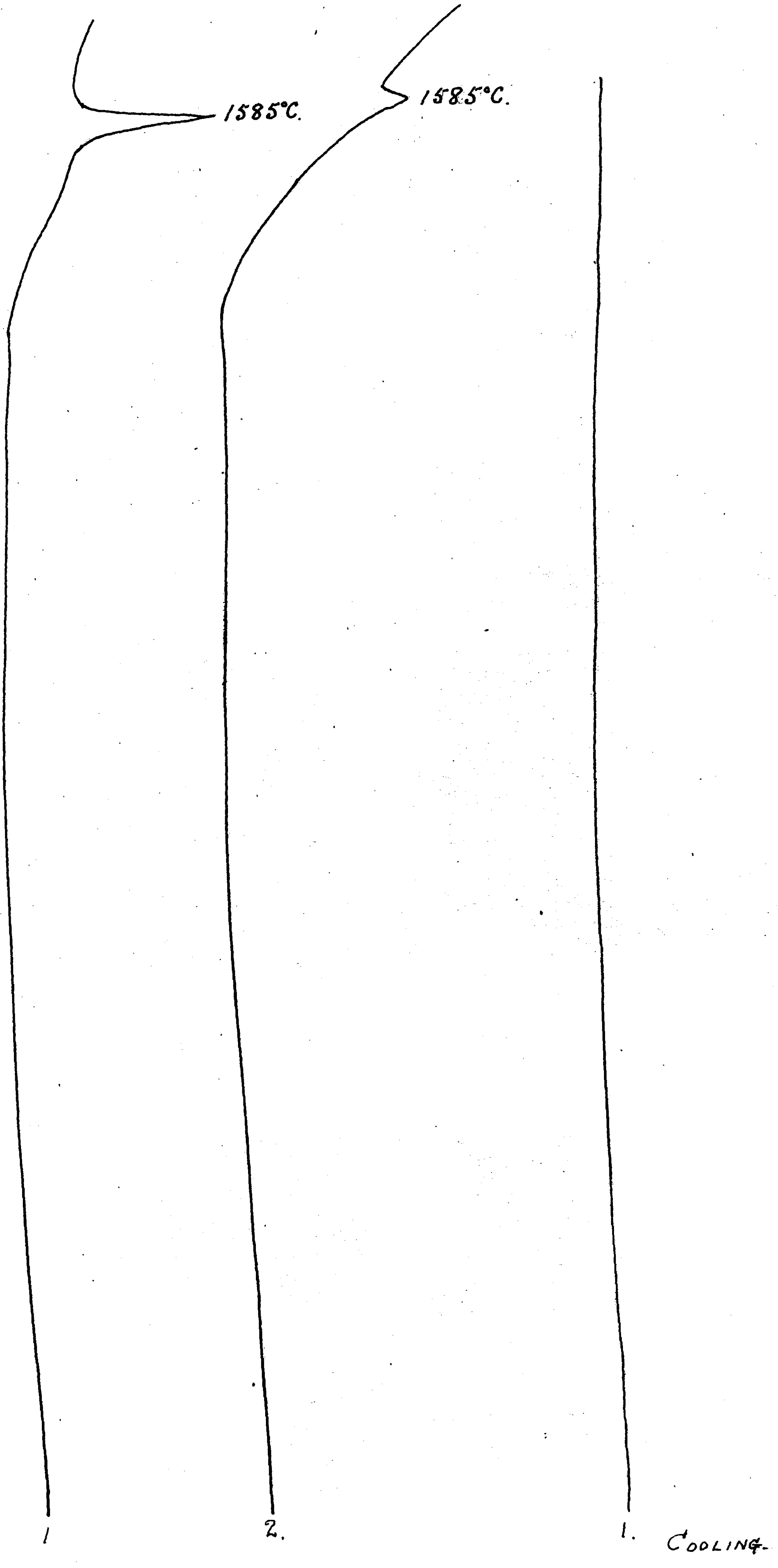
FIG. 13.



HEATING.

FeO. 10%.
MnO. 90%.

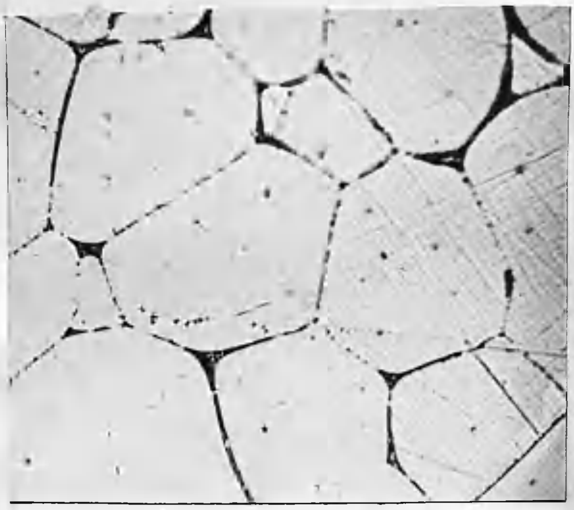
Fig. 14



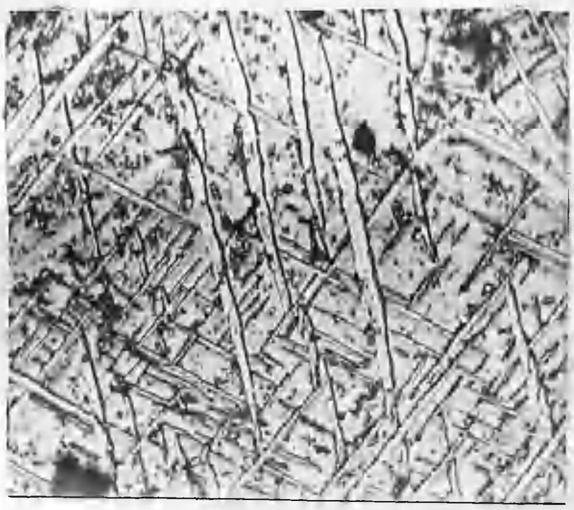
MnO. 100%.

Fig. 15.

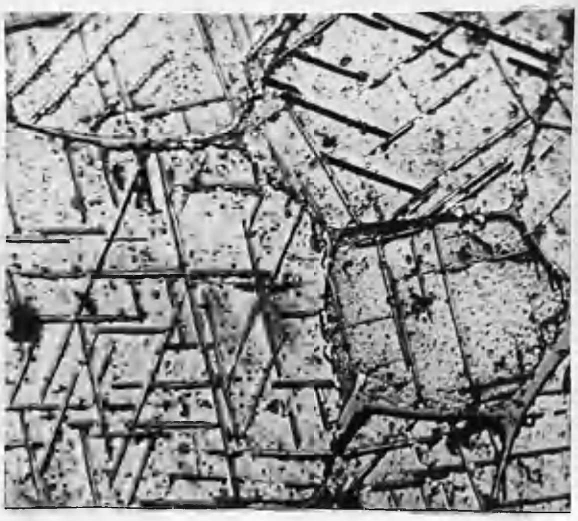
(a) FeO × 500.



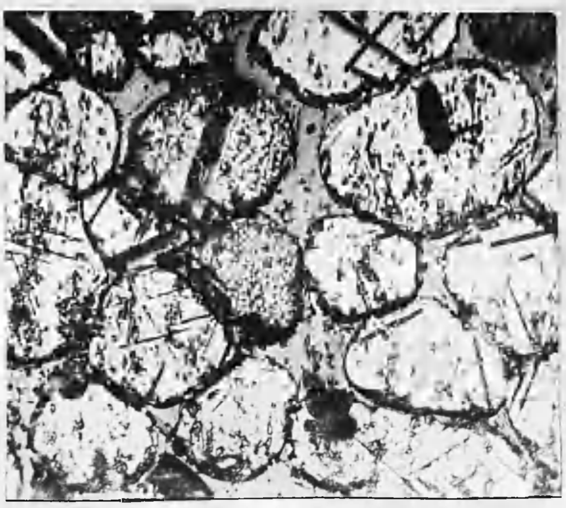
(b) FeO 90%. MnO 10%.
× 250.



(c) FeO 50%. MnO 50%.
× 500.



(d) FeO 35%. MnO 65%.
×350.

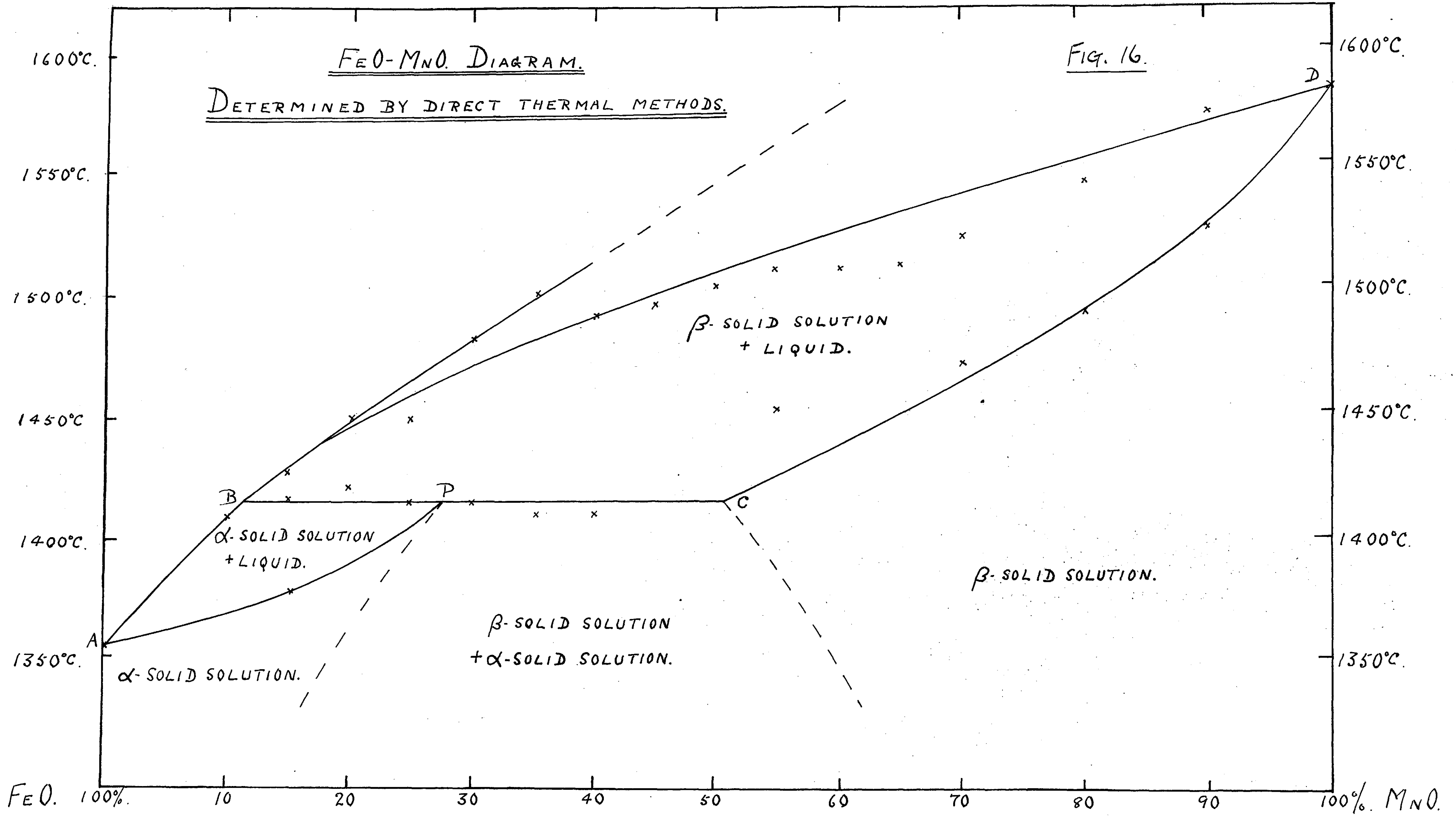


(e). FeO 20%. MnO 80%.
× 300.

FeO-MnO Diagram.

Determined by direct thermal methods.

Fig. 16.



Section II. The Investigation of the Thermal Equilibrium Diagram of the System $MnO-SiO_2$.

Tentative diagrams for this system have been put forward by Doerinckel (Metallurgie, VIII. 201. 1911), Herty and collaborators (Metals and Alloys, Dec. 1930. p. 883) and Benedicks and Lofquist have constructed a provisional diagram, which is included in their book "Non-metallic inclusions in iron and steel".

In all cases only the lower melting point mixtures have been at all accurately investigated. A number of the of the results seem decidedly speculative and it would appear that the whole system would amply bear more detailed investigation.

It was decided to attempt to work out the system as completely as possible. In the earlier stages of the investigation the methods of attack and of working on the problem were the same as in the previous section. The same type of furnace and cracking train, pythagoras tube and thermocouple were employed.

The MnO used was prepared in exactly the same way as formerly. The silica used was in the form of very fine white sand, guaranteed to be about 99% pure.

The problem of finding a suitable refractory again cropped up. Magnesia, lime and fireclay crucibles were all ruled out owing to interaction with the melt. Alundum crucibles were also very severely corroded by the melts and were of very little use. Carbon crucibles and carbon thermocouple sheaths were employed in the early stages. The crucibles were cylindrical in shape and were about ¾ in. internal diam. 1¼ in. external diam. and 2½ in. in height. The sheaths were made by drilling holes 3/16 in. diam. in carbon electrodes 5/16 in.diam

It was found that, particularly with the melts richer in MnO, beads of metallic manganese collected in the bottom of the crucible. This occurred when melting was carried out in a Pythagoras tube in an atmosphere of nitrogen. There must, therefore, be a very appreciable reduction of MnO by carbon at these high temperatures.

As the use of carbon crucibles would have resulted in a continual change in the composition of the melt, they were finally discarded. But quite a number of melts were made and a large number of heating and cooling curves obtained.

Salamander crucibles and carbon sheaths were next used. These salamander crucibles are a mixture of carbon and fireclay and the reduction of MnO was still very appreciable. After a number of melts had been made the use of these crucibles was discontinued.

Various attempts were made to use metallic crucibles, e.g. iron and nickel, for the lower melting point mixtures but in every case these were very badly corroded.

Doerinckel in his investigations on this system used platinum crucibles, but it was found that a few melts at high temperatures caused such grain-growth in the platinum, that the slightest rough handling broke the crucible and the removal of the melted material was impossible. The problem of finding a satisfactory refractory material seemed almost insoluble.

Two other very serious difficulties were experienced. First, it was almost impossible to obtain heating curves which showed any decided thermal arrests. In this connection the curves obtained are shown in figs. 17-27. The absence of any decided arrests is no doubt due to the very sluggish nature of all phase changes in silica or compounds containing silica. In an attempt to remedy this the thermocouple sheaths were made as thin as possible, but very little improvement was noted. In quite a number of experiments the junction of the thermocouple was inserted straight into the melt, but even this had practically no effect. It was noted that the wires of the couple were unaffected by the melt and remained bright and clean.

A second difficulty lay in the fact that the furnace used was not capable of reaching a sufficiently high temperature to completely melt the mixtures containing higher percentages of MnO. This was not suspected for a time, but a few thin sections

sections/ of some of the melts were prepared for examination by transmitted light, and the presence of unmelted particles of MnO was clearly demonstrated.

It became evident at this stage of the work that the available methods were insufficient and that if the system were to be completed very marked progress must take place along three lines

(a) In the provision of furnaces capable of attaining much higher temperatures than formerly.

(b) In the discovery of a refractory material which would contain the melts at these high temperatures without contamination or change in composition of the melt taking place.

(c) In the perfection of some method of thermal measurement which would allow those very small or very long drawn out phase changes to be measured accurately.

It will be shown how each of these requirements was met, to some extent at least, in the course of the work.

(a) The provision of furnaces capable of attaining much higher temperatures was the easiest of the problems. A molybdenum-wound furnace of the type already described was used. The use of a Pythagoras tube was dispensed with. The molybdenum sheet grid was fixed to the outside of an alundum sheath. This allowed the internal diameter of the furnace tube to be reduced from 3 to 2½ ins. The thickness of the wall of the tube was about 3/32 in. and the efficienc of the furnace was very markedly increased by making use of the fact mentioned previously, namely, forming a very thick coating of alundum (½-¾ in.) over the winding. The sheath carrying the grid was about 16 in. long with an internal diam. of about 2 in. The walls were made as thin as possible, and flanges about 2½ in. external diam. were fitted to the top and bottom; these fixed the position of the sheath in the furnace tube and left a small clearance between the furnace tube and the outside wall of the sheath for the molybdenum sheet. The bottom flange was about ½ in. long and the top one about 4 in. long. A furnace constructed in this fashion lasted much longer than those used formerly and a recorded temperature of 1865°C was obtained in one instance.

(b) To obtain a satisfactory refractory material was a more difficult problem. A clue to this was furnished when it was noted that the thermocouple junction was unaffected by contact with the molten materials, and the idea of using either molybdenum or tungsten as a refractory material presented itself. It was thought that it would be a more feasible idea to try molybdenum first. An attempt was made to procure molybdenum crucibles, but these are not manufactured by any firm. The only form, suitable for the purpose in which it could be obtained was as solid rod, the thickest of which was only 11.5 m.m. in diam. A supply of this rod was procured and lengths ($1\frac{1}{4}$ in.) were cut off and drilled. The crucibles so formed were about 3.1 cms. long, 8 m.m. internal diam. and 11.5 m.m. external diam. About 3 m.m. of solid material was left undrilled at the bottom. A small lid, with a flange, was machined to fit tightly on to the top of the crucible and two holes were drilled in it to allow the thermocouple leads to pass through. The crucibles contained about 2 gms. of material.

Using these crucibles for melting no contamination of the fused material could be detected even by spectrographic tests.

Investigations were then carried out with the materials contained in these crucibles, using the type of furnace just described. With the very small weight of charge which could be used the difficulty of obtaining definite thermal arrest points was as great as ever. Conditions (a) and (b) noted above had been satisfied. A sufficiently high temperature could be obtained, and a refractory material which held the molten materials without change in composition or contamination taking place had been found.

It would probably be desirable to survey the data which had been obtained up to this point relating to the various mixtures of MnO and SiO_2.

Discussion of the results obtained in the $MnO-SiO_2$ determinations by the direct thermal method.

Thermal curves, obtained by the methods just described are shown in figs. 17-27. The data available is obviously not very satisfactory and the arrests noted in the curves are in many cases so small that it was only due to the fact that they occurred with such constancy on a number of curves that their significance was realised.

Included in the system are the two well-known geological minerals:- Tephroite (the bisilicate, $2MnO.SiO_2$) and Rhodonite (the monosilicate; $MnO.SiO_2$). Tephroite contains 29.5% silica and 70.5% MnO, rhodonite contains 45.7% silica and 54.3% MnO.

In considering the thermal curves for these substances as shown in figs. 20 and 25, it will at once be evident that neither gives the arrests characteristic of the simple solid to liquid phase change of a pure substance.

In the case of rhodonite, fig. 25 there is a long continued arrest beginning at 1210°C, reaching a maximum at 1275°C and tailing off to a finish at about 1320°C. In order to determine the exact significance of these arrests; a charge of rhodonite was ground up and heated to just above the 1275°C arrest and allowed to cool. The thermal curves obtained are shown in fig. 26. The arrest at 1275°C is still in evidence and there is quite a pronounced arrest on the cooling curve. Subsequent examination showed that the charge had never been properly molten. It would then appear that this arrest at 1275°C must mark the occurrence of a peritectic reaction and that rhodonite has not a true melting point but dissociates at 1275°C into free silica and a rich MnO phase.

A similar state of affairs seems to exist in the case of tephroite. There is a trace of an arrest at 1210°C, a more pronounced arrest at 1325°C and the final arrest at 1375°C will mark the temperature at which the charge becomes completely molten. It may be reasonably assumed that tephroite also dissociates before melting. Free MnO and a silica rich liquid being formed about 1320-1330°C.

A well-marked arrest at 1320-1330°C, corresponding to the peritectic reaction is found to occur on the heating curves for mixtures containing from 10-33% silica, figs. 18,19 and 20. The slope of the liquidus for this part of the diagram is very steep and a wide gap exists between it and the solidus and it is very difficult to arrive at any definite conclusions regarding the exact position of the liquidus line. A very small and indefinite arrest at about 1580°C on the 85/15 MnO/SiO_2 mixture is the highest temperature at which evidence for the position of the liquidus is to be found by these methods. The following are the upper arrests for the mixtures within this region:-

Melt.		Upper arrest temperature in °C.
MnO %.	SiO_2%.	
85	15	1582
75	25	1475
70.5	20.5	1375.

The position of the liquidus has been arrived at from these points.

In mixtures containing more than 46% silica the arrest at 1275°C, corresponding to the rhodonite peritectic reaction is evident on the thermal curves, fig. 27. Two mixtures in this range the 50/50 and 40/60 MnO/SiO_2, were investigated; in both cases there are arrests at about 1275°C, but upper points corresponding to the position of the liquidus could not be detected. In the light of the results described in section III, it is now believed that in the higher temperature regions of these compositions there appears to be the formation of two immiscible liquids, and the thermal arrests will necessarily be so small in magnitude and the temperatures so high that they cannot be detected by the present methods.

Between 29.5% and 45.8% SiO_2, representing the compositions of tephroite and rhodonite respectively there is a eutectic range. Mixtures within these limits of composition consist, after solidification, of a mixture of tephroite and rhodonite.

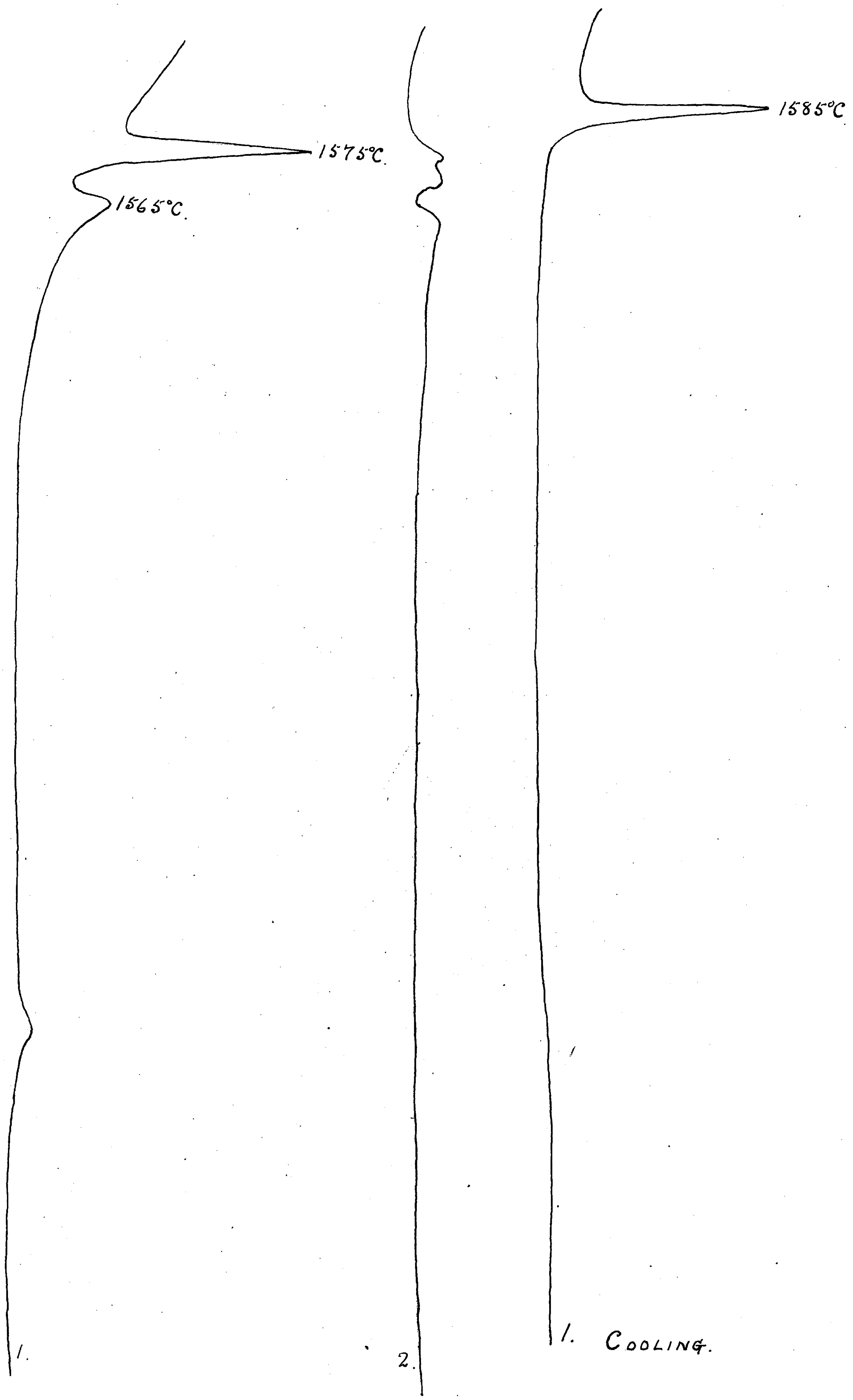
The eutectic temperature occurs about 1210°C. See the lower arrest points on the curves in figs. 21, 23 and 24. The eutectic composition is about 37.5% SiO_2.

An unexpected feature of the diagram is the deep narrow trough which is formed by the liquidus in the eutectic region. The slope of the liquidus on either side of the eutectic composition is very steep, but has been fairly well established.

In summing up, it may be said that the portion of the diagram around the eutectic has been provisionally fixed, but from about 50-100% SiO_2 very little definite data has been obtained. On the MnO rich side of the diagram the same uncertainty exists and the position of the liquidus line is based on rather speculative evidence, especially above 75% MnO.

The diagram which has been tentatively constructed from the consideration of the foregoing data is shown in fig. 28.

FIG. 14.



Heating.

MnO. 95%.
SiO_2. 5%.

MnO. 100%.

Melting carried out in alundum crucibles using alundum thermocouple sheaths.

FIG. 18.

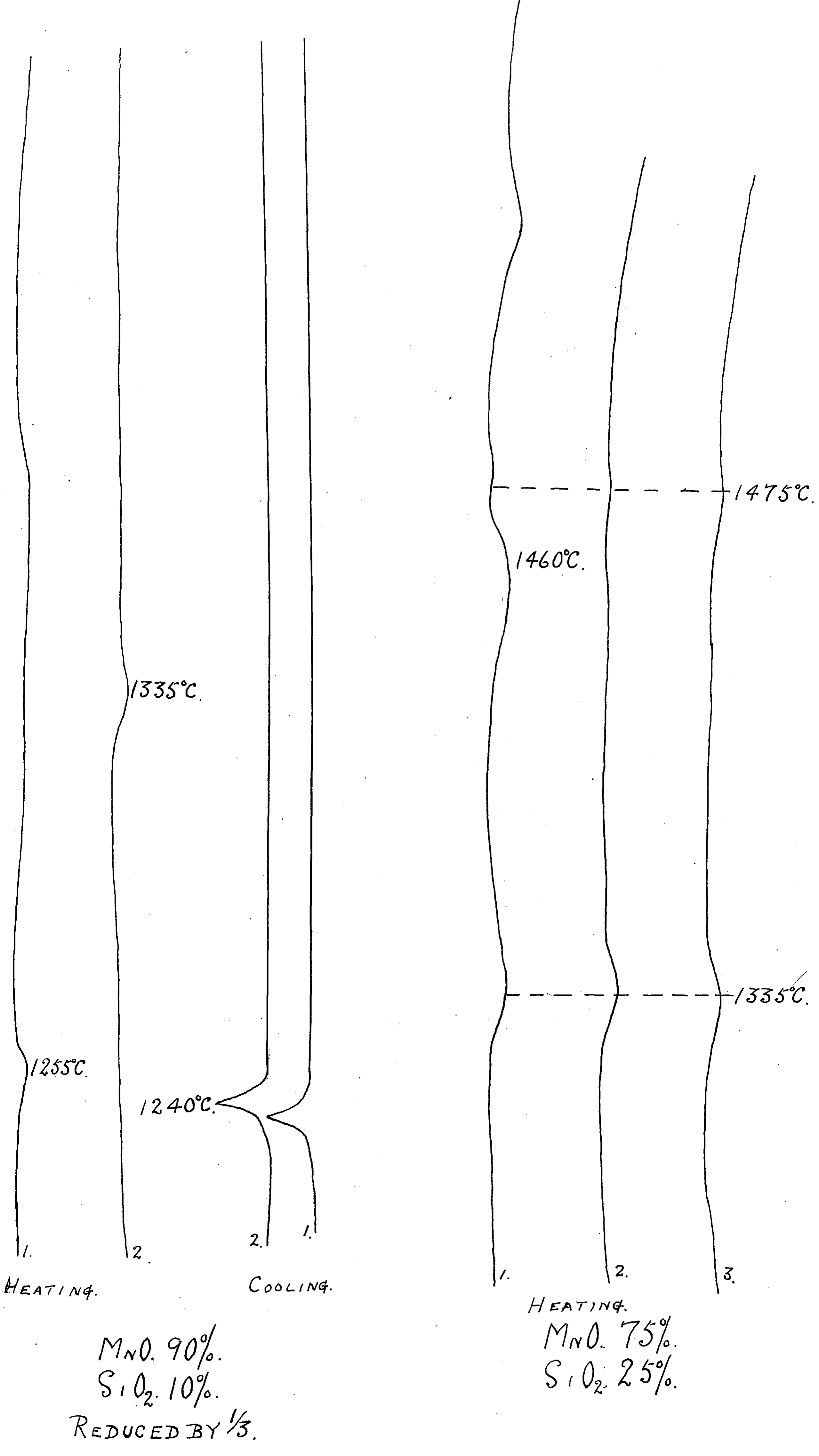
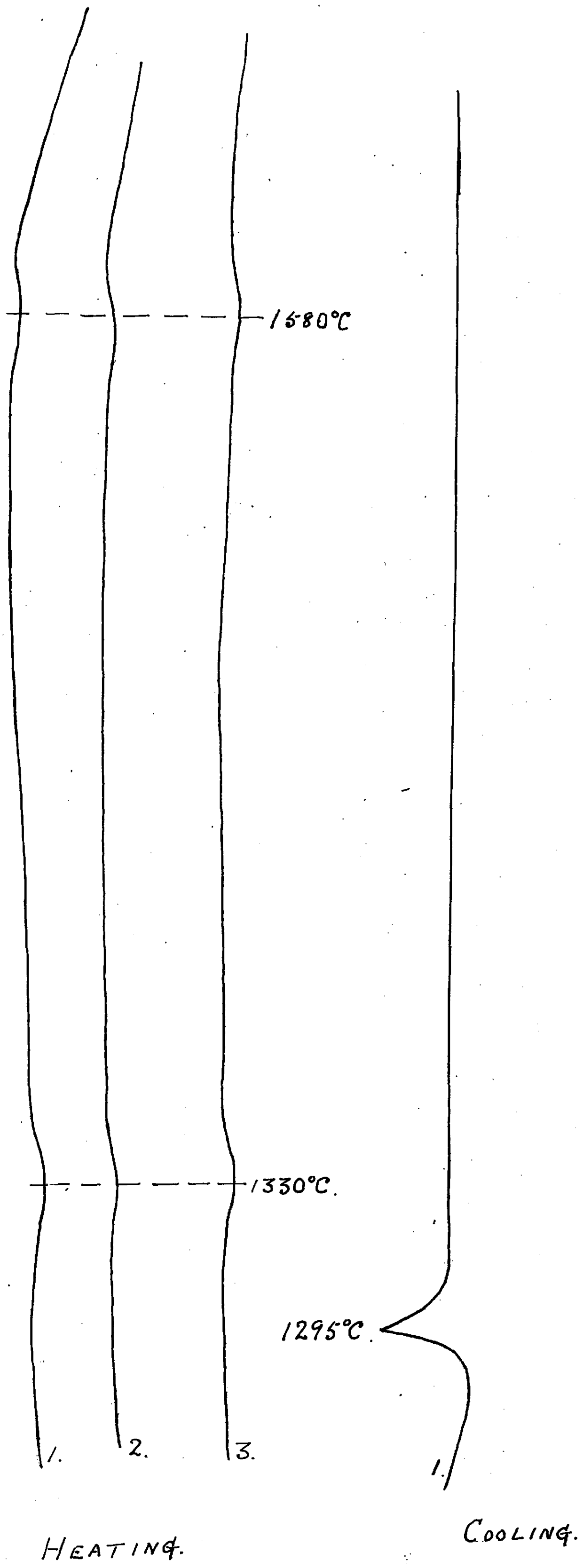
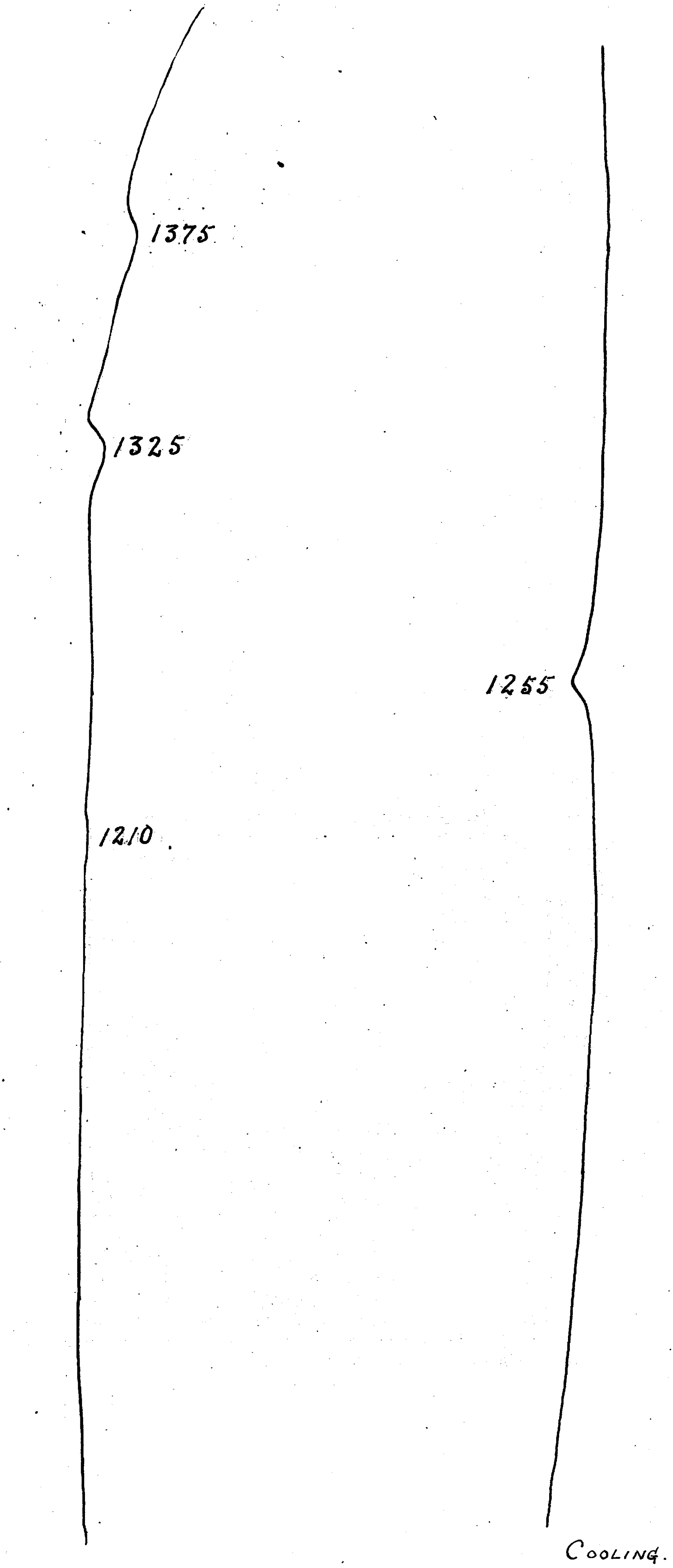

1335°C.
1255°C.
1240°C.
1.
2
2.
1.
HEATING.
COOLING.
MnO. 90%.
SiO_2. 10%.
REDUCED BY 1/3.
1475°C.
1460°C.
1335°C.
1.
2.
3.
HEATING.
MnO. 75%.
SiO_2. 25%.

FIG. 19.



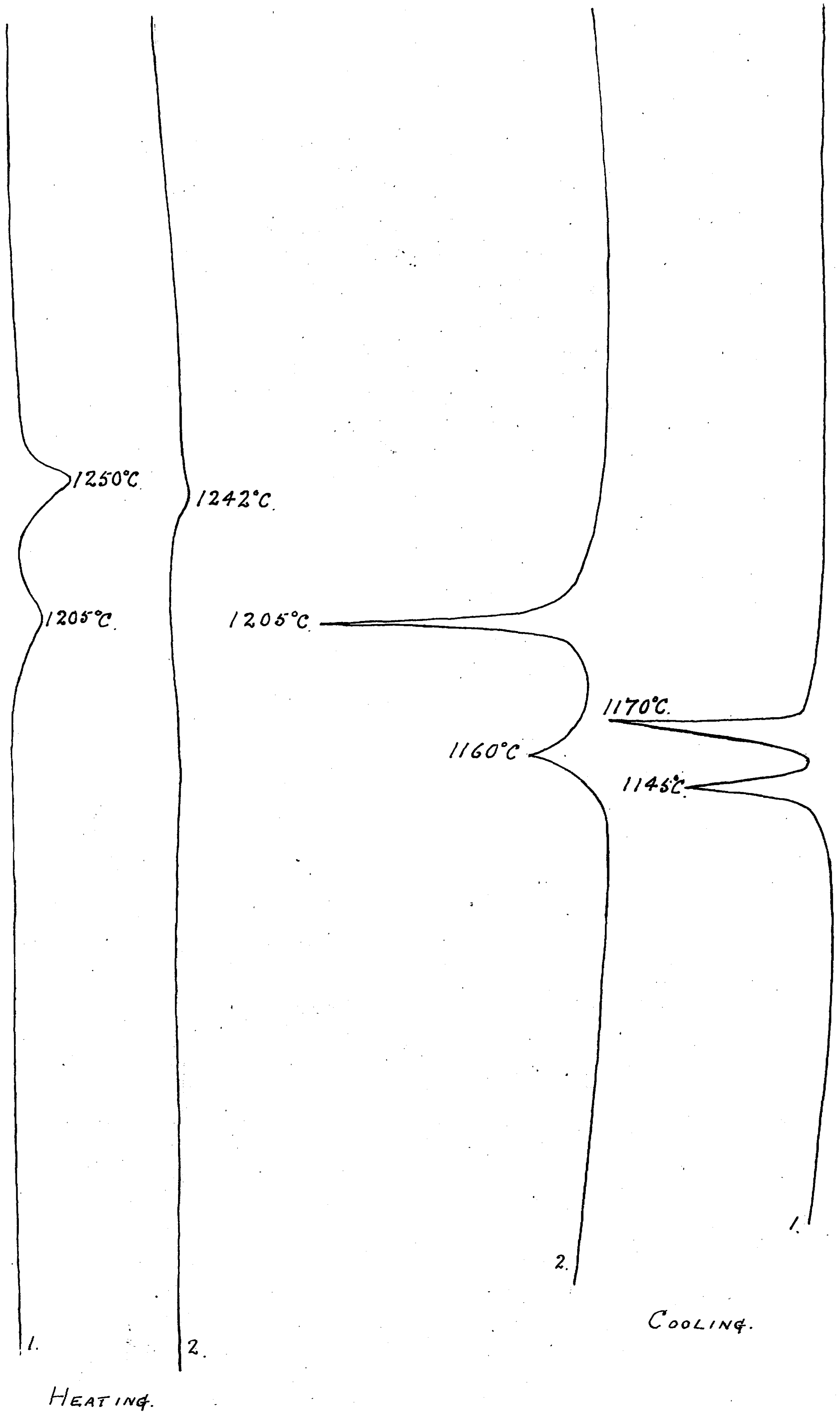
MnO. 85%.
SiO_2. 15%.
REDUCED BY 1/3.

FIG. 20



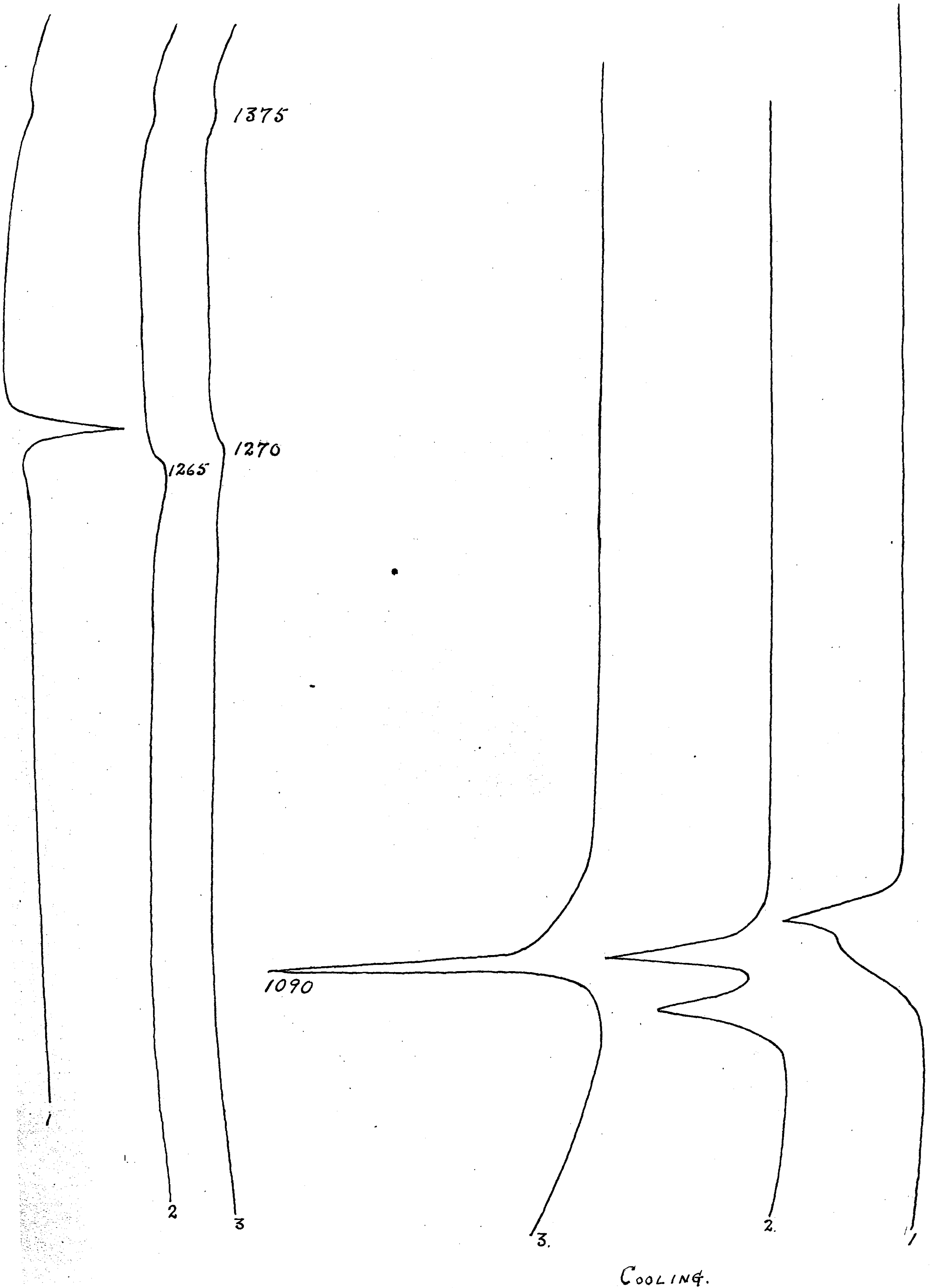
MnO. 70·2%.
SiO_2. 29·8%.
TEPHROITE.

Fig. 21.



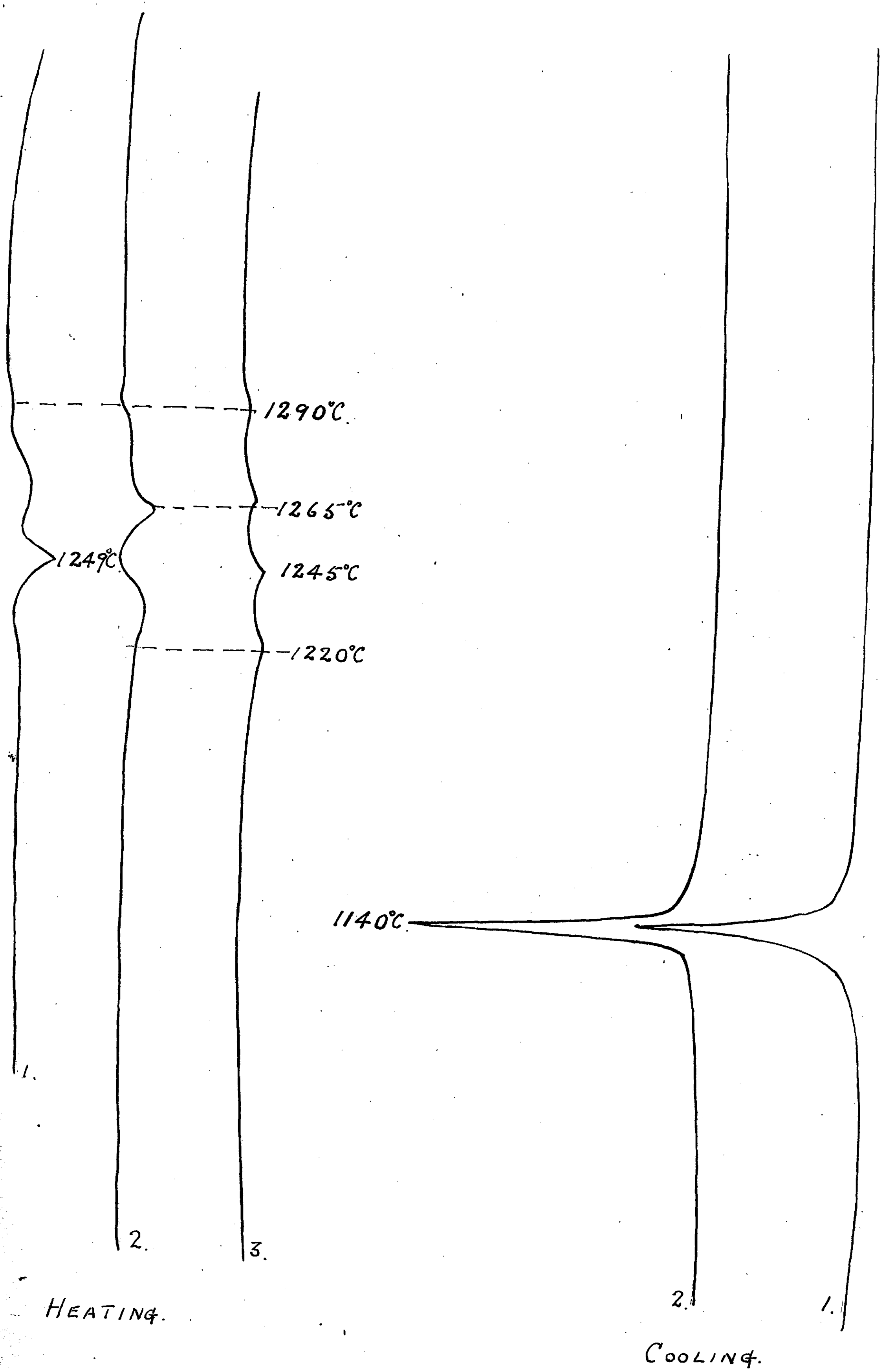
MnO. 63·4%.
SiO_2. 36·6%.

FIG. 22.



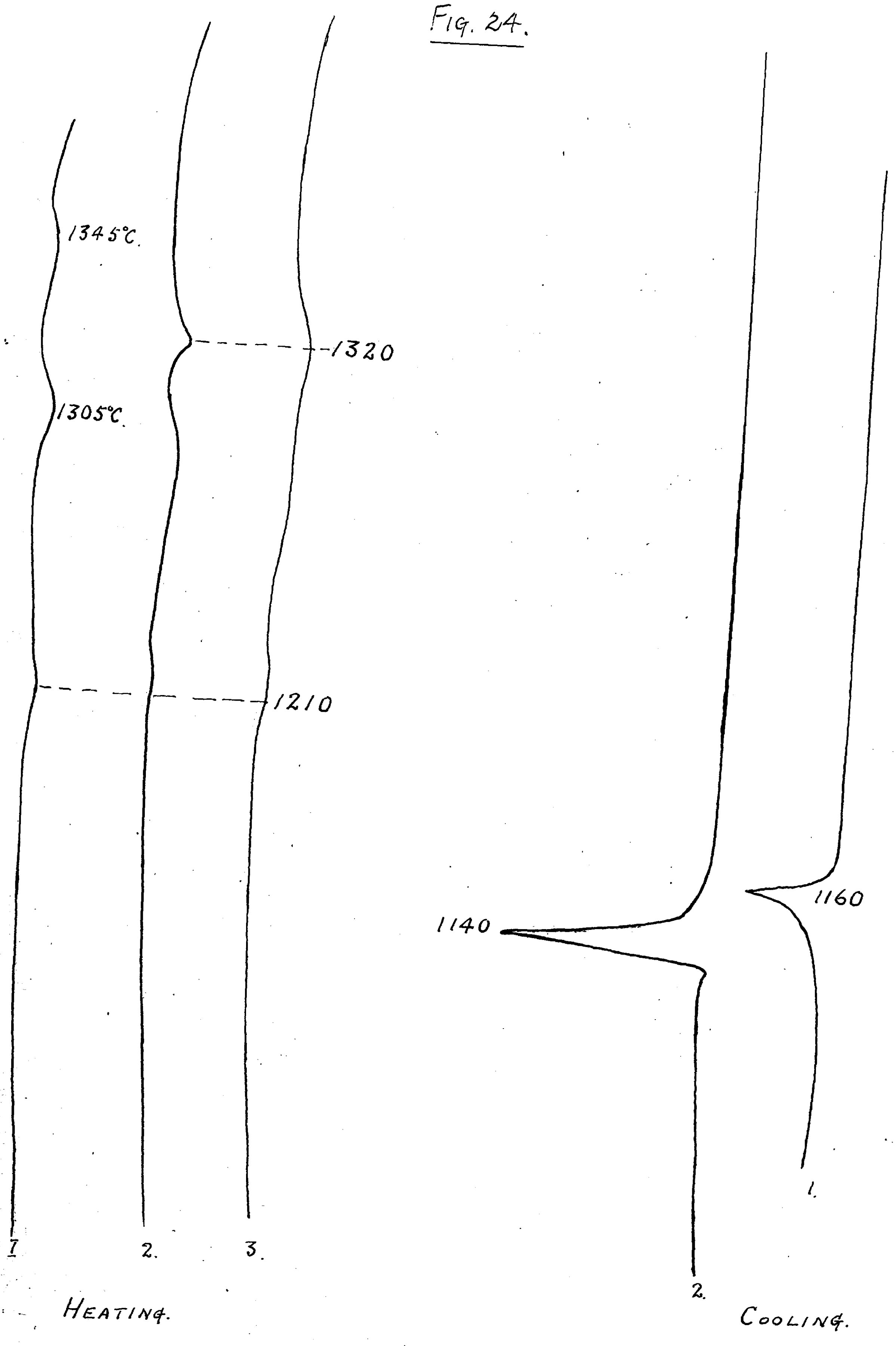
MnO. 61·1%.
SiO$_2$. 38·9%.

Fig. 23.



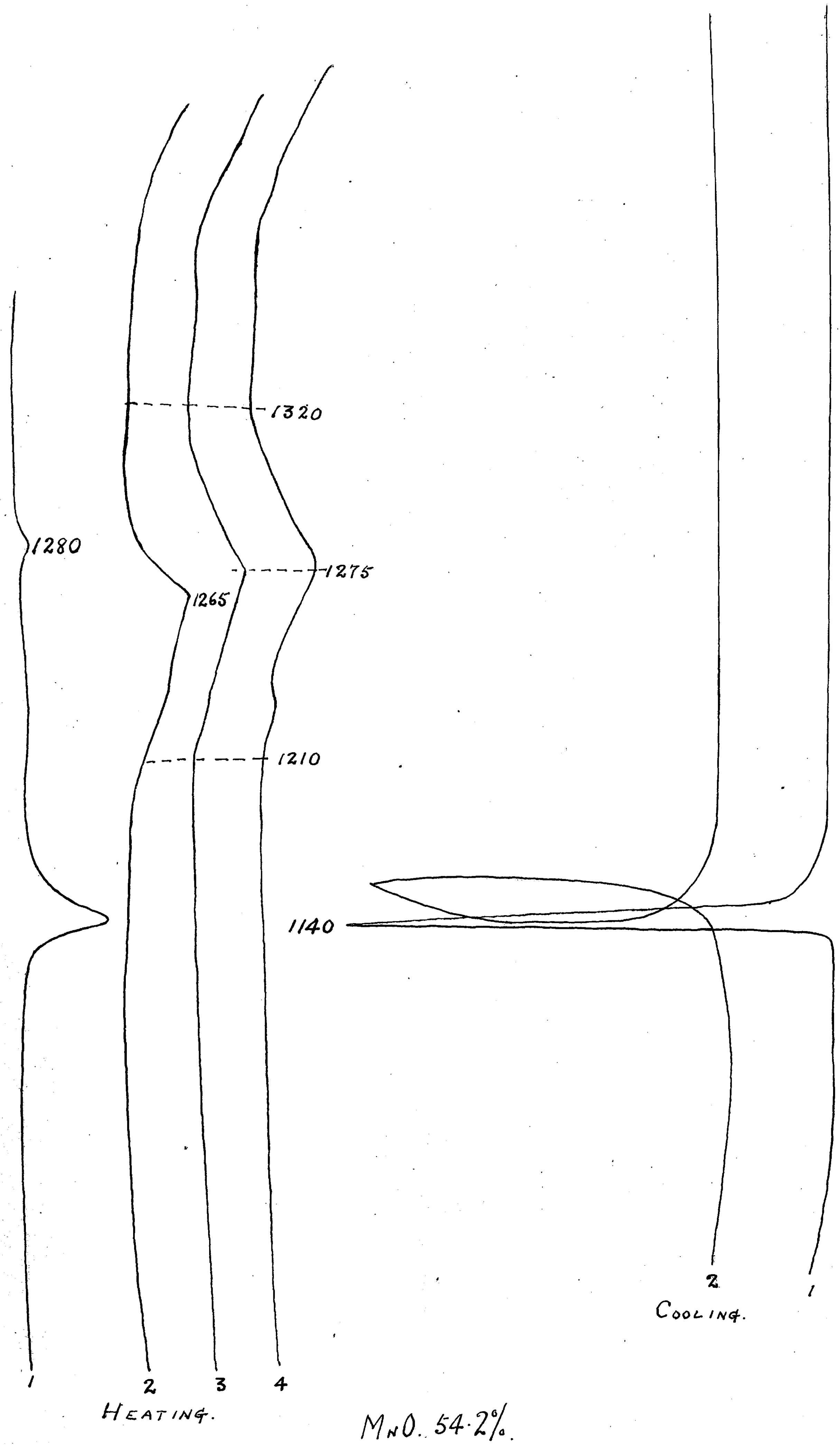
MnO. 58·8%.
SiO_2. 41·2%.

Fig. 24.



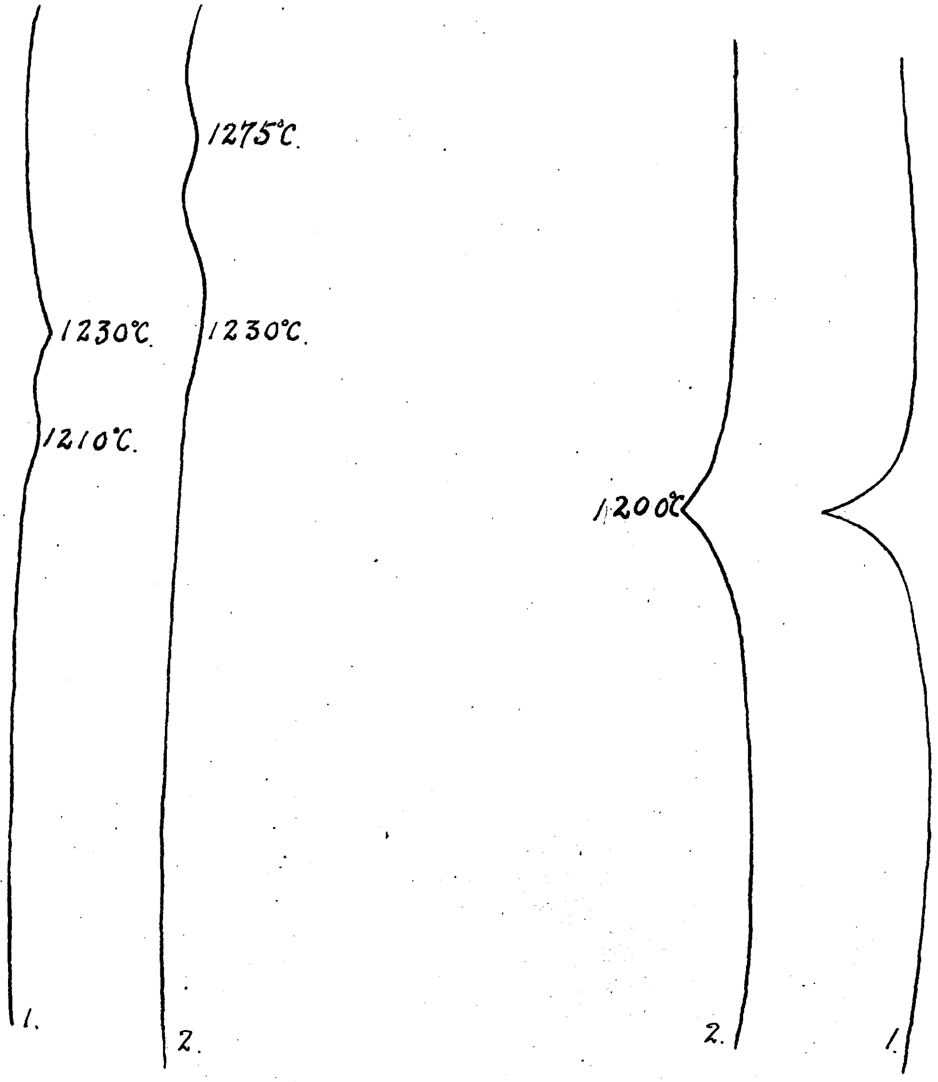
MnO. 57%.
SiO_2. 43%.

Fig. 25.



MnO. 54·2%.
SiO_2. 45·8%.
Rhodonite.

Fig. 26.



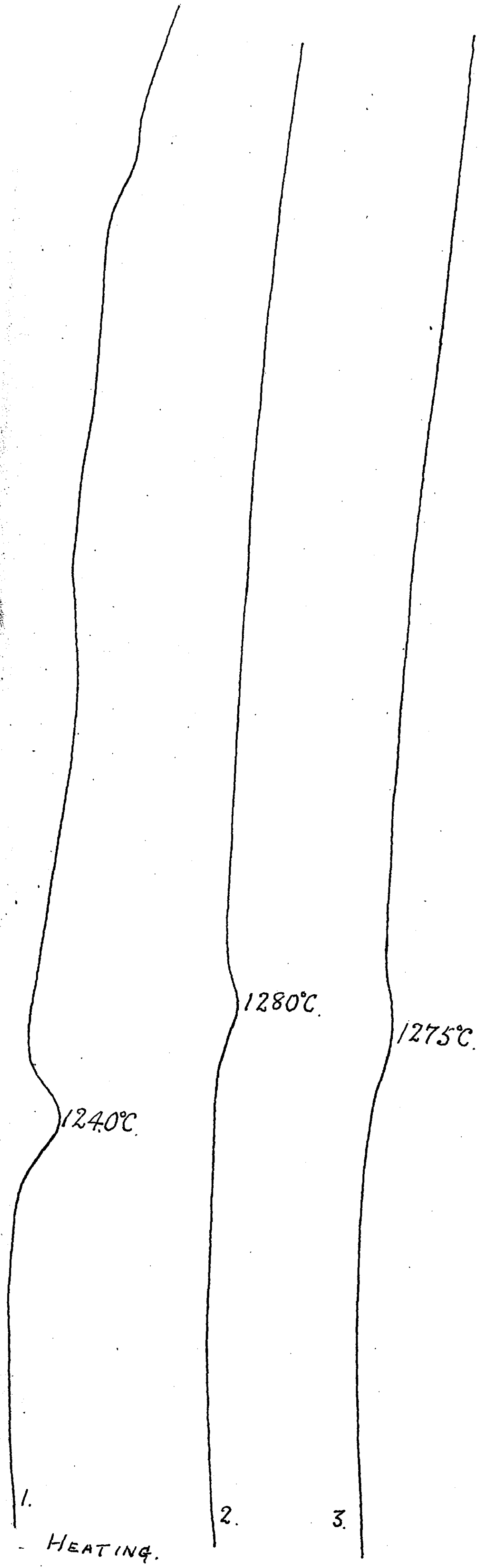
Heated up to 1300°C.

Cooled from 1300°C.

MnO. 54·2%.
SiO_2. 45·8%.

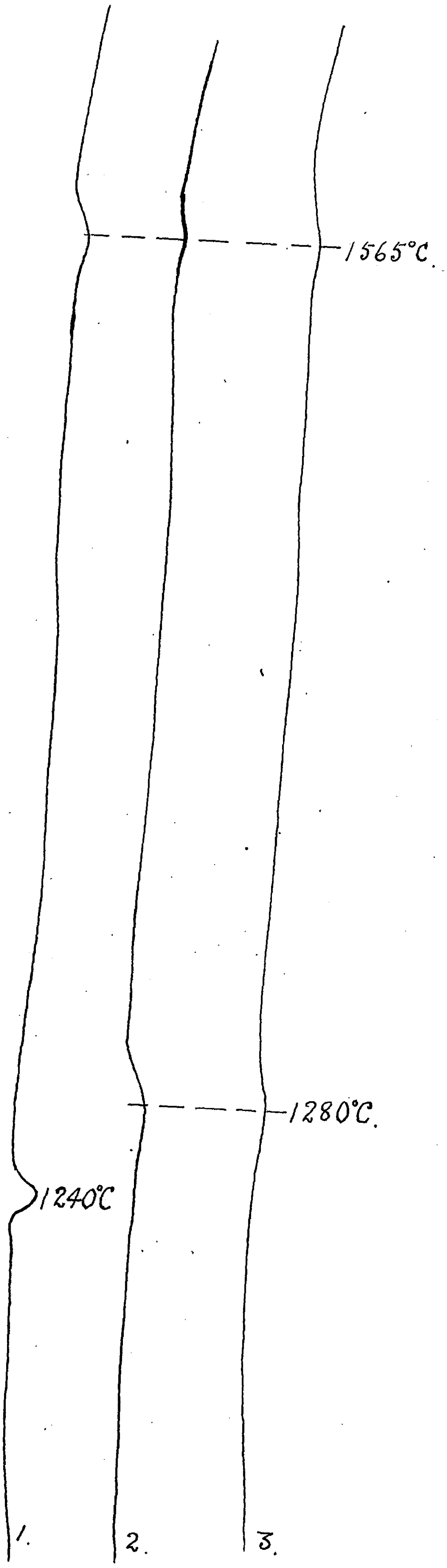
Rhodonite.

Fig. 24.



Heating.

MnO. 50%.
SiO_2. 50%.



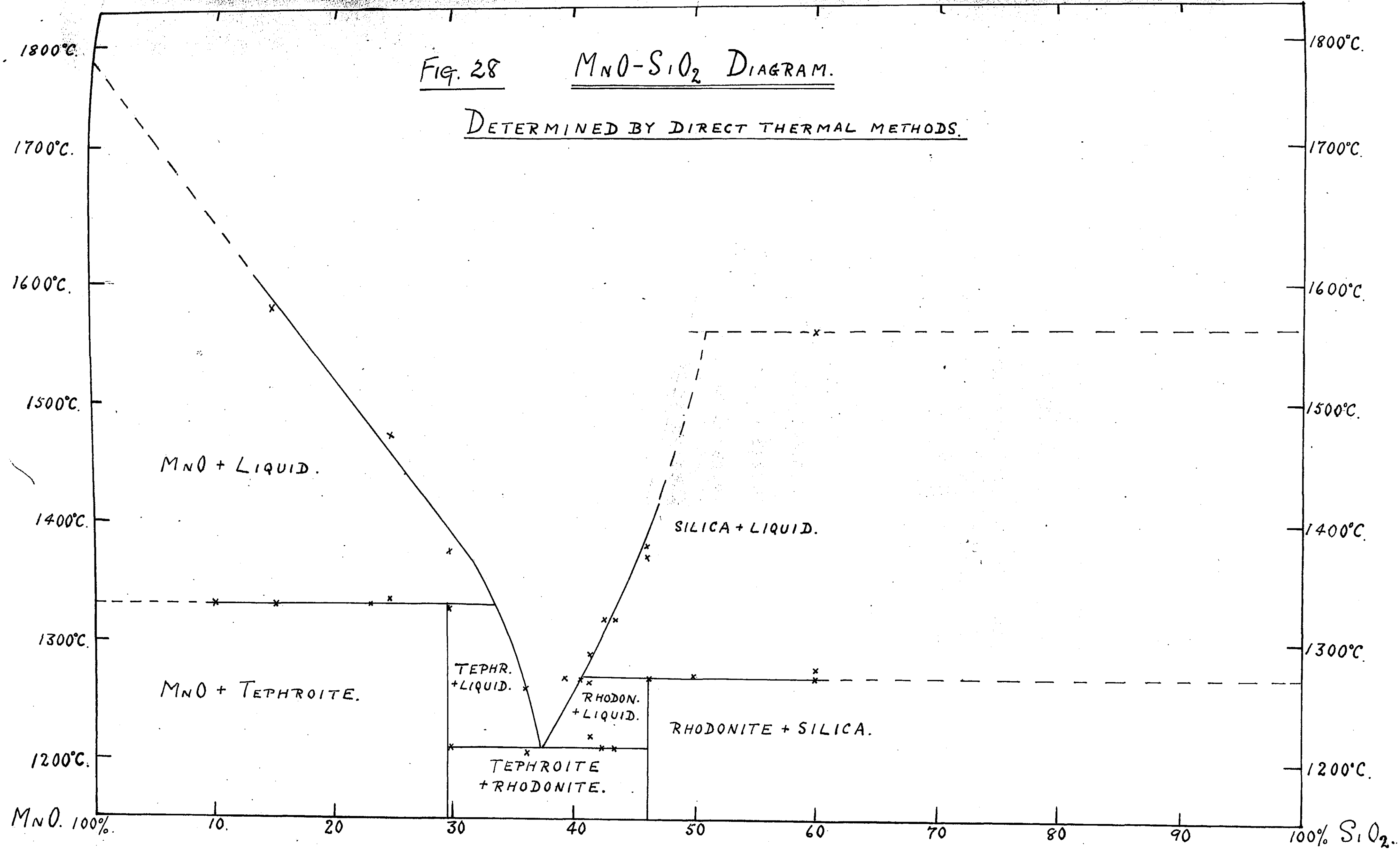
Heating.

MnO. 40%.
SiO_2. 60%.

Reduced by 1/3.

Fig. 28 MnO-SiO_2 Diagram.

Determined by direct thermal methods.



Section 111. The Investigation of the Thermal Equilibrium Diagram of the System MnO-SiO_2 by the Differential Thermocouple Method.

The fragmentary and indefinite nature of the evidence obtained for the system MnO-SiO_2 by the methods just described made it imperative to obtain a method of thermal measurement which would allow very small or very long-drawn out phase changes to be recorded accurately. It was realised that only by this means could the diagram be satisfactorily completed.

The use of a differential thermocouple arrangement was next suggested.

The differential couple was first introduced by Roberts-Austen for "The alloys research committee of the Institute of Mechanical Engineers"; in the fifth report of the committee. This arrangement has proved of great value in determining small thermal changes during the heating or cooling of metals or alloys.

The method consists essentially in eliminating the general heating or cooling effect during the observation and noting any difference in temperature of the metal under observation and another metal of similar thermal capacity. This neutral body must give a perfectly regular thermal curve during the range of temperature under consideration, and should be as nearly as possible of the same shape and size as the body being investigated so that the two may heat or cool with equal rapidity.

Two galvanometers are required, one connected with a simple thermocouple in the usual way to indicate temperatures. The second being connected with a compound couple, which only indicates any differences in temperature between the two metals used. As the two metals are heated or cooled at the same rate a ray of light from the second galvanometer will only move when heat is given out or absorbed by phase changes taking place in the metal under observation.

The diagrams of connections is shown in fig. 29. B is the specimen under observation and is bored with two holes, one for the thermocouple D, connected through the cold junction E and resistance F to galvanometer G. C is the standard. It is bored with one hole containing a thermocouple. One wire (e.g. the Pt wire) passes to the cold junction E_1, through a resistance F_1, to the galvanometer G_1. The other wire (e.g. the Pt-Rh wire) passes to H_1 where it forms with another Pt wire, a second thermocouple, which is placed in the second hole of the metal under examination. The Pt wire passes through the cold junction E_1 and resistance F_1 to the galvanometer G_1, thus completing the circuit. Any absorption or evolution of heat caused by phase changes in the metal under examination gives rise to a difference in temperature between the two bodies $(\theta - \theta_1)$ and the galvanometer coil is deflected. The thermal curves are obtained by plotting $(\theta - \theta_1)$ against θ, and show heat changes with great clearness, indicating both the commencement and termination of the points.

In adopting the differential couple for the work under consideration, some slight alterations were made. Molybdenum and tungsten wires were used as formerly. The neutral body was a length of molybdenum rod of approximately the same weight of the crucible and charge combined. The hot junction of an ordinary molybdenum-tungsten thermocouple was bound to the crucible containing the charge or inserted into the charge. No difference in the results obtained could be detected in either case. The compound couple was made up with two lengths of molybdenum wire and a short length of tungsten wire connecting the junctions on the neutral body and crucible as shown in diagram fig. 30. The ordinary temperature recording couple was taken through a cold junction and the leads connected to a Tinsley potentiometer by means of which the E.M.F. was measured. The molybdenum leads from the differential couple we were also taken through a cold junction and connected with a sensitive galvanometer.

It is necessary to ensure that both crucible and neutral body should be heated or cooled at as nearly as possible the same rates. To accomplish this all the connections were made and the crucible and neutral body were embedded in a mass of alundum, the alundum was dried and the whole introduced into the furnace. Later it was found advantageous to have the crucible and neutral body enclosed in a properly made alundum container. This was a cylindrical receptacle about $1\frac{7}{8}$ in. diam. and 2 in. long. Along the diameter two holes were bored, the centre of each hole being equidistant from the centre line of the container and each was about $\frac{1}{2}$ in. diam. and about $1\frac{1}{4}$ in. deep, so that the crucible would fit fairly closely into one and the neutral body into the other. An alundum lid, with a deep recess in the under side was made to fit closely on to the top of the container, and an elliptical hole through which the thermocouple leads passed was bored in the lid. A diagram of the crucible and connections is shown in fig. 30. By the use of this container the position of the crucible and neutral body was fixed relative to the furnace windings and the possibility of unequal rates of heating or cooling was minimised.

As mentioned previously, the leads of the differential couple were connected to a galvanometer and a spot of light reflected from the coil was received on a graduated scale. If the crucible and neutral body are heating or cooling at equal rates there should be no movement of the spot of light. In practice, due to small differences in the thermal capacities of the crucible and neutral body, there is a gradual but perfectly regular movement of the spot over the scale. The general form of the curve is consequently not a perfectly straight line. On this curve will be superimposed any variations in the rate of heating caused by phase changes in the material in the crucible. The first absorption of heat by the material in the crucible will be marked by a deviation of the curve from the normal. As the absorption of heat continues the curve will deviate more and more from the normal until the phase change is completed, the curve will then return gradually to the

the/
normal, approaching it in an asymptotic fashion. So that in the interpretation of the curves the first deviation is assumed to mark the beginning of, and the maximum deviation the completion of, the phase change.

A complication may arise when a second point is close to the first. In this case the curve may not have returned to the normal, e.g. may be at the point F in fig. 31. So that in this case a second bulge will be superimposed on the first. If no second point had occurred, the first curve would have returned to the normal along FOB, but at F there is the first sign of a deviation from this path and this point may be taken, in exactly the same way as formerly to mark the beginning of the second phase change, The point G, at which this second deviation reaches its maximum value may be taken to mark the completion of the change.

Procedure in the MnO-SiO_2 determinations by the differential thermocouple method.

In every case a charge of approximately 2 gms. was used. MnO and SiO_2 in the desired percentages were accurately weighed out, finely crushed and intimately mixed together and introduced into the crucible. The crucible and neutral body with the wires connected as indicated in the diagram fig. 30, were then carefully inserted into the container. The lid was then slipped down into position and tied to the container. The annular space between the lid and body of the container was luted with alundum. The elliptical hole in the lid, through which the leads passed was also filled with alundum. So that penetration of furnace gases to the charge was reduced to a minimum. The whole was then lowered into the furnace. The top of the furnace was loosely closed with a bung, thorugh a hole in which the leads passed.

The thermocouple leads were connected through a cold junction to a potentiometer, and the differential couple leads through a cold junction to the terminals of a galvanometer. The spot of light from this galvanometer was received on a graduated scale, and the position of the spot on this scale was noted and a record kept. Any deviation of this spot will be a measure of the difference in temperature between the two bodies when a phase change is taking place in the material in the crucible. The curves were obtained by plotting the readings of the positions of the spot against the temperature reading as measured on the potentiometer.

Usually three heating and two cooling curves were taken. It was usually found that the first heating curve differed in general outline from the subsequent curves, and it is assumed that this is due to heats of reaction, solution, etc. The second and third curves were, in every case, almost identical. Very close agreement can also be observed in the cooling curves.

Discussion of the results obtained in the investigation of the system $MnO-SiO_2$ by the differential thermocouple method.

The investigation of this system by the use of the differential thermocouple yielded some rather interesting results. Some of the upper points on the liquidus, which cause a thermal change too small to be detected by ordinary methods, can be determined by this means. The higher portions of the liquidus on the MnO end have been determined with a very fair degree of accuracy.

The information gained previously was of assistance in so far that a rough outline of the diagram had been arrived at. The peritectic dissociation of rhodonite and tephroite had been fairly well established. The temperatures of these peritectic reactions had been determined, and that of the eutectic between rhodonite and tephroite provisionally fixed.

The curves for rhodonite, fig. 39 amply confirm what had already been suspected regarding the thermal changes in this mineral. A large arrest, beginning at 1250°C and ending about 1300°C, marks the peritectic. A small upper arrest at 1420°C will indicate complete liquefaction of the material, this higher arrest furnishing the last link in the chain of evidence regarding the thermal changes which the mineral undergoes.

All the evidence again goes to show that there is a eutectic between rhodonite and tephroite. In the curves for all the mixtures between 45.8 and 29.5% silica, the existence of an arrest beginning about 1210°C is quite clearly indicated, figs. 35-38, and this temperature 1210°C has been assumed as the eutectic temperature.

One rather strange fact emerges as a result of the study of some of the thermal curves for mixtures within this region. In the heating curves for the 64/36 and 60/40 MnO/SiO_2 mixtures in figs. 36 and 37. In both curves there is evidence of an arrest beginning at 1210°C, there are fairly definite arrests at 1250°C and

and/
1240°C, respectively. These upper points may be taken as marking the position of the liquidus. But in both cases there is definite evidence of arrests at 1260-1270°C and 1330°C. It is difficult to account for the occurrence of these arrests in material which is assumed to be in the molten state, and the fact that these arrests occur in the curves for all the mixtures within this range makes the problem still more complicated. It might be explained by lack of homogeneity in the melt due to the very slow rate of diffusion which is characteristic of silicate systems, but the close agreement to be observed in several heating curves is against this explanation. The other and more probable explanation is that rhodonite and tephroite, whether in the liquid or solid state undergo a chemical dissociation at a constant temperature, or in other words, that the peritectic reaction can still take place even when the substance is molten. It would appear then that rhodonite in its dissociation produces tephroite and free silica, and that tephroite in turn breaks down into MnO and silica.

It is impossible, from phase rule considerations, to have the two peritectic lines stretching, one above the other, across the eutectic range. In view of the fact that all the arrests on the heating curves of mixtures within this range begin at 1210°C, it seems only reasonable to assume this as the eutectic temperature, and it necessarily follows that the liquidus lines must meet this line at some point.

Enormous assistance in arriving at definite conclusions regarding this part of the diagram was obtained by the use of a high-temperature microscope. This was just a very small molybdenum-wound furnace with water-cooled sides and lid. The lid of the furnace was fitted with a small quartz window, so that the inside of the furnace could easily be seen. The mixture was contained in a shallow molybdenum crucible and the junction of a molybdenum-tungsten couple was inserted into the bottom of the crucible.

A low-power microscope was focussed on the

the/
surface of the charge. The furnace was heated up and, by means of the microscope the changes taking place in the material during the heating could be observed.

The following mixtures were examined by this means and the results obtained are shown in tabular form:-

Sample No.	Composition MnO %.	Temp. at which liq. first appeared.	Temp. at which majority of liq. appeared	Temp. at which final solid disappeared
1.	68	1160°C	1280°C	1360°C.
2.	53	1210°C	1280°C	1525°C.
3.	52	1210°C	1280°C	-
4.	50	1210°C	1280°C	-

It will be observed from these results that in all cases melting had begun at 1210°C and that the larger part of the material was molten at 1280°C. Results which are in complete agreement with the assumption that the eutectic does exist at the temperatures stated.

In the examination of the mixture containing 53% MnO, sample 2, a composition very close to that of rhodonite the following very interesting observations were made during the melting of the sample:-

Particles of rosette shape floated on the surface of the liquid about 1280°C (possibly tridymite). Between 1455°C and 1460°C the amount of floating solid increased. No further change was observed till 1525°C, when the whole suddenly melted. A subsequent melt showed that the surface actually set solid at about 1440°C and became liquid again about 1520°C. Holding the temperature at 1450°C caused the solid to continue to separate, thus showing that the change did not depend on a progressive rise in temperature. In addition it was not reversible on cooling. The surface tension of the melt was very low and the material tended to spread over the surface of the crucible.

Such observations give some idea of the very

very/
complex changes which may take place in a system such as this.

In that portion of the diagram from 50 to 100% silica, the evidence obtained is not so conclusive. The existence of the peritectic at about 1275°C seems quite definite, see figs. 41 to 46, and is evident even on the curves for the 97/3 SiO_2/MnO mixture. There would also appear to be traces of an arrest at about 1530°C which may mark an ill-defined cristobalite to tridymite change brought about by the MnO acting as a flux. Regarding the region above 1530°C there is no reliable data and the probability is that there is a region within which two immiscible liquids exist - one high in silica and the other a rich MnO liquid.

In the 97/3 SiO_2/MnO curves there is very dubious evidence of an arrest at about 1640°C, which may however be an indication of the lower temperature limit of the region of the two immiscible liquids.

In regard to the liquidus from 100 to 66 per cent MnO the evidence available is much more definite. The gap between the solidus and liquidus is very great, and in view of the very prolonged period during which liquefaction of the mixture is taking place, it is a remarkable tribute to the efficiency of the method of measuring these small thermal arrests, that this quite definite evidence has been obtained. The upper arrest points for the mixtures are as follows;-

Mixture.		Upper arrest temperatures in °C.
MnO %.	SiO_2 %.	
68	32	1360
82	18	1555
92	8	1680
100		1785.

See figs 32 to 35. These are the points which have been used in arriving at the position of the liquidus in this part of the diagram.

Another unexpected feature of the diagram is the very steep slope of the liquidus between 40% and 50% silica. The evidence is not so conclusive as that for the rich MnO melts, but there is a fairly definite evidence of the upper point on the 42.5/57.5 SiO_2/MnO and the rhodonite melts, figs. 38 and 39. The upper arrests on the curves for the melts, which have been used in arriving at the position of this part of the liquidus are as follows:-

Mixture.		Upper arrest temperature in °C.
MnO %.	SiO_2 %.	
57·5	42·5	1320
54·2	45·8	1420
52·5	47·5	1500
50·0	50·0	1600.

See figs. 38 to 41.

The heating and cooling curves for pure MnO provided very unexpected features. The melting point of this oxide has been the subject of considerable discussion in the past. In the previous part of this work the value found was 1585°C. Microscopic examination led to the belief that considerable amounts of impurities were present, these being due to contamination of the oxide by alumina from the crucible. The value for the melting point given in the International Critical Tables is 1650°C. Benedicks and Lofquist in their book on Non-metallic Inclusions estimate it as above 1700°C.

In this section of the work several attempts were made to melt the oxide before success was obtained. In the first case the oxide was heated to about 1680°C, but on examination no sign of melting was observed. A second attempt was made by heating to 1730°C, there was still no sign of melting except for a slight fritting of the top layer. In the third attempt a temperature of 1790°C was obtained and the heating curve is shown in fig. 32. The curve deviates from the normal at this point and it was at first assumed that this was due to defective functioning of the couple since, as is evident from the curve, there had been considerable fluctuations at lower temperatures.

On this occasion there were definite signs that melting had begun, and the attempt was repeated with the same charge. The furnace was pushed to its utmost limit and a temperature of 1865°C was recorded. On subsequent examination the MnO was found to be completely melted. The heating and cooling curves are shown in fig. 32. It will be evident from the latter that the melting point of the oxide is about 1785°C.

This value is much higher than any previous determination but in view of the evidence brought forward there would seem to be no reasonable doubt that the real value for the melting point must be very close to the figure assigned to it here.

All the available data has been incorporated in the diagram shown in fig. 48. As described below an attempt was made to verify the diagram by identifying the phases present in each melt by means of a determination of the refractive indices.

The eutectic composition is shown at 37.5 % of silica and the melting point at 1210°C. Doerinckel gave the eutectic composition at 41.5% silica and the melting point at 1195°C. In Herty's diagram the eutectic occurs at 35% silica and the melting point 1225°C. The melting point of MnO as given by Herty is 1610°C while it is here given as 1785°C.

The Determination of the Optical Properties of the Constituents of the System MnO-SiO_2.

A thermal-equilibrium diagram cannot be considered to have been definitely established by the use of purely thermal data. It is very desirable to have some means of determining the nature of the phases present, and where possible, their relative amounts, the composition at which any one phase disappears, and that at which a new phase makes its appearance.

A very valuable check on the thermal data is thus obtained and the completed diagram then gives information as to the ranges of composition over which different phases exist, the thermal changes to which each phase is subject and the actual nature of the phases.

It is the usual practice to attempt to verify the thermal data by microscopic examination of the mixtures after the thermal determinations have been carried out. It is found, however, that with materials like MnO and SiO_2; it is difficult to obtain a satisfactory method of polishing and that the detection of the phases present is by no means an easy task.

A number of melts made in the salamander and carbon crucibles were polished and examined, and several of the molybdenum crucibles were cut across and the section of the material polished. The results obtained were not very satisfactory.

In order to examine the materials by transmitted light thin sections of a number of mixtures were prepared, but the time involved and the cost of preparation of these samples was scarcely justifiable and in many cases it was still exceedingly difficult to identify the phases present with any accuracy.

When melting was carried out in the small molybdenum crucibles the problem became still more difficult. After melting the material could not be extracted in pieces sufficiently large to be polished and it was rather expensive to section a crucible for the

the/
examination of each melt. The fused material was usually drilled out of the crucible and the problem was to find some method of determining and identifying the phases present in the powdered material. The only optical property which could be expected to be of real use in the identification of substances in the powder form is the refractive index. Beck (Petrographic methods by Weinschenck; Clark's translation, p. 33) has described a very satisfactory method for the determination of the refractive index of material in the powder form. This method was subsequently employed with very satisfactory results.

A number of liquids with different refractive indices can be employed according to this method. The highest refractive index readily obtainable with liquids is 1.74 and the refractive index of many slag constituents is greater than this. Merwin and Larsen (Amer. J. Sci. 1912, 34, p. 42-47) have described a method for measuring refractive indices between 1.98 and 2.92. They employed mixtures of sulphur and selenium which on cooling form glasses. The powdered material is placed on a glass slip and covered with the sulphur-selenium mixture. The slip is gently heated till the mixture melts and then a cover-slip is pressed down on the material, care being taken to avoid the formation of air-bubbles. The refractive indices of the various mixtures employed was checked by using a number of minerals of known refractive indices.

By these methods it was found possible to determine the refractive indices of the various constituents present in the melts. According to the diagram only four constituents need be looked for, viz.:- MnO, tephroite, rhodonite, and one of the crystalline forms of silica, which was subsequently identified as tridymite. These have the following refractive indices:-

MnO	------------- 2.16	Rhodonite	--------- 1.76
Tephroite	------- 1.78-2.00	Tridymite	--------- 1.49.

Also only two of these can occur in any one melt and it was a comparatively easy task to determine the refractive indices of the constituents and thus obtain a very useful check on the thermal

thermal/
determinations.

In spite of the fact that the material had been ground rather finely in the process of extraction from the crucible it was found that quite a number of definite crystals of the constituents could still be observed when the powder was examined under the microscope. A large number of these crystals were sufficiently thin to permit of other optical properties being determined, e.g. pleochroism, whether isotropic or anisotropic, and if anisotropic, the angle of extinction. The various results obtained are shown in t tabular form in fig. 47 and it will be evident that they are in very close agreement with the thermal results.

Fig. 29.

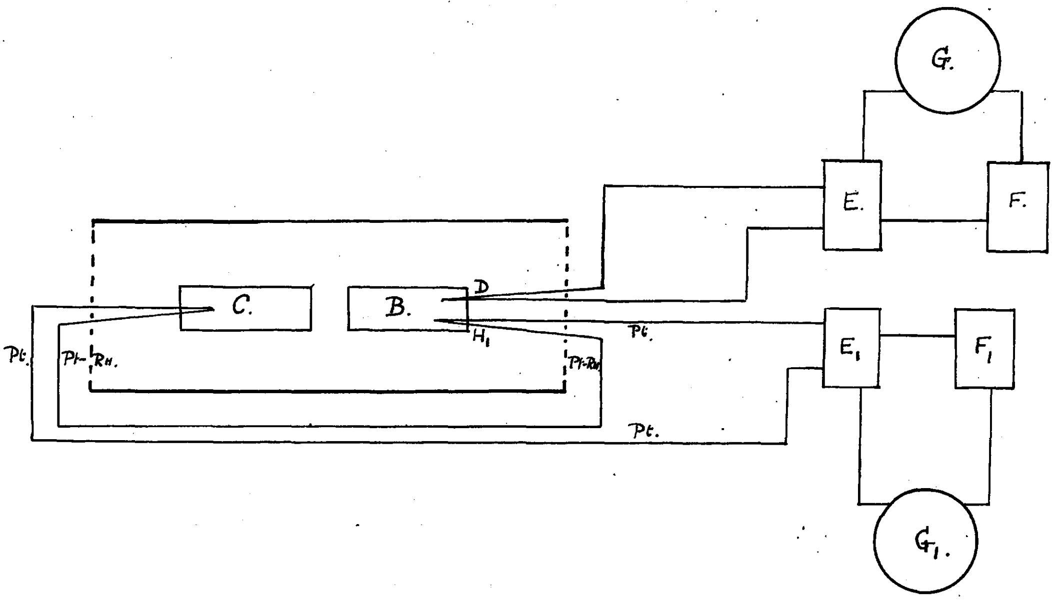
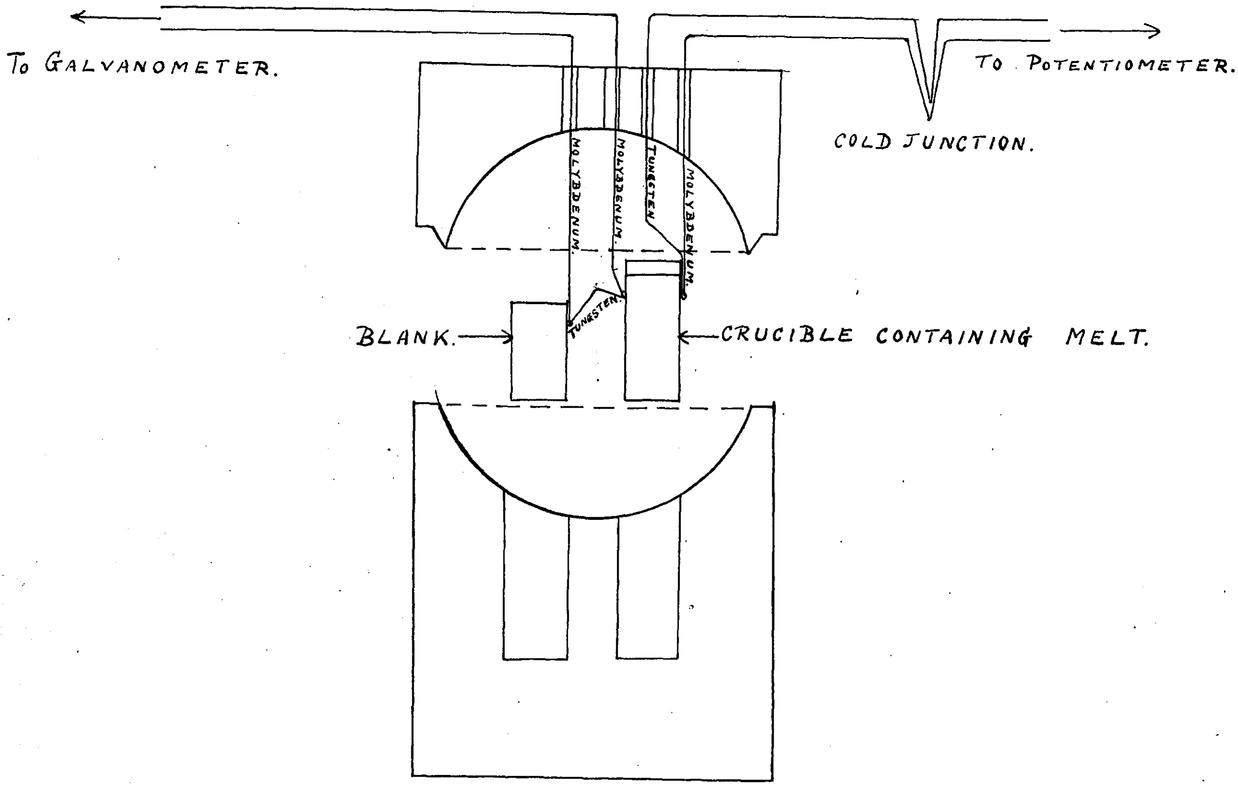


DIAGRAM OF CONNECTIONS FOR DIFFERENTIAL THERMOCOUPLE.

FIG. 30.



ALUNDUM CONTAINER FOR CRUCIBLE AND BLANK.
DIAGRAMMATIC SKETCH SHOWING ARRANGEMENT OF THERMO-COUPLE AND DIFFERENTIAL CONNECTIONS.

FIG. 31.

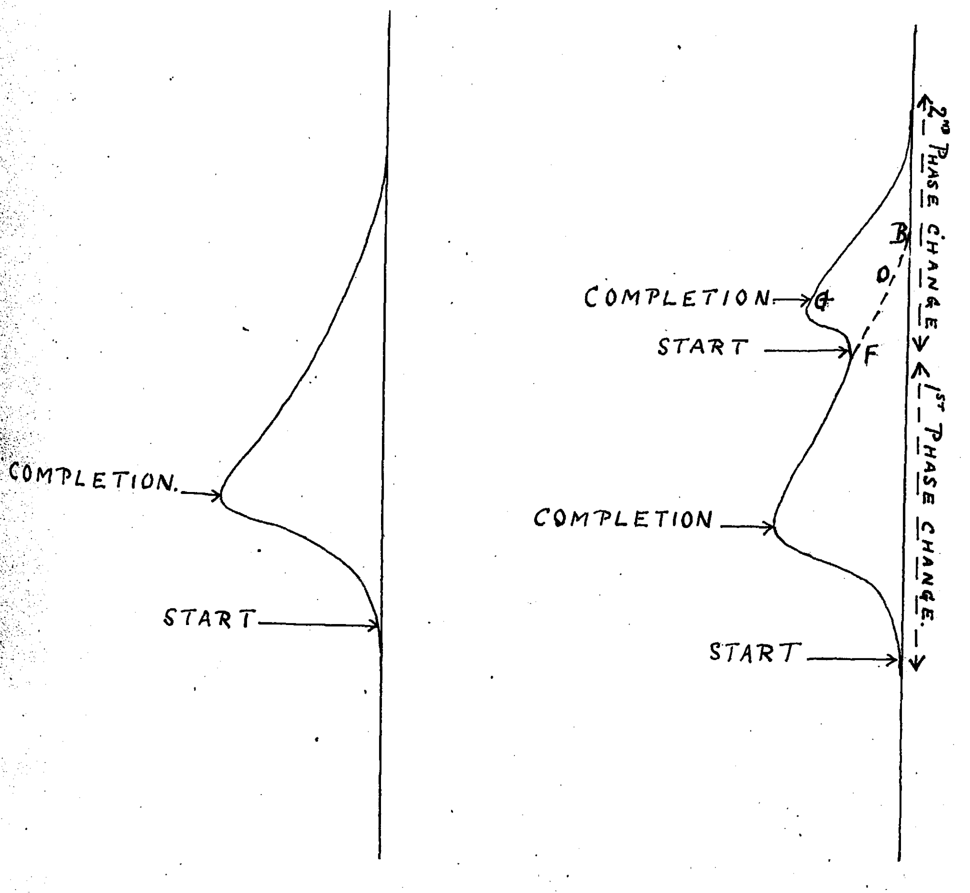
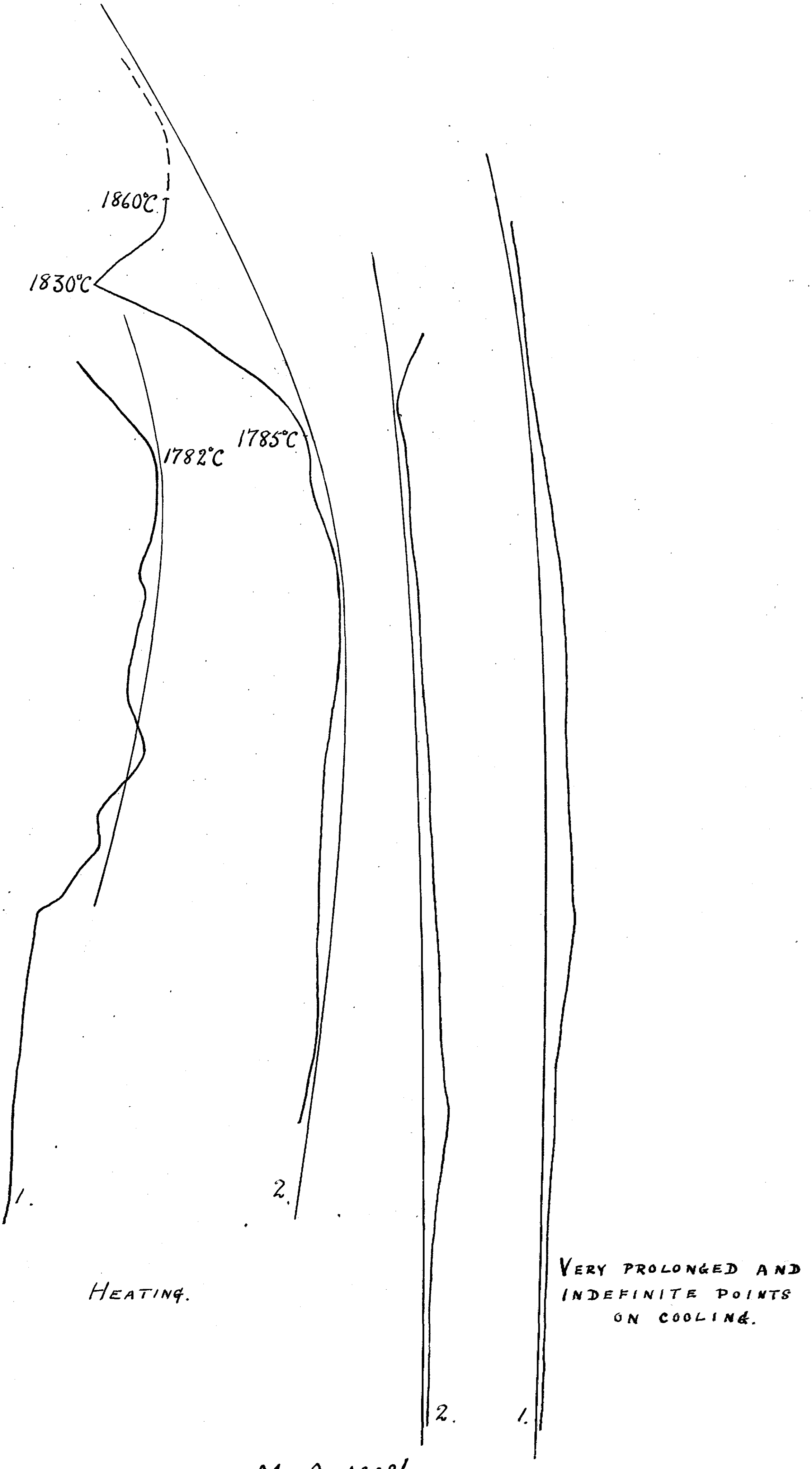


DIAGRAM SHOWING METHOD OF INTERPRETING DIFFERENTIAL CURVES.

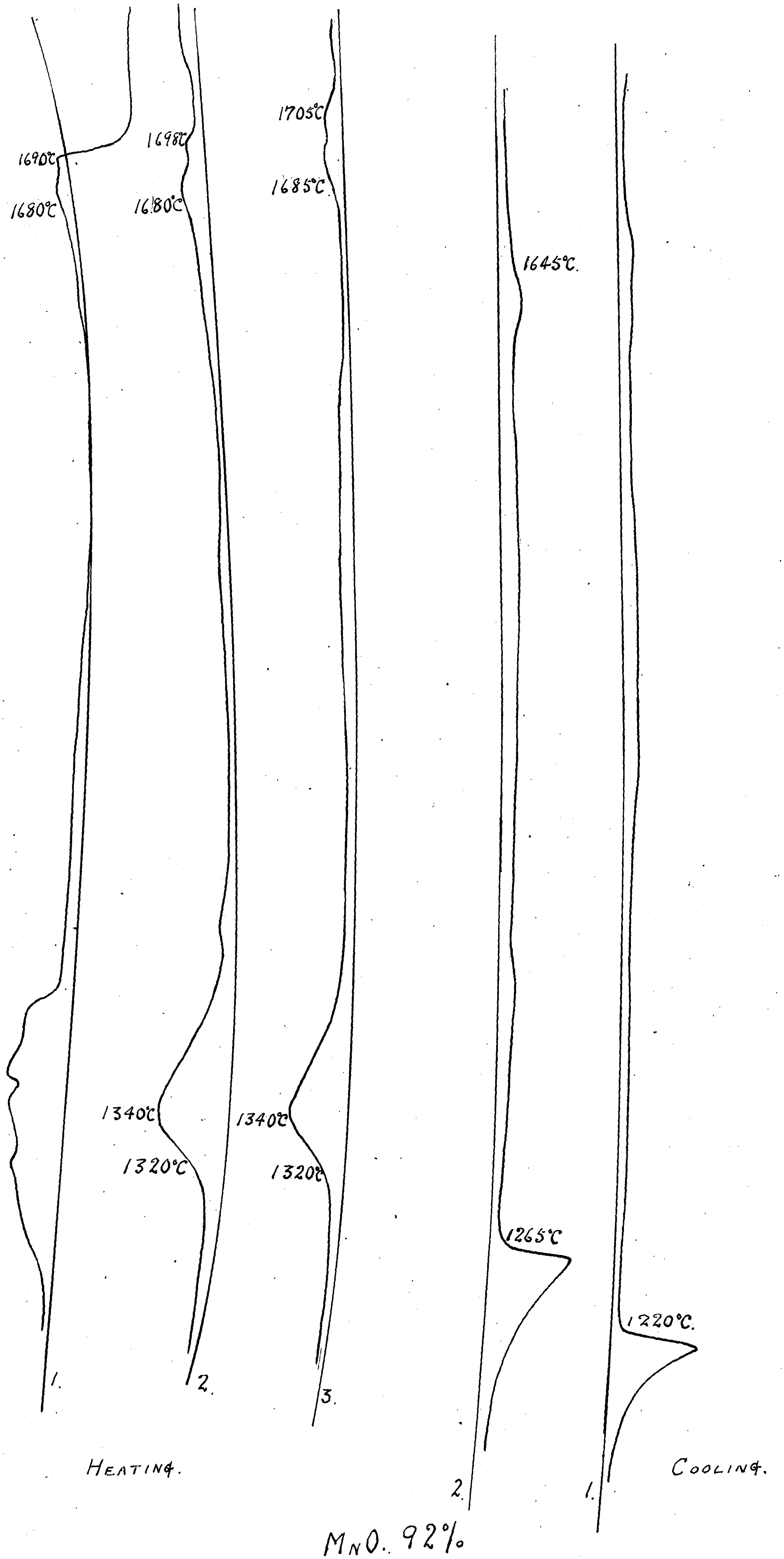
FIG. 32



MnO. 100%.

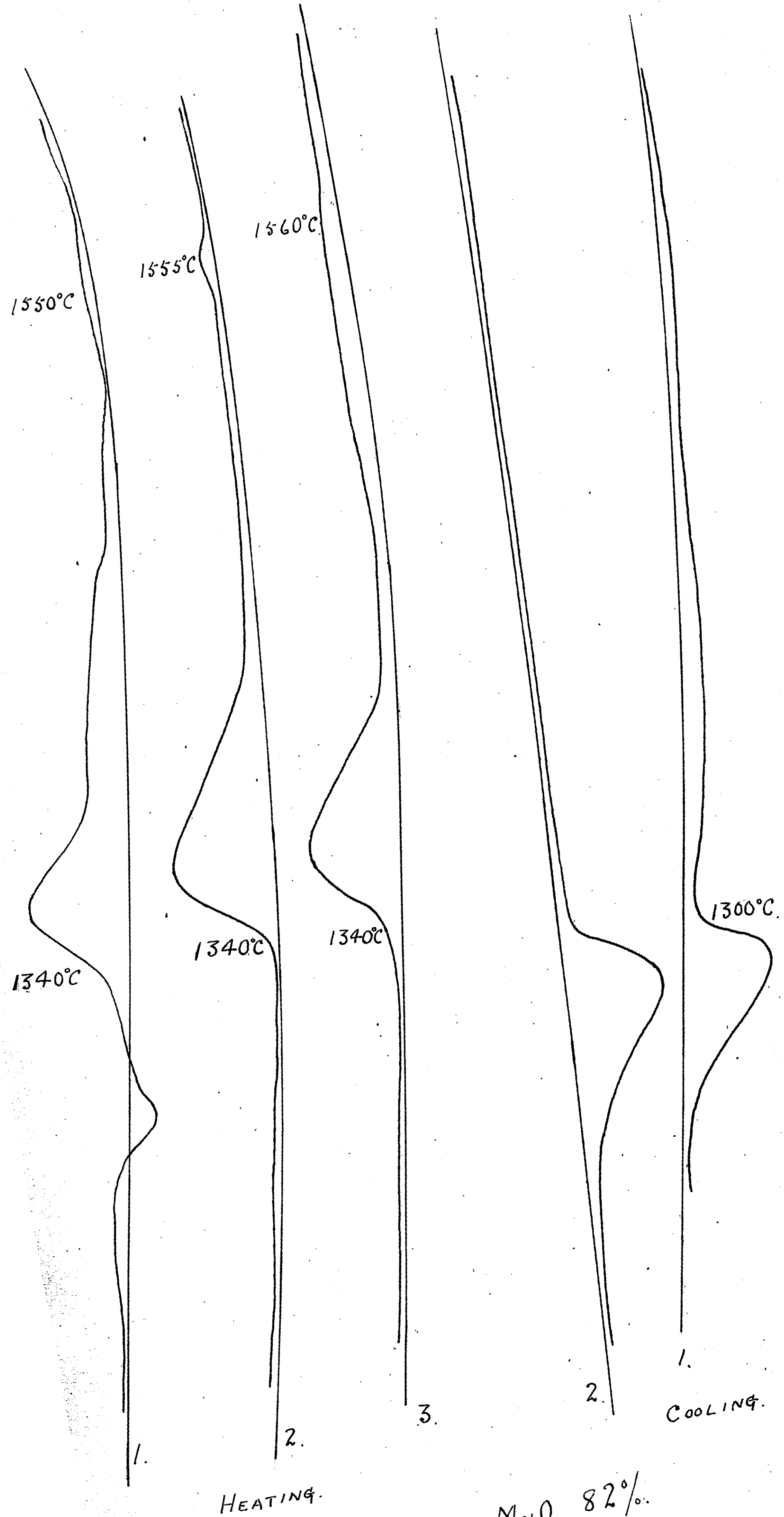
ALL CURVES TRACED FROM ORIGINALS BY AN EIDOGRAPH AND REDUCED BY 1/3.

Fig 33.



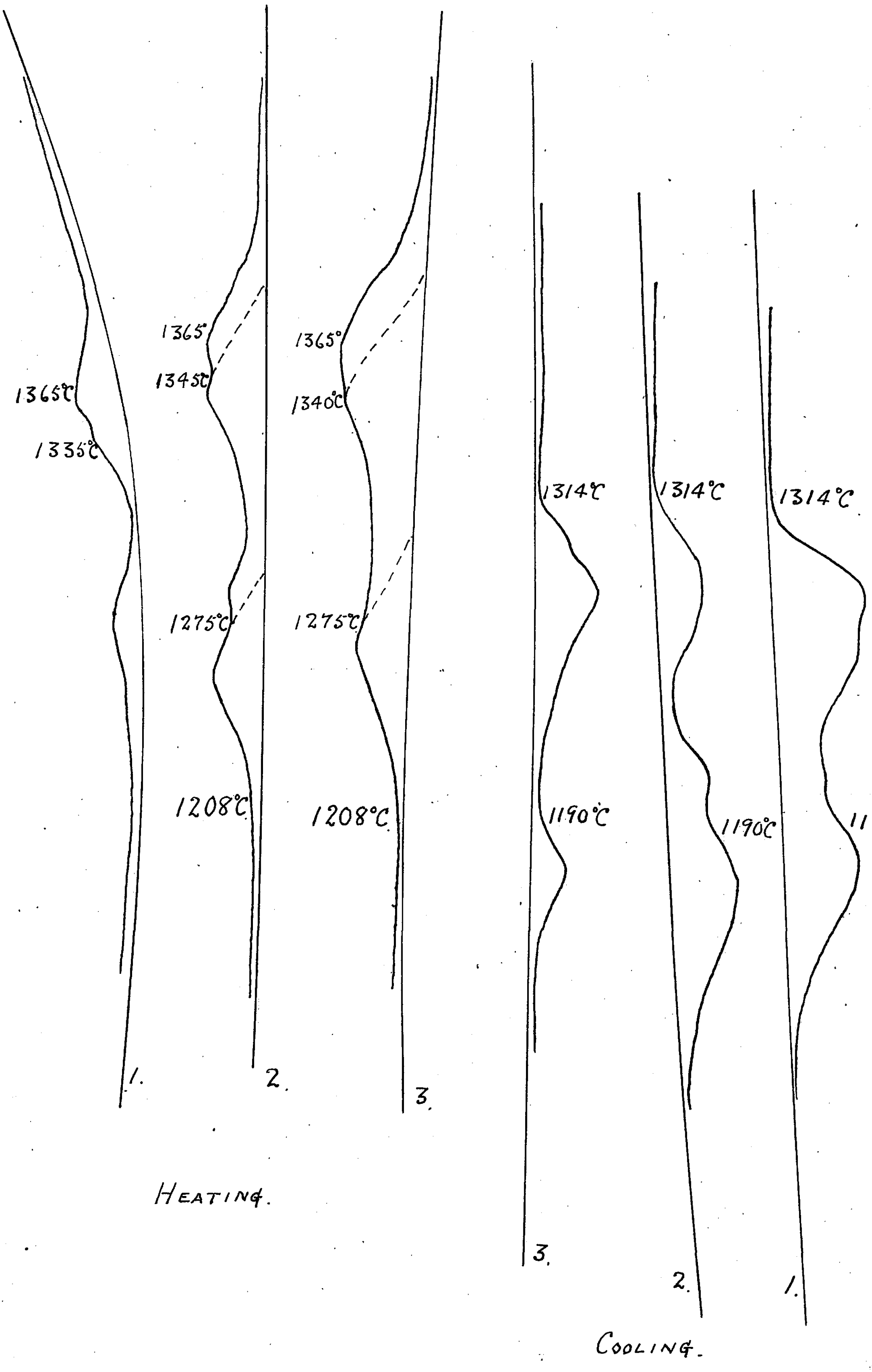
MnO. 92%
SiO_2. 8%.

Fig. 34.



MnO. 82%.
SiO_2. 18%.

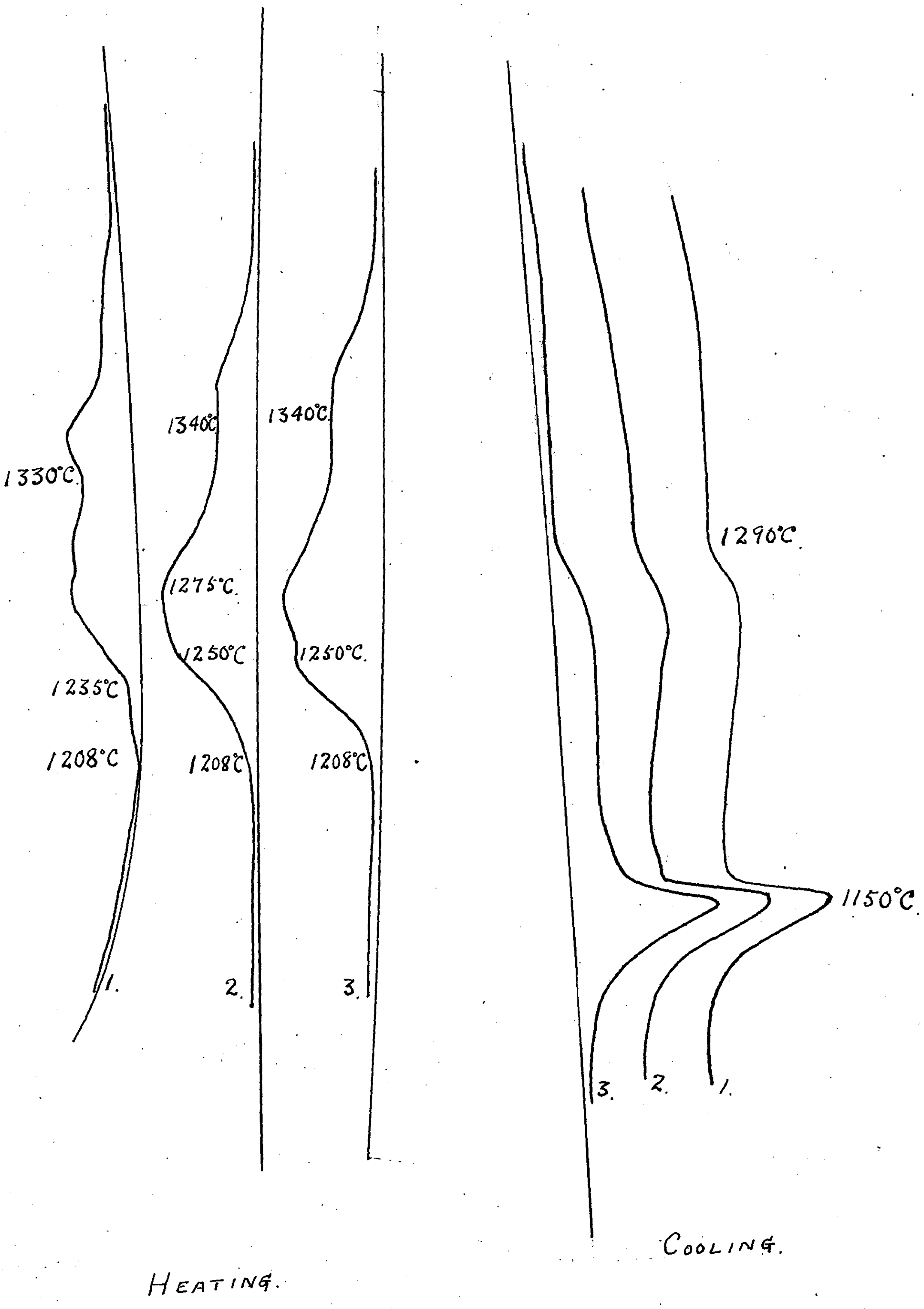
Fig. 35



MnO. 68%.

SiO_2. 32%.

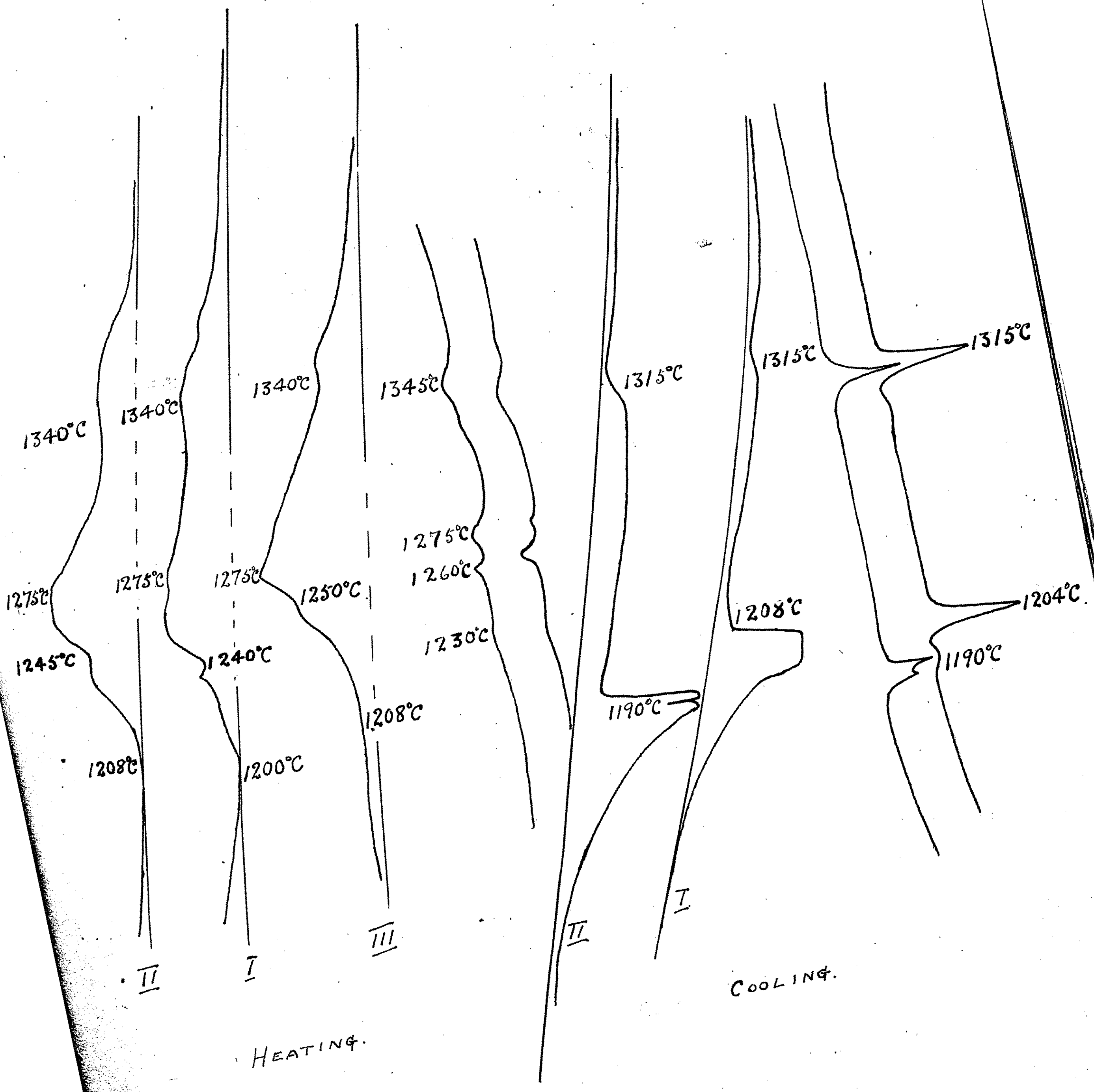
Fig. 36.



MnO.. 64%

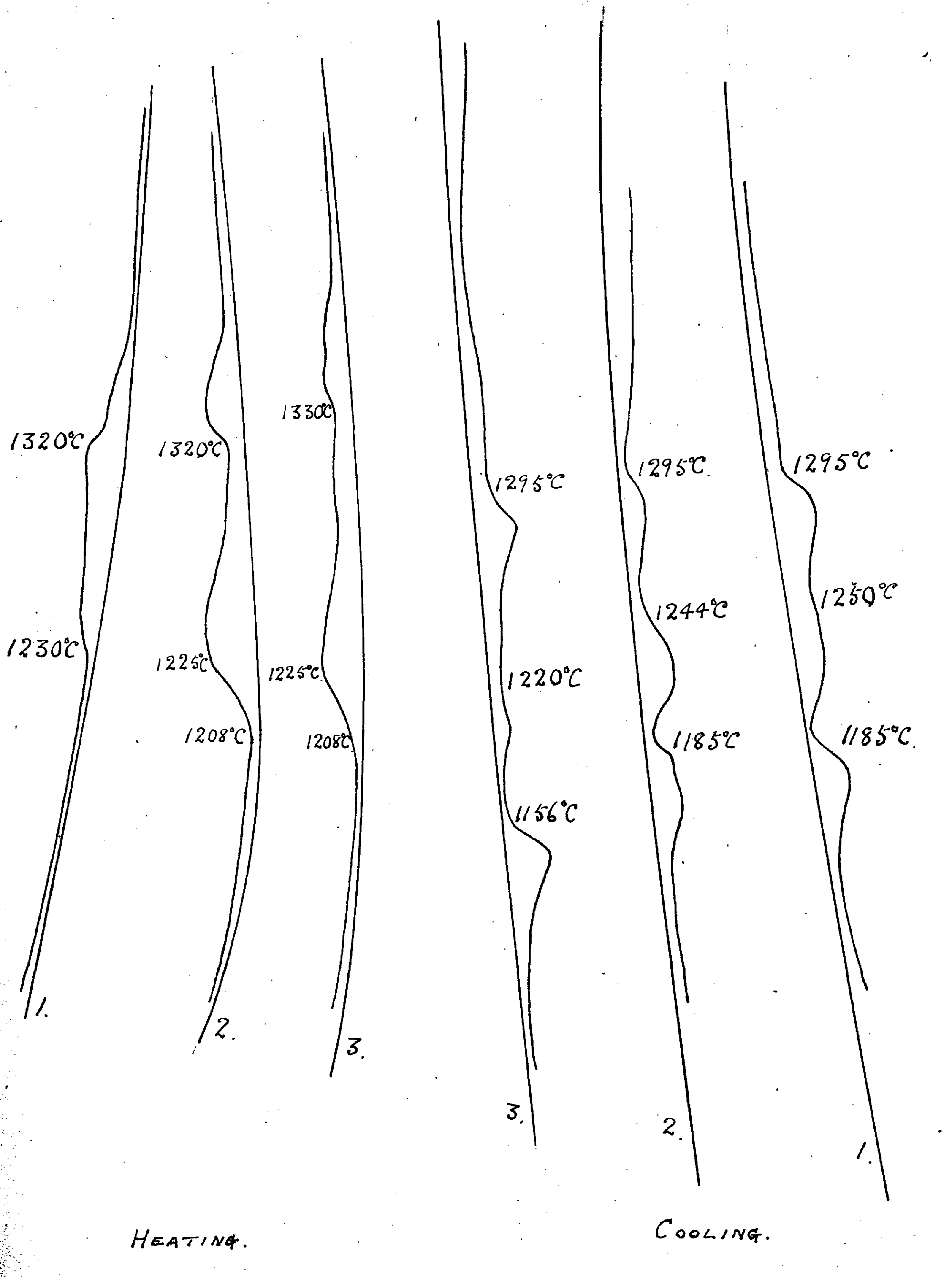
SiO_2.. 36%.

FIG. 34.



MnO. 60%
SiO_2. 40%

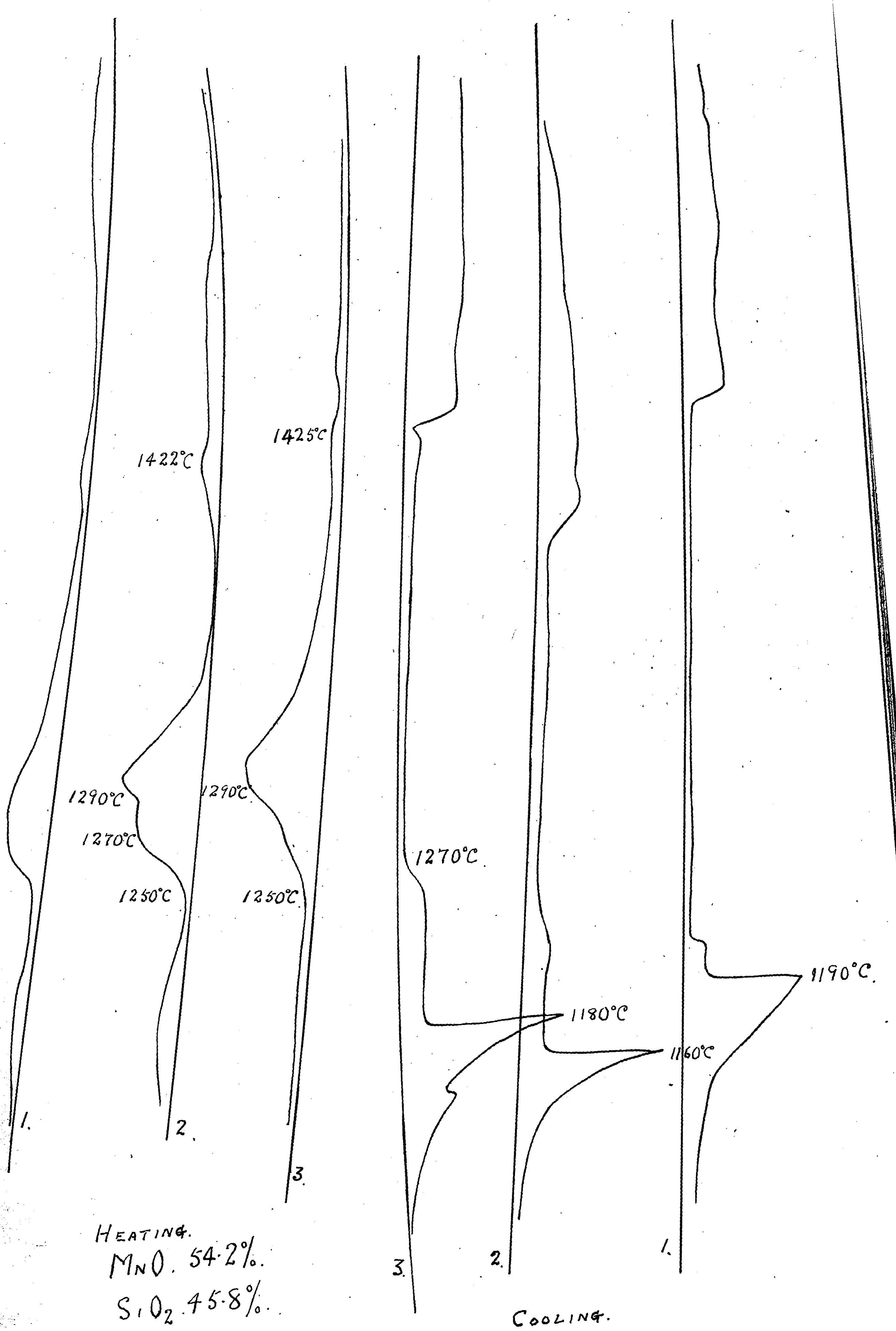
FIG. 38.



MnO. 57·5%

SiO_2. 42·5%

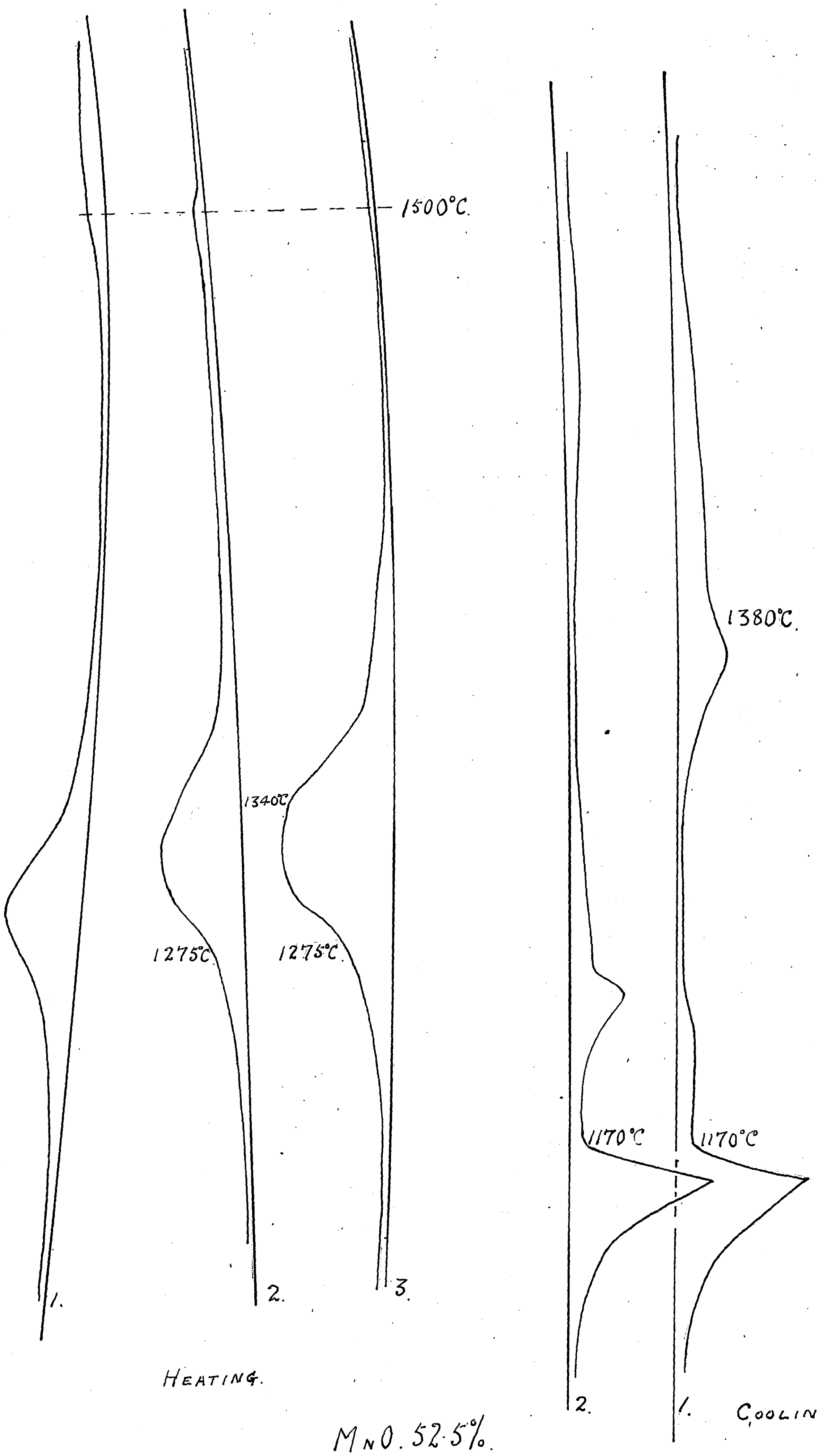
Fig. 39.



MnO. 54·2%.
SiO₂. 45·8%.

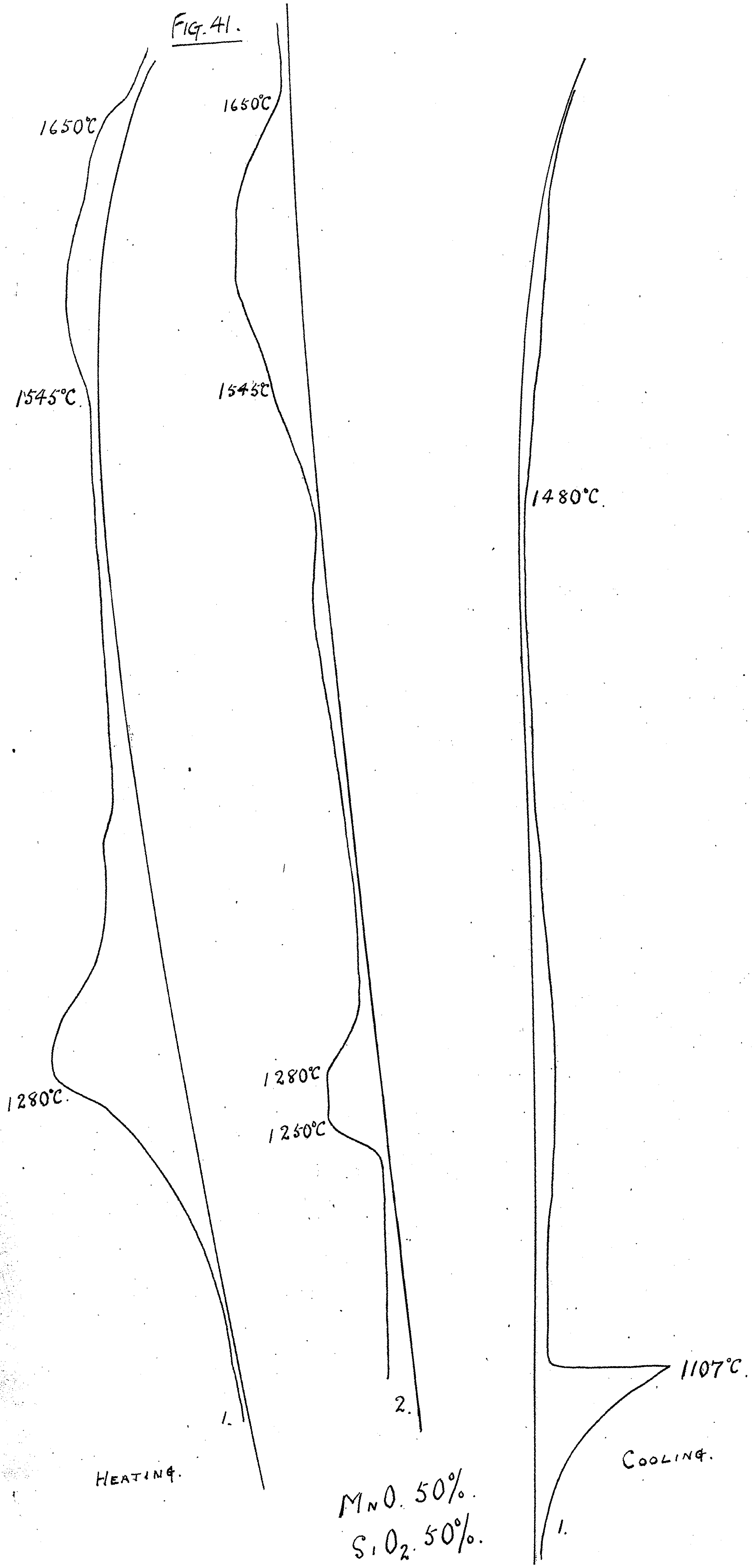
RHODONITE.

Fig. 40.



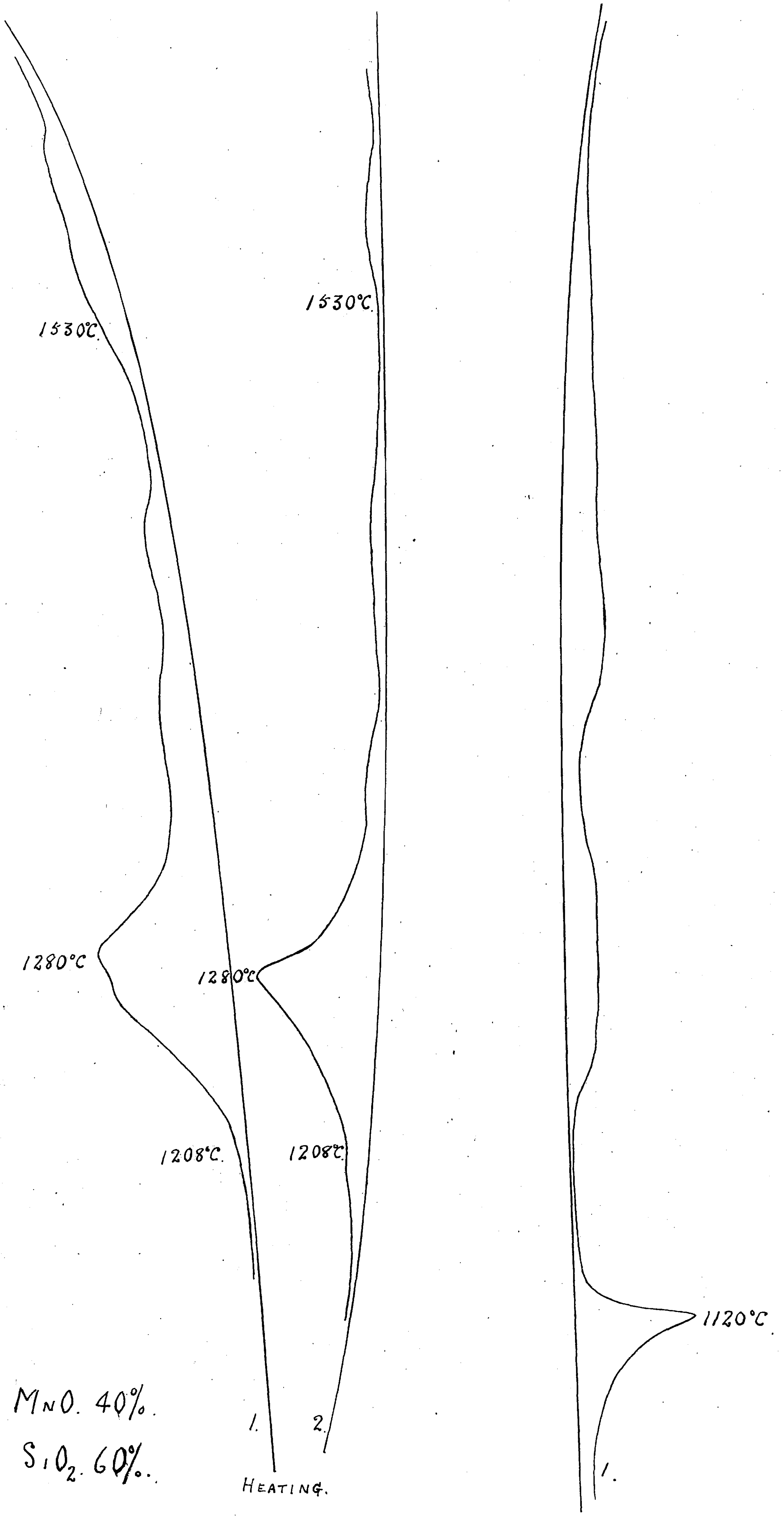
MnO. 52·5%.
SiO$_2$. 47·5%.

FIG. 41.



MnO. 50%.
SiO_2. 50%.

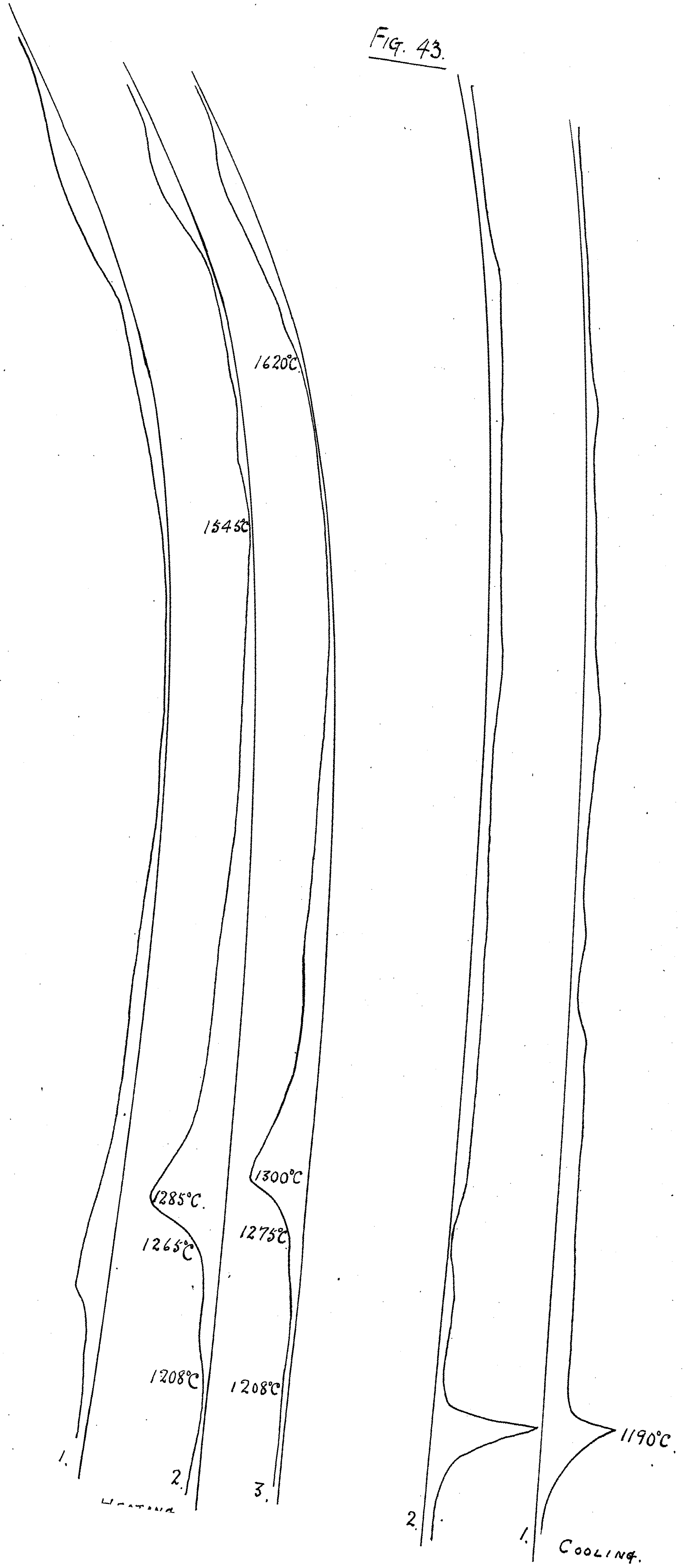
FIG. 42.



MnO. 40%.

SiO_2. 60%.

Fig. 43.



MnO. 25%
SiO$_2$. 75%.

FIG. 44.

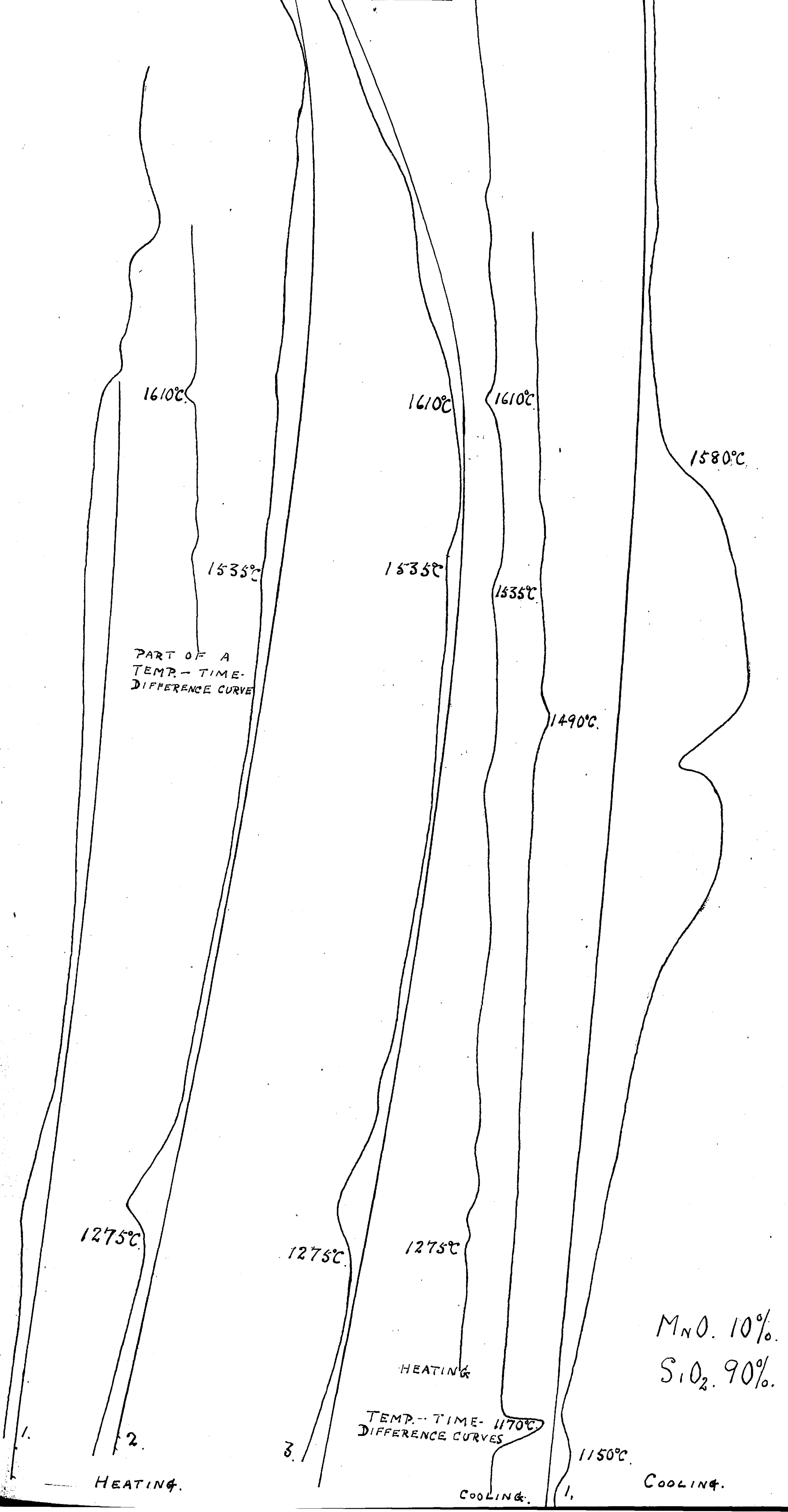
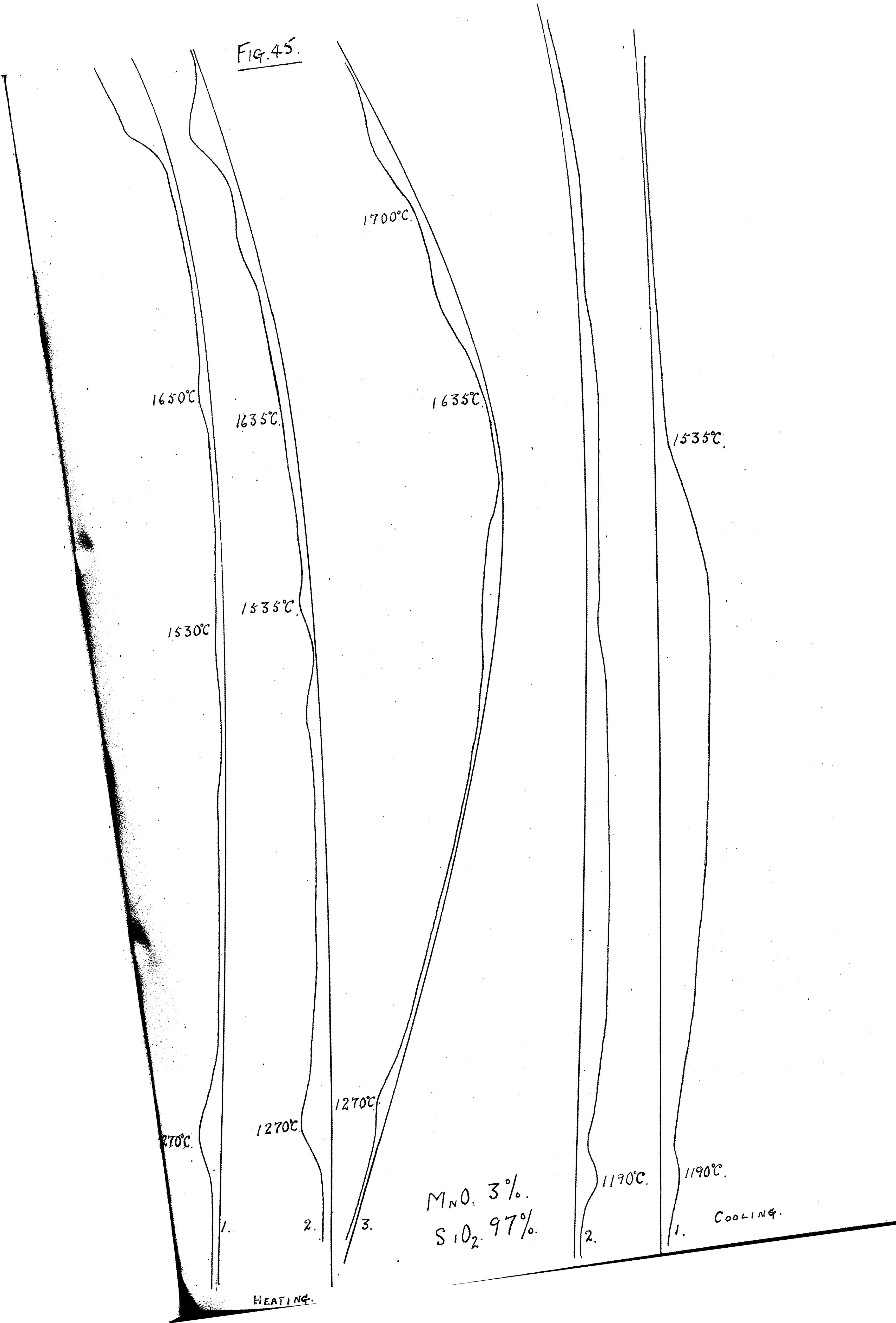
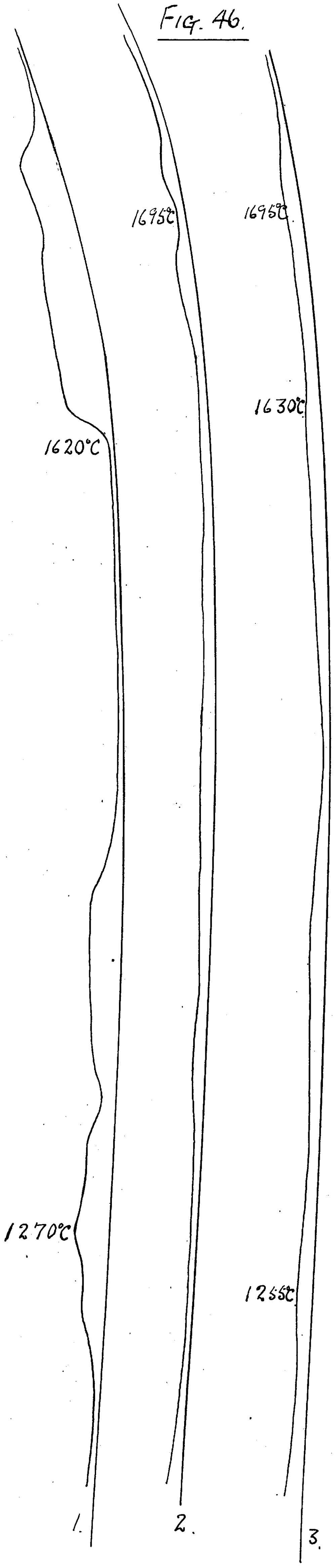

1610°C
1535°C
PART OF A TEMP. – TIME-DIFFERENCE CURVE
1275°C
1610°C
1535°C
1275°C
1610°C
1535°C
1490°C
1275°C
HEATING
TEMP. – TIME-DIFFERENCE CURVES
1170°C
1580°C
1150°C
1.
2.
3.
1.
HEATING.
COOLING.
COOLING.
MnO. 10%.
SiO2. 90%.

Fig. 45.



MnO. 3%.
SiO_2. 97%.

Fig. 46.



Heating.

MnO 1%
SiO_2 99%.

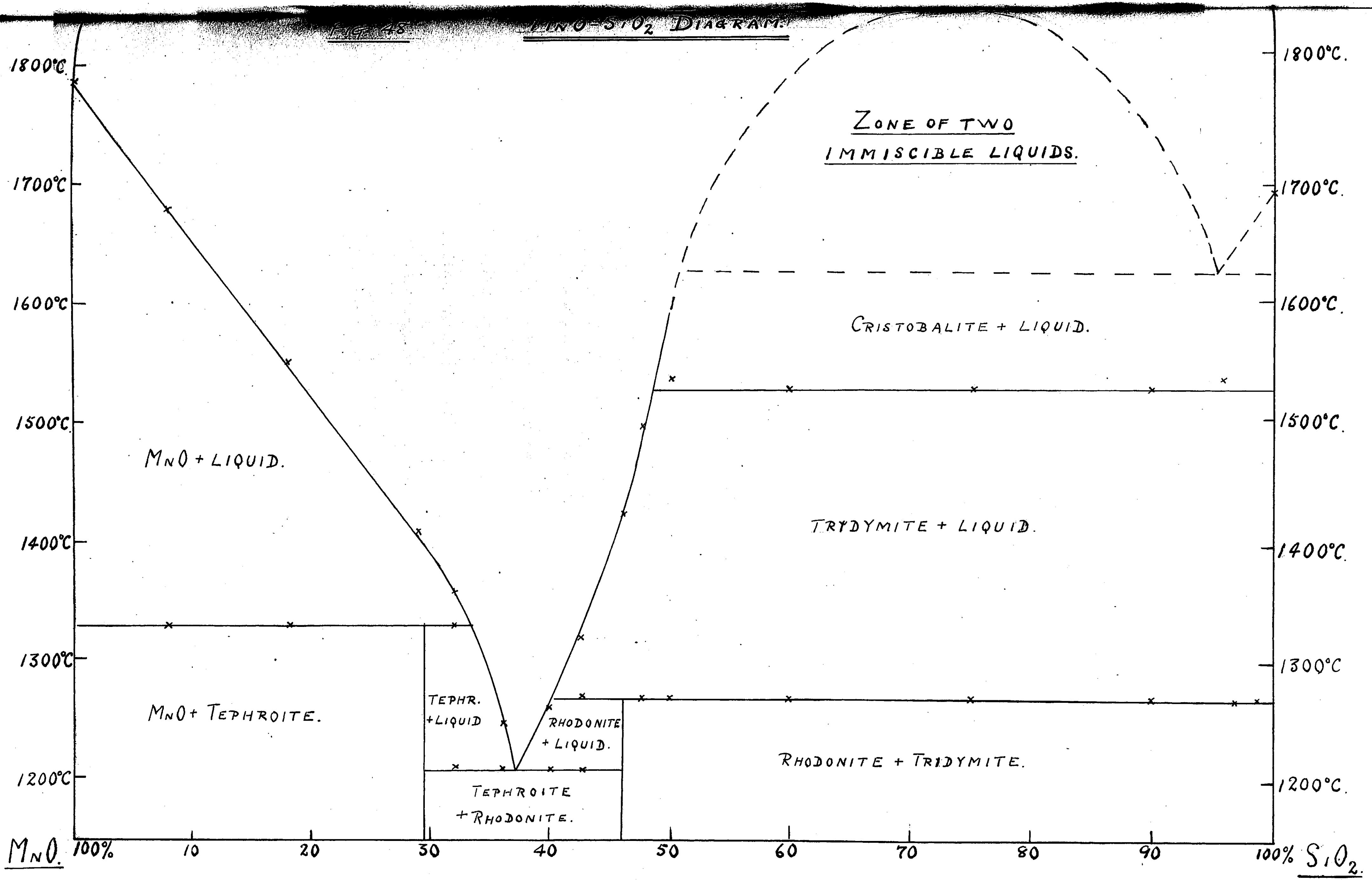
Fig. 47. The Optical Properties of the System MnO-SiO_2.

Melt.		Phases present.	Colour of phases.	Refractive Index.
MnO.	SiO_2.			
100%.		MnO	Bright green.	2.16
95%.	5%.	MnO Tephroite	Bright green. Colourless.	2.16 1.78-2.00
82%.	18%.	MnO Tephroite	Bright green. Colourless.	2.16 1.78-2.00
70.4%.	29.6%.	Tephroite	Colourless.	1.78-2.00
68%.	32%.	Tephroite Rhodonite	Colourless. Brown.	1.78-2.00 1.76
64%.	36%.	Tephroite Rhodonite	Colourless. Brown.	1.78-2.00 1.76
60%.	40%.	Tephroite Rhodonite	Colourless. Brown.	1.78-2.00 1.76
57.5%	42.5%.	Tephroite Rhodonite	Colourless. Brown.	1.78-2.00 1.76
54.2%.	45.8%.	Rhodonite	Brown.	1.76
50%.	50%.	Rhodonite Tridymite	Brown Colourless.	1.66-1.74 1.49-1.50
40%.	60%.	Rhodonite Tridymite	Brown Colourless.	1.66-1.74 1.49-1.50
30%.	70%.	Rhodonite Tridymite	Brown Colourless.	1.66-1.74 1.49-1.50
10%.	90%.	Rhodonite Tridymite	Brown Colourless	1.66-1.74 1.49-1.50
3%.	97%.	Rhodonite Tridymite	Brown Colourless.	1.76 1.49-1.50
1%.	99%.	Tridymite Rhodonite (Trace)	Colourless. Brown	1.49-1.50 1.76

Other Optical Properties Determined.

Phase.	Pleochroism.	Polarisation colour.	Extinction angle.
MnO.	-	High.	Straight.
Tephroite.	-	High.	Straight.
Rhodonite.	Faint.	Medium.	45°.
Tridymite.	-	Low-grey.	Straight.

FIG. 48. MnO-SiO$_2$ DIAGRAM.



Section IV. The Investigation of the Thermal Equilibrium Diagram of the System FeO-MnO by the Differential Thermocouple Method.

The wide discrepancy between the values for the melting point of MnO, as determined by the methods described in Section 1, and by those described in Section 111, immediately aroused doubts as to the accuracy of the FeO-MnO diagram which had been derived in Section 1. As was noted, when discussing the diagram, there is a break in the liquidus at about 35% MnO and the upper part of the diagram does not fit in at all well with the values obtained for the lower part.

An attempt to obtain more accurate data regarding the system was then made by the use of differential thermocouple methods and molybdenum crucibles. This constituted the last stage of the work outlined here.

The FeO and MnO used in the determinations were carefully prepared as detailed in Section 1.

The general arrangement of the differential thermocouple and of the crucible and neutral body was the same as described for $MnO-SiO_2$ in Section 111. Owing to the presence of FeO, however, the work had to be carried out in an inert atmosphere. A pythagoras tube, connected through a manometer with the nitrogen supply as described in Section 1, was used. It has already been mentioned that pythagoras tubes soften appreciably above 1600°C. The investigation was consequently limited to a study of those mixtures which did not require temperatures much in excess of this for melting. Actually a temperature of about 1700°C was reached, but the life of the tube, when used in this way was very short, the heated zone very quickly becoming buckled and distorted.

Just as before a charge of approximately 2 gms. was used. The required percentages of FeO and MnO were accurately weighed out, finely crushed and intimately mixed together and then introduced into the crucible. The heating and cooling curves were determined in exactly the same manner as formerly. It was usually found that the first heating curve differed in general outline from the subsequent curves due, no doubt, to heats of reaction, solution, etc. The remaining heating curves were in every case almost identical. Very close agreement was also observed in the cooling curves.

Discussion of Results Obtained in the FeO-MnO Determinations.

The thermal curves obtained in the investigation are reproduced in figs. 49-55.

The curves for various samples of FeO are shown in figs. 49 and 50 and these have already been referred to in the discussion on the thermal curves for FeO in Section 1. It will be noted that in each sample the arrest at 1350-1355°C is most pronounced, this arrest corresponding to the peritectic dissociation of the mixture into two phases, one iron with a very small amount of oxygen in solid solution, and the other an oxygen-rich liquid.

In each case there is an arrest at 1410°C, which will mark the allotropic change in iron, the temperature of the transformation being raised by the presence of oxygen in solution. The material becomes completely molten at about 1480°C.

As was indicated in the discussion of the system earlier, the existence of a peritectic reaction within the system seems to be quite well established. A study of the curves for the 70/30, 60/40 and 50/50 FeO/MnO mixtures in figs. 53, 54 and 55, respectively, will reveal in each case a well-defined point commencing at 1425-1430°C, and 1430°C has been taken as the peritectic temperature. It would appear that there is not the complete solubility between the oxides which the very close resemblance between their crystalline form would lead one to expect.

The limit of solubility of MnO in FeO, α-solution, appears to be about 12-13%. In the curve for the 90/10 FeO/MnO mixture, fig. 51, melting begins about 1360°C reaches a maximum at 1400°C and liquefaction is complete about 1430°C. This is the only point available for fixing the position of the α-solution liquidus line. The position of the α-solution solidus line can be fixed approximately by the lower arrests on the 90/10, 80/20 and 70/30 FeO/MnO thermal curves. These arrests occur at the temperatures shown and have been taken as fixing the position of the line:-

Mixture.		Lower Arrest Temperature in °C.
FeO. %.	MnO. %.	
90	10	1365
80	20	1370
70	30	1390.

See figs. 51-53.

The limit of solubility of FeO in MnO seems to be about 45%. The position of the β-solution liquidus line has been arrived at by noting the temperature at which the upper arrest is completed, and these temperatures occur in the various mixtures as shown:-

Mixture.		Temperature at which upper arrest is completed in °C.
FeO. %.	MnO. %.	
80	20	1500
70	30	1550
60	40	1610
50	50	1650
40	60	1700.

See figs. 52-55.

The final point on the liquidus, the melting point of MnO, has already been determined as 1785°C.

The part of the liquidus between 60 and 100% MnO has been extrapolated and is shown in the diagram in dotted lines.

One or two anomalous points may be noted. First in the 50/50 mixture, fig. 55, there is an arrest at 1370°C. The existence of this point may be explained by assuming an increase in the solubility of the materials on heating. With rapid heating the

the/ diffusion of the α-solution into β-solution does not take place gradually, but occurs suddenly at that temperature.

In the curve for the 80/20 FeO/MnO mixture after the lower arrest at 1370°C, there is a continuous arrest from 1400-1500°C. This may be very simply explained by the fact that the peritectic reaction and melting of the mixture follow one another so closely that the arrests are not separated on the thermal curves.

In some cases the cooling curves do not correspond very closely with the interpretations put upon the heating curves. In the curves for the 90/10 FeO/MnO mixture the first trace of a cooling arrest seems to occur above the upper arrest on the heating curve. In the curve for the 50/50 mixture there are a series of arrests on the cooling curve which can only be explained by assuming that precipitation does not take place regularly but in a series of steps.

The data obtained has been incorporated in the diagram in fig. 57.

The occurrence of the two different phases has been checked by the usual optical methods.

The diagram put forward is in general agreement with the provisional one suggested by Benedicks and Lofquist in their book on "Non-metallic Inclusions in Iron and Steel" but differs slightly in the limits of solubility of the α and β-solutions and in the temperature of the peritectic.

It differs quite markedly from the diagram put forward by Herty (Metals and Alloys. Dec. 1930. P. 883). In this diagram complete solubility between the two oxides is postulated, and the melting point of MnO is given as 1610°C.

The Optical Properties of the System FeO-MnO.

An attempt was made to determine the optical properties of the constituents of this system by employing Beck's method for powdered material exactly as described for the system $MnO-SiO_2$ in Section 111.

This investigation demonstrated the existence of the two distinct phases. A fact which had been strongly suspected as a result of a study of the thermal data. The refractive indices of solid solutions will vary with the composition of the solution, and this is borne out by a study of the results tabulated in fig.56, There is no marked difference in the refractive indices of the two phases. This is quite in accordance with what would be expected due to the very close similarity in crystalline form which does exist between the two oxides.

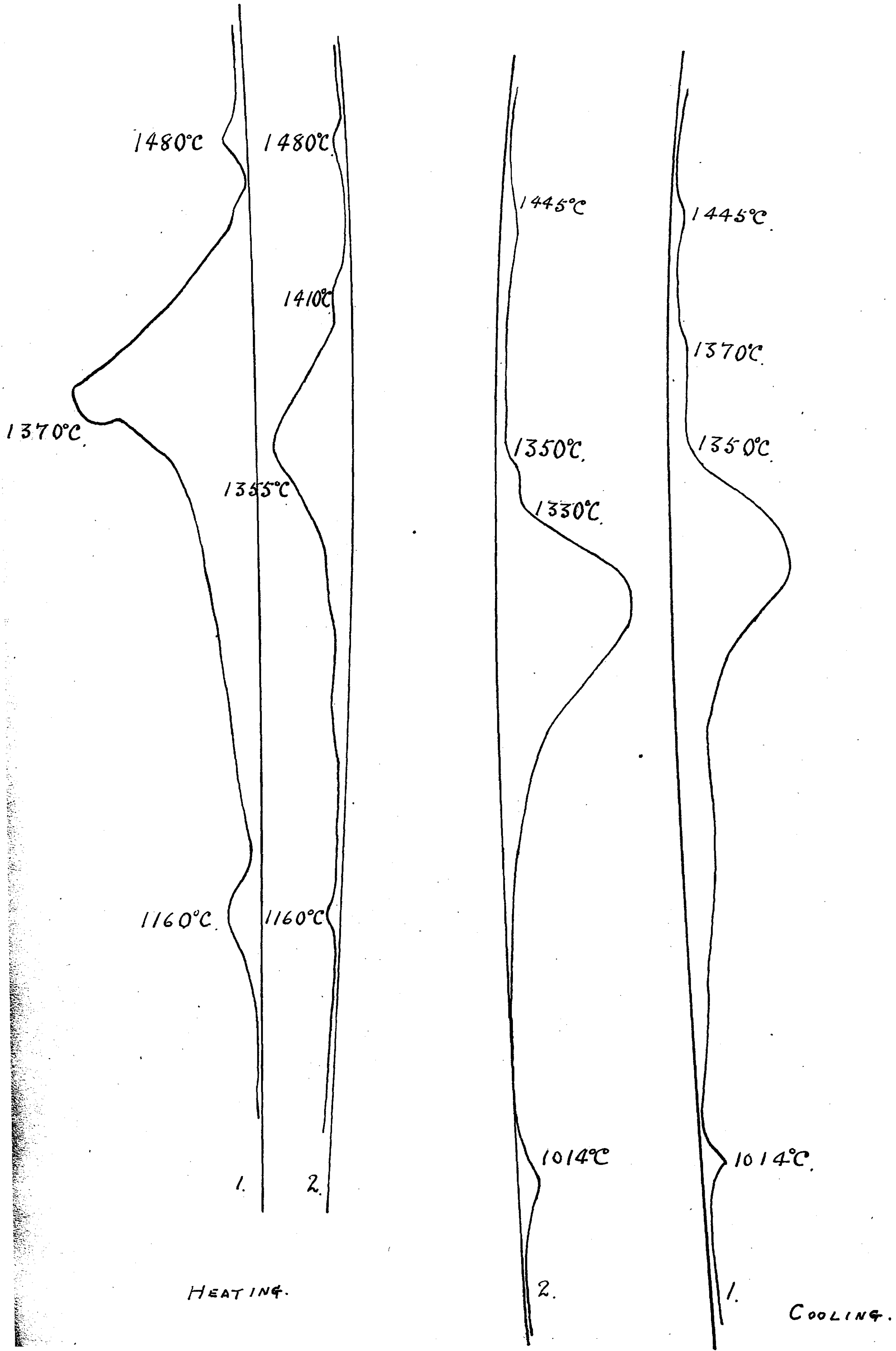
Fig. 56. The Optical Properties of the System FeO-MnO.

Melt. FeO.	Melt. MnO.	Phases present.	Colour of phases.	Refractive Index.	Extinction Angle.
100%.			Dull grey (Thin section) Steel blue (Reflected light).	1.78-2.00	Isotropic.
90%.	10%.	α.	Dull grey.	2.00	Isotropic.
80%.	20%.	α.	Dull grey.	2.05	Isotropic.
		β.	Slight evidence of 2nd. phase.	-	-
70%.	30%.	α.	Dull grey.	2.05	Isotropic.
		β.	More of 2nd. phase present.	-	-
60%.	40%.	α.	Red brown.	2.08	Isotropic.
		β.	Light green.	2.13	Isotropic.
50%.	50%.	α.	Red brown.	2.11	Isotropic.
		β.	Light green.	2.13	Isotropic.
	100%.		Green.	2.16	Isotropic.

There was very little trace of pleochroism or polarisation colours in any of the melts examined.

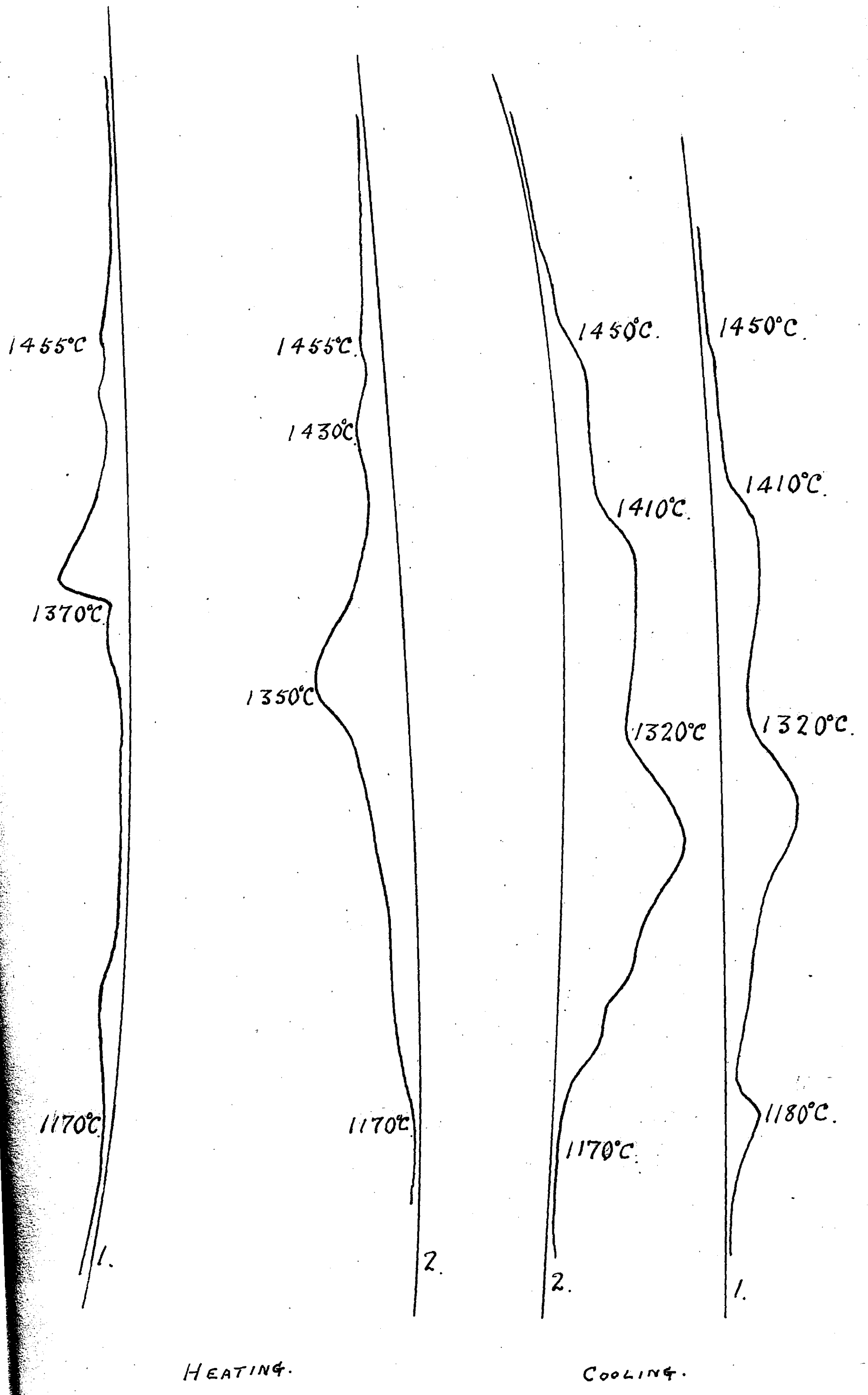
Fig. 49.

All curves traced from originals by an Eidograph and reduced by 1/3.



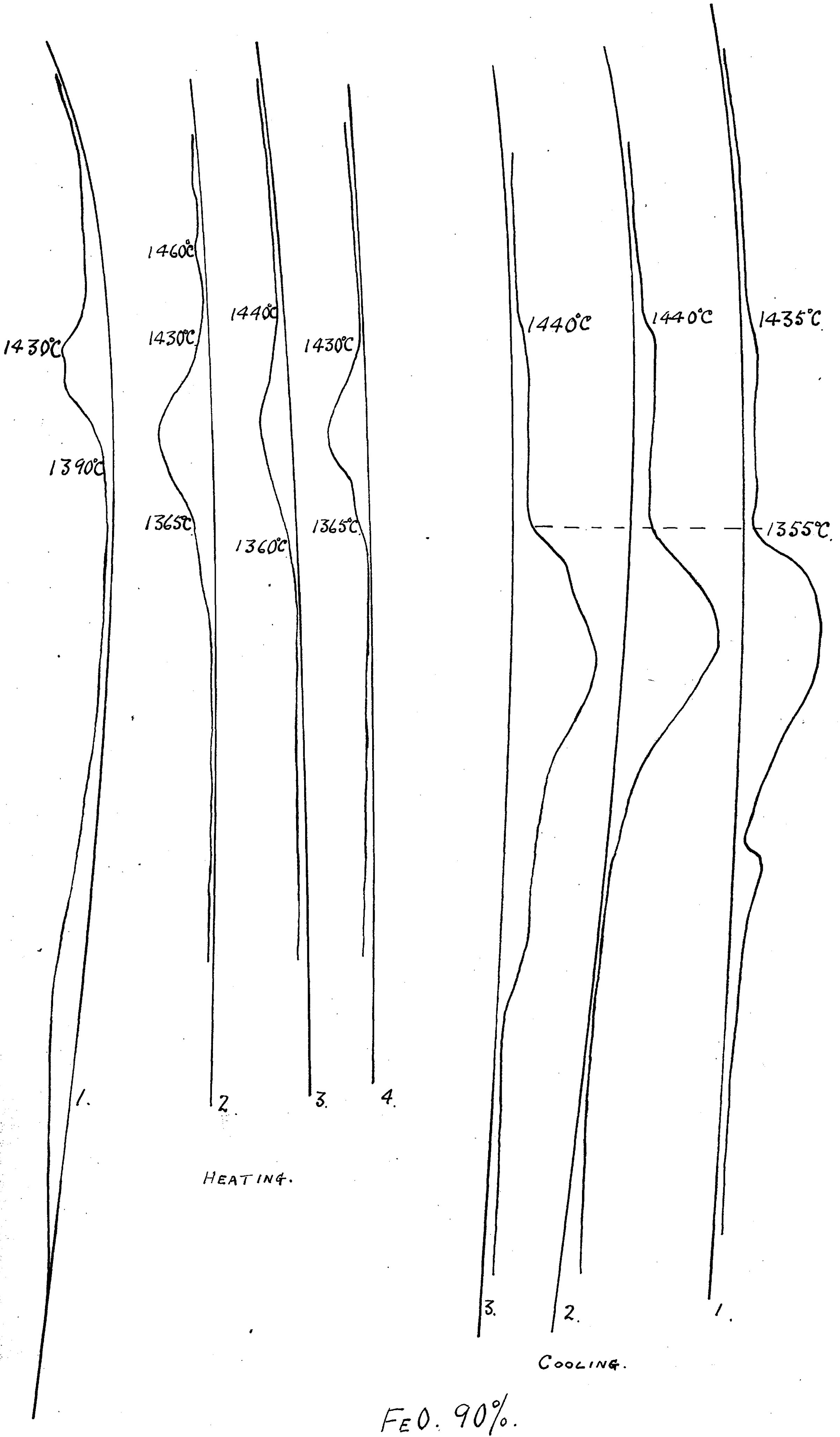
FeO. 100%.
Non-Magnetic.

Fig. 50.



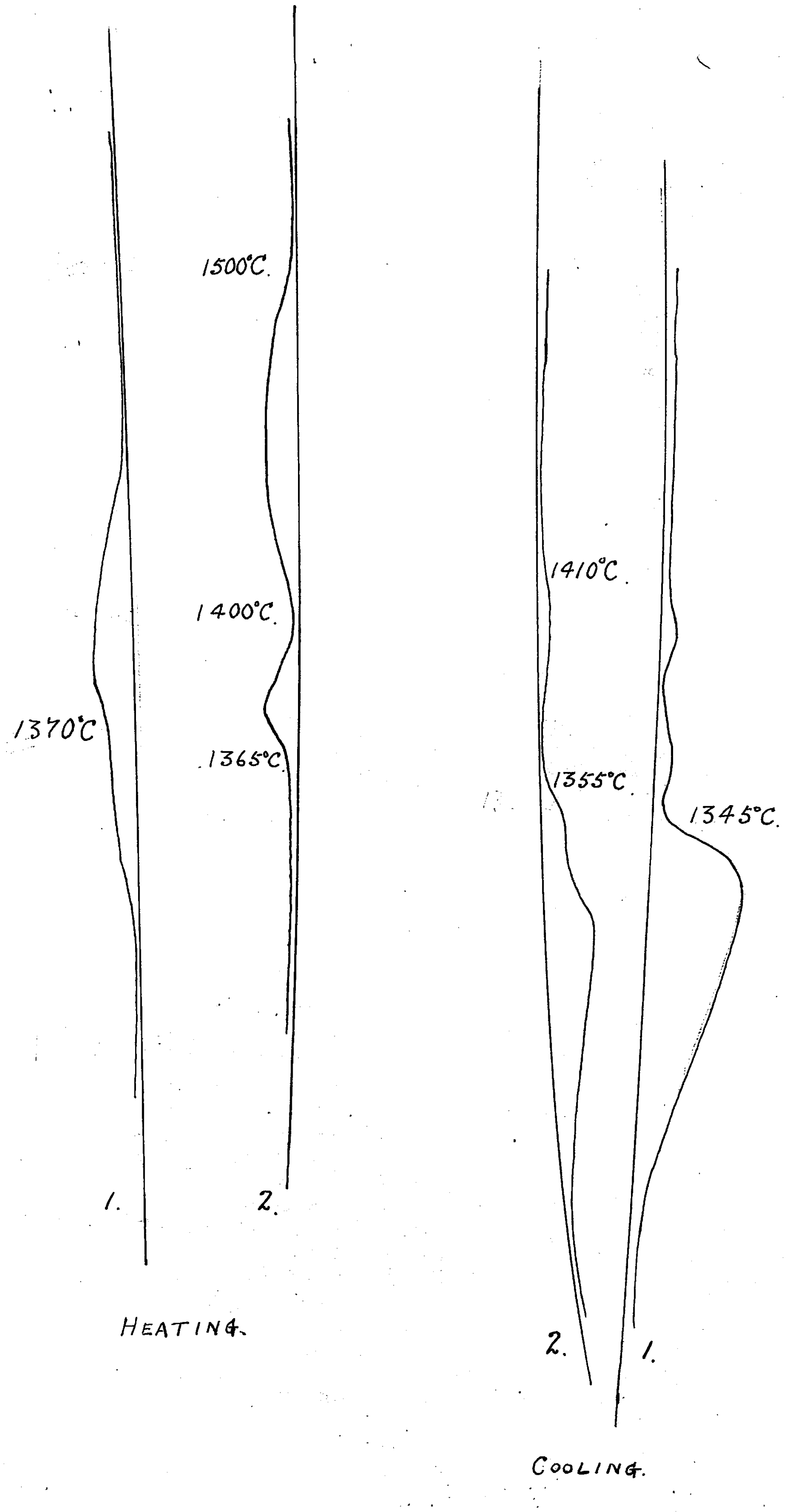
FeO 100%.
Magnetic.

FIG. 51.



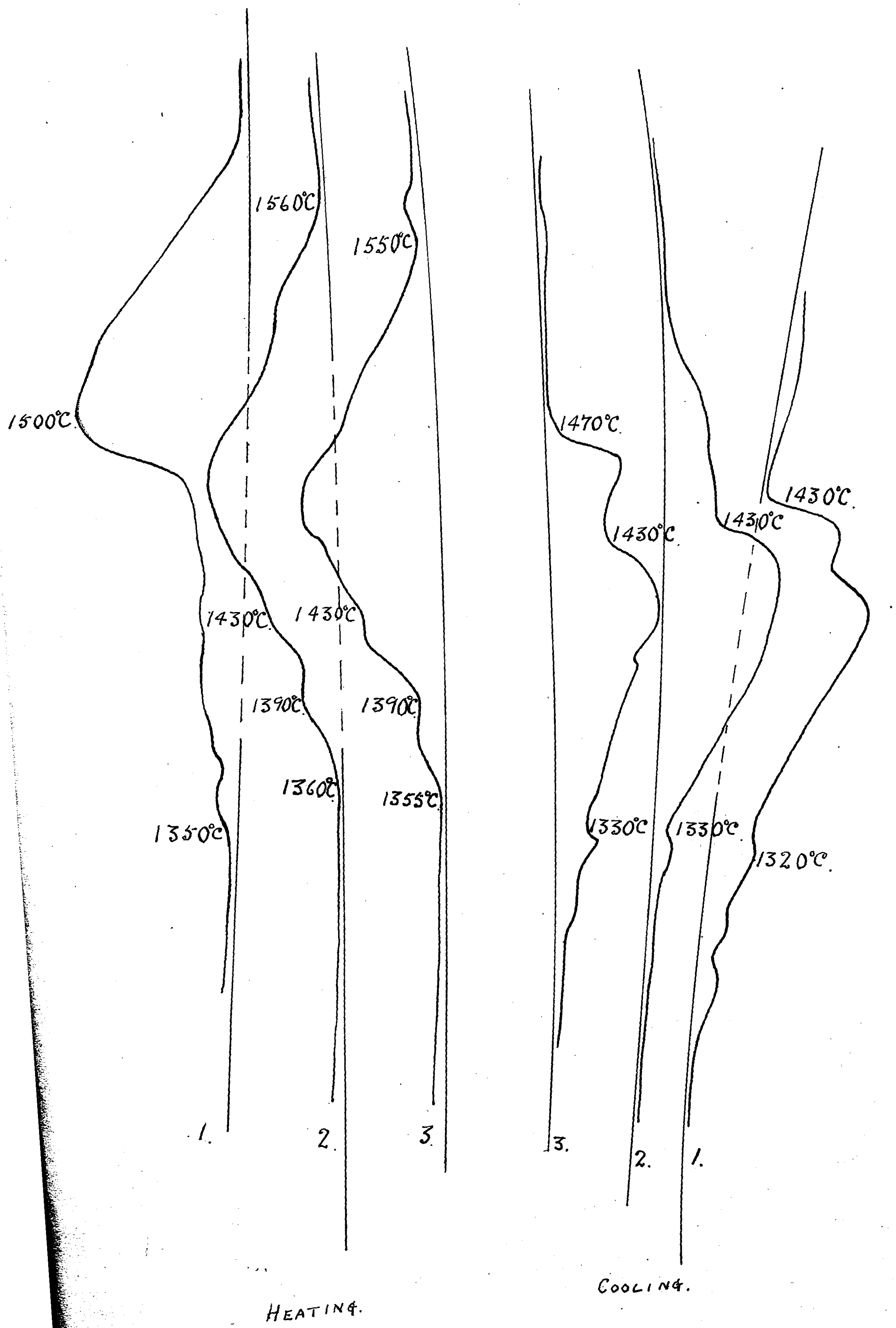
FeO. 90%.
MnO. 10%.

Fig. 52.



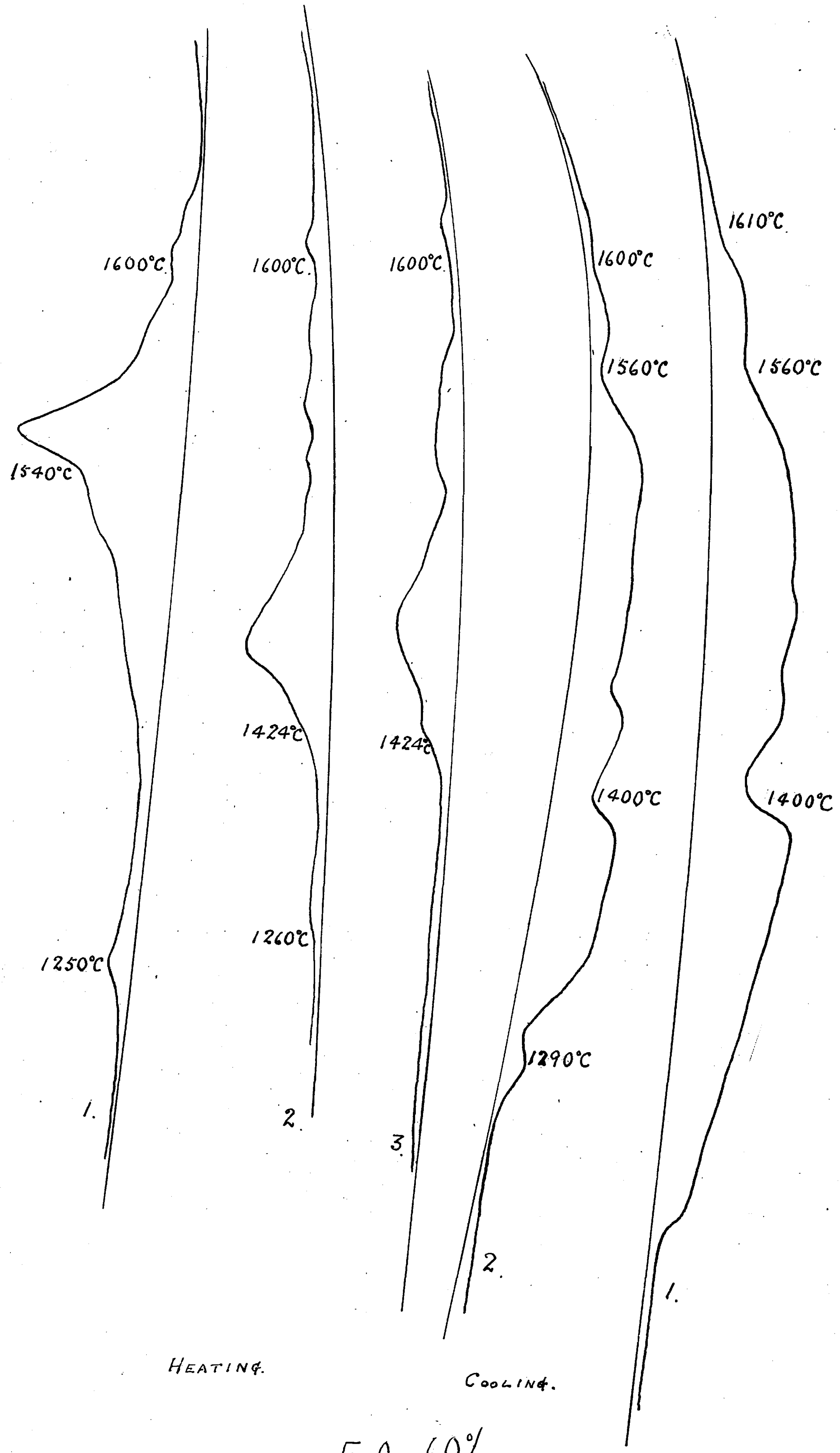
FeO. 80%.
MnO. 20%.

Fig. 53.



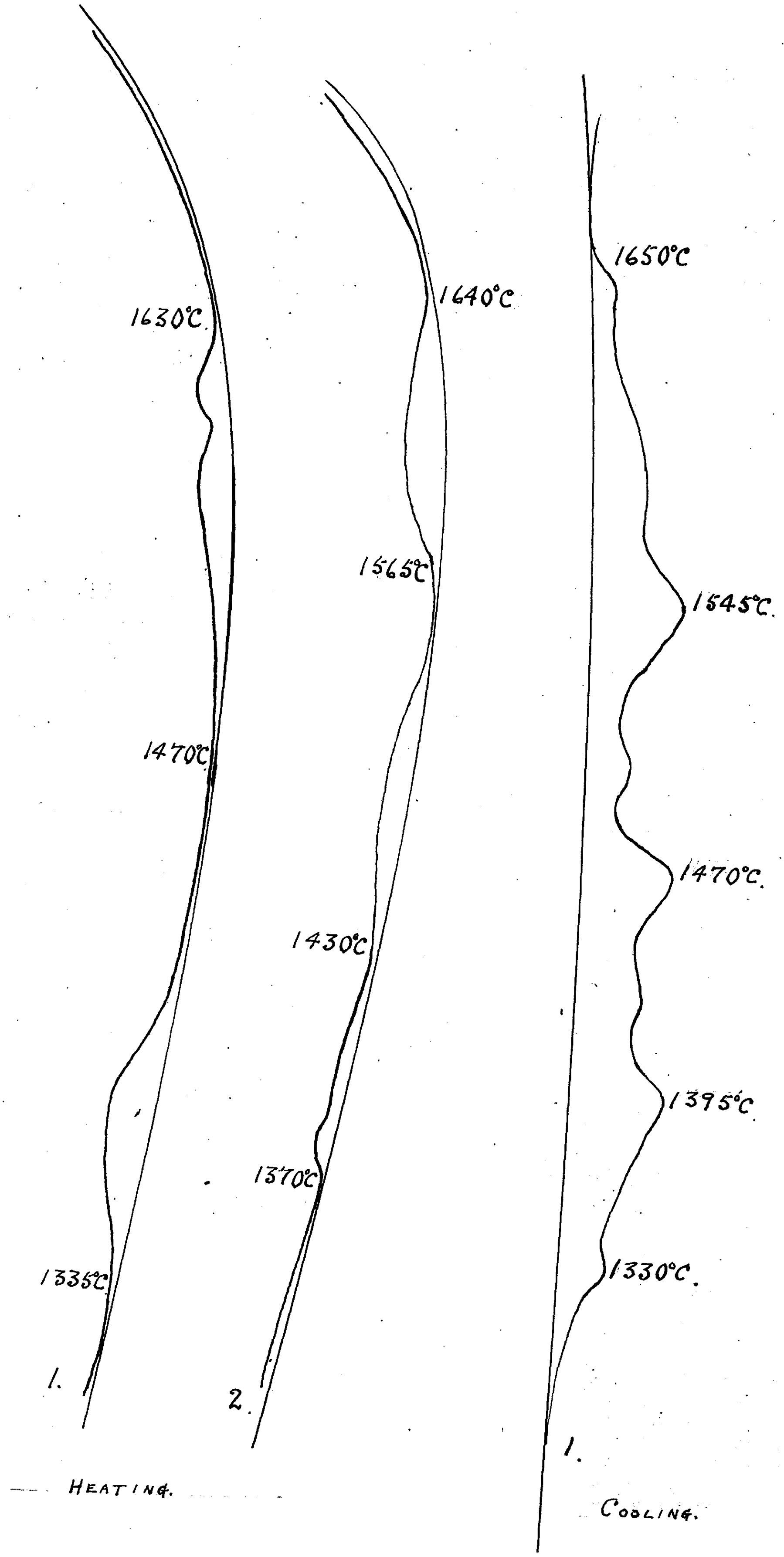
FeO. 70%.
MnO. 30%.

Fig. 54.



FeO. 60%.
MnO. 40%.

Fig. 55.



FeO. 50%.
MnO. 50%.

Fig. 57. FeO-MnO Diagram.