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[F O U R T H S E R I E S .]



ART. XL.—*The Binary System MgO-SiO₂*; by N. L. BOWEN
and OLAF ANDERSEN.

INTRODUCTION.

IN the course of work on two supposed binary systems of which $MgSiO_3$ was one component, the writers have found that $MgSiO_3$ is unstable at its melting point and can itself be treated only as part of a binary system and not as a separate component. The supposed binary systems mentioned must therefore be treated as ternary systems and before proceeding to the study of our separate ternary systems we have worked out jointly the binary system $MgO-SiO_2$ which is common to both.

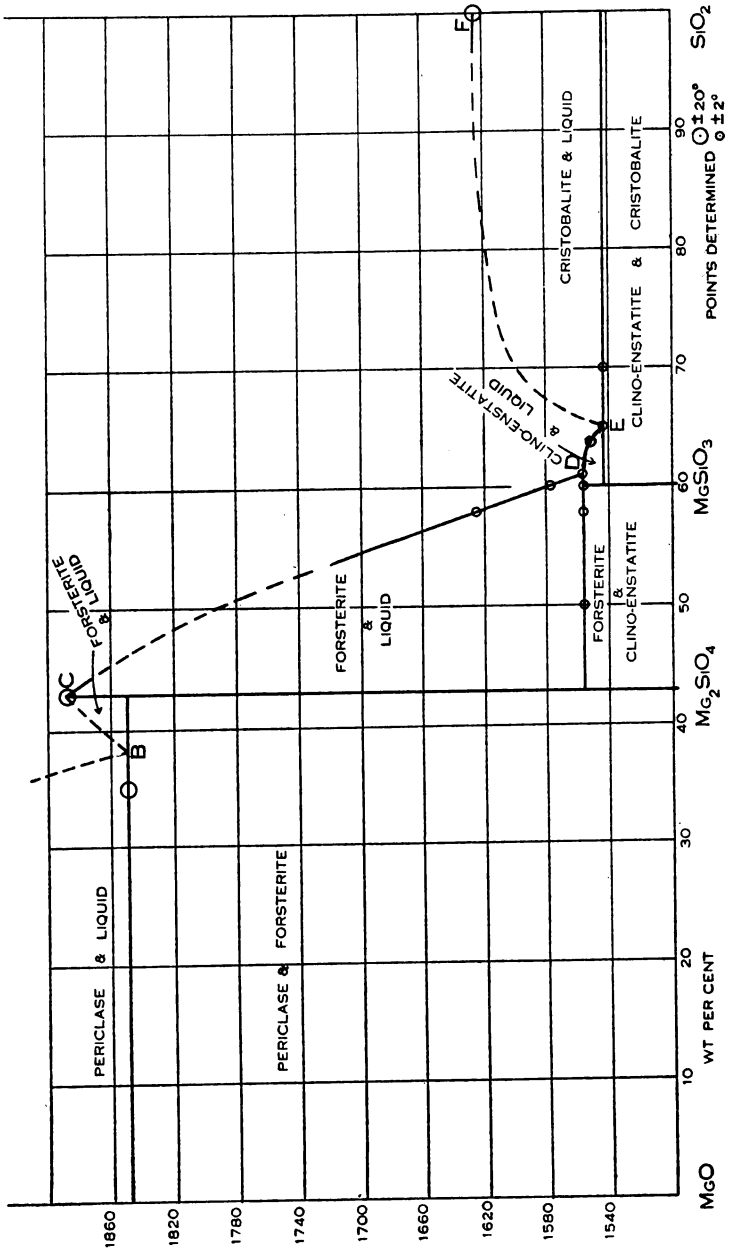
In compositions towards the magnesia end the temperatures are beyond the range of accurate determination and towards the silica end viscosity is so great as to preclude great accuracy, so that only approximate results are possible, but in the intermediate mixtures the determination of compounds and the fixing of the invariant points have been accomplished with precision.

THE METHOD OF WORKING.

The mixtures used were made up from selected quartz, ground and treated with HCl, and magnesia obtained by igniting the precipitated carbonate to constant weight.

In studying equilibrium in the system we have depended almost entirely on quenching experiments. The method has frequently been described in publications* from this laboratory. It consists in holding a small charge of a mixture of known composition at a measured temperature, in a platinum resistance furnace, until equilibrium is attained, then cooling

* e. g., Shepherd & Rankin, this Journal (4), xxviii, 308, 1909.



instantaneously to room temperature by allowing the charge to fall into a dish of mercury, and examining the charge under the microscope to determine the phases present. In this manner the phases present at all attainable temperatures, in all compositions, can be definitely fixed. The thermoelement of Pt-Pt:Rh, used to measure the temperature, is frequently calibrated by quenching charges of pure, artificial minerals of known melting point, usually diopside and anorthite. As will appear from an examination of the tabulated results, the actual procedure with any given mixture is to locate by quenching, between as narrow limits as possible, the temperature at which a phase appears or disappears.

To reach some of the higher temperatures an iridium furnace was used and the temperatures were measured optically.

RESULTS.

The completed results are now presented in tabular and diagrammatic form before proceeding to their discussion.

TABLE I.

QUENCHING RESULTS. PLATINUM RESISTANCE FURNACE. TEMPERATURE MEASURED WITH THERMOELEMENT.

(a) *Liquidus of Forsterite.*

Oxides	Composition Compounds	Temperature	Time	Result	
MgO 42	SiO ₂ 58	{ Mg ₂ SiO ₄ 11·7 } { MgSiO ₃ 88·3 }	1625°	1 hr.	glass and minute amount forsterite
40·1	59·9	MgSiO ₃ 100	1576° 1578°	1 hr. 1 hr.	glass and forsterite glass only

(b) *Temperature of Invariant Point, Forsterite-Clino-enstatite-Liquid.*

50	50	{ Mg ₂ SiO ₄ 58·5 }	1555°	1 hr.	clino-enstatite and forsterite
		{ MgSiO ₃ 41·5 }	1559°	1 hr.	glass and forsterite
42	58	{ Mg ₂ SiO ₄ 11·7 }	1555°	1 hr.	clino-enstatite and forsterite
		{ MgSiO ₃ 88·3 }	1559°	1 hr.	forsterite and glass
40·1	59·9	MgSiO ₃ 100	1556°	1 hr.	clino-enstatite
			1558°	1 hr.	glass and forsterite

Temperature = 1557° ± 2°

(c) *Composition of Invariant Point, Forsterite-Clino-enstatite-Liquid.*

Oxides	Composition Compounds	Temperature	Time	Result	
MgO 38·8	SiO ₂ 61·2	{ MgSiO ₃ 97 } { SiO ₂ 3 }	1557° 1555°	1 hr. 1 hr.	glass only glass and clino-enstatite

Oxides	Composition Compounds	Tempera- ture	Time	Result
MgO 39	SiO ₂ 61	{ MgSiO ₃ 97·5 } { SiO ₂ 2·5 }	1558° 1556°	1 hr. glass only 1 hr. glass and clino-enstatite
39·2	60·8	{ MgSiO ₃ 98 } { SiO ₂ 2 }	1560° 1558°	1 hr. glass only 1 hr. glass and forsterite

Composition = MgSiO₃ 97·5%, SiO₂ 2·5%

(d) *Temperature and Composition of Eutectic
Clino-enstatite-Cristobalite.*

MgO	SiO ₂	{ MgSiO ₃ 90 }	1540°	2 hrs.	Clino-enstatite and cristobalite
36	64	{ SiO ₂ 10 }	1545°	2 hrs.	Clino-enstatite and glass
35	65	{ MgSiO ₃ 87·5 }	1542°	2 hrs.	Clino-enstatite and cristobalite
		{ SiO ₂ 12·5 }	1544°	2 hrs.	glass only
30	70	{ MgSiO ₃ 75 }	1540°	2 hrs.	Clino-enstatite and cristobalite
		{ SiO ₂ 25 }	1545°	2 hrs.	glass and cristobalite

Temperature = 1543° ± 2°
Composition = MgSiO₃ 87·5%, SiO₂ 12·5%

(e) *Liquid of Clino-enstatite.*

MgO	SiO ₂	{ MgSiO ₃ 97 }	1557°	1 hr.	glass only
38·8	61·2	{ SiO ₂ 3 }	1555°	1 hr.	glass and clino-enstatite
36	64	{ MgSiO ₃ 90 }	1554°	2 hrs.	glass only
		{ SiO ₂ 10 }	1550°	2 hrs.	glass and clino-enstatite

OBSERVED IN IRIIDIUM FURNACE.
TEMPERATURE MEASURED WITH OPTICAL PYROMETER.

Oxides	Compounds	Temperature
MgO 57·2	SiO ₂ 42·8	Mg ₂ SiO ₄ 100% melting point 1890° ± 20°
65	35	{ Mg ₂ SiO ₄ 86 } { MgO 14 } eutectic melting 1850° ± 20°

SUMMARY OF INVARIANT POINTS.*

Solid Phases	Liquid Phase	Temperature
Periclase (MgO)	MgO 100 %	2800° (Kanolt)
{ Periclase (MgO) } { Forsterite (Mg ₂ SiO ₄) }	{ < 14% MgO } { > 86% Mg ₂ SiO ₄ }	1850° ± 20°
Forsterite (Mg ₂ SiO ₄)	Mg ₂ SiO ₄ 100 %	1890° ± 20°
{ Forsterite (Mg ₂ SiO ₄) } { Clino-enstatite (MgSiO ₃) }	{ MgSiO ₃ 97·5% } { SiO ₂ 2·5% }	1557° ± 2°
{ Clino-enstatite (MgSiO ₃) } { Cristobalite (SiO ₂) }	{ MgSiO ₃ 87·5% } { SiO ₂ 12·5% }	1543° ± 2°
Cristobalite (SiO ₂)	SiO ₂ 100 %	1625° (Fenner)

* These points are, of course, invariant only when the system is considered as a condensed system.

DISCUSSION OF RESULTS.

Magnesia.—We have found magnesia in only one form, as isotropic crystals corresponding with the mineral periclase. When it occurs embedded in glass, it is always in rounded grains with crystal outline at best only suggested. We have not tried to determine its melting point. Kanolt places it at $2800^\circ C.$;* Ruff, above 2500° .†

Silica.—Silica occurs in contact with liquid in magnesia-silica mixtures only as cristobalite. The inversion temperature cristobalite-tridymite, 1470° ,‡ lies below the range of temperatures at which any of our mixtures are liquid. We have taken Fenner's value 1625° as the melting point of cristobalite.

Compounds.—There are two binary compounds, the orthosilicate, Mg_2SiO_4 , and the metasilicate, $MgSiO_3$. We have not found any compounds, corresponding with the lime-silica compounds, åkermanite and tricalcium silicate, or traces of any phase other than the metasilicate, the orthosilicate and the end components, occurring in contact with liquid in the binary system.

Mg_2SiO_4 .—Magnesium orthosilicate occurs in orthorhombic crystals corresponding with the natural mineral forsterite. The melting point of forsterite was determined in an iridium furnace, the temperature being measured by means of an optical pyrometer of the Holborn-Kurlbaum type. The pyrometer was calibrated for the known points: 2050° , melting-point of Al_2O_3 ;§ 1755° , melting-point of platinum; 1557° , dissociation (with melting) of $MgSiO_3$. The lamp-filament was matched against a piece of thin iridium foil lying on the surface of the charge of the powdered mineral contained in an iridium boat. On the occurrence of melting, movement of the foil is observed. By this method the melting-point of forsterite was found to be 1890° . The error of a measurement made in this manner may be as much as 20° or 25° , an accuracy very much less than that attained for points lying within the temperature range of the platinum furnace and Pt-Pt:Rh thermoelement ($\pm 2^\circ$). We have therefore distinguished on the diagram the points determined by these two methods, indicating the latter by small circles and the former by larger circles.

$MgSiO_3$.—Magnesium metasilicate has no true melting point, i. e., there is no temperature at which the solid $MgSiO_3$ is in equilibrium with liquid of its own composition. The thermoelement records a strong absorption of heat at 1557° and this temperature has heretofore been considered the melting point, but quenching has shown that 1557° is the temperature of dissociation of $MgSiO_3$ into forsterite and liquid in the propor-

* Kanolt, C. W., Bureau of Standards, Reprint No. 212, 19, 1913.

† Ruff, O., Zs. anorg. Chem., lxxxii, p. 373, 1913.

‡ Fenner, C. N., The Stability Relations of the Silica Minerals, this Journal (4), xxxvi, 337, 1913.

§ Kanolt, C. W., Bureau of Standards, Reprint No. 212, 19, 1913.

tions, forsterite 5.5 per cent, liquid 94.5 per cent. The temperature must then be raised to 1577° before the solution of forsterite is complete and the whole becomes liquid.

Magnesium metasilicate was studied formerly at this laboratory and four forms described, the stable monoclinic pyroxene clino-enstatite, and three monotropic forms described as orthorhombic pyroxene, orthorhombic and monoclinic amphibole.* Later another orthorhombic form termed α -MgSiO₃ was added and described as enantiotropic with clino-enstatite (β -MgSiO₃), the latter being the low temperature form and the inversion point about 1365°.† The present work does not add any new information concerning the monotropic forms mentioned, but, concerning the material called α -MgSiO₃, a revision of the former statements is necessary in the light of the completed results of the binary system.

If a mixture of composition MgSiO₃ is cooled from the liquid condition, forsterite first separates out and with further cooling the remaining liquid crystallizes to a mixture of silica and MgSiO₃. The product then consists of clear, strongly-birefringent grains of forsterite embedded in a dusty matrix of indefinite properties, the dusty appearance being caused by the tiny specks of silica of very low refraction dotted through the MgSiO₃. It was these clear, strongly-birefringent grains of forsterite which were described as α -MgSiO₃ and were considered to be the product of inversion of clino-enstatite at a high temperature. They were really the product of dissociation of clino-enstatite at a high temperature and were not, as we have pointed out, a form of the metasilicate, but were the orthosilicate, forsterite.

The measured crystals described as α -MgSiO₃‡ and showing the forms (010), (110) and (011), referred to the axes $a : b : c = 1.19 : 1 : 0.47$ should have been termed forsterite. A rotation of the crystals through 90° on the b axis will give the forms (010), (021) and (110) referred to the axes $a : b : c = 0.47 : 1 : \frac{1.19}{2}$.

These latter ratios are those of forsterite, within the errors of measurement, and the forms are common in that mineral.§ The form (010) is more prominent than is usually the case in larger crystals, but there is a well-recognized tendency in small and quickly formed crystals toward special development parallel to the plane of the best cleavage and we have observed this tendency in crystals of artificial forsterite.

* Allen, Wright and Clement, *Minerals of the Composition MgSiO₃*, this Journal (4), xxii, 388, 1906.

† Allen, White, Wright and Larsen, *Diopside and its Relations to Calcium and Magnesium Metasilicates*, this Journal (4), xxvii, 1, 1909.

‡ Allen, White, Wright and Larsen, this Journal (4), xxvii, 31, 1909.

§ See artificial crystals of forsterite, Allen, Wright and Clement, this Journal (4), xxii, 391, 1906.

The cleavage noted as parallel to (100) becomes, on rotation of the crystal, parallel to (001), which in natural forsterites, unlike other olivines, is the second best cleavage.* To this cleavage ($//001$) the plane of the optic axes is parallel in the measured crystals, and here again there is correspondence with forsterite. In crystallographic properties, including the axial ratios themselves, in refractive indices, and in the relation between the position of the optical ellipsoid and crystallographic directions, the crystals called α - $MgSiO_3$ correspond with forsterite. The only supposed difference remaining is in the measured value of the optic axial angle. In view of the possible disturbance due to a slight strain in the crystals this minor difference noted in the former measurements cannot be regarded as establishing a species, in the face of the identity of the more distinctive properties with those of forsterite and of the proof by means of quenching that material so obtained must contain forsterite.

In the table below, the degree of correspondence is shown between the constants given for the crystals which were called α - $MgSiO_3$, after rotation through 90° on the b axis, and the values noted for artificial crystals of forsterite in an earlier publication from this laboratory, already referred to.

It was a difficult matter to identify the clear grains in the dusty material as originally prepared, but, by quenching, identical material can be prepared in two steps which make

TABLE II.

	Forsterite	" α - $MgSiO_3$ "
Crystal system	orthorhombic	orthorhombic
Axial ratios	0.463 : 1 : 0.584	0.47 : 1 : 0.59
Forms observed	010, 021, 110 and others	010, 021, 110
Cleavages	$//010$	not noted (crystals tabular $//010$)
	$//001$	$//001$
Axial plane	$//001$	$//001$
Refractive indices	$\alpha = 1.645 \pm .003$ $\gamma = 1.668 \pm .003$	$\alpha = 1.641 \pm .003$ $\gamma = 1.663 \pm .003$
Optic axial angle	86°	60°

the relations clear. A mixture of composition $MgSiO_3$ may be held at the temperature 1560° , a little above the dissociation point, and then quenched. The product consists of clear grains embedded in glass and the properties of these grains are definitely those of forsterite. Moreover, corresponding with

* It appears that in artificial forsterite cleavage after (001) may sometimes be as good as after (010), for Wright notes "cleavage perfect after (001) and (010)" for crystals of forsterite made in a flux.

the deficiency of silica in the forsterite there is an excess silica (above the composition MgSiO_3) in the glass as revealed by the fact that the refractive index of the glass, 1.575, is definitely lower than that of MgSiO_3 glass, 1.580. If this material is returned to the furnace at a lower temperature and crystallized, the product consists of clear forsterite grains surrounded by dusty material (MgSiO_3 and silica), the whole precisely the same as the material obtained in one step by cooling from the liquid state. On the other hand, a clear, forsterite-free, MgSiO_3 glass, which can be obtained only by quenching from a temperature above 1577° , may be crystallized at any temperature between 1200° and 1557° and the product is only clean clino-enstatite, without the strongly-birefracting forsterite grains which were called $\alpha\text{-MgSiO}_3$ and without the dusty appearance (silica). This clino-enstatite may be held for an indefinite period at any temperature up to 1557° without showing any tendency to invert to another form.

It should be noted, moreover, that this method of holding the mixture MgSiO_3 above 1577° , then quenching and crystallizing the glass below 1557° , is the *only dependable method* of obtaining pure clino-enstatite free from forsterite and silica, though *occasionally* the melt can be cooled quickly enough in the furnace, through the range 1577° - 1557° , to avoid the crystallization of forsterite. The occasional non-appearance of the material called $\alpha\text{-MgSiO}_3$ in the earlier work is due to this latter fact.

In summary, then, it may be stated that there is no enantiotropic inversion of clino-enstatite into $\alpha\text{-MgSiO}_3$. The substance which was called $\alpha\text{-MgSiO}_3$ is the product, not of inversion of clino-enstatite, but of dissociation of clino-enstatite and is the mineral forsterite, Mg_2SiO_4 .

Since we are dealing with equilibrium, the form clino-enstatite is the only form of MgSiO_3 , which appears on our diagram. It always occurs in the characteristically twinned form described in former publications and in the optical part of this paper.

The Eutectic, Periclase-Forsterite.—The melting temperatures of all mixtures of MgO and Mg_2SiO_4 are beyond the range of the platinum resistance furnace used for most of the work, but we studied one mixture between these two in order to decide the presence or absence of a eutectic point. Silica and magnesia were mixed in the proportion to give Mg_2SiO_4 , 86 per cent, MgO 14 per cent, and ground together and the material heated for half an hour at about 1600° . Grinding and heating were repeated and then the material was examined. It proved to be clearly a fine-grained mixture of forsterite and periclase and gave no trace of any compound intermediate between these two. A small charge of this mixture was then

carefully heated on a small piece of platinum foil in the oxy-hydrogen flame. The mixture melted about the same time as the platinum and as the edge of foil melted away, the liquid silicate ran back upon the still unmelted portion and was thereby saved for examination. The larger of the liquid globules recrystallized on removal from the flame to a mixture of forsterite and periclase, both well crystallized. Some of the more quickly cooled material, however, consisted of periclase and glass, indicating that the composition dealt with lies on the magnesia side of the eutectic.

The behaviour of this mixture was then examined in the iridium furnace, after the manner of the determination of the melting-point of forsterite. The mixture became liquid at 1850° , 40° below the melting point of forsterite. The diagram has been drawn in accordance with these results, showing a eutectic between forsterite and periclase at 1850° and with the composition close to forsterite (less than 14 per cent MgO). The determination of the composition of the eutectic is, of course, the roughest approximation.

The Liquidus between Mg_2SiO_4 and $MgSiO_3$.—Points on the liquidus between Mg_2SiO_4 and $MgSiO_3$ were determined up to a temperature of 1626° by means of the thermo-element, Table I (a). Above this temperature no points were determinable except the melting point of forsterite itself (1890°).

The Invariant Point, Forsterite-Clino-enstatite-Liquid.—Between forsterite and clino-enstatite there is no eutectic, for the reason that clino-enstatite itself is unstable at its melting point, breaking up into forsterite and liquid. The composition of the liquid capable of existing in contact with both clino-enstatite and forsterite (D) was fixed in the following manner: Its composition was first approximately determined by holding a charge of $MgSiO_3$ at 1560° , a little above the dissociation point, and quenching. The product consists of forsterite crystals and glass and the refractive index of the glass was determined. The refractive index of pure $MgSiO_3$ glass is 1.580, that of the glass in the quenched product as obtained above was $1.575 \pm .001$. From the indices of refraction of glasses of mixtures of $MgSiO_3$ and SiO_2 in known proportions the composition of this glass was found to correspond approximately with $MgSiO_3$, 97 per cent, SiO_2 , 3 per cent. Mixtures of various compositions close to this were then made up and the first crystal separating from them (primary phase) determined by quenching. In this manner it was found that in 3 per cent SiO_2 the primary phase was clino-enstatite, in 2.5 per cent SiO_2 clino-enstatite, and in 2 per cent SiO_2 forsterite. Thus the composition of the point D (fig. 1) was determined at 2.5 per cent SiO_2 .

All mixtures of compositions lying between Mg_2SiO_4 and the

point D should break up when the temperature is raised to 1557° into a liquid of composition D and forsterite. We have confirmed this behaviour in several of these mixtures (see Table I (b)).

The Crystallization of Mixtures of Mg₂SiO₄ and MgSiO₃.—The crystallization of mixtures lying between Mg₂SiO₄ and MgSiO₃ takes place, when perfect equilibrium obtains, in the following manner: Forsterite crystallizes out first and increases in amount until the temperature 1557° is reached. At this temperature the liquid has the composition D and clino-enstatite begins to crystallize out, forsterite to redissolve, this process continuing until all the liquid is used up and the whole consists of forsterite and clino-enstatite. In pure MgSiO₃ the early separation of forsterite takes place in the same way, but at the reaction temperature (1557°) the last of the liquid and the last of the forsterite are used up at the same instant and the whole consists of clino-enstatite. In compositions between Mg₂SiO₄ and the point D, forsterite separates first as before, at the reaction point it is completely resorbed, leaving clino-enstatite and some liquid. With further lowering of temperature clino-enstatite continues to separate until, at 1543°, when the liquid has the composition E, cristobalite separates also and the whole crystallizes at this temperature, giving a mixture of clino-enstatite and cristobalite.

Such is the behaviour of these mixtures when complete equilibrium is attained. We have already seen, however, that with quick cooling, equilibrium is not attained and a preparation of composition MgSiO₃ will then crystallize to a mixture of clino-enstatite, silica, and forsterite. The same fact is true of all mixtures lying between Mg₂SiO₄ and D, the reason being that with quick cooling the liquid of composition D, instead of reacting with (redissolving) forsterite at 1557°, simply crystallizes, as the temperature falls quickly below this point, to a mixture of MgSiO₃ and silica. Such mixtures containing both forsterite and silica are unstable but will persist indefinitely.

The Eutectic, Cristobalite-Clino-enstatite.—The eutectic point between cristobalite and clino-enstatite was located by quenching charges of various compositions to determine the primary phase. The composition MgSiO₃, 90 per cent, SiO₂, 10 per cent shows clino-enstatite as the primary phase. The composition MgSiO₃, 87.5 per cent, SiO₂, 12.5 per cent is completely crystalline at 1542° and completely liquid at 1544° and therefore corresponds sensibly with the eutectic composition. Cristobalite is the primary phase in mixtures richer in SiO₂ (see Table I (d)). The eutectic melting was observed at the same temperature (1543°) in mixtures on both sides of the eutectic.

In the mixtures on the silica side we were not able to determine the liquidus with great assurance on account of the high viscosity of the mixtures. There are, however, indications that

the liquidus is very steep close to the eutectic. It would then be very flat close to silica, if 1625° is the melting point of cristobalite.

Previous Work on the System $Mg_2SiO_4-MgSiO_3$.—A recent paper by Deleano presents the results of an investigation of the system $Mg_2SiO_4-MgSiO_3$.^{*} Deleano found that all the compositions close to $MgSiO_3$ soften at the same temperature (within the error of measurement). These results are in accord with our determination that there is no eutectic between $MgSiO_3$ and Mg_2SiO_4 , but a dissociation-temperature at which all compositions between D and forsterite (fig. 1) break up into liquid and forsterite, though Deleano presents a diagram showing a eutectic.

Deleano concludes, on the basis of finding periclase in a melt of forsterite composition, that forsterite is unstable at the melting-point. It is to be noted that the mixtures used were made up by mixing silica and a calculated weight of $MgCO_3 \cdot 3H_2O$. This latter compound is very difficult to obtain free from basic carbonate, the presence of which would result in an excess of magnesia in the product.

We made the forsterite mixture, as we did our other mixtures, by mixing silica and magnesia in calculated proportions, the magnesia being obtained by igniting the precipitated carbonate to constant weight. When the mixture is so made and when perfect mixing is accomplished by repeated grinding and heating, the product may then be melted and crystallized repeatedly and the crystalline product is always pure forsterite without a trace of periclase.

OPTICAL STUDY.

The product of each quenching experiment was examined in powder form under the microscope and the optical properties of the various phases determined. In this manner, not only the nature of the crystalline phases is noted, but, at times, the composition of the liquid phase may be obtained by determining the refractive index of the glass. The various optical constants were measured on suitable material and are recorded below.

Periclase.—Periclase was the only form of MgO noted. It occurs in the preparations, when embedded in glass, as rounded grains of isotropic character and index 1.73. We have also examined periclase made by the Norton Company by fusing magnesite. It is in coarse granular lumps showing the excellent cubic cleavage and the optical properties of periclase. The hardness of this material is about equal to that of apatite (5) and distinctly less than that of orthoclase (6).

^{*} Zs. anorg. Chem., lxxxiv, 423, 1914.

Cristobalite.—Silica occurs in our melts only as cristobalite. As viewed under the microscope at room temperature the crystals are birefringent, α -form, but have the crystal form of the isotropic β -form in which they crystallized at the temperature of the furnace. When embedded in glass the crystals are sometimes sharply outlined octahedra, modified by the cube, but usually the cube is the more prominent form and the crystals are, by distortion, stout prisms due to slight elongation parallel to one of the cubic axes. The birefringence is barely discernible with the aid of the sensitive-tint plate, this apparently low value being probably due to the mutual compensation of a number of twinning lamellæ. Occasionally polysynthetic twinning was observed. The mean refractive index, $1.485 \pm .001$, agrees with the values found by Fenner.*

Forsterite.—We have found Mg_2SiO_4 only in the form corresponding with the natural mineral forsterite. Measured artificial crystals of this mineral are figured in a former publication from this laboratory.† Crystals from this same stock, prepared by fusing together magnesia, silica and magnesium chloride in an atmosphere of HCl, were used to determine the optical constants of forsterite more accurately. The acute angle of the unit prism was used as a wedge and the refractive indices α and β determined for sodium light on the goniometer, by the method of minimum deviation. The optic axial angle was then measured directly on the Wülfing apparatus in sodium light, the crystal being immersed in a liquid of index β . From these values the index γ was calculated. The results are given below:

$$\begin{array}{rcl} \beta = 1.651_0 & 2V = 85^\circ 16' \pm 4' & \\ \alpha = 1.635_1 & \gamma = 1.670_4 & \\ & \gamma - \alpha = .035_3 & \end{array}$$

The cleavage is distinct after (010) and (001).
The optical orientation is $c = b$ and $a = c$.

A determination of the density of these crystals was made in Rohrbach's solution by the flotation-refractive index method of Merwin.‡ The crystals used were small and were examined under the microscope and found free from inclusions of any kind. The density found was $3.216 \pm .002$.

Clino-enstatite.—With the exception of the occasional appearance of the monotropic amphibole form of $MgSiO_3$ in quickly cooled melts, the stable monoclinic pyroxene, clino-enstatite, was the only form of the metasilicate observed in our quenches.

* The Stability Relations of the Silica Minerals, this Journal, (4), xxxvi, 1913, 354.

† Allen, Wright and Clement, Minerals of the Composition $MgSiO_3$, this Journal, (4), xxii, 1906, 391.

‡ This Journal, (4), xxxi, 425, 1911.

We have therefore made no observations which throw further light on the relation between enstatite and clino-enstatite. The two are very similar in physical properties but clino-enstatite is monoclinic.

Clino-enstatite crystals have been measured and the figures given in a former publication of this laboratory. It has the characteristic, perfect prismatic cleavage of the pyroxenes. Usually rough cracks //(001) show as well. Polysynthetic twinning after (100) is exceedingly characteristic. The plane of the optic axes is normal to (010) as would be the case in enstatite if it were oriented after the manner of the monoclinic pyroxenes. Sections //(010) do not, therefore, show the highest interference colors as in most pyroxenes. The angle $C \wedge c = 22^\circ$. The optic axial angle is difficult to measure on account of the polysynthetic twinning. Wright and Larsen give the value 53.5° .* The refractive indices were determined on material crystallized from a clear glass and therefore free from inclusions of silica, which tend to give a value slightly too low. The results were $a = 1.651 \pm .001$, $\gamma = 1.660 \pm .001$ determined by immersion in liquids of known refractive index.

BEARING OF THE RESULTS ON PETROLOGIC PROBLEMS.

In the chemically pure products described it has been shown that, over a wide range of compositions, the olivine, forsterite, crystallizes out and is later either partly or completely redissolved, reacting with the liquid to give the pyroxene, clino-enstatite. This resorption takes place as a necessary result of equilibrium and during the normal course of crystallization. In natural rocks the resorption of olivine and the formation about the olivine crystals of reaction-rims of enstatite has often been noted.† Such reaction between the crystals in a magma and its still liquid portion has sometimes been assumed to imply some drastic change of conditions such as the sudden relief of pressure. It has also been considered possible that such crystals may have sunk into magma of such a composition that they became unstable. In the case of olivine it is probable that such assumptions are unnecessary. Olivine crystals may perhaps be partly or wholly resorbed during the normal course of crystallization as a simple result of cooling, as in the case of the more simple mixtures described.

It has been shown also that certain crystalline products, when quickly formed, may contain forsterite and free silica (cristobalite) together and this condition may persist indefinitely although it does not represent equilibrium. Dr. Cross‡ has found cristobalite in cavities of olivine-bearing lavas from

* This Journal, (4), xxvii, 30, 1909.

† Harker, A., Natural History of Igneous Rocks, p. 269.

‡ Personal communication.

Hawaii, but in that case we are probably dealing with a quite different matter, perhaps with the decomposition of silicates and the setting free of silica as cristobalite by the action of vapors.

A mixture of total composition MgSiO_3 , 98 per cent, SiO_2 , 2 per cent, can be cooled in such a manner that it consists of forsterite and glass. We have then what might be termed an olivine-bearing lava in simplified form, though the actual total composition of the mixture shows no olivine but an excess of free silica. This simple case emphasizes the fact that, in spite of the great usefulness of a purely chemical classification of rocks, a classification in terms of the actual phases (minerals) present is extremely desirable because these phases are an expression of equilibrium under the conditions of their formation.

SUMMARY.

Equilibrium in the binary system MgO-SiO_2 was studied by applying the method of quenching.

There are two compounds, the orthosilicate Mg_2SiO_4 and the metasilicate MgSiO_3 , capable of existing in contact with liquid in the binary system. The former crystallizes in a form corresponding with the mineral forsterite and the latter forms crystals similar to enstatite in most properties but of monoclinic symmetry, clino-enstatite.

Clino-enstatite is the only stable form of MgSiO_3 encountered. It has no true melting-point but breaks up at 1557° (formerly considered the melting-point) into forsterite and liquid and the temperature must be raised to 1577° before complete solution of the forsterite takes place.

In an earlier publication from this laboratory, crystals termed $\alpha\text{-MgSiO}_3$ were described as a high-temperature form of magnesium metasilicate. They were considered to be the product of inversion of clino-enstatite ($\beta\text{-MgSiO}_3$), but the crystals described have now been proved to be a product of the dissociation at 1557° and to be the orthosilicate, forsterite, not a form of the metasilicate.

On account of the break up of clino-enstatite into forsterite and liquid there is no eutectic between the two compounds, and the liquids show, on cooling, the partial or complete re-solution of forsterite at the reaction point, 1557° , the liquid reacting with the forsterite crystals to give clino-enstatite.

A discussion is given of the geological significance of this resorption of the olivine, forsterite, by reaction with the liquid to give the pyroxene, clino-enstatite.

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