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THE LIME-SILICA SERIES OF MINERALS.[1]

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Any one who has followed the work of the eminent Norwegian scientist, Prof. J. H. L. Vogt, during the past three or four years, must realize that an extraordinarily effective weapon has come into the service of petrology, the full power of which cannot at once be understood or appreciated. We refer to the methods and established generalizations of physical chemistry. The older science of chemistry has made such strides under these new theories of solutions that we really have little more to do than to apply them ready-made to our own problems, like a smooth and powerful machine tool of guaranteed effectiveness. Mineral solutions are after all only chemical solutions over again with slightly different components and a different, a very different range of temperatures and pressures.

It has been the purpose of this laboratory to attempt this task by a direct application of the principles and methods of quantitative physics and chemistry, or, in a word, to study mineral and rock formation by direct measurement at the temperatures where the minerals combine and separate like the solutions of ordinary chemistry under ordinary conditions. We further determined, wherever possible, to prepare chemically pure minerals for this purpose in order that such conclusions as we might reach should not be dependent upon dangerous assumptions regarding

[1] An extract from a paper of the same title read before the American Chemical Society at Ithaca, June 28, 1906.

the harmless character of the 5 or 10 per cent. of "impurities" not infrequently present in hand specimens from natural sources. It is at once obvious that in order to succeed the first experiments must be restricted to the simplest reactions and that these will not always be the most important or the most interesting, but the results will always be in definite terms and final when the materials used are pure. Furthermore, the accumulated experience obtained from simple cases will safely and surely lead to successful methods of a scope to meet the more complicated problems of rock formation.

This plan was really entered upon several years ago in a very small way and with very limited resources. The first paper,[1] which was published in 1904–5, contained a laboratory study of a typical isomorphous pair, the soda-lime feldspar series, carried out in the spirit of the above plan. The second,[2] which appeared in February of the present year, was a very careful study of enantiotropic mineral inversion between the mineral wollastonite and the pseudohexagonal form which has been obtained by several observers but which appears not to have been found in nature. The present paper, which is the third of the mineralogical series, undertakes to carry through a fairly complete set of measurements upon a typical eutectic pair—the lime-silica series. It is still incomplete in some particulars, notably at the ends of the series. Mixtures very rich in lime possess temperature constants which are beyond the reach of existing apparatus, while on the silica side the extreme viscosity and consequent inertness which were encountered in the soda feldspars effectually veil or prevent the development of the phenomena which occur there. Some approximate measurements have been made even in these regions (represented by dotted lines in the diagram, Fig. 2), but they have not the same accuracy as those portions of the curve which are represented by full lines. All the mixtures used were prepared with the greatest care and were chemically pure within one or two tenths of 1 per cent.

Lime-Silica Minerals.—In the lime-silica series only one well-defined mineral is known—wollastonite, which when melted

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[1] Arthur L. Day, E. T. Allen and J. P. Iddings: Am. J. Sci. 19, 93 (1905). Publications of the Carnegie Institution of Washington, No. 31 (1905).

[2] E. T. Allen, W. P. White and Fred Eugene Wright: "On Wollastonite and Pseudo-Wollastonite, Polymorphic Forms of Calcium Metasilicate," Am. J. Sci. 21, 89 (1906).

usually crystallizes in a pseudohexagonal form of the same composition. This mineral has already been carefully studied by Allen and White, and the relation between the natural mineral and its second crystal form thoroughly cleared up. Pursuing the conventional methods of reasoning, we might also expect to have an intermediate mineral for the trisilicic acid, $2CaO \cdot 3SiO_2$; an åkermanite analogue, $4CaO, 3SiO_2$; an orthosilicate, $2CaO, SiO_2$; and a tricalcium silicate, $3CaO, SiO_2$. All of these minerals are deducible from the various silicic acids. We have undertaken to prepare and study the entire series of mixtures of lime and silica.

Boudouard's Measurements.—So far as known there has been only one serious attempt to determine the constitution of this series of minerals.[1] According to Boudouard, the freezing-point curve for the lime-silica minerals consists of four eutectics and three maxima (compounds), the maxima corresponding to the metasilicate, the orthosilicate and the tricalcium silicate. Unfortunately, the method used by Boudouard was a very inaccurate one. He prepared small cones of the various mixtures and placed these in a furnace alongside of Seger cones. The furnace was then heated and allowed to cool down again, after which the crucible was opened and the cone observed to see whether or not the mineral had melted. It is a common method in industrial practice, but has rarely been thought accurate enough for original determinations.

This method is peculiarly unsuited for such investigations for several reasons: Suppose the mixture to contain an eutectic with a greater or less excess of one of the components. The cone would begin to weaken as soon as the eutectic began to melt, and its further progress would be governed entirely by the relative quantity of eutectic present and its viscosity *after melting*. No information whatever regarding inversions in the solid or of the component in excess could be obtained, and errors of more than 500° would certainly occur (in fact did occur in Boudouard's case) in the interpretation of the softening temperature in some parts of the lime-silica curve. Let us illustrate by a perfectly obvious hypothetical case (Fig. 1): Assume first that the freezing-points change rapidly following a steep liquidus AB (see also Fig. 2, Curve DE). The amount of eutectic in concentrations X and Y will be so great as to soften the cone long before the

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[1] Boudouard: J. Iron and Steel Inst., 1905, p. 339.

freezing-points Z and W are reached. If, on the other hand, the liquidus slopes gently (AC), the amount of liquid eutectic as compared with the solid phase is smaller and the temperature of softening of the cone will approximate more closely to the change in freezing-point.

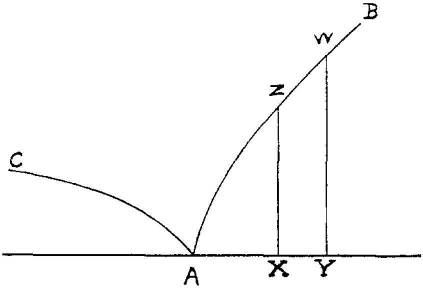

Fig. 1.

Furthermore, if the cones are made up from the initial components ($CaCO_3$ and SiO_2 for example), the heat of combination is liberated as the cone approaches the melting temperature and raises the temperature of the cone above that of the furnace, producing sudden fusion, of which the neighboring Seger cone can receive no record.

Incidentally, one finds here the explanation of Hoffmann's experiments[1] on the temperature of formation of slags. Contrary to his statement that the "temperature of formation is above the temperature of fusion," just the reverse is true. Under normal conditions these mineral combinations occur at temperatures lower than the melting-point, the exceptions occurring only when the materials are so coarsely ground or poorly mixed that combination is retarded until the melting-point of the slag is passed. The orthosilicate of calcium is a very good instance of the formation of a compound below its melting temperature. We shall show later that while this compound melts at about 2080°, it is possible to prepare it below the melting-point of platinum, in fact in platinum vessels, by heating the finely ground material in the Fletcher furnace, regrinding, mixing, and reheating. By this process it is possible to obtain a compound which gives the optical tests for the orthosilicate and is entirely without free lime or silica.

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[1] H. O. Hoffmann: Trans. Amer. Inst. Min. Eng. **29**, 682 (1899).

Apart from the criticism which this particular application of cones appears to us to deserve, it is also well-known that the time factor is always very important in dealing with a Seger cone. Boudouard himself states (p. 343): "A very small difference in temperature or *a few minutes' additional heating*[1] often suffices for the softening stage to pass into one of complete fusion." If this statement was made understandingly, the method merited rejection by Boudouard himself. Furthermore, the use of Seger cones for exact work will always be unsatisfactory because it depends upon the judgment of the operator to say when a cone has "fallen" sufficiently to be considered melted, and different observers almost always obtain widely different results under like conditions. As has been pointed out by Day and Allen,[2] any method of measurement which is not based upon some reasonably sharp physical change must be expected to give different results in different hands. Suppose this method were to be applied, for example, to the determination of the melting temperature of orthoclase or albite, or even pure quartz, which have been shown to possess a viscosity entirely comparable in magnitude with the rigidity of the solid crystalline mineral; almost any conclusion could have been reached under these conditions.

It is stated by M. Boudouard that all mixtures of lime and silica between 30 and 90 per cent. of lime melt below 1500°. This certainly cannot be the case. Pure orthosilicate of calcium when heated in a platinum crucible will stand without showing the slightest trace of melting while the platinum containing vessel melts down. The temperature must therefore be at least as high as the fusion point of platinum (1720°). We found no lime-silica mixtures richer than 60 per cent. in lime which could be melted in platinum vessels.

Apart from the uncertainty in the temperature measurements offered by Boudouard, we shall also undertake to show in its proper place that there is no pure lime-silica compound corresponding to tricalcium silicate. We are therefore somewhat at a loss to explain in any satisfactory way how the published curve which has attracted so much attention in England, was really obtained.

In this kind of investigation it is always desirable to begin with

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[1] Italics are ours.

[2] Loc. cit.

a careful determination of the physical properties of the pure components, although in the present case it must be admitted that this was the most inaccessible and difficult portion of the field over which we worked.

Lime.—Calcium oxide melts at a temperature so high that it is not yet possible to make a satisfactory determination of its melting-point. It can be fused in the electric arc under favorable conditions to a clear liquid of low viscosity which crystallizes readily into a well developed cubic structure. Near its fusing temperature, lime either becomes quite volatile or the carbon of the arc reduces it to the metal which volatilizes and is immediately reoxidized outside of the heated zone. We are unable to offer conclusive evidence in favor of the one hypothesis or the other, but the fact that pure lime at 2000° shows no signs of a high vapor pressure points rather to the second explanation as the correct one.

For experiments with lime fusion, we obtained some artificial graphite,[1] practically free from all impurities, so that no contaminating substance was introduced into the fused lime from the electrodes. To further guard against possible contamination, only that part of the cake which formed above the (horizontal) arc was used in determining its physical properties.

Density of Lime.—The density of fused calcium oxide was determined as follows: A selected portion of the crystalline mass was finely ground, ignited to drive off adsorbed water, and weighed in carefully dried turpentine after the method of Day and Allen. The results are not in very good agreement, due to the difficulty of weighing out the product without its becoming superficially hydrated or absorbing carbon dioxide.

	Fused CaO. H_2O at 25° = 1.
	3.313
	3.307
	3.329
Mean density,	3.316 (25°)

This crystallized lime is much less readily attacked by water than is the amorphous oxide. It is, however, not indifferent to water. Five grams of the crystals when ground and mixed with a small quantity of water in a test-tube scarcely raised the tempera-

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[1] Prepared especially for us by the International Acheson Graphite Company, Niagara Falls, N. Y.

ture at all, but upon standing for some five minutes, the charge exploded with considerable violence. Unpowdered blocks of the crystalline oxide when placed in cold water dissolved slowly without appreciable heating. Hot water attacks them more rapidly, but the action of the water is slow in both cases when compared with the amorphous lime.

The hardness, according to Mohr's scale, is between 3 and 4.

Silica.—The melting temperature of silica has been variously estimated from 1200° to 2000°, but so far as known no careful determination of it has ever been made. Since this oxide melts to an extremely viscous liquid, attempts to determine the melting temperature by observing the softening of the charge are wholly misleading. The molecular deorientation proceeds very slowly, extending over a considerable range of temperature, as albite and orthoclase have been found to do,[1] but with the disadvantage that this temperature region is too high to be reached with a thermoelement and no other method of temperature measurement possesses sufficient sensitiveness in this region to locate the melting temperature by the heat absorbed during slow fusion. Determinations of the freezing-point are out of the question, owing to the inertness of the viscous melt.

An approximate determination of the melting temperature was made in this way: A gram or two of finely powdered quartz was placed in a small iridium crucible and heated in an iridium tube furnace.[2] Experience has shown that melting and inversion phenomena in very viscous substances take place much more readily if the material is finely divided. A tiny fragment of platinum foil was then laid on the top of the charge and the furnace slowly heated until the foil was observed to melt. Upon removing the charge from the furnace and examining it microscopically, evidence of fusion was found throughout the mass. The crystal grains had inverted to tridymite and the superficial liquefaction had caused them to sinter tightly together, but no displacement of the grains had taken place. At the temperature of melting platinum, therefore (1720°), silica shows positive evidence of fusion. Other similar charges were then prepared

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[1] Day and Allen: Loc. cit.

[2] No detailed description of the apparatus used or the methods of operating it can be included in this brief abstract. They are nearly all accessible in other publications from this laboratory or in contemporary pyrometric literature.

and the operation repeated with longer exposures and temperatures slightly below the melting-point of platinum, the temperatures being measured with a Holborn-Kurlbaum optical pyrometer[1] focused on the platinum fragment. By repeating this process at short temperature intervals and with about twenty minutes' exposure, melting was definitely established as low as 1625°.

The iridium furnace is unfortunately not adapted for long-continued heating, and the platinum coil furnace will not reach this temperature, so that an effort to discover a definite temperature below which the solid is stable and above which it will melt, if given time enough, was abandoned. If the heating is moderately rapid, the crystalline solid will persist far above the melting-point of platinum; if slow enough, it liquefies completely at 1625° or even lower. It is probably a fair assumption that pure crystalline silica begins to melt at about 1600°,[2] and will continue to complete fusion, if given time enough—above that point the higher the temperature the more rapid the melting. A charge of quartz was heated for a long time in a platinum furnace at 1550° without producing a trace of fusion.

There is little satisfaction in pursuing an inquiry of this kind. As has been stated elsewhere with reference to an entirely similar case,[3] the term "melting-point" does not appear to be well applied to cases of this character in which the crystalline structure persists for days or weeks at temperatures above the point where melting begins. If the change of state is to be defined by the

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[1] Holborn and Kurlbaum: Ann. Physik. 10, 225 (1903).

[2] In a recent number of this Journal (July) Mr. Alexander Lampen publishes an experimental determination of the melting-point of a "piece of pure quartz" as follows (five minutes exposure):

Edges rounded	1650°
Fused	1700°

Our experience inclines us to the belief that these temperatures are too low for the stages of the melting described for two reasons: (1) We found no crystalline quartz fragment upon which rounded edges could be observed from without the furnace after five minutes' heating even at the temperature of melting platinum (1720°), a fixed point in which great confidence can be placed; (2) if Mr. Lampen was able clearly to see incipient melting through red glass within his furnace, as he has stated, the radiation which he measured cannot have been "black" and his instrument *must* have read too low.

This note is added by request since the reading of the paper.—THE AUTHORS.

[3] Publication 31, Carnegie Institution of Washington, p. 74 (3).

absorption of heat, and the absorption of heat extends over a wide range of temperatures and conditions, our forms of expression should be revised somewhat to include these hitherto unrecognized cases.

Tridymite.—The relation between tridymite and quartz appears to be a simple one, although the literature of the subject is unsatisfactory. But few trustworthy observations have been recorded and the conclusions drawn from them are vague and contradictory. So far as known, quartz has never been crystallized as such from mineral fusions except where catalyzers were present. Tridymite has probably been obtained by several individuals through the accidental crystallization of fused silica vessels,[1] but no especial attention appears to have been given to the circumstances in which it occurs, and its identification has not aways been positive.

Like the melting temperature, the inversion of quartz to tridymite and the recrystallization of fused silica are very difficult phenomena to study, owing to the extreme inertness of the material, but a number of experiments have been successfully carried out which appear to clear up the situation, even though the inversion temperature cannot be determined with any great accuracy.

First of all, we heated a large charge of finely ground quartz and followed the temperature curve carefully from 400° to 1600°. It was found after the experiment that the quartz crystals had, for the most part, gone over into tridymite and the change in the volume accompanying the inversion had generated enough pressure to completely shatter the open platinum crucible which contained the charge. The change was so gradual, however, that no record of it appeared upon the thermal curve. Subsequent experiments in which we endeavored to change crystalline quartz into tridymite at lower temperatures were successful as far down

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[1] Prof. Dr. L. Holborn, of the Physikalisch-technische Reichsanstalt, Dr. M. Herschkowitsch, of the firm of Carl Zeiss in Jena, Dr. Küch, of the firm of Heraeus in Hanau, and the Rev. Theodor Wulf, S. J., formerly of Göttingen, in the preparation and use of quartz glass vessels, have noticed that the glass devitrifies at high temperatures in the presence of water vapor or after long usage. So far as we are aware, all of these observations have remained unpublished. Hahn, in the Int. Cong. f. angewandte Chemie, Berlin, 1903 (Vol. I, p. 714), notes the devitrification of a quartz glass tube at 1100°. He also identified the crystal formation under the microscope as tridymite.

as 1100°. To be sure, entire crystals showed no change whatever after six hours' exposure at 1400°, but powdered quartz is completely changed into tridymite after a few hours at that temperature. On the other hand, if finely divided amorphous silica, *i. e.*, fused ("quartz glass"), or better, precipitated silica, be allowed to remain for a short time at any temperature above 1000°, it changes promptly to tridymite—the precipitated material very rapidly, the quartz glass much more slowly. Neither the glass nor the precipitated silica ever crystallized as quartz at temperatures above 1000°, nor is there any difference in the optical properties of the tridymite obtained at the different temperatures, either from the quartz crystals or the amorphous silica. The rate of change is much influenced by the fineness of the powder, although there is no difficulty in crystallizing large blocks of solid quartz glass at the higher temperatures. In our experiments in the preparation of quartz glass,[1] we frequently obtained isolated spherulites of tridymite several millimeters in diameter, even with rapid cooling, which appeared to have been started by a grain of graphite or carborundum powder accidentally falling into the melt. On one occasion the entire block was coated with tridymite to a depth of a millimeter or more.

We have therefore succeeded, by direct experiment upon pure silica, in establishing the fact that tridymite, and not quartz, is the stable crystalline form of silica for all temperatures above 1000°.

At lower temperatures than this it is impossible, in view of the inertness of the substance, to obtain any further reaction, even with the finest precipitated silica, within the time available for a laboratory experiment. A month's exposure at 900° produced no change. We therefore followed the example of several distinguished predecessors in this field, and tried various catalyzers.

Formation of Quartz.—Hautefeuille thought he had produced quartz crystals by fusing amorphous silica with sodium tungstate at 900°, but the methods of high temperature measurement commonly employed in his time were very imperfect, and the temperature is undoubtedly too high. He has also stated that he obtained it by fusion with lithium chloride. Both Hautefeuille and Margotet have recorded the fact that in the presence of lithium chloride amorphous silica changes to tridymite at high

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[1] Day and Shepherd, "Quartz Glass," Science, 23, 670 (1906).

temperatures and to quartz at low temperatures. We obtained quartz crystals from glass by the use of 80 per cent. potassium chloride and 20 per cent. lithium chloride, at all temperatures below 760°, while at temperatures of 800° and higher, only tridymite crystals appeared. The same results were obtained with vanadic acid and with sodium tungstate. The inversion point

quartz $\rightleftarrows$ tridymite

therefore occurs at about 800°. This conclusion is subject to the assumption that the inversion temperature is not lowered by the catalyzing agent—an assumption which seems to be justified by the fact that the quartz crystals obtained in this way (judged by the optical properties) appear to hold none of the reagent in solid solution.

The situation is, then, briefly this: Both quartz and amorphous silica at high temperatures change to tridymite. Quartz is consequently the unstable form of silica from 800° upward, and will go over into tridymite whenever conditions favorable to the change are present. The melting temperature of silica is therefore properly the melting temperature of tridymite and not of quartz as it is commonly described. We have once or twice succeeded, by extremely rapid heating, in melting quartz as such, or more correctly speaking, in carrying a quartz charge past the melting temperature of tridymite, melting a portion of it and finding a residue of quartz afterward which had neither inverted nor melted. It would hardly be possible by any known method, however, to obtain a separate melting temperature for quartz independently of tridymite.

The reverse operation, showing that tridymite inverts to quartz at temperatures below 760°, cannot be carried out in the laboratory without the use of catalyzers on account of the extreme slowness of the change. In the presence of 80 per cent. potassium chloride and 20 per cent. lithium chloride, quartz begins to appear from tridymite in quantities sufficient for positive identification after an exposure of five or six days at about 750°. No effort was made to invert the entire charge, on account of the slowness of the change and the fact that its character was now fully established. The glass crystallizes to quartz below 760° and to tridymite above 800°; crystalline quartz goes over to tridymite above 800°, and tridymite to quartz at 750°; the change is therefore enantiotropic and not monotropic.

Incidentally, a sufficient reason has been given for the complete failure of experimenters to produce quartz without catalysis. If dry silica at 900° is so inert as to undergo no reaction at all during a month's exposure under favorable conditions, how can we expect reaction below 800° where the viscosity is even greater? Silica must be crystallized below 800° to produce quartz.

Density of Silica.—The density of the quartz used and obtained in our experiments was determined with the following result, the aggregate impurity being not over one-tenth of 1 per cent.

Purified natural quartz.	Quartz glass.	H_2O at 25° = 1.
2.655	First preparation........	2.209
2.653	" "	2.215
2.654	" "	2.212
	Second "	2.213
	" "	2.215
Mean, 2.654 (25°)		Mean, 2.213 (25°)

It will be noted that there is a difference of more than 16 per cent. between the density of the glass and that of the quartz crystals.

A charge of powdered crystalline quartz heated for several days at 1200° appeared under the microscope to be homogeneous tridymite. Some observations of its density are contained in the subjoined table under the heading "tridymite from quartz." A similar charge obtained by crystallizing the glass at 1200° (three days) also showed no residual glass under the microscope. Its density is given under the heading "tridymite from glass." A second table contains confirmatory measurements upon a second preparation heated to a slightly different temperature.

Tridymite (H_2O at 25° = 1).

First preparation (1200°).		Second preparation (6 days at 1160°).	
From quartz.	From glass.	From quartz.[1]	From glass.
2.325	2.316	2.327	2.319
2.330	2.318	2.325	2.318
2.325	2.316		2.316
	2.319		
Mean, 2.326 (25°)	Mean, 2.317 (25°)	Mean, 2.326 (25°)	Mean, 2.318 (25°)

Whether the quartz had not completely changed to tridymite, or the glass was incompletely crystallized, or perhaps both, is of little moment. It is a very slow change and the agreement between the values obtained by the two methods is sufficiently

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[1] This preparation was afterward found to contain some unchanged quartz.

good, when considered in the light of their identical optical properties, to establish the absolute identity of the tridymite formed from the glass and from the quartz crystals.

The Lime-Silica Series.—Having determined the properties of our two component minerals, we are prepared to enter upon the study of their relation to each other in mixtures of various proportions. It will be borne in mind that inasmuch as we found no proper melting-point for pure silica on account of the inertness (if we may so describe it) with which it resists molecular de-orientation when heated, so compositions which are immediately adjacent to the silica end of the series may be expected to show the same property and to yield but little information from a direct application of the usual pyrometric methods. Similarly, pure calcium oxide and its immediate neighbors are well out of reach of accurate measurement by any existing pyrometers. But even without these important measurements, we have been able to obtain sufficient information in the more inaccessible portions of the curve to enable us to describe all the reactions involved with little probability of error. Inasmuch as lime is probably the most refractory mineral known, it will require no apology if we simply leave its thermal constants until greater perfection in pyrometric measurements shall have been attained.

Preliminary Orientation.—Given chemically pure and *well mixed* (by grinding and *repeated melting*) preparations, it is not a difficult matter to secure a preliminary survey of a field of this kind. The mineral wollastonite is known, and more than that, is known to possess a melting temperature lower than either lime or silica. There is, therefore, immediate reason for anticipating eutectic relations somewhere in the series. If wollastonite forms a eutectic with components on one or both sides of it, mixtures containing slightly more lime or slightly more silica than wollastonite will have lower melting temperatures than it. A simple and effective mode of preliminary procedure is therefore to take a tiny pinch of a number of the percentage mixtures adjacent to wollastonite, place them in order upon a narrow platinum ribbon which can be heated electrically to uniform brightness, and observe the order in which they melt. No temperature measurement is worth while; the information obtained can only serve for orientation and must be verified by more reliable pyrometric methods.

If a eutectic is present on either side of the compound, it will be the first to melt, and the compound last; the intermediate mixtures are not important. If the materials are not too viscous the melting will be sharp and the material will crystallize again on slow cooling. A few repetitions, or the introduction of intermediate compositions in doubtful cases, will usually enable a preliminary curve to be drawn in which the compounds and eutectics which are within reach will be correctly located. In fact, for many substances they can be very exactly located in this way; intermediate compositions, on the other hand, may be very misleading, depending upon the behavior of the eutectic present after the melting temperature of the latter has been passed.

Proceeding in this way, a eutectic will be readily located between silica and wollastonite at the composition 63 per cent. SiO_2, 37 per cent. CaO, and another on the other side of wollastonite at the composition 46 per cent. SiO_2, 54 per cent. CaO. We will allow the other component of this second eutectic to remain unidentified for the moment, as no stable lime-silica mineral richer in lime than wollastonite is known. If we continue our platinum ribbon experiment with continually increasing percentages of lime, we shall find that after one or two steps beyond this second eutectic the platinum ribbon will burn out without melting the little grains. In other words, the melting temperature of lime-silica mixtures richer in lime than 60 per cent. are all higher than that of platinum. To meet this difficulty, we substituted iridium for platinum ribbon, and proceeded as before laying out a whole series of compositions from 60 per cent. CaO on. We soon discovered a third and very sharp eutectic with the composition $67^1/_2$ per cent. CaO, $32^1/_2$ per cent. SiO_2, and a maximum indicating a probable compound at 65 per cent. CaO, 35 per cent. SiO_2, which corresponds to the anticipated orthosilicate. No other points were obtained up to 2100°.

Thus in a very short time and in this simple and expeditious way we were able to locate three eutectics (37, 54 and $67^1/_2$ per cent. CaO) and two compounds (48 and 65 per cent. CaO) between lime and silica, canvassing for the purpose practically all the compositions from pure lime to pure silica at intervals of 1 or $2^1/_2$ per cent. and all temperatures from 500° to 2100°. Beyond 75 per cent. lime and below 32.5 per cent. the method yields no information for reasons which have been elaborated elsewhere. All the important determinations were verified by numerous repetitions.

If we now compare the compounds obtained by this preliminary investigation with those which we were led to anticipate from Boudouard's observations, as well as from the hypothetical silicic acids, we find that we have located two—the metasilicate and orthosilicate—and missed two—the åkermanite analogue ($4CaO.3SiO_2$) and the tricalcium silicate. The next step was therefore obviously to bring all our resources to bear upon these particular compositions in order definitely to ascertain whether such compounds can exist when the components are pure, and if so, under what conditions and with what properties. That we succeeded in reaching a positive conclusion upon this point is due in large measure to the skilful microscopic examinations by Mr. Fred Eugene Wright of this laboratory, of which a detailed record prepared by him will be found with the full text of this paper soon to be published.

The Åkermanite Analogue.—The åkermanite analogue ($4CaO.3SiO_2$) was first taken up and the neighboring concentrations investigated at intervals of 1 per cent. with the greatest care. A large charge of this particular composition was repeatedly melted and examined under the microscope but it failed to show homogeneous structure or any characteristic property of a compound. On the other hand, the pseudo-wollastonite and the orthosilicate appeared in the proportion appropriate to its place in the series. Furthermore, since the melting temperatures of these mixtures were within the reach of our platinum furnaces, and therefore of our most sensitive pyrometric measurements, we were able to hold the temperature constant at any desired point and then by rapid cooling (quenching in mercury) to fix any phase which might have been present and become unstable below that temperature. Here again we found that pseudo-wollastonite and the calcium orthosilicate were the only phases which could be separated from this or any mixture of the pure components in the neighborhood. It is our belief, therefore, that the åkermanite mineral cannot exist between the pure components and is only possible when other substances are present. This is further indicated by the fact that the metasilicate of calcium in the presence of magnesium oxide forms a solid solution of which the limiting concentrations are relatively wide and which would easily account for the åkermanite mineral produced from the fusion of the three components.

The Orthosilicate of Calcium, Ca_2SiO_4 (65 per cent. CaO).[1]—It has long been known that the orthosilicate of calcium, although not found in nature, can be formed by the fusion of the pure components. The temperature of fusion is very high and the crystalline material obtained disintegrates spontaneously at the lower temperatures. The cause of the disintegration has not been carefully studied heretofore, and optical determinations of it are difficult, owing to the extreme fineness of the disintegrated product. Our investigation establishes the fact that the orthosilicate of calcium can exist in three polymorphic forms which we have designated as α, β and γ, in the order in which they form from fusion. The α-form is the only modification which is stable in contact with the melt. Its specific gravity is about 3.27, determined in methylene iodide solution upon fresh crystals. Its hardness is 5-6, Mohr's scale; crystal system, monoclinic.

Below 1410° the α- changes into the β-form, of which the density, 3.28 (measured by comparing the indices of refraction), is but little different from that of the α-modification. The substance was too unstable for determinations of the density to be made in the ordinary way. It crystallizes in the orthorhombic system. The inversion point between the α- and β-varieties is well marked and distinguishable over almost the entire range of compositions of which the orthosilicate is a component, as indicated in the diagram (Fig. 2, line *MN*). The inversion of β into γ occurs at about 675° with a large increase of volume, which at once explains the disintegration of the material. The temperature at which this inversion occurs is somewhat variable, and it is not readily reversible. It is much too slow a change to admit of pyrometric determination, but it is possible to locate it approximately by quenching the material from selected temperatures in the neighborhood of the inversion point. The usual procedure was to take a small portion of the disintegrated material, fold it tightly between thin strips of platinum and place these in the furnace. The temperature was then raised to any chosen value

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[1] The metasilicate of calcium has been made the subject of a special paper by Allen, White and Wright (loc. cit.), and will not receive detailed consideration here.

and maintained constant for periods of time varying from six hours to three or four days. At temperatures far enough removed from the inversion point, the transition from one form into the other was fairly rapid, but as the temperature of inversion approaches, equilibrium is attained with increasing difficulty. After the furnace had remained at this constant temperature for a length of time, it was opened, the platinum strips containing the orthosilicate were removed, and quickly plunged into mercury. In this way, from temperatures just above the inversion point, it was possible to fix the β-form long enough to allow of its optical determination.

The disintegration on cooling appeared to depend considerably upon whether or not the α-form had first been allowed to change into the β-form. For example, if a small portion of the orthosilicate is fused before the oxyhydrogen blast and then plunged directly from the flame into mercury, the quenched material will usually be stable for a considerable time. If the flame is removed but a moment and the slightly cooled specimen plunged from white heat into mercury, disintegration is immediate. This phenomenon was further verified by fusing the material and dropping it into a furnace held at about 1200°. After a few moments the charge was then removed and quickly plunged into mercury. Treated in this way, all of α goes over into β, which in turn will disintegrate completely with little or no delay after reaching the $\beta \rightleftarrows \gamma$ inversion temperature. One will sometimes get the α-form by slow cooling, but never the β-form.

The γ-form of the orthosilicate crystallizes in the monoclinic system. Its density, determined in turpentine, by the pycnometer method, is

2.973
2.975
Mean, 2.974 (25°)

The difference in volume between the γ- and α- or β-forms is therefore nearly 10 per cent., and since the α- and particularly the β-form goes over into the γ at low temperatures with the greatest readiness, the disintegration of the fused orthosilicate is readily explained.

Neighboring mixtures containing the orthosilicate as a component disintegrate beginning with compositions containing only 51 per cent. of lime. The disintegration of this preparation is, however, very slow, and usually does not take place at all unless the mixture has been held for some time at a relatively high temperature. The 54 per cent. mixture can also be readily obtained without disintegration, but with more than 54 per cent. of lime, disintegration always occurs under the ordinary conditions of preparation.

If the orthosilicate be heated to temperatures only slightly above *QR* (Fig. 2) so as to produce the β-form without sintering, disintegration does not appear on cooling for the reason that the change in volume is not apparent in the powdered material. If the charge be heated to about 1400°, or above 1410° where the α-modification appears, it sinters tightly together and the disintegration phenomenon is again observed. Charges sintered together at 1400° to 1500° and held continuously at any temperature above *QR* do not disintegrate so long as this temperature is maintained, but as soon as the temperature drops below *QR*, disintegration recurs, but not at a constant temperature nor at any characteristic rate, the change being very dependent upon the conditions obtaining at the time.

The orthosilicate is easily attacked by water, giving an alkaline reaction, even when the water is cold, while with boiling water it is possible to wash out as much as 10 per cent. of lime. This probably accounts for the absence of this mineral in nature. Ammonium chloride solution even when cold decomposes all the mixtures of lime and silica.

The Tricalcium Silicate,[1] $3CaO,SiO_2$.—This silicate owes its supposed existence mainly to those investigators who have found it necessary to postulate such a compound in order to explain the constitution of Portland cement. So far as the literature shows, no one has ever isolated and described a pure and homogeneous compound of this composition or defined its properties.[2] Many and varied attempts to make it have uniformly resulted in mixtures in which poor optical properties have made the conclusions insufficiently positive.[3]

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[1] In the literature of the cement industry the hypothetical compound, $3CaO,SiO_2$, is almost universally referred to as the "tricalcic silicate." The substitution of "tricalcium silicate" in conformity with common chemical usage will of course cause no confusion.

[2] It is sometimes described as "nearly homogeneous."

[3] A moment's consideration should suggest that there is no real necessity for assuming the existence of the tricalcium silicate in order to explain

We began the investigation of this composition by fusing the components in the proper proportions and examining the fused product microscopically as others had done. Most previous investigators, however, appear to have depended for microscopic evidence upon the ordinary optical figures and interference colors. Now, it so happens that this mixture when fused crystallizes in an extremely fine structure in which the interference colors are quite different from those of the orthosilicate to be sure, but this is merely the result of the fine state of division and the overlapping of the crystals, and not to another compound. If one examines any of the compositions in which the tricalcium silicate might be expected to figure, using the very sensitive index of refraction as a test of homogeneity, he will find that in every preparation containing more lime than 65 per cent. (orthosilicate composition), there is an excess of free lime which can be positively identified. We have fused the tricalcium silicate composition, cooled it rapidly and slowly in various ways without once failing to find free lime present in quantity. Through the kindness of Dr. Clifford Richardson, we were also given an opportunity to examine some of the tricalcium silicate prepared and described by him, and while its ordinary appearance under the microscope differed from that of the orthosilicate, a study of the index of refraction showed the supposed tricalcium silicate to be a mixture of the orthosilicate with free lime. Having failed to obtain a single tricalcium silicate which did not contain free lime, and because every specimen which we examined, including many which had been prepared by others, also showed the orthosilicate to be present, we were forced to conclude that the tricalcium silicate has no real existence. We also tried fusing the tricalcium silicate composition with a flux, but the product was always the orthosilicate of calcium.

the nature of Portland cement. It is a system of at least three components with a great number of possibilities. The real difficulty appears to have been that crystallized lime is relatively inert and does not readily give the reactions common to ordinary lime, consequently the tests which were thought to demonstrate the absence of free lime in these preparations have proved very misleading. For example, we have found that crystals of lime are but very slowly attacked by water (see p. 1094). Another argument which is freely offered—that there can be no free lime present "because if free lime is added the cement dusts spontaneously," is obvious fallacy. Free lime does not cause the dusting, and if it did the fact that the *addition* of free lime caused dusting would be no proof that none was present.

Although we are anticipating pyrometric studies which follow, a single glance at our diagram (Fig. 2) will show that we have found and measured the $\beta \rightleftarrows \alpha$-inversion of the orthosilicate in all the compositions up to 90 per cent. lime which we could never have done with a tricalcium silicate intervening unless the tricalcium silicate be assumed to possess an identical inversion—which would be a rare coincidence. We have therefore complete optical and pyrometric evidence of the persistence of the orthosilicate throughout the supposed tricalcium silicate region, and no compound of tricalcium silicate composition can exist there.

By way of completing the search for hypothetical compounds, we also examined compositions corresponding to the trisilicic acid, but found that the mixtures of lime and silica from which the salt of this acid might be expected to crystallize did not give any new phases. These mixtures showed well developed pseudowollastonite with the tridymite eutectic, and neither rapid cooling nor crystallization of the glass at low temperatures gave any indication whatsoever of the hypothetical compound.

The Temperature Constants.—We have now definitely located the compounds of lime and silica which can exist between the pure components together with the eutectics which they form. It only remains to study their thermal properties somewhat more consistently by accurate pyrometric apparatus. It was not found possible to determine the presence of the eutectic (line *HBI*, Fig. 2) in the 10 and 20 per cent. compositions, for reasons which will have become sufficiently clear already, but the microscopic evidence shows the tridymite to be normal, whether it forms from pure silica or in the presence of lime, so that the eutectic must extend over to the silica axis. From 30 per cent. on there was no difficulty in observing it pyrometrically. Mean values of the observations obtained are included in Table I.

TABLE I.

(Line *HI*, Fig. 2.)

Eutectic. Tridymite—pseudo-wollastonite.

Percentage of CaO	30	32	35	40	45
Eutectic melts...............	1420°	1418°	1418°	1421°	1413°

The liquidus *AB* (Fig. 2) has been drawn as a dotted line. The value assumed for the melting temperature of silica is based upon considerations which have been elaborated elsewhere (p. 1095). It requires no further comment except perhaps to call attention to the fact that it is much lower than the temperature usually assigned to it. As the mixtures grow richer in lime, the melting of the excess of silica seems to be considerably facilitated, but there are no points sufficiently sharp to serve any purpose as quantitative determinations until we reach the composition 30 per cent. CaO, 70 per cent. SiO_2. The microscopic evidence is, however, both satisfactory and sufficient as to the nature and continuity of the curve.

Along the branch *BC* (Fig. 2) of the liquidus, the pseudo-wollastonite is the solid phase. It crystallizes from these mixtures in laths between which an extremely fine-grained, almost sub-microscopic eutectic appears.

It may be remarked in passing that the "eutectic structure" in minerals is by no means so characteristic as in the case of the alloys. Owing to the great viscosity of these melts and consequent slowness of diffusion, it is evident that there is no opportunity for the formation of the characteristic grain structure which we have come to associate with the eutectics of the alloys. This almost complete absence of diffusion in silicate melts makes it necessary to proceed with great caution in applying to minerals the methods which are easily and effectively applied to the alloys. For example, in alloys it is possible to crystallize out a portion of the solid phase, then to separate the mother-liquor and by analysis of the two to determine the composition of the solid phase. In the case of mineral mixtures, the segregation of the eutectic is, for laboratory experiments at least, very indefinite. We have repeatedly examined different regions of a charge in which the eutectic was known to separate, in the hope of finding it segregated towards the middle of the charge, as commonly happens with alloys, but in no case were we able to detect more of the eutectic in one part of the charge than in another. It is usually finely divided and intimately mixed with the primary crystals.

The properties of the pseudo-wollastonite which separates along the branch *BC* are not quite identical with those of the compound when prepared pure, from which it is evident that a certain amount of silica must be taken up by it in solid solution. The amount thus held in solution is certainly less than 2 per cent., but its exact determination microscopically is very difficult indeed. Furthermore, this pseudo-wollastonite when changed to

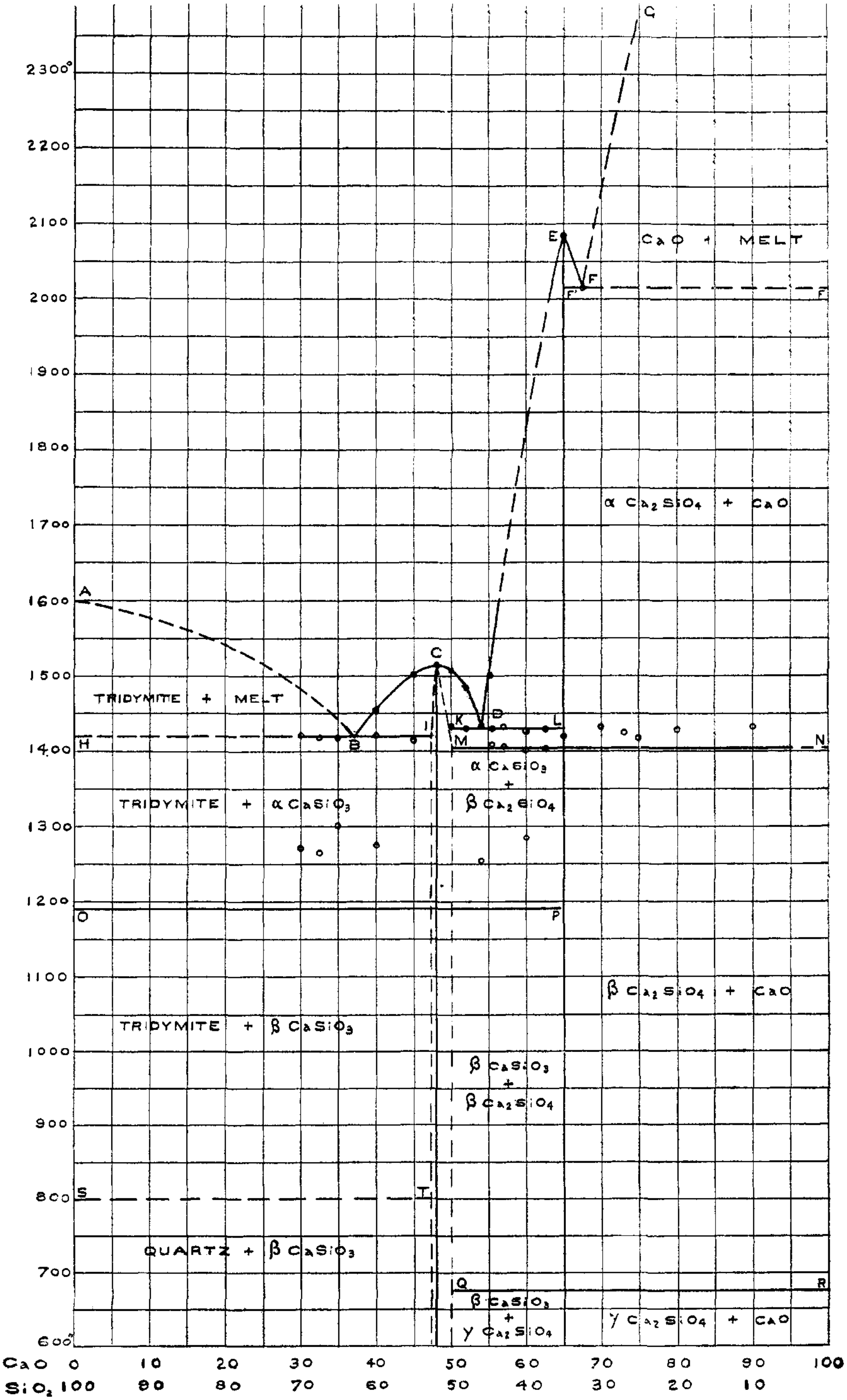
G
E
F
F'
F'
CaO + MELT
α Ca₂SiO₄ + CaO
A
C
TRIDYMITE + MELT
D
K
L
H
B
I
M
N
α CaSiO₃ + β Ca₂SiO₄
TRIDYMITE + α CaSiO₃
O
P
β Ca₂SiO₄ + CaO
TRIDYMITE + β CaSiO₃
β CaSiO₃ + β Ca₂SiO₄
S
T
QUARTZ + β CaSiO₃
Q
R
β CaSiO₃ + γ Ca₂SiO₄
γ Ca₂SiO₄ + CaO
2300°
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600°
CaO 0 10 20 30 40 50 60 70 80 90 100
SiO₂ 100 90 80 70 60 50 40 30 20 10

Fig 2.

wollastonite still shows a slightly different optical character from the pure material, showing that the solid solution apparently continues after the inversion. For brevity, the pseudo-wollastonite has been designated α-$CaSiO_3$, and wollastonite β-$CaSiO_3$, in (Fig. 2). The branch of the liquidus *CD* was readily determined, as well as the beginning of the branch *DE*. It was not possible, however, to follow the branch *DE* beyond 57 per cent. owing to the steepness of the curve, which rapidly carries it out of the range of the accurate thermoelectric methods.

Mean values of the observations along the curve of melting-points are continued in Table II.

TABLE II.

(Curve *A B C D E F G*, Fig. 2.)

Curve of Melting-points.

Percentage of CaO	40.0	45.0	48.2	50.0	52	54	55.5	65	67.5
Component in excess melts	1453°	1500°	1512°[1]	1508°	1484°	1433°	1503°	2080°[2]	2015°[2]

The eutectic *KL* (pseudo-wollastonite + α-calcium orthosilicate), Table III, was found in all compositions containing more than 50 per cent. and less than 65 per cent. of lime. No trace of it could be detected in the 65 per cent. composition, though diligent search was made for it. A great many determinations were made of it of which only the mean values are given in Table III.

TABLE III.

(Line *KL*, Fig. 2.)

Eutectic. Pseudo-wollastonite + α-Calcium Orthosilicate.

Percentage of CaO	50	52	54	55.5	57	60	62.5
Eutectic melts	1432°	1430°	1433°	1429°	1431°	1426°	1429°

The properties of the metasilicate separating along *CD* are also slightly different from those of the pure pseudo-wollastonite, and up to 50 per cent. the mixture appears homogeneous, so that the metasilicate probably takes up about 1 per cent. of orthosilicate in solid solution.

The melting-point of the orthosilicate determined in the iridium furnace was found to be

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[1] Determined by Allen and White, Loc. cit.

[2] Determined with the Holborn-Kurlbaum optical pyrometer in the iridium furnace.

2077°
2085°
2083°
Mean, 2082°

Another charge observed at 2035° was found to be entirely unmelted. Optical methods of temperature measurement are not competent to determine the melting temperature of the orthosilicate in the presence of the eutectic for reasons already explained (p. 1091), but the eutectic or the compound is readily measured by itself once the composition has been determined. Applying the method to the $67^1/_2$ per cent. mixture, therefore, it was found to melt very sharply at 2015°. Neither the orthosilicate nor the 70 per cent. lime composition showed any trace of fusion at this temperature. Since the microscopic properties of the orthosilicate remain unchanged in the presence of an excess of lime or of silica, it follows that the orthosilicate does not form solid solutions with either lime or silica. Both eutectics will therefore continue up to the orthosilicate. Above the lime-orthosilicate eutectic the pyrometer affords no further information regarding the melting-point curve.

The line *MN* (Fig. 2) represents the temperature at which the inversion of β-orthosilicate occurs. It will be noted that the inversion is frequently delayed by superheating, especially in the region remote from the eutectic, but it was always possible to show by quenching the material from above and below these temperatures that the variation is merely due to the inevitable lag of the reaction. Between 50 and 65 per cent. of lime, the two heat changes at *MN* and *KL* lie so close together that it was very difficult to separate them. The pyrometer shows two points plainly but each is somewhat displaced by the other. We were able, however, to distinguish them beyond possibility of confusion by holding the furnace constant at 1425° and quenching the charge in water. These conditions yield α-orthosilicate + pseudo-wollastonite, while if the temperature is held at 1390–1400°, β-orthosilicate + pseudo-wollastonite results. The inversion temperatures are contained in Table IV. Mean values are, of course, without significance.

TABLE IV.

Inversion. β-Orthosilicate to α-Orthosilicate.

Percentage CaO.	55.5	57.0	60.0	62.5	65.0	70	73	75	80	90
Inversion temp.	1407°	1395°	1404°	1396°	1426°	1409°	1426°	1415°	1407°	1438°
	1414	1412	1411	1397	1421	1405	1425	1421	1429	1432
	1403	1419	1411	1405	1415	1412			1432	1433
	1411	1415	1398	1398	1414				1425	
		1406	1402	1408	1412					
		1406	1404	1407	1413					
		1404	1405	1401	1417					
			1388		1423					
					1411					

The scattered points lying below 1300° (Fig. 2) occur only in the compositions in which the metasilicate is present, and correspond, as a microscopic examination at once shows, to the change from wollastonite to the pseudo-hexagonal form. With falling temperature, the points occur very much lower or are lost, since the inversion does not occur quite as readily on cooling. Allen and White observed that this inversion could be brought about only with great difficulty with the pure metasilicate, but in the presence of an excess of either lime or silica, we found it to occur with comparative readiness (Table V) in many compositions. The line *QR* is the temperature at which the reaction β into α takes place. As observed in the discussion of the properties of the orthosilicate, this reaction does not occur promptly, but is liable to very serious superheating or undercooling.

TABLE V.

Inversion. β-Metasilicate to α-Metasilicate.

Percentage CaO.	30	32.5	35	40	45	57
Temperature of inversion..	1273°	1274°	1257°	1288°	1254°	1286°
		1263	1399	1266		
			1323			
			1328			

SUMMARY.

There are only two definite compounds of lime and silica capable of existing in contact with the melt. These two compounds are:

(1) The pseudo-hexagonal metasilicate melting at 1512° and inverting into wollastonite at about 1200°. The metasilicate is able to take up a small amount of either lime or silica in solid solution.

(2) The orthosilicate of calcium which melts at 2080° possesses three polymorphic forms:

The α-form, which crystallizes in the monoclinic system, has a density of 3.27 and a hardness of between 5 and 6.

The β-modification crystallizes in the orthorhombic system and has a density of 3.28.

The γ-modification has a density of 2.97, and also crystallizes in the monoclinic system. The disintegration or "dusting" of the orthosilicate and of all lime mixtures above 51 per cent. lime is due to the 10 per cent. volume change accompanying the $\beta \rightleftarrows \alpha$ inversion.

The inversion point α to β occurs at 1410°, β to γ at 675°.

There are three eutectics in the series: Tridymite + the metasilicate at 37 per cent. lime, 1417°; the metasilicate + orthosilicate at 54 per cent. of lime, 1430°; and orthosilicate + lime at $67^1/_2$ per cent. of lime, 2015°.

The orthosilicate is readily attacked by water, which dissolves out the lime in large quantities. This is probably the reason why it is not found as a natural mineral.

The density of fused lime is 3.32; its hardness 3+. It fuses in the electric arc but its fusion temperature is not accurately measurable. Lime crystallizes in the isometric system and possesses no polymorphic forms.

Silica begins to melt at about 1600° to an extremely viscous liquid, so that an exact melting-point cannot be determined. It has been shown that for all temperatures above 1000° pure quartz changes into tridymite, and pure quartz glass crystallizes as tridymite; so that above this temperature tridymite is unquestionably the stable phase. In the presence of fused chlorides quartz glass crystallizes as quartz at temperatures up to 760° and as tridymite above 800°, crystalline quartz inverts to tridymite above 800° and tridymite goes back to quartz at 750°. The inversion temperature is therefore about 800°, and the change is enantiotropic. The density of pure tridymite was found to be 2.318, and that of quartz glass 2.213. The pure natural quartz used had a density of 2.654, the artificial crystals of 2.650.

Neither the salt of the trisilicic acid, $2CaO, 3SiO_2$, the åkermanite analogue, $4CaO, 3SiO_2$, nor the tricalcium silicate, $3CaO, SiO_2$, can exist in the two-component system.

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