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THE CONSTITUTION OF BONE CHINA

PART I

High Temperature Phase Equilibrium Studies In the System Tricalcium Phosphate-Alumina-Silica

by

P. D. S. St. Pierre

MINERAL DRESSING AND PROCESS METALLURGY DIVISION



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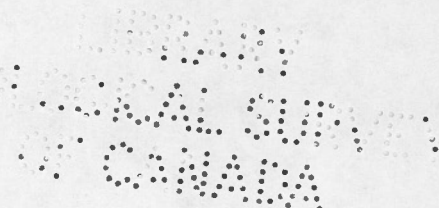
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THE CONSTITUTION OF BONE CHINA

I. High Temperature Phase Equilibrium Studies in the System Tricalcium Phosphate-Alumina-Silica.

by

P. D. S. St. Pierre

Metallurgist,

Mineral Dressing and Process Metallurgy Division.

INTRODUCTION

The present investigation represents a first attempt to interpret the thermal behaviour and constitution of bone china by means of a phase equilibrium study on an idealized system. The results are of interest not only to ceramists who make bone china, but also to technologists wishing to make it from materials other than those traditionally used.

Although petrologists have used high temperature phase equilibrium studies as a means of investigating constitutional and thermal problems for nearly fifty years, it is only in comparatively recent times that ceramic technologists have shown interest in this approach to their problems. The cement and glass industries have been the leaders in this respect. With the exception of certain ceramics used in electrical applications, the whiteware branch of the ceramic industry has been slow to appreciate the potentialities of phase equilibrium studies.

If this work can serve as a foundation for further research on bone china bodies then its object of promoting knowledge of the value of phase equilibrium methods will have been achieved.

History

Bone china was first developed and produced commercially in England by Josiah Spode II at the end of the eighteenth century. Originally this new whiteware was intended to compete with the porcelains imported from foreign lands, but it quickly became established on its own merits by virtue of certain desirable properties. The most important of these for the buyer were a whiteness and translucency that were superior to many of the costly European and Chinese hard porcelains. Another factor which greatly enhanced the value of bone china was the lower firing temperature that permitted a greater variety of brilliant underglaze colours than was possible with high-fired hard porcelain. Technologically Spode's product also had the advantage that it could be manufactured more easily and cheaply than the soft porcelain developed by the French. Today, bone china is probably the best known of fine English ceramic products and is much sought after in the world's markets.

Purpose of Investigation

Although bone china has been made in England for a great many years little research has been published on its constitution and fabrication. Complications in manufacture have limited its production almost entirely to England where the art of compounding and firing the ware has been highly developed. English factories, however, have always accepted high losses as a normal part of manufacture and as a consequence this fine ware is expensive.

The chief difficulties encountered in making bone china are, 1) Tendency of bodies to go "off-colour" on firing, 2) Short firing range, and 3) High shrinkage on firing. Most investigations on bone china have been concerned with measures to overcome these three faults.^{1, 2, 3, 4, 5, 6 & 7*} The present study differs from previous work in that the subject is treated in a more general manner. The view is held that knowledge of the constitution of bone china will hold the key to an understanding of the above-mentioned unfavourable properties.

Treatment of Subject

The first published scientific work seems to have been carried out early in this century. The methods of investigation were crude, but the information obtained, though meagre, was useful and will be referred to later. Nothing further was published until 1932 and 1935 when German and French papers^{8, 9} were issued describing experiments on bone china. Subsequent technical publications^{10, 11} have been in the nature of reviews which contributed no new knowledge to the subject. In the present investigation an attempt has been made to lay a sound foundation on which further scientific work may be built.

The best means of comprehending the thermal equilibrium behaviour of complex mixtures is through the medium of the phase diagram. In the type of phase diagram most commonly used in ceramic work the fields of primary crystallization of phases encountered in the system are shown and liquidus temperatures are

* All references are placed at the end of paper.

plotted either as ordinates in two-component systems or as isotherms in ternary systems. The value of the diagram to the ceramist may be compared to that of a topographical map to a traveller. A map enables a traveller to determine the best path to his objective, while a phase diagram permits the ceramist to predict the crystallization path of any mixture in a given system. In this way the properties of mixtures in the system may be anticipated and suitable ones chosen for specific purposes.

The compilation of a phase diagram requires careful selection of components so that the properties of the mixtures may be suitably plotted to yield the maximum of information. In order to describe graphically the constitution of bone china and the thermal relationships of its phases it is necessary to express composition by not more than four components. Table I shows the range of composition of bone china bodies in terms of the raw materials used in its manufacture. Table II gives typical analyses of some common bone china bodies.

TABLE I
General Range of Composition
of Bone China Bodies¹²

Raw Material	Proportion
China clay	20-30%
Bone ash	27-46
Cornish stone	20-32

TABLE II
Composition of Some Bone China Bodies¹²

Sample	Bone Ash	China Clay	Flint	Cornish Stone
a	45%	26%	3 %	26%
b	46	24	3	27
c	48	31	3	18
d	42	29	5	24
e	44	24	-	32
f	38	12	25	25

If these substances were pure stable compounds they could be used to describe accurately bone china, but unfortunately they are unstable, complex mixtures and so cannot be applied in this way. The difficulty may be overcome by expressing the composition of bone china in terms of the oxides which make up the raw materials. In order to restrict the components to four in number, only the major oxides can be considered, the rest being neglected completely. Clearly then, the phase diagram can only be considered as an approximation, but nevertheless it provides a useful and practical guide to phase relationships in commercial bodies. A four-component system is too complex to be studied in a few years and simplification to a three-component system is necessary. This may be done with little further approximation as will be shown presently.

The four major oxide components of bone china are lime (CaO), alumina (Al_2O_3), phosphorus pentoxide (P_2O_5), and silica (SiO_2). The presence of magnesia, alkali oxides, iron oxides, and fluorine will be neglected since, generally, they amount to less than 3% of

the total composition, and individually do not exceed 1.5%. Experience with other systems shows that such minor impurities have little or no effect on crystallization sequences; they simply lower the melting points predicted from the idealized diagram. A correction must therefore be made when applying the data from the diagram to practical mixtures.

Thus, melting point and phase equilibrium data for the system can be shown graphically by means of a tetrahedron as indicated in Figure 1, page 7.

Mixtures of the oxides are located by means of a tetrahedral coordinate system. The fields of primary crystallization of the various phases encountered in the system are expressed in the tetrahedron by spaces bounded by continuous irregular surfaces. Isotherms of liquidus and solidus points may be indicated similarly. A study of the system may be facilitated by investigating only the plane nearest to the region where typical bone china compositions fall. This may be represented best by the plane $3\text{CaO} \cdot \text{P}_2\text{O}_5 - \text{Al}_2\text{O}_3 - \text{SiO}_2$, because its three components melt congruently. Thus the composition of bone china bodies will be expressed, as a first approximation, in terms of tricalcium phosphate-alumina-silica. The $\text{CaO}/\text{P}_2\text{O}_5$ ratio of many bone china bodies falls between the limits of 1.18 and 1.58 required by tri- and tetra-calcium phosphates respectively. Although most bone china compositions would be better expressed mathematically in terms of tetracalcium phosphate, the use of this compound as a component in phase studies is precluded by its decomposition on melting. It will be seen later, however, that

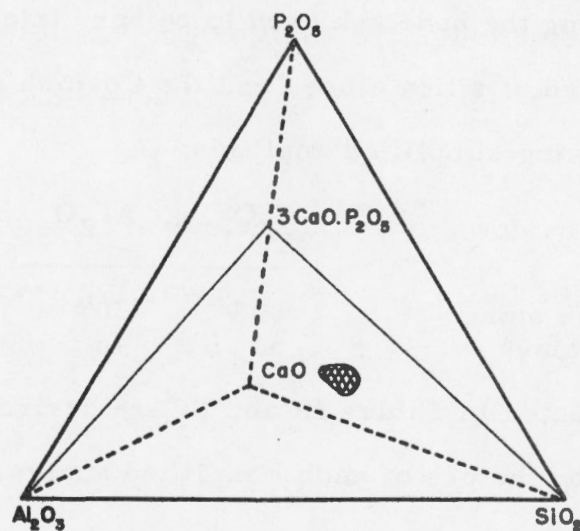


Figure 1. - Space tetrahedron for system CaO , Al_2O_3 , P_2O_5 and SiO_2 showing the range of composition of bone china bodies.

temporary neglect of the higher $\text{CaO/P}_2\text{O}_5$ ratio does not hinder the description of the constitution of bone china.

In order to locate bone china compositions in the $3\text{CaO P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-SiO}_2$ plane of the tetrahedron, the analyses of Tables I and II must be expressed in terms of the aforementioned components. This may be achieved by considering the bone ash used to be pure tricalcium phosphate, the flint to be composed of silica alone, and the Cornish stone and china clay to have the following simplified analyses:-

	SiO_2	Al_2O_3
Cornish stone	80%	20%
China clay*	54	46

The figures quoted in Tables III and IV are derived from Tables I and II respectively by the use of such simplified analyses.

TABLE III

General Range of Composition of Bone China Bodies Treated as Simple Ternary Mixtures*

Component	Proportion
$3\text{CaO.P}_2\text{O}_5$	27-46%
Al_2O_3	13-20
SiO_2	27-42

*After dehydration of clay: $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} - \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$

TABLE IV

Composition of Bone China Bodies
Treated as Simple Ternary Mixtures*

Sample	3CaO.P ₂ O ₅	Al ₂ O ₃	SiO ₂
a	46.7%	16.1%	37.2%
b	47.6	15.4	37.0
c	50.2	16.6	33.2
d	43.7	17.1	39.2
e	45.5	15.9	38.6
f	38.7	9.9	51.4

Previous Research

Although high temperature phase equilibrium relationships have been carefully studied for the system CaO-Al₂O₃-SiO₂¹³ little or nothing is known of the other systems represented by the tetrahedron shown in Figure 1. Barrett and McCaughey¹⁴, however, have published approximate data on the essential equilibrium relationships in the system CaO-P₂O₅-SiO₂.

At first sight it would appear that information on one internal plane (viz. 3CaO.P₂O₅-Al₂O₃-SiO₂) would be insufficient to gain much of an insight into the phase assemblages of such a complex mixture as bone china. In practice, however, correlation of the phase distributions in the aforementioned plane with those of the base plane (i. e. CaO-Al₂O₃-SiO₂) facilitates reasonably accurate prediction of phase distributions in other pertinent planes.

* After dehydration of clay: $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$

Experimental Methods

The experimental procedures used to compile phase diagrams fall into two general classifications, 1) Dynamic methods and 2) Static methods.

The heating and cooling curve technique used in metallurgical studies is representative of the first class. In this treatment the liquidus and solidus temperatures of a mixture are determined by noting the temperature at which the break in its heating or cooling curve occurs due to the absorption or release of the latent heat of melting. Thus, the data yielded by this method are obtained by subjecting the specimen to a series of continuously changing equilibrium states, and noting in particular the one at which latent heat is absorbed or released. In this sense the method is dynamic. Unfortunately the sluggish transformations in most silicate systems preclude the use of this method in ceramic studies.

The static method used in silicate chemistry was developed at the beginning of this century by workers at the Geophysical Laboratory, Washington, D. C.¹⁵. Briefly, the technique may be described as follows:- The constituents of the system are mixed in suitable proportions and fused in a platinum crucible to form a homogeneous glass. Small samples (25 mg.) of this glass are heated and held at various known temperatures to attain equilibrium and then quenched in water. In this way conditions at high temperatures are retained in the specimen, which is later examined at room temperature. Powdered fragments of the quenched samples are immersed in suitable oils and observed under

the petrographic microscope. The liquidus of a given composition is determined by seeking the temperature below which quenched samples contain a trace of crystal and above which they are all glass, the latter condition representing an all-liquid state at the elevated temperature. Thus, liquidus temperature and primary crystal are obtained simultaneously.

The quench method is very accurate though slow, for each run may take several hours to reach equilibrium and many quenches may be required before the limiting runs for a particular mixture are found. Commonly, however, thirty minutes at constant temperature suffices for equilibrium conditions to be reached. Initially twelve or more runs may be necessary to locate the liquidus temperature of a mixture to within $\pm 2^{\circ}\text{C}$. However, as the investigation proceeds, more accurate estimates of the liquidus of new mixtures may be made, and therefore the number of runs necessary to determine it may be reduced.

Wherever possible the quench method¹⁵ was used in this present study and details of the technique are discussed in the next four chapters. Mixtures which were too refractory for study in the quench furnaces were investigated by cone fusion methods. In all, about one hundred mixtures were made up and investigated by these two methods. Sufficient information was obtained to survey the whole $3\text{CaO} \cdot \text{P}_2\text{O}_5 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system. Clear, homogeneous

glasses were not formed in every case, but all had properties which made it possible to recognize the liquid state in the quenched samples. The composition of this minority of non glass-forming mixtures lay in the more refractory areas of the diagram adjacent to tricalcium phosphate and alumina.

It is common in silicate technology to designate oxides by the first letter of their chemical formulae, and this method of abbreviation will frequently be used throughout the present work. The system under examination will thus be known by the symbols CAPS, wherein C = CaO, A = Al_2O_3 , P = P_2O_5 and S = SiO_2 . Compounds may be indicated as follows, C_3P = tricalcium phosphate, A_3S_2 = mullite, CAS_2 = anorthite, etc.

THE COMPONENTS

The reason for selecting the components $3\text{CaO} \cdot \text{P}_2\text{O}_5$, Al_2O_3 , and SiO_2 for this study of bone china was explained in the previous section. The properties of these components as individual phases will now be described.

Tricalcium Phosphate, $3\text{CaO} \cdot \text{P}_2\text{O}_5$

In commercial bone china the source of this component is always calcined beef bone. It is claimed that synthetic phosphate lacks even the slight plasticity of calcined bone and is not, therefore, a suitable addition to a ceramic body which is not very plastic at any time. Some typical analyses of the bone used are quoted in Table V.

TABLE V
Analyses of Bone¹²

	1	2	3	4	C ₃ P	C ₄ P
CaO	47.8	55.0	52.0	41.7	54.2	61.2
P ₂ O ₅	35.0	39.6	39.9	26.5	45.8	38.8
K ₂ O	----	----	1.3	2.9	----	----
Na ₂ O	----	----	0.8	0.2	----	----
C	16.0	4.5	5.5	27.7	----	----
CO ₂	1.0	1.0	0.7	0.9	----	----
Fe ₂ O ₃	0.002	0.002	0.002	0.002	----	----
CaO	1.37	1.39	1.30	1.57	1.18	1.58
P ₂ O ₅						

Tricalcium phosphate is extraordinarily difficult to obtain as a pure compound with its components in the strict stoichiometric ratio demanded by the formula. After many experiments a simple method of preparation was evolved which permitted the synthesis of the phosphate during the preparation of glass mixtures. Details of preparation, etc., are discussed in Appendix 1.

The melting point of C₃P was found to be $1750 \pm 20^\circ\text{C}$ as determined by cone fusion observations. The experimental details of this determination are given in the section on the binary system Tricalcium Phosphate-Alumina (CAP system).

High and low temperature crystal modifications of tricalcium phosphate exist. Some of their properties were studied and the results are summarized below:-

α , high temperature form, refractive indices $\alpha = 1.588$ and $\gamma = 1.591$, principal x-ray lines with copper radiation 2.90, 2.61, 3.92.

β , low temperature form, refractive indices $\alpha = 1.620$ and $\gamma = 1.622$, principal x-ray lines with copper radiation 2.89, 2.60, 3.18.

It has been stated²³ that the β to α transformation takes place at 1350°C. Quenching runs made to verify this value show that although the statement is essentially correct it must be discussed in more detail, if it is to be interpreted correctly. In the present work it was found that if a sample of β tricalcium phosphate was heated at 1348°C for one hour and then quenched a complete transformation to the α modification took place. However, if the specimen was heated for the same period at 1294°C a mixture of α and β resulted. Similarly, if α tricalcium phosphate was heated for one hour at 1404°C a minute trace of β tricalcium phosphate was detected under the petrographic microscope. Heating the α form at progressively lower temperatures brought about a greater development of β until at 1300°C the α quench product resembled closely the 1294°C β quench mentioned above. Starting with either the α or β modification no transformation took place in a one hour run at 1250°C. No doubt, on prolonged heating a transformation would take place, but in view of the lengthy experiments required this investigation was not undertaken.

It will be appreciated then, that some qualification is necessary when quoting a transformation temperature. A metastable transformation range similar to this one is also found in the case of calcium pyrophosphate (See Appendix II).

The above data check closely with those given in "Data on Chemicals for Ceramic Use" (Bulletin 118, June 1949, National Research Council, Washington, D. C.), the reference handbook on constants used throughout this work. Microscopically, both forms of tricalcium phosphate may easily be recognized. Index, birefringence and twinning serve to identify the α form. α tricalcium phosphate crystallizes very rapidly and it is impossible to quench molten mixtures containing an abundance of this compound to a homogeneous, isotropic glass. Such mixtures, which are noted later, yield a strained glass structure when quenched from above the liquidus temperature. The anisotropic glass may be rendered crystalline by annealing below the liquidus. This strained condition causes the glass fragments to exhibit anomalous extinction between crossed nicols under the microscope.

Hydroxyapatite ($3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$) which is readily formed from tricalcium phosphate under certain circumstances is easily distinguished under the microscope by its higher refractive indices, $\omega = 1.645$ and $\epsilon = 1.641$. At no time was this compound detected during the phase investigation, and therefore no complications due to its presence arose. The formation of this compound is more

fully discussed in Appendix 1. It should be noted, however, that once formed this hydroxyapatite is difficult to decompose since it retains chemically combined water up to temperatures as high as 1400°C.

Alumina, Al_2O_3

Alumina in bone china is mostly derived from china clay which is one of the constituents of the body, though the Cornish stone makes a definite contribution (See analyses of clay and stone). From the point of view of phase relationships, of course, it makes no difference whether a component be derived from one or more sources.

Several allotropes of this oxide are said to exist, but the existence of only two is well established. The α and γ forms of alumina are respectively high and low temperature modifications whose properties may be summarized as follows:-

α , hexagonal crystal system, melting point 2000-2030, refractive indices $\omega = 1.768$, $\epsilon = 1.760$, principal x-ray lines 2.08, 1.60, 2.55.

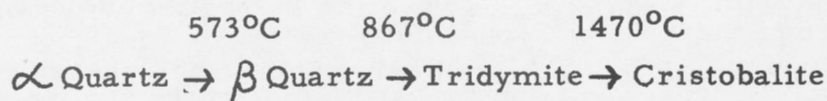
γ , cubic crystal system, transition to α 750-1000°C, refractive index 1.696, principal x-ray lines 1.40, 1.98, 2.39.

The presence of alumina in the present study was readily detected under the petrographic microscope, since only the α form was encountered. This high temperature modification crystallizes into small, well formed hexagonal plates with very high refractive indices and low birefringence. In crystal habit α alumina might be confused

with β $3\text{CaO} \cdot \text{P}_2\text{O}_5$ but the higher refractive index of the alumina (1.760 vs. 1.622) usually reveals its identity. Confirmation of identity, however, can always be made by x-ray examination.

Silica, SiO_2

Both the Cornish stone and china clay contribute to the presence of this component in bone china. Four stable forms of silica are known and their ranges of stability may be summarized thus:-



Except for the two forms of quartz the inversions are very slow and generally an accelerator such as sodium tungstate is required to bring them about within a reasonable period. Tridymite and cristobalite undergo minor metastable inversions at low temperatures giving rise to the so called "high and low forms". The latter inversions take place very rapidly and generally the upper form cannot be stabilized at room temperature. In the course of the present investigation, however, high cristobalite was occasionally observed.

Since high temperature products are being studied the properties of only tridymite and cristobalite need be considered:-

Low tridymite, rhombic, transition to lower high tridymite 117°C , refractive indices $\alpha = 1.478$, $\gamma = 1.481$, principal x-ray lines 4.29, 4.07, 3.80.

Lower high tridymite, hexagonal, transition to upper high tridymite 163°C.

Upper high tridymite, hexagonal, transition to cristobalite 1470°C.

Low cristobalite, tetragonal, transition to high cristobalite 220°C, refractive indices $\omega = 1.487$, $\epsilon = 1.484$, principal x-ray lines 4.02, 2.47, 2.83.

High cristobalite, cubic, melting point 1713°C, refractive index 1.466, principal x-ray lines 4.14, 2.53, 1.64.

All the modifications of silica have low refractive indices and this property may be used to distinguish them from other phases encountered in the system. In the specimens examined during the course of the present work siliceous material was usually seen as fine, low-index dots. In the CPS system mixtures containing small quantities of silica always crystallized with the cristobalite in the form of rosettes (See Figure 2, page 19).

EXPERIMENTAL PROCEDURE

Preparation of Mixtures

The constituents used in making up the required mixtures were calcium pyrophosphate, calcium carbonate, alumina and silica. Details on their preparation, purity, etc., are given below.

Calcium Pyrophosphate, $2\text{CaO} \cdot \text{P}_2\text{O}_5$

This constituent was made from the specially prepared dicalcium phosphate dihydrate whose synthesis and properties are described in

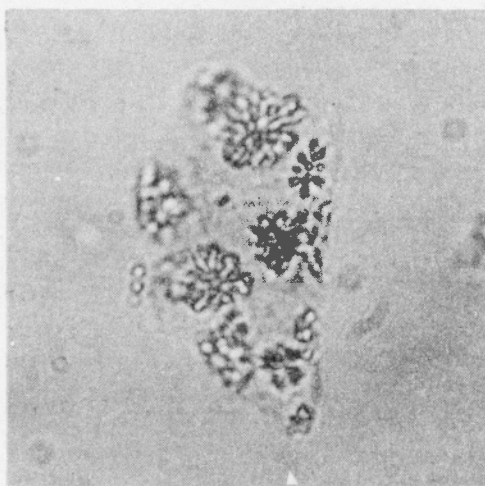


Figure 2. - Rosettes of cristobalite crystallized from a highly phosphatic melt.

the appendices. The dicalcium phosphate dihydrate was ignited at 900°C to ensure that the reaction $2\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}_2\text{P}_2\text{O}_7 + 5\text{H}_2\text{O}$ would go to completion and also to burn out any sugar absorbed during the synthesis of the dicalcium salt. The stock of pyrophosphate so prepared was stored in an oven at 110°C and weighed out as required.

This constituent was, of course, a source of both lime and phosphorous pentoxide. The lime needed to bring the lime/phosphorous pentoxide ratio to that required by tricalcium phosphate was obtained by the addition of calcium carbonate to the mixtures.

Calcium Carbonate, CaCO_3

The necessity for this constituent has just been explained. Baker's special low alkali C. P. calcium carbonate was used. Traces of water were driven off by ignition at 400°C followed by storage in an oven maintained at 110°C. The material was weighed out when necessary after first cooling in a desiccator.

Alumina, Al_2O_3

Alumina was obtained by the ignition of Baker's C. P. $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. This latter compound decomposes readily on gentle heating, though strong heating is required to remove the last trace of moisture. Generally the procedure for dehydration was as follows:- A sample of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ was warmed very gently in a large beaker. The material appeared to boil and erupt constantly. Much care was required to keep dusting losses to the minimum. After a while the

sample subsided and stronger heat was applied. The partially dehydrated alumina was then transferred to suitable platinum ware and gradually heated to about 1250°C , at which temperature it was kept for three hours. Samples were cooled in a desiccator and kept in ground glass stoppered bottles.

Most fine powders are hygroscopic and fine alumina is particularly so. It was found best always to calcine the prepared alumina for a few minutes in a Bunsen furnace prior to weighing. After cooling in a desiccator, weighing was effected as rapidly as possible in order to minimize errors due to water pick-up. The short calcination had the double advantages of removing last traces of water and also agglomerating the powder so that it presented less active surface to the air.

Silica, SiO_2

This was obtained by igniting Baker's C.P. silicic acid $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, after first leaching out impurities with hydrochloric acid. As received, the silicic acid was quite pure, but did contain some iron salts. Leaching in warm hydrochloric acid for several days seemed to be an effective method of removing these trace impurities. Leaching was continued until no iron was detected in the washings by the ammonium thiocyanate test. Testing, by volatilizing the silica with hydrofluoric acid, showed that only 0.023 per cent solids were left on ignition. The dehydration treatment following the leach was identical with that

given for alumina. The silica obtained, however, was coarser than the alumina and therefore required less elaborate precautions to keep it dry. The stock was kept in an oven at 110°C and used as required.

The required amounts of the constituents were weighed to an accuracy better than ± 1 mg. on an analytical balance. Calcium carbonate and silica, both of which tended to adhere to the weighing pan, were removed by washing with alcohol. Mixtures were calculated to yield 4 gm. of glass, since the raw materials for this amount just filled a 10 c. c. platinum crucible.

The raw constituents were first mixed on glazed paper and then gently ground together in a corundum mortar. This latter treatment not only promoted mixing but also helped to reduce the volume of the fluffy calcium pyrophosphate.

After charging the mixture into a 10 c. c. platinum crucible it was heated slowly to about 1000°C in a Bunsen furnace. This ignition served to decompose the calcium carbonate, and also to sinter the mixture prior to the more rapid heating to which it was subsequently subjected. Next, the sinter was fused rapidly at 1700°C in the small oxy-gas blast lamp furnace shown in Figure 3, page 23.

After twenty to thirty minutes at 1700°C the sample was quenched by dipping the crucible into cold water. The glass so formed was broken up in a hard steel Plattner mortar, and afterwards any traces of iron picked up during the grinding were removed with a powerful magnet. Following this treatment the powdered glass was remelted in the manner previously described.

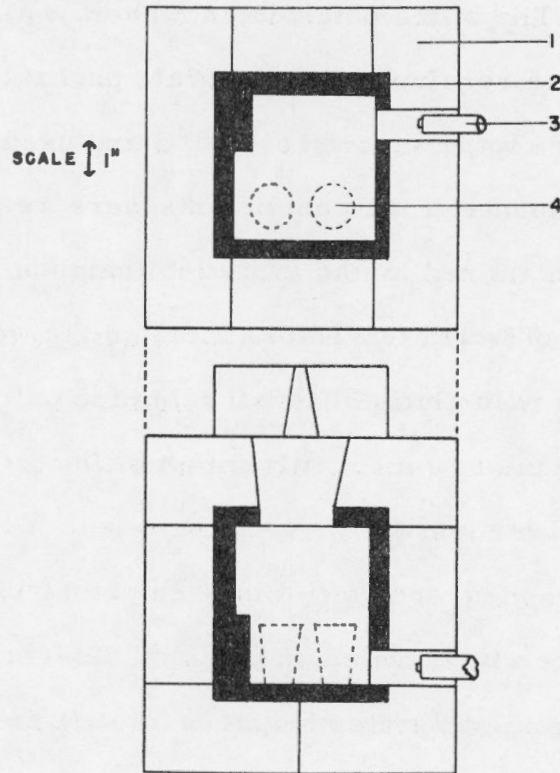


Figure 3. - Blast lamp furnace.

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| 1. Fireclay insulating brick. | 3. Oxygen-city gas burner. |
| 2. Bubble Alundum insulating inserts coated with sillimanite cement. | 4. Alundum crucible flame shields. |

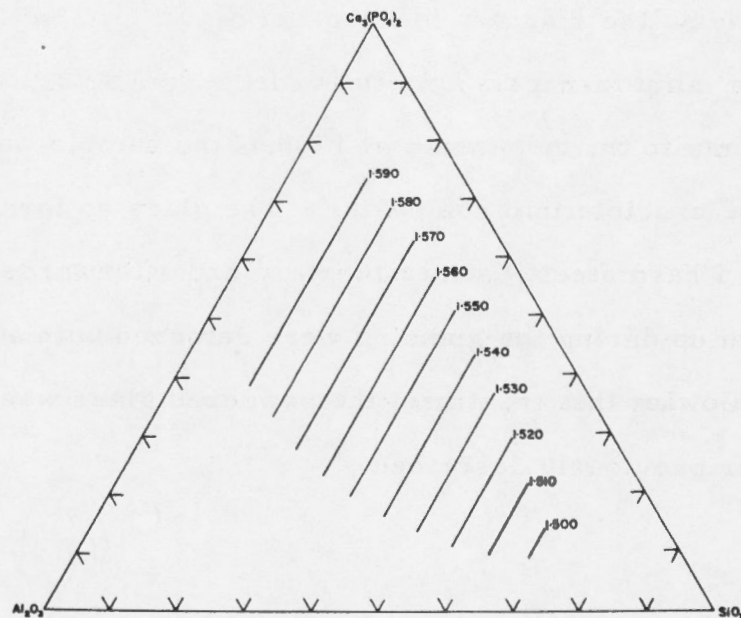


Figure 4. - Isofract diagram for glasses in the CAPS system.

Because of their high viscosity, mixes rich in silica required as many as six melts before a homogeneous glass was obtained. Generally, however, four fusions were sufficient to produce the desired glass. The criterion of homogeneity was uniformity in the refractive index of glass fragments examined by the immersion method under the petrographic microscope. To carry out this technique fragments of glass were immersed successively in different oils of known refractive indices. When the index of an oil matched that of the glass the bright line (Becke line) which normally moved into or out of the fragment on racking the microscope up and down vanished completely. In view of the variation of index with wavelength of light, determinations were made using monochromatic sodium light as the source of illumination.

As the various glasses were made, their refractive indices were noted and plotted on a triangular composition diagram. Since it is well established that the refractive indices of glasses in a system vary in a smooth and continuous manner with compositional change, it is possible to construct an Isofract diagram which can be used to verify the compositions made. Such a diagram is shown in Figure 4, page 23, for the CAPS system. Unfortunately the scope of the diagram in this particular system is limited, for only mixtures centrally located in the composition triangle form true isotropic glasses.

A further limitation to the use of this diagram in checking compositions is caused by the alignment of the isofracts across the diagram. It will be noted that the only compositional variations readily detected

by index changes are those which take place along lines radiating from the silica corner of the diagram.

Besides the aforementioned application, isofract diagrams may be used to study courses of crystallization. For instance, if a partially crystallized mixture is quenched, an estimate of the composition of the liquid co-existing at high temperatures may be made by comparing the index of the glass with the isofracts on the diagram. Thus changes in liquid composition may be followed during the crystallization sequence. In the present system, however, this technique may only be applied to sequences involving a change of silica content.

Not all the mixtures formed glasses when quenched in a platinum crucible, and it was impossible, therefore, to check the homogeneity of these fusions. It is believed, however, that representative samples could be taken for quench work after six melts. In any event all mixtures were very finely ground prior to sampling.

Initially, it was anticipated that there might be volatilization losses of phosphorous pentoxide at the high temperatures reached in making the glasses. Precautions were taken to ensure that glasses were always treated in an oxidizing atmosphere. Checks on half hour fusions at 1700°C showed a loss of 0.04% in the weight of the mixture over that expected due to the decomposition of carbonate. This loss is negligible and it may be considered that both volatilization and reduction of the phosphorous pentoxide were effectively prevented.

Apparatus

Quench Furnace

The melting studies were carried out by heating samples of glass weighing 10 to 25 mg. in a vertical tube furnace. The essential details of the furnace are indicated in Figure 5 and the accompanying legend, page 27.

It will be observed that three different insulating materials are used in concentric rings around the heating element. Light calcined magnesia is much superior to any other high temperature insulating material, but suffers from the disadvantage of sintering badly on continued use at high temperatures (i. e. above 1500°C). Sintering, of course, seriously impairs the insulating properties of the magnesia. For this reason an intermediate zone of bubble zirconia is interposed between the hottest part of the furnace and the magnesia. Because it conducts electricity at elevated temperatures, zirconia insulation cannot be used immediately next to the heating element, hence the need for the Alundum grain.

The Alundum refractories may be used safely up to 1750°C , but the mullite tube requires occasional replacement when heated frequently above 1650°C . For use at high temperatures the mullite tube is supported at the top, so that it hangs straight when hot. Even this precaution, however, is insufficient to overcome warpage completely, and eventually most tubes are rejected because they develop slight bends which interfere with the free passage of specimens

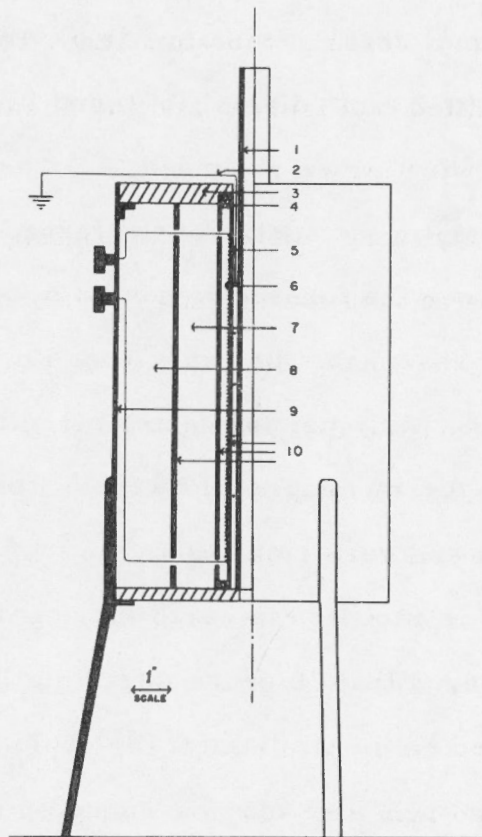


Figure 5. - Quench furnace.

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|---|---|
| 1. Mullite tube. | 6. 120 mesh Alundum grain insulation. |
| 2. Grounded platinum shield wound on the mullite tube. | 7. Bubble zirconia insulation. |
| 3. Transite board. | 8. Light calcined magnesia insulation. |
| 4. Alundum cement plug. | 9. Cylindrical sheet iron furnace casing supported on three steel legs. |
| 5. Winding, 27 ft., 20 gauge (B&S), 60-40 platinum-rhodium alloy, painted over with Alundum cement. | 10. Alundum tubes. |

being quenched. It is possible that Alundum tubes would warp less than mullite, but on the other hand Alundum is more liable to fracture on thermal shock. Since the furnace is often opened while hot, a refractory with good thermal shock resistance is essential.

Fine platinum wire (0.2 mm. diam.) is wound in large open turns on the mullite tube. This wire, when grounded, acts as a shield which protects the thermocouple in the centre of the furnace from stray electrical currents. Since the furnace is heated by A.C. electricity, induced currents might reasonably be expected. Fortunately these A.C. currents do not affect the D.C. potentiometer circuit used to measure the microvoltage of the thermocouple. However, some ionization takes place in the hot furnace and very small D.C. voltages are picked up by the couple. The shield is required to earth these parasitic e. m. f.s.

It is commonly believed that 20 gauge 60/40 platinum-rhodium wire is too brittle to be wound on small diameters. This is not correct, in fact if suitably annealed such wire may be wound on its own diameter (0.8 mm.) without difficulty. The success of the present investigation depended upon the use of 60/40 wire, because furnaces wound with the more common 90/10 or 80/20 wires may only be used safely to 1600°C. In the past, higher temperatures have been achieved by the use of costly iridium tube furnaces. The melting point of 60/40 wire is approximately 1920°C and furnaces wound with it may be run safely at 1700°C. Little is gained by employing increased rhodium content wire, for the melting point of pure rhodium is only 46°C higher.

The size of the furnace is kept to the minimum in order to achieve flexibility in heating and cooling. Several runs are generally necessary to determine the liquidus point of a mixture, making rapid adjustment of temperature between runs essential.

The samples, wrapped in platinum foil envelopes, (approximately 6 mm. x 6 mm. foil, 0.01 mm. thick) are suspended from the quench rig in the middle of the furnace. Details of the rig are shown in Figure 6, page 31.

The drawing is a half section and therefore only one quench lead and one leg of the thermocouple are visible. The sample is tied with platinum wire to an alumina ring through which is threaded more fine platinum wire. The ends of this latter wire are wrapped round the quench leads. The whole assembly is set vertically in the furnace and when it is time to drop the specimen a current is passed through the quench leads. When correctly adjusted, the current is just sufficient to fuse the fine wire stretched between the ends of the leads. Excessive current causes molten platinum to spatter the furnace walls and this increases the danger of subsequent specimens sticking to the tube. On fusion of the platinum wire the sample drops freely out of the furnace into a beaker of cold water where it is quenched.

Both the quenching rig and central tube of the furnace are subject to rapid temperature changes. The quenching rig experiences particularly severe shock when it is put into and taken out of the hot furnace at the beginning and end of a run respectively. The central

tube is cooled by the air circulation (Stack Effect) when the rig is being inserted or removed. Mullite seems to be the only material capable of withstanding the repeated thermal shock, but the sheathing of the thermocouple and quenching lead, located in the hottest part of the furnace, is made of alumina. This refractory has a higher softening point than mullite and specimens are less liable to stick to it. However, its poor spalling resistance makes fairly frequent replacement necessary.

Temperature Measurement

As well as the quenching leads, the quenching rig also carries a platinum-platinrhodium (90/10) thermocouple. The couple is placed as close as possible to the specimen, in order to facilitate accurate temperature measurement. Since the hot zone of the furnace is relatively short it is important to place both specimen and couple in the centre of the zone.

The free ends of the couple are insulated from one another and run into the cold junction through a terminal block set at the top of a Dewar vacuum flask. At the cold junction, which is contained in a glass tube surrounded by ice, two gold wires are joined to the leads from the couple. These gold wires are brought up to the top of the assembly, where they are connected through pin jack terminals to the copper leads from a potentiometer. A noble metal is used immediately next to the platinum wires in order that a welded junction may be made. In this way it is possible to have a small junction free

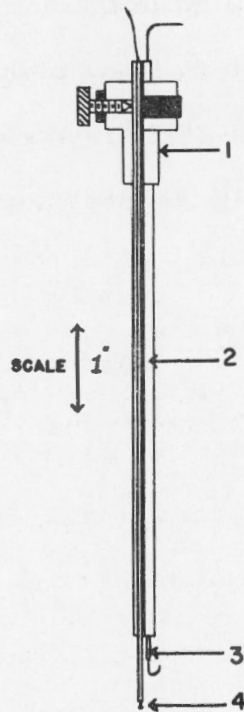


Figure 6. - Quench rig.

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|---------------------|--|
| 1. Soapstone block. | 3. Quench leads. |
| 2. Mullite sheath. | 4. Thermocouple. Platinum
90/10 Platinum-Rhodium. |

from parasitic e. m. f. s. The wires of the thermocouple are 0.4 mm. diameter, but those in the cold junction only 0.2 mm. diameter. The couple requires a thick wire to withstand frequent flexing, whereas the junction wire should be small enough to reduce heat conduction to the minimum. The e. m. f. -temperature tables for thermocouples are drawn up for a cold junction at 0°C. It is important, therefore, to ensure that the junction is maintained constantly at this temperature. This may be achieved by setting the glass tube high in the vacuum flask. so that it is always surrounded by floating ice.

The e. m. f. of the thermocouple was measured by a White potentiometer¹⁶. This instrument was specially designed for this type of work and is known to be particularly free from parasitic e. m. f. s. The usual ancillary equipment consisting of a low-resistance reflecting galvanometer, cadmium cell, and lead accumulator was required in conjunction with the potentiometer.

Temperature Control

In the early stages of the investigation the temperature of the furnace was regulated by a "Brown Thermocouple Controller". This instrument was actuated by a control thermocouple placed close to the heating element of the furnace. The e. m. f. of the couple was applied to a sensitive low-resistance galvanometer, the path of whose pointer was limited by a reciprocating chopper device positioned at the required temperature on the galvanometer scale. When the needle reached the control point the travel of the chopper

was interrupted and this caused it to trip a mercury switch. The switch cut the current to the furnace and brought about cooling. As soon as the galvanometer pointer permitted the free travel of the chopper again the heating was resumed and the cycle of operations repeated.

This type of non-proportional control works satisfactorily on furnaces with a large heat reserve, but wide temperature fluctuations are inevitable with small furnaces. These were minimized in the present instance by placing a by-pass rheostat across the terminals of the controller. Thus, even when the controller was in the "off" position some power was still applied to the furnace. By careful adjustment of the gap between the current passing during the "on" period and that passing during the "off" period the temperature variation could be reduced to $\pm 1^{\circ}\text{C}$.

This apparatus was eventually replaced by a Roberts type Wheatstone bridge controller which maintained temperature within $\pm 0.25^{\circ}\text{C}$ of the desired value. The basic design used was that described by Crandall et al. in the Bulletin of the American Ceramic Society, March, 1950. After modifying the circuit given in the aforementioned bulletin, a controller was built by E. F. V. Robinson, electronics engineer with the National Research Council, Ottawa, and tested by the author. A wiring diagram is shown in Figure 8, page 35. The original controller and a second model made later are shown, together with the quench furnaces, in Figure 7, page 35.

This type of controller is truly proportional in its action, for the power it applies to the furnace is directly related to the deviation of temperature from standard conditions. Reaction is rapid, because the thermosensitive element is the furnace winding itself. The principle of operation is as follows:- The furnace winding is incorporated in an A.C. Wheatstone bridge circuit. When the desired temperature is reached the bridge is balanced manually by adjusting the resistance of the bridge arms until a minimum voltage is recorded by a D.C. voltmeter connected to the grid of the thyatron tube, FG17. Any temperature variations which take place after balancing immediately bring about resistance changes in the sensitive furnace winding. The control circuit then becomes unbalanced with respect to voltage and phase angle across the bridge. After suitable amplification the signals are applied to the control grid of the thyatron tube. Incorporated in the thyatron circuit is a transformer (1:50 ratio) whose impedance is regulated by the thyatron. A part of the current to the furnace passes through one side of this transformer and is impeded by the reactance of the coil. An oscilloscope, connected across the thyatron side of the transformer, shows a characteristic waveform when the control point is approached. The current input to the furnace is then adjusted to make the thyatron fire for approximately one quarter of the A.C. cycle indicated on the oscilloscope. Should the furnace cool the firing cycle lengthens proportionately and thereby lowers the average impedance of the

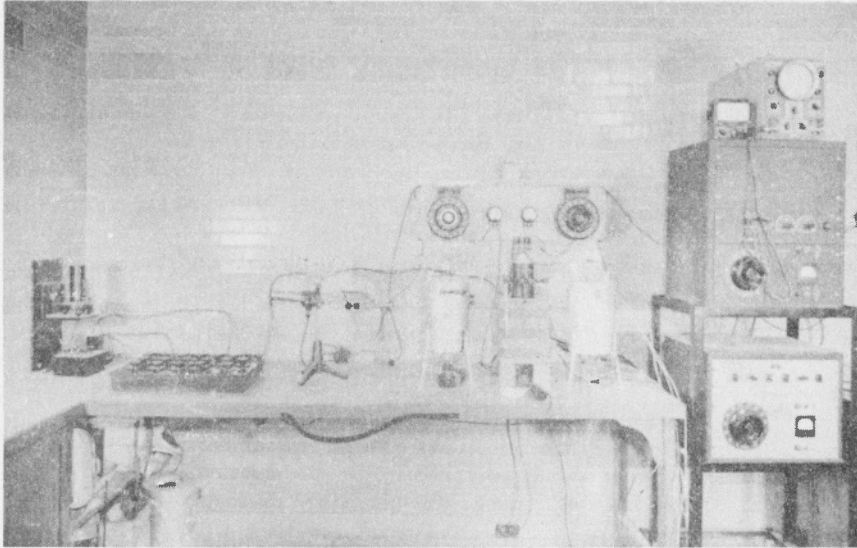


Figure 7. - View of quench furnaces, controllers, potentiometer and cold junction.

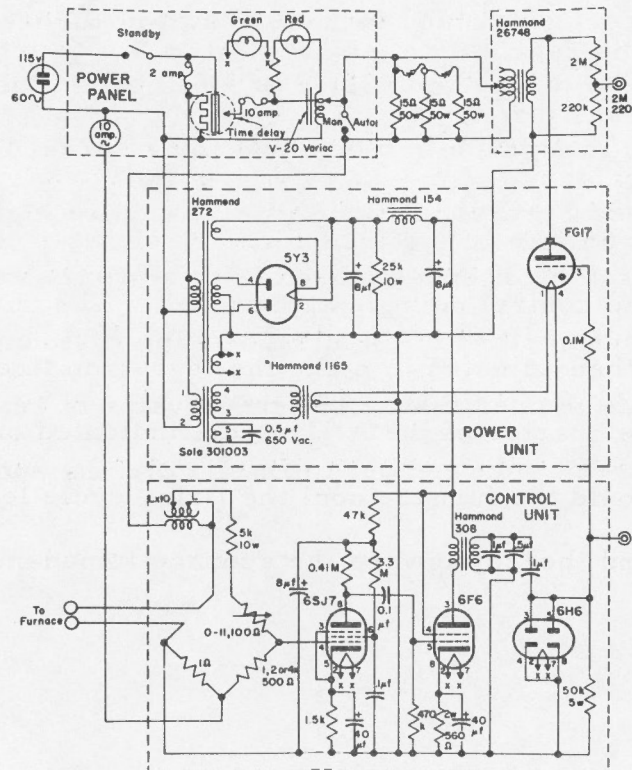


Figure 8. - Wiring diagram of Wheatstone bridge furnace controller.

transformer permitting more current to flow to the furnace. If the furnace overheats the opposite action takes place. Since the magnetic flux in the transformer is controlled by the firing cycle of the thyatron it will be appreciated that the current is linked to temperature fluctuations in the furnace.

The sensitivity of control ultimately depends on a high coefficient of increase in resistance with temperature of the furnace winding. Platinum and its alloys are ideal in this respect.

The application of the controller is described in the next section. Specifications and circuit details are to be found in the reference quoted above.

High Frequency Furnace

Some mixtures were too refractory for study in the quench furnaces. These were studied by the cone fusion method in the high frequency, horizontal tube furnace shown in Figure 9, page 37.

Essentially, the furnace consisted of an Alundum tube (18" long x 3/4" bore) placed in a graphite block susceptor surrounded by carbon black insulation and several turns of a water-cooled high frequency coil. The temperature of cones placed in the furnace was measured with two optical pyrometers of the disappearing filament type, placed one at each end of the open tube. The mean value of readings by two observers was taken as the temperature of softening and melting.

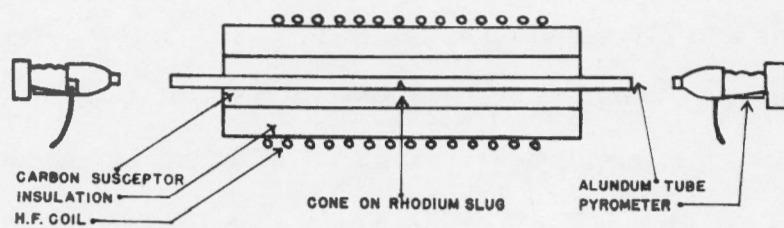


Figure 9. - High frequency furnace apparatus.

A gentle stream of air removed carbon monoxide penetrating the Alundum tube at high temperatures. In this way reduction of the phosphate was avoided.

Operation of Apparatus

Before proceeding with a presentation of the data obtained during the investigation, it would be well to consider the manner of operation of the apparatus described in the foregoing sections. The determination of the liquidus point of a mixture using the quench furnace apparatus will first be described.

The sample, attached to the quench rig, was lowered into a hot quench furnace, the temperature of the latter being somewhat below the estimated liquidus. The sample was then allowed to devitrify by holding it at this lower temperature for a few minutes. The furnace was then heated to the required temperature in about ten minutes, and held there for thirty to sixty minutes. Samples containing over sixty percent silica generally took the longer period to reach equilibrium, because of their high viscosity when molten. Devitrification of the specimen assisted observation by providing nuclei for crystal growth, and thereby preventing supercooling of melts. Thus, if a specimen was heated for a short time slightly above the desired temperature, there was no danger of it failing to crystallize on returning to the control point.

The temperature of the sample was accurately measured by the thermocouple next to it on the quenching rig. The e. m. f.

generated in the couple was determined by the temperature required and therefore the necessary microvoltage settings were made on the potentiometer prior to placing the couple in the furnace. When the furnace reached operating temperature the potentiometer circuit was balanced, using a sensitive reflecting galvanometer to determine the null point. It was important to avoid overheating the specimen, since this destroyed the crystal nuclei. Overshooting by more than 1°C could not be tolerated and when it occurred the run was repeated.

Controller adjustments were critical during the early stages of a run, if overshooting was to be avoided, and initial heating of the furnace was carried out with the controller on the "manual" circuit. This meant that the energy input to the furnace winding was controlled by hand through a "Variac" autotransformer. Constant practice enabled one to estimate power requirements quite accurately for given temperatures. When the furnace was within, say, 10°C of operating temperature the bridge circuit was balanced and the controller switch turned over to the "automatic" position.

Initially an oscilloscope and voltmeter were needed to determine the balance point of the bridge circuit, but after several runs had been made the furnace records indicated the settings for the various temperatures. All runs were logged, since the power consumption of the furnace changed as the insulation sintered together. It was interesting to note that although the controller would regulate temperature to $\pm 0.25^{\circ}\text{C}$, there was an overall drift of 2°C per hour on high temperature runs due to the sintering. Fortunately

this drift was always such as to cause the furnace to cool and so overshooting did not occur. The drift was generally compensated for by adjusting the bridge setting manually when necessary. Although the final results were not more accurate than $\pm 2^{\circ}\text{C}$, constancy of temperature within finer limits during the run was desirable because fluctuations could have caused solution and reprecipitation of phases at unequal rates. Thus the observed state of the specimen could, under some circumstances, have represented a condition above or below that expected for the average temperature of the run.

Constant use at high temperature caused an e. m. f. drift in the thermocouple, due to a differential in the rates of evaporation of its component parts. This and other sources of error were minimized by calibrating the couple at definite time intervals. A running time of 2,000 minutes was found to be a satisfactory interval for temperatures below 1500°C . Above this temperature the interval was reduced to 600 to 1,000 minutes. When the correction for a couple exceeded 125 microvolts at a fixed point, the end of the couple was cut off and the wires rebaded in an oxy-gas flame. The fixed points used in the present study were the melting points of gold (1063°C), diopside (1391°C) and palladium (1549°C). In common with most work of this type the Geophysical Scale of temperature has been used.

Calibration at the gold and palladium points was done by suspending a small Alundum ring from a piece of the appropriate pure wire placed close to the thermocouple, and when the ring fell out of

the furnace, due to the wire melting, the microvoltage of the couple was noted.

Diopside is a calcium magnesium silicate ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) which has a very sharp melting point when its components are in strict stoichiometrical proportions. This compound was synthesized in the laboratory and the calibration was done by treating the material in the same manner as that used for the phosphate glasses, i. e., by quenching to determine the liquidus.

The corrections at the fixed points were plotted against time, so that an estimated correction could be computed for runs made during the interval between the calibrations. Corrections for a particular temperature at a given time could then be made by interpolation between the estimated fixed-point corrections. This treatment assumes simple linear relationships between the correction, time and temperature functions. Deviations from this assumption, however, are not likely to be serious since couples are rebathed when the corrections exceed 10°C .

Some very refractory compositions in the binary CAP and CPS systems were studied in the high frequency furnace described in a previous section. A cone, one-half inch high, was made from the sample by grinding and bonding it with a little 10 per cent polyvinyl alcohol solution. The cone was then mounted on a rhodium plaque and inserted in the furnace. After a trial run to determine the liquidus, other cones were heated more carefully to obtain

accurate results. The temperature of the specimen and its melting behaviour were observed with optical pyrometers.

The cone fusion technique was of limited value only, since the deformation temperature of the cone was determined by the amount of eutectic present. A further difficulty lay in the viscous character of high silica melts, which made cones remain upright even though molten. In the case of the CAP and part of the CPS system this latter objection was not valid since the melts formed are extremely fluid.

THE SYSTEM TRICALCIUM PHOSPHATE-SILICA

Previous Investigations

The only published, completed research which covers the above binary is that of Barrett and McCaughey¹⁴ on the system $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$. However, they were primarily interested in mapping, approximately, the field boundaries of the ternary system, and a study of the binary $3\text{CaO.P}_2\text{O}_5\text{-SiO}_2$ was incidental to the main investigation. Their results, in the form of a phase diagram, are reproduced in Figure 10, page 43.

According to this diagram the binary system $3\text{CaO.P}_2\text{O}_5\text{-SiO}_2$ has a eutectic at 7% SiO_2 and a region of liquid immiscibility extending from 52% SiO_2 to almost 100% SiO_2 .

Since the publication of Barrett and McCaughey's work, Tromel¹⁷ has shown that tetracalcium phosphate melts incongruently. It is

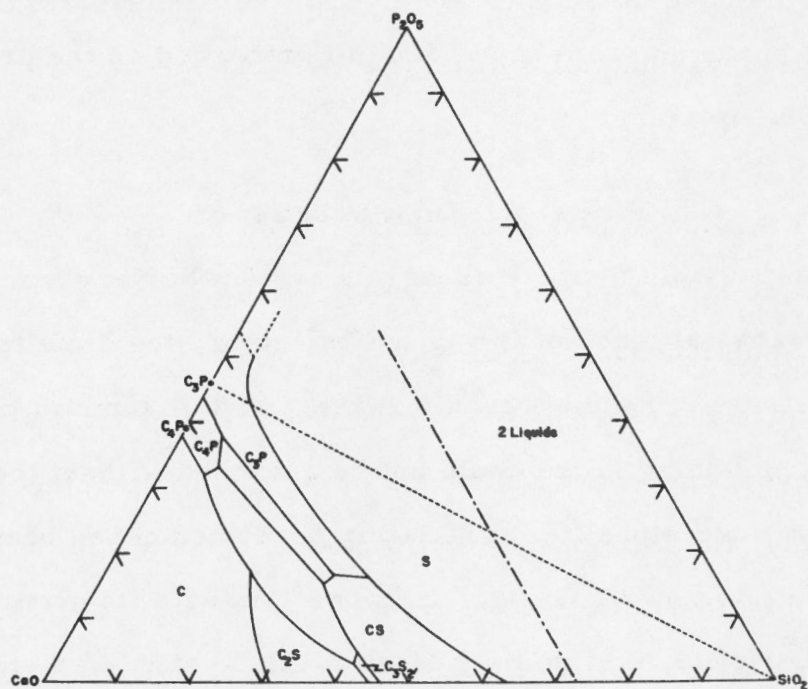


Figure 10. - Phase equilibrium diagram for the system CaO-P₂O₅-SiO₂.

probable then, that the region of C₄P shown in the diagram will have to be revised.

Lately Bredig¹⁸ has put forward evidence to suggest that the phases described as Nagelschmidtite and Silicocarnotite are really alpha dicalcium silicate. This hypothesis will be discussed later in connection with the results of the present work. The areas of Nagelschmidtite and Silicocarnotite shown on the original Barrett and McCaughey phase diagram have been left unmarked on the present reproduction.

Present Investigation

It was impossible to study all of this system by the quench method, because a) much of it was too refractory to be melted in 60/40 platinum-rhodium wound furnaces, and b) some of the fluid melts containing silica could not be quenched without the precipitation of cristobalite. The latter phenomenon has been discussed fully by J. W. Greig¹⁹ in connection with its occurrence in other silicate systems. Most of this system was studied by the cone fusion method, but three compositions close to the eutectic were investigated by the quench technique.

Data

The information given in the table below is that from which the phase diagram shown in Figure 10 is drawn.

TABLE VI

Thermal Data for the C₃P-S Binary System

a) Cone Fusions

Composition	Remarks
100% C ₃ P:0%S	Melted sharply at 1730°±10°C (Geophysical scale). Refractive index of button correct for α C ₃ P, therefore no reduction or apatite formation during heating.
95% C ₃ P:5%S	Melted very sharply at 1560°C to a homogeneous button. Microscope examination shows a few dendrites of C ₃ P in a eutectic of C ₃ P and cristobalite. May be very near eutectic composition on C ₃ P side.
90% C ₃ P:10%S	Melted in same manner as previous cone at 1600°C. Residue seemed to consist of primary bipyramids of cristobalite in C ₃ P matrix. Probably on S side of eutectic composition.
80% C ₃ P:20%S	Cone started to slump noticeably at 1650°C and was truly molten at 1710°C. Residue free from coring shown in next sample.
70% C ₃ P:30%S	The cone finally slumped at 1750°C. The button was observed to consist of a small central clear hard cone surrounded by a larger quantity of milky white glass. Cone was highly siliceous and contained blebs of C ₃ P. The milky white glass seemed to consist of C ₃ P with much fine cristobalite precipitated in it.
60% C ₃ P:40%S	The melting behaviour of this specimen was identical with the previous one, though the proportion of cone to milky white glass was greater.
50% C ₃ P:50%S	Behaviour as per previous two samples.
10% C ₃ P:90%S	During heating cone bled slightly. After run it was noted the cone consisted almost entirely of a silica core with only a small quantity of milky glass surrounding it. Composition probably close to end of two liquid region.

b) Quench Runs *

Composition	Duration of Run (Minutes)	Temperature °C	Microscope Examination
95% C ₃ P:5%S	20	1562 1558	All strained glass. Glass + trace of cristobalite + C ₃ P. Probably on eutectic composition.
92.5% C ₃ P:7, 5%S	20	1608 1604	Strained glass. Glass + a little cristobalite. On silica side of eu- tectic.
90% C ₃ P:10%S	20	1632 1628	Strained glass only. Glass + trace cristobalite.

Because of varying viscosity and liquid immiscibility, some cones only approximately reached equilibrium during the heating cycle. The only cones whose melting points could be determined accurately were those which melted sharply (viz. the C₃P and eutectic compositions). The main value of the cone fusion study lay in determining the extent of liquid immiscibility in the system and in establishing approximately the eutectic temperature and composition.

Cones, whose compositions lay in the field of liquid immiscibility, always bled when heated to high temperatures and yielded buttons with hard siliceous glassy cones surrounded by milky white glass. Referring to the proposed phase diagram shown in Figure 10, page 43, it

* Throughout the present work only limiting runs are described.

might be argued that most cones on heating to the eutectic temperature would "bleed" since the eutectic is a fluid phosphatic composition. Thus as the eutectic melt drained out of the cone, the remaining composition would become more siliceous and, therefore, viscous. While such an explanation of the core structure cannot be dismissed entirely, experiment showed that the phenomenon only occurred in certain compositions and that heating to temperatures in excess of 1700°C was necessary to bring it about. It was noted, for instance, that a composition containing 20 per cent silica could not be made to exhibit coring, yet one containing 30 per cent silica showed the effect when heated to 1775°C ($\pm 25^{\circ}$). Further evidence of liquid immiscibility is to be found in the fact that compositions containing 30 per cent or more silica did not melt completely in platinum crucibles at 1710°C . Since the system is a simple binary one, all liquidus points between 30 and 100 per cent silica must fall below the melting point of silica (1713°C). It would appear that the liquidus of all these compositions must be close to that of silica. Such behaviour can readily be explained by an area of liquid immiscibility. The data given in Table VI indicate that this condition was observed in specimens between 30 and 90 per cent SiO_2 and probably extended for 5 per cent on each side of these limits. The temperature at which unmixing occurred was not determined accurately, but Greig¹⁹ has shown that it occurs between 1690°C and 1700°C for most silicate systems. General experimental evidence indicated that this was likely to be true also for the present system.

The fusion work indicated that a eutectic between tricalcium phosphate and silica might be expected at 5 to 10 per cent SiO_2 . Accordingly, attempts were made to locate the point by the quench method.

In normal glass forming mixtures it is a simple matter to determine the liquidus by interpolating between the temperature at which quenched samples are all glass and that at which a trace of crystal is observed. Unfortunately mixtures rich in tricalcium phosphate are not good glass-formers and at best form only an anisotropic glass, described hereafter as "strained glass". It is not easy to distinguish such glass from phosphate crystal, but differentiation can generally be made by a comparison of refractive indices. The indeterminate extinction of the strained glass under crossed nicols is also one of its characteristics.

It would appear from the quench runs that the eutectic falls at approximately 5 per cent silica. Since the field of bone china lies some distance away from this binary system it was considered unnecessary to locate the eutectic more accurately.

Crystallization Sequence

It will be necessary later to trace the courses of crystallization of mixtures in a ternary system, and in order to appreciate fully the various features discussed it would be advisable to discuss comparable developments in the simpler binary systems. Thus in the three sections dealing with the binaries that bound the ternary $\text{C}_3\text{P-A-S}$ system the crystallization sequences of pertinent melts will be studied.

Consider first the crystallization path of a melt having the composition marked X (3% SiO₂) on Figure 10, page 51. On cooling such a melt, the first substance to crystallize is tricalcium phosphate. Precipitation of this compound occurs as soon as the liquidus temperature is reached and continues down to the eutectic temperature. At this point the liquid, which has been changing composition along the liquidus curve as its phosphate content decreased, freezes sharply to yield an intimate mixture of tricalcium phosphate and cristobalite. Thus all mixtures between pure tricalcium phosphate and the eutectic (5% SiO₂) have a freezing range which is defined by the temperature interval between the liquidus curve and eutectic temperature.

The ratio of solid to liquid at any given temperature may be found by the so called "lever arm" rule. The derivation of the rule may readily be understood by regarding the abscissa between tricalcium phosphate and the liquidus curve at any given temperature as a pseudo binary system. By this treatment it will be seen that at the eutectic temperature, composition X consists of $\frac{100}{5} \times 3 = 60\%$ eutectic (containing 95% C₃P, 5% S) and $\frac{100}{5} \times 2 = 40\%$ C₃P (primary phase). In practice it will be noticed that this procedure bears a resemblance to the methods used in lever problems in applied mathematics.

The crystallization of melt Y is similar to that of X, differing only in the primary crystal precipitated. In this and all other mixtures on the right hand side of the eutectic, cristobalite is the first

compound to crystallize out. Determination by the lever rule of the development of primary crystal during the cooling of melt Y shows that the increase is small. This is due to the steep liquidus curve and the distance of Y and the eutectic from the composition of the pure primary phase. As a result, the liquidus of such mixtures is difficult to determine because the crystal to glass ratio changes so slowly with varying temperature.

The behaviour of melt Z, however, is somewhat different from the other two. Apparently energy considerations in the system are such that all mixtures between approximately 25 and 95 per cent silica attain maximum entropy only by forming two liquids on melting. At 1700°C the compositions of the two liquids for all the mixtures so affected are given by the points A and B in Figure 11, page 51. At higher temperatures the compositions of the two liquids approach one another as shown by the dotted lines, and at some very high temperature the compositions coincide to form a homogeneous melt. Thus, on cooling such a melt, unmixing occurs first and the compositions of the two liquids formed change continuously along the dotted lines as cooling proceeds. The relative proportions of the two liquids may be found at any temperature by applying the lever arm rule as previously described. At 1700°C liquid B decomposes, precipitating cristobalite and forming liquid A. After this, the manner of crystallization is identical with that of melt Y.

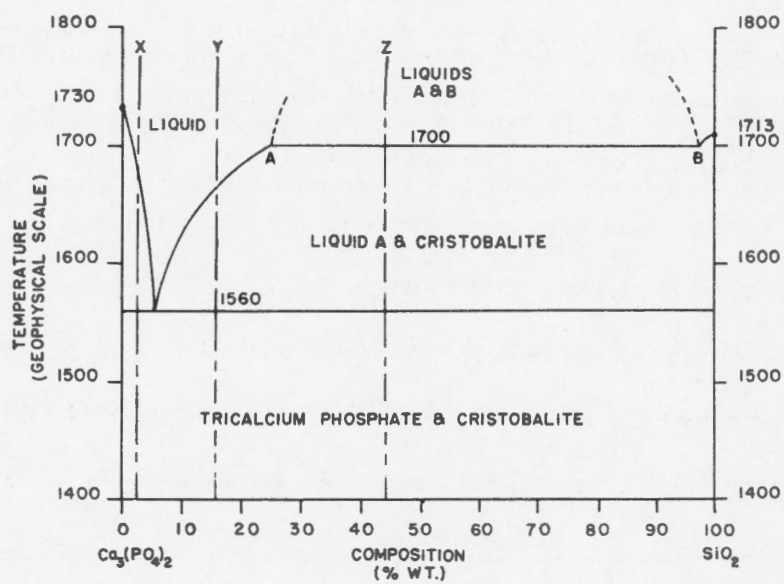


Figure 11. - The system tricalcium phosphate-silica.

THE SYSTEM ALUMINA-TRICALCIUM PHOSPHATE

Present Investigation

There appears to be no information published on this system. The results of the present investigation may then be considered forthwith.

This system is even more refractory than the C_3P -S and is just as susceptible to crystal formation. Thus, quench work was limited by the maximum operating temperature of the furnace, and also by the difficulty of quenching mixtures to a glass. Cone fusion studies were first made in the high frequency furnace apparatus and from the results obtained some mixtures were selected for quench runs. By this means it was found possible to draw a reliable phase diagram.

Data

TABLE VII

Thermal Data for the A- C_3P Binary System

a) Cone Fusions

Composition	Remarks
95% C_3P :5% A	Cone softened at $1680^{\circ}C$. Down at $1700^{\circ}C$.
90% C_3P :10% A	Similar to previous cone in behaviour.
80% C_3P :20% A	Cone melted quite sharply at $1680^{\circ}C$. Probably on or near eutectic point.
75% C_3P :25% A	Behaves in manner similar to the first two cones.
65% C_3P :35% A	Cone softened at $1680^{\circ}C$. Down at $1750^{\circ}C$. Probably past eutectic.

Microscope examination of all the fused cones indicated that tricalcium phosphate and alumina are the only solid phases in the system.

b) Quench Runs

Composition	Duration of Run Minutes	Temperature °C	Microscope Examination
85% C ₃ P:15%A	20	1687	Mixture of glass, α C ₃ P and α A. Liquidus out of range of furnace.
80% C ₃ P:20%A	20	1678	All glass + very minute trace A. Right on liquidus.
		1674	Well developed C ₃ P and α A. Probably right on eutectic point since change so rapid on dropping 4°C.
75% C ₃ P:25%A	20	1687	Similar to first mixture. Liquidus out of range of furnace. On alumina side of eutectic.

The phase diagram shown in Figure 12, page 55, has been drawn from the data given in Table VII. It will be noted that the system is a simple one with a eutectic composition at 20 per cent alumina. The melting point of the eutectic (1678°C) governs the melting behaviour of most of the cones since at this temperature all mixtures in the system contain liquid. Thus, those cones whose compositions lie near the eutectic contain much liquid at 1678°C and therefore they all collapse close to this temperature.

Crystallization Sequence

The binary system contains one invariant point, namely the eutectic, and only at this composition does a mixture have a sharp

melting point. The end members of the system, alumina and tricalcium phosphate also have sharp melting points.

On cooling, alumina is the primary crystal separating from melts whose compositions fall on the alumina side of the eutectic. As the alumina crystallizes the remaining liquid changes composition steadily until the eutectic is reached, at which point the last primary alumina precipitates and the liquid freezes sharply, as the eutectic mixture. The ratio of liquid to crystal at any point during the crystallization may be determined by the lever-arm rule previously mentioned. Compositions on the tricalcium phosphate side crystallize in a similar manner except that the primary crystal is tricalcium phosphate. All melts complete solidification on reaching 1678°C (the eutectic temperature) the last liquid to freeze yielding an intimate mixture of alumina and tricalcium phosphate.

THE SYSTEM ALUMINA-SILICA

Previous Investigations

This binary is perhaps the best known of all silicate systems since it was one of the first to be studied and has subsequently proved invaluable to those engaged in the ceramic industry. The phase diagram, first described by Shepherd, Rankin and Wright, was later modified by Bowen and Greig²⁰, and the accuracy of the later diagram is now so well established that no further checks were considered

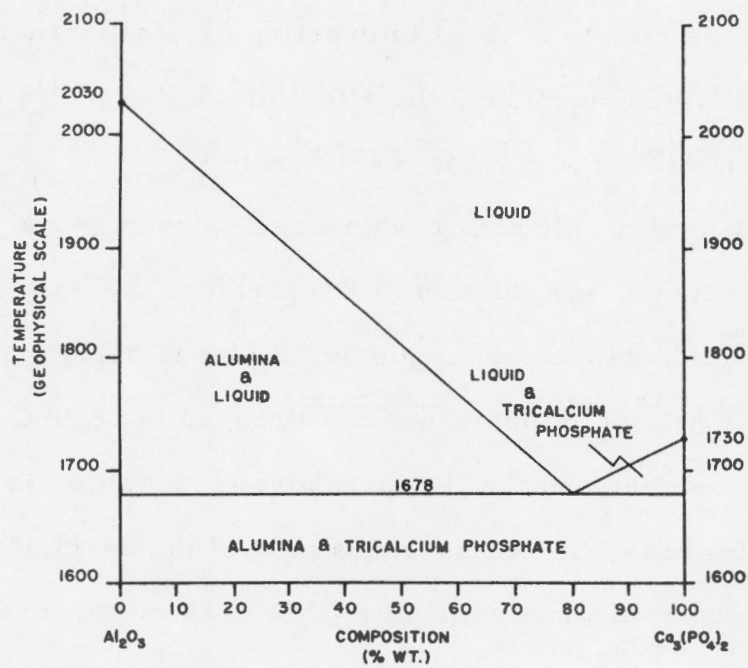


Figure 12. - The system alumina-tricalcium phosphate.

necessary. The diagram shown in Figure 13, page 57, is that given by Bowen and Greig.

Crystallization Sequence

This diagram (Figure 13) differs from the others in that an incongruently melting compound, mullite, occurs in the system. Thus, besides the eutectic at $5\frac{1}{2}\%A$ there is another invariant point in the system. This gives rise to several interesting crystallization sequences that may be studied by considering the effect of cooling melts with the compositions marked X, Y and Z, in the diagram.

In the case of melt X, alumina crystallizes as soon as the liquidus temperature is reached. As the alumina separates, the composition of the residual liquid changes continuously, its locus being the liquidus curve. When the temperature has dropped to $1810^{\circ}C$ a reaction point is reached and the liquid, whose composition is now approximately 55% A 45% S, reacts with a part of the precipitated alumina to form the compound mullite (A_3S_2). The mixture is now completely frozen and the relative proportions of alumina to mullite in the mixture may be determined in the usual manner by the lever-arm rule.

Initially, melt Y behaves in the same manner as melt X, but when the reaction point is reached all the primary alumina is redissolved to form mullite. After this reaction the excess liquid continues cooling with the precipitation of mullite. The composition

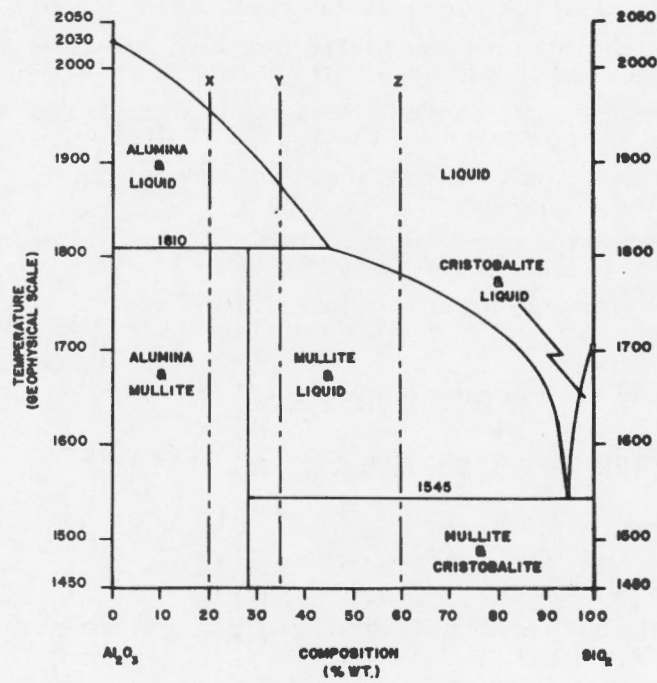


Figure 13. - The system alumina-silica.

of the cooling liquid changes in the usual way as the mullite crystallizes and when it reaches the eutectic composition it freezes sharply as an intimate mixture of mullite and cristobalite. The final crystal assemblage contains only mullite and cristobalite, and therefore differs from mixture X in phase composition.

Melt Z crystallizes in the same way as any other non-eutectic composition in a simple binary eutectic system. In this instance mullite is the primary crystal and freezing is completed when the last liquid present reaches the eutectic composition. The final phase assemblage is similar to that of melt Y, differing only in the relative proportions of mullite and cristobalite.

THE SYSTEM

TRICALCIUM PHOSPHATE-ALUMINA-SILICA

Present Investigation

No information has been published on this system and therefore the discussion that follows is based on the results of the present study.

The phase equilibrium relationships in the system were studied almost entirely by the quench method. Compositions in the central portion of the ternary diagram formed clear homogeneous glasses without difficulty. Such compositions could be studied admirably by the quench method and it was fortunate therefore that bone china compositions fell within this area.

In the alumina and silica corners of the diagram mixtures were found to be too refractory for treatment in platinum ware. Further to this, highly siliceous mixtures were very viscous and did not devitrify easily. It will readily be appreciated that runs of considerable duration would be necessary to ascertain accurately the liquidus temperature of these compositions. Mixtures rich in tricalcium phosphate were also found to be refractory and investigation was made more difficult by the ease with which tricalcium phosphate crystallized. For this latter reason mixtures containing more than 65% $\text{Ca}_3(\text{PO}_4)_2$ were almost impossible to quench to a true glass. Generally these compositions yielded a mixture of strained devitrite and true glass on quenching. Hence, for the reasons just given, few mixes were made close to the component corners.

Phases

The phases were identified chiefly by petrographic methods, but in difficult cases X-ray studies were made to check the results of the microscope examination. The optical properties of the various phases occurring in the system have been well described by petrologists and therefore recognition of well formed crystals was a relatively simple matter.

Both high and low temperature forms of tricalcium phosphate appeared in the system. The rapid crystallization of the high

temperature modification prevented the formation of well defined crystals. This allotrope was always found in a granular form with the optical and X-ray constants already quoted in an earlier section. The low or β form normally crystallized from mixtures capable of forming a true glass. As a result of the slower crystallization, well formed crystals were usually seen. Its normal habit was as small hexagonal plates, but in a few instances crystals formed which were well developed in three dimensions. Such crystals were observed to exhibit the rhombohedral habit of whitlockite, as described in Dana's Mineralogy (Ed. 7, p. 685).

The optical constants of these crystals were the same as those of the pure compound. It would appear then, that there was little or no solid solution of silica in tricalcium phosphate. This is surprising since it should be fairly easy for silicon to substitute for phosphorus in the PO_4 lattice of tricalcium phosphate.

Alumina always crystallized in the α form (corundum) as small hexagonal plates of high refractive index. The β tricalcium phosphate had similar crystal habit, but a lower index and birefringence. Since the primary fields of α alumina and β tricalcium phosphate were adjacent, care was required in examining compositions near the field boundary.

Anorthite, whose primary field was found in the central portion of the ternary phase diagram, crystallized in the form of plate-like rhombs. Observation of the rhombs in quenched samples was

sometimes difficult, since in part of the system the index of the glass matrix closely matched that of the crystal. Consequently the observer was frequently more conscious of those crystals which were oriented on edge. Crystals in this position had a lath-like appearance, and under crossed nicols showed limited polysynthetic twinning (plagioclase type) and inclined extinction. The so-called laths could be distinguished from mullite by their inclined extinction and stubby habit.

Mullite was found in the system mostly in its usual radiating needle-like form. It also appeared as fine blebs with a moderately high refractive index in samples which had been quenched close to the liquidus. This latter property served to distinguish it from cristobalite and tridymite whose fields were adjacent to that of mullite.

Cristobalite and tridymite have very low refractive indices (approx. 1.48) and this made recognition simple because of the higher index of phases in adjoining fields. Generally these modifications of silica tended to be needle-like in habit, but some specimens were observed in which a bipyramidal form had been assumed.

Data

The final results of the quench runs made on compositions in the system are summarized in Table VIII, page 64. The table

is subdivided by grouping together compositions with the same primary crystal. The refractive indices of all true, homogeneous glasses are recorded in the table. It was from this information that the isofract diagram shown in Figure 4 was constructed. The limiting runs made to bracket liquidus temperatures were not more than 4°C apart in all cases. Thus nominally the accuracy of the temperatures given is $\pm 2^\circ\text{C}$. Uncertainties in calibration, composition, etc., reduce the overall accuracy so that it probably falls between $\pm 2^\circ\text{C}$ and $\pm 5^\circ\text{C}$. In most cases equilibrium was established in a thirty- to forty-minute run, but compositions containing more than 65 per cent silica and those devitrifying below 1350°C were run for sixty minutes. On an average, six runs were necessary to establish each liquidus point.

Frequently, the behaviour of the quenches could be anticipated by observing the nature of the product from the synthesis of the glass mixture. Mixtures containing 60 per cent or more tricalcium phosphate in the primary field of this compound often yielded an opal glass on quenching in a platinum crucible. These so called glasses were in actual fact seen to be extensively crystallized when viewed under the microscope. The small samples of such mixtures taken for equilibrium studies quenched in an irregular fashion, sometimes a true glass was obtained, but generally birefringent strained glass or crystal resulted on chilling in water. Replacing the water by mercury brought about no improvement in the quenching. It was thus difficult to distinguish between bire-

fringent strained glass and crystal (α tricalcium phosphate) which had a similar birefringence. In most cases liquidus was taken as the point between quenches which were all "strained glass" and those in which small hexagonal shaped crystals of β tricalcium phosphate appeared. This cannot be regarded as entirely satisfactory since the liquidus was frequently close to the region of the sluggish α to β transformation, and it was possible therefore, to quench to this indefinite transition point rather than the true liquidus. Fortunately this condition occurred in very few compositions and had no bearing on the conclusions drawn later.

TABLE VIII

Quench Runs in the C₃P-A-S Ternary System

A. Primary Field of Tricalcium Phosphate

C ₃ P	Composition		Refractive Index Glass	Liquidus Temp. °C
	A	S		
90	7.5	2.5	-----	----
80	14.4	5.6	-----	----
80	10	10	-----	----
75	12.5	12.5	-----	----
70	17.5	12.5	1.588	1457
70	15	15	1.585	1435
70	12.5	17.5	1.582	1444
65	20	15	1.586	1430
65	17.5	17.5	1.582	1427
65	15	20	1.580	1457
60	22.25	17.75	1.580	1413
60	20	20	1.578	1413
60	17.5	22.5	1.577	1419
60	15	25	1.571	1423
57.5	18.5	24	1.575	1415
55	20	25	1.570	1392
55	17.5	27.5	1.568	1406
50	20	30	1.564	1379
50	17.5	32.5	1.562	1405
44	23	33	1.556	1331
44	20	36	1.550	1369
40	22.5	37.5	1.548	1328
40	20	40	1.546	1356
35	22.5	42.5	1.540	1302

B. Primary Field of α Alumina (Corundum)

C ₃ P	Composition		Refractive Index Glass	Liquidus Temp. °C
	A	S		
75	20	5	-----	1649
74	23	3	-----	1689
70	21.6	8.4	1.596	1595
65	22.5	12.5	1.590	1502
60	28.8	11.2	1.592	1615
55	27.5	17.5	1.580	1494
50	30	20	1.580	1499
44	33	23	1.572	1518
40	43.2	6.8	1.583	-----
40	35	25	1.570	1538
35	40	25	1.570	1637
35	35	30	1.559	1516
35	32.5	32.5	1.559	1442
30	40	30	1.560	1627
30	35	35	1.552	1508
20	57.6	22.4	-----	-----
20	44	36	1.550	-----

C. Primary Field of Anorthite

C ₃ P	Composition		Refractive Index Glass	Liquidus Temp. °C
	A	S		
57	24	19	1.580	1407
55	25	20	1.578	1405
55	22.5	22.5	1.575	1392
50	27.5	22.5	1.575	1408
50	25	25	1.570	1388
44	28	28	1.564	1392
40	30	30	1.560	1399
40	25	35	1.552	1321
35	30	35	1.552	1379
35	25	40	1.544	1310
30	30	40	1.543	1356
30	25	45	1.535	1273
27.5	23.75	48.75	1.530	1294
25	27.5	47.5	1.532	1302

D. Primary Field of Silica

Composition			Refractive Index	Liquidus
C ₃ P	A	S	Glass	Temp. °C
70	9	21	-----	1470
50	15	35	1.552	1468
40	15	45	1.539	1492
35	20	45	1.536	1352
35	15	50	1.530	1516
30	21	49	1.532	1307
25	22.5	52.5	1.527	1331
25	17.5	57.5	1.518	1469
20	20	60	1.511	1403
20	16	64	1.509	1512
13	15	72	1.497	1523
10	18	72	1.496	1510

E. Primary Field of Mullite

Composition			Refractive Index	Liquidus
C ₃ P	A	S	Glass	Temp. °C
28	34	38	1.544	1481
27.5	31.25	41.25	1.544	1419
26	34	40	1.546	1494
25	32.5	42.5	1.538	1478
23	27	50	1.530	1359
20	40	40	1.544	1649
20	30	50	1.528	1495
20	24	56	1.518	1305
17	27	56	1.520	1491
15	37.5	47.5	1.534	1669
15	22.5	62.5	1.509	1421
10	27	63	1.508	1612

A few compositions were prepared in order to study the extent of liquid immiscibility occurring with the ternary system. These mixtures were investigated by the cone fusion method in the high frequency furnace apparatus. The results are summarized in Table IX below.

TABLE IX
Thermal Data for the C₃P-A-S Ternary System
Cone Fusions

Composition	Remarks
60% C ₃ P:4%A:36%S	Cone heated to 1740°C. No evidence of coring. Not in 2 liquid field.
40% C ₃ P:6%A:54%S	Cone heated to 1720°C. No evidence of coring. Not in 2 liquid field.
20% C ₃ P:8%A:72%S	Cone heated to 1720°C to bring about complete collapse. No evidence of coring. Not in 2 liquid field.

The data given in the above tables is summarized in the form of the phase diagram shown in Figure 14, page 69. It is customary to place silica at the apex of triangular phase diagrams. In this instance tricalcium phosphate has been placed in this position, since observation is facilitated by this arrangement when studying the C₃P-A-S place in the C-A-P-S tetrahedron (See next section).

Crystallization Sequence

The phase diagram shows that the system is not a true ternary, since a phase, anorthite, appears that cannot be described in terms of the three components. The implications arising from this condition are of great importance and will be discussed later.

It is impossible to describe fully the crystallization sequences in this partial system, since all mixtures contained therein involve the crystallization of anorthite. Immediately the crystallization path of a mixture reaches the point at which anorthite separates, the residual liquid becomes enriched in phosphorus pentoxide and the crystallization proceeds in a direction out of the C_3P -A-S plane.

Consider, for example, the various stages of crystallization of a mixture located in the primary field of tricalcium phosphate near to the fields of silica and anorthite. This composition would closely approximate a bone china body. Tricalcium phosphate will crystallize first from such a mixture. As the phosphate precipitates the composition of the remaining liquid changes continuously along the projection of the line made by joining the tricalcium phosphate corner to the original composition of the mixture. When the composition of the liquid reaches the anorthite field boundary, both tricalcium phosphate and anorthite crystallize concurrently. As the crystallization of these compounds proceeds the composition of the liquid then changes along the field boundary towards the phosphorus pentoxide corner of the quaternary system C-A-P-S. Since nothing is known of the field boundary in this direction it is impossible to trace the course of crystallization further.

Taken by itself, knowledge of the phase distribution in the plane C_3P -A-S is of limited value when interpreting the properties of bone china. However, when this plane is considered in con-

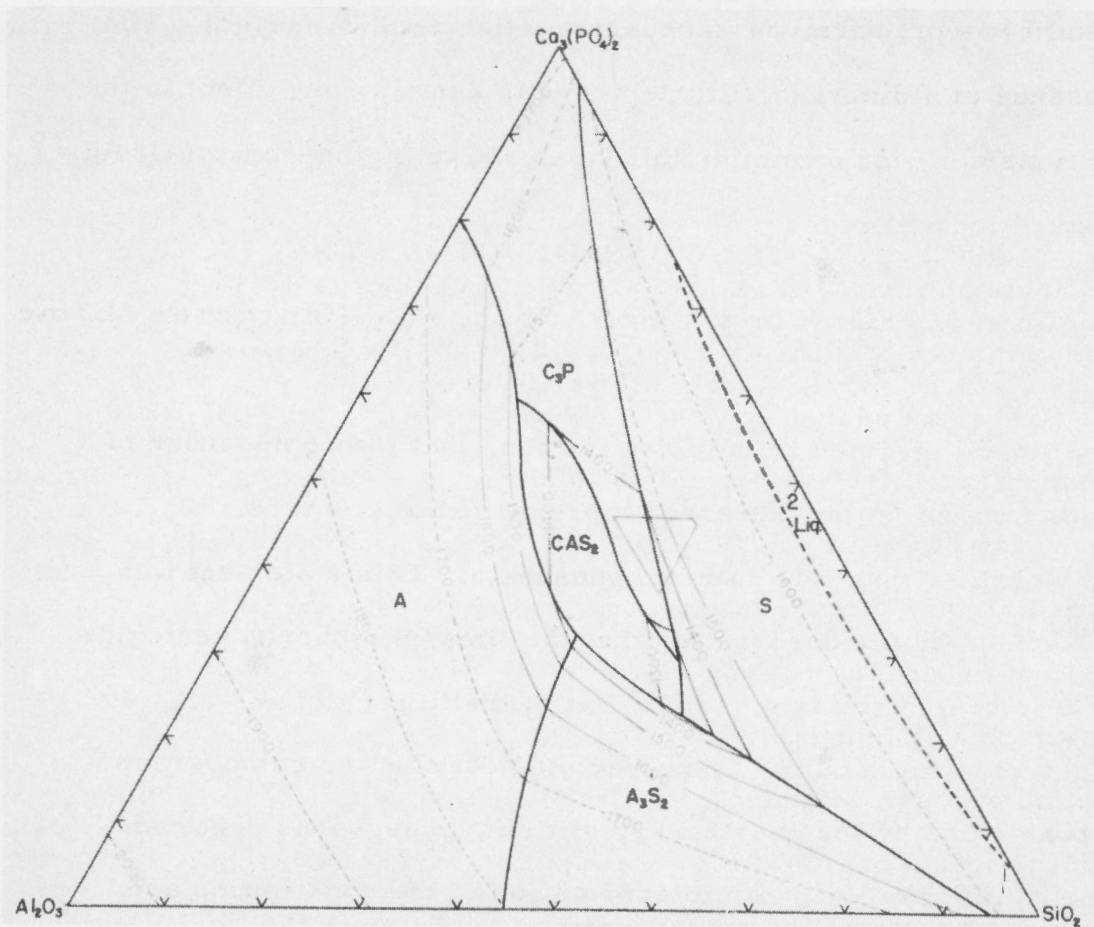


Figure 14. - The system tricalcium phosphate-alumina-silica. The trapezoidal area represents the limits of composition of bone china bodies. Estimated isotherms are shown as dotted lines.

junction with the quarternary system, of which it forms a part, its value becomes more apparent. This treatment will be discussed in detail in the next section.

The region of liquid immiscibility found in the binary C_3P-S system has practically disappeared in the ternary system. The presence of alumina in silicate systems has a strong effect in the prevention of liquid immiscibility, as shown by the work of Greig.¹⁹

DISCUSSION OF DATA

The Quarternary System Phosphorus Pentoxide-Lime-Alumina-Silica

It was suggested in the first section, that the composition of bone china might be expressed more accurately in terms of tetra- rather than tri- calcium phosphate. This statement was occasioned by the observation that the lime/phosphorus pentoxide ratio in bone china is closer to that of the tetracalcium salt. It would be more accurate, however, to describe the composition of bone china by the quarternary system, phosphorus pentoxide-lime-alumina-silica. An interpretation of the constitution and thermal behaviour of bone china should therefore be preceded by a discussion of this quarternary system applying the data presented in the preceding sections.

Referring to Figure 15, page 71, it will be seen that except for tricalcium phosphate, all the fields found in the plane

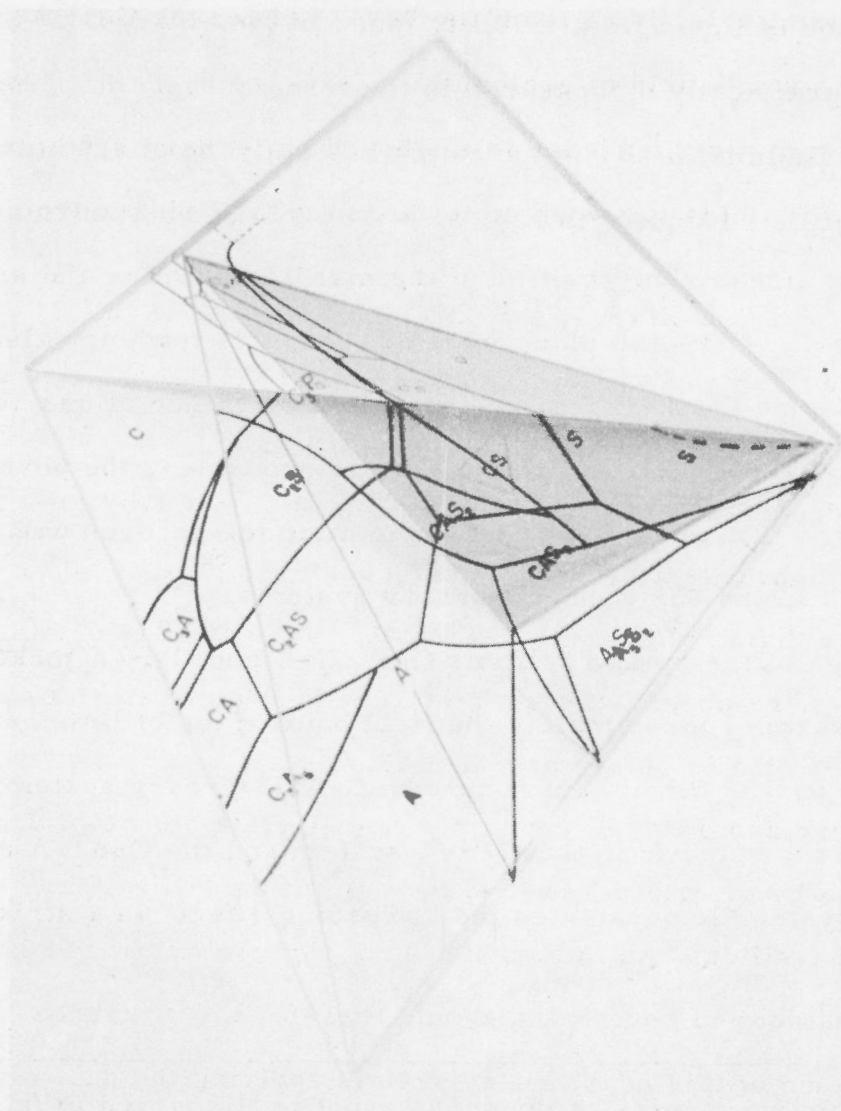


Figure 15. - Photograph of a plastic model of the C-A-P-S system. The apex (P) and the alumina corner (A) are the points nearest to the viewer. The C-A-P and A-P-S planes have been removed from the model in order to reveal the C₃P-A-S and C₃P-CAS₂-S planes. The latter plane appears darker and has no markings of any kind. Tie lines are shown joining C₃P with A₃S₂, and A₃S₂ with CAS₂. These lines, together with the appropriate joins made by the plastic planes, delineate the probable compatibility tetrahedron (C₃P-CAS₂-A₃S₂-S) in which bone china compositions fall (See lightly marked trapezoidal area).

C_3P -A-S also appear on the base plane C-A-S. These fields must therefore intercept any intermediate plane from the A-S binary (e. g. , C_4P -A-S). Intermediate planes may, however, have additional fields where they cut other phase fields rising from the base. Thus, the C_4P -A-S plane may contain a small field of gehlenite.

There is a distinct tendency in the bounding ternary systems, C-P-S and C-A-P, for fields to sweep up towards the C-P binary from the C-S and C-A base lines. The position of the mullite, alumina and silica intercepts on the C_3P -A-S plane indicates that this tendency also finds expression inside the tetrahedron. Since the existence of quaternary compounds within the tetrahedron is very improbable*, the phase fields occurring in the C- C_3P -A-S portion of the main tetrahedron will be those present in the surrounding ternary systems.

Knowledge of the binary systems C-P, C-A and C_3P -A makes it possible to sketch approximately the field boundaries of lime and alumina (in part) in the hitherto unknown C-A-P ternary system. The join between the eutectic in the C_3P -A system and the C_3A_5 -A eutectic in the C-A system demonstrates the "sweeping effect" in a striking manner.

* The stability of complex compounds cannot be discussed in full here. From discussions with Professor A. E. van Arkel (University of Leiden) it would appear that geometrical considerations in packing atoms make the existence of stable compounds of this type unlikely.

The field of dicalcium silicate (C_2S) shown by Barrett and McCaughey¹⁴ in their phase diagram of the system C-P-S seems to be unnaturally small when considered in conjunction with the C_2S field in the C-A-S system. If, however, the areas they marked "nagelschidtite" and "silico-carnotite" are included in the dicalcium silicate field the proportioning in the space model improves. While this suggested modification is mere speculation, it deserves serious consideration in view of Bredig's¹⁸ hypothesis mentioned earlier in this paper.

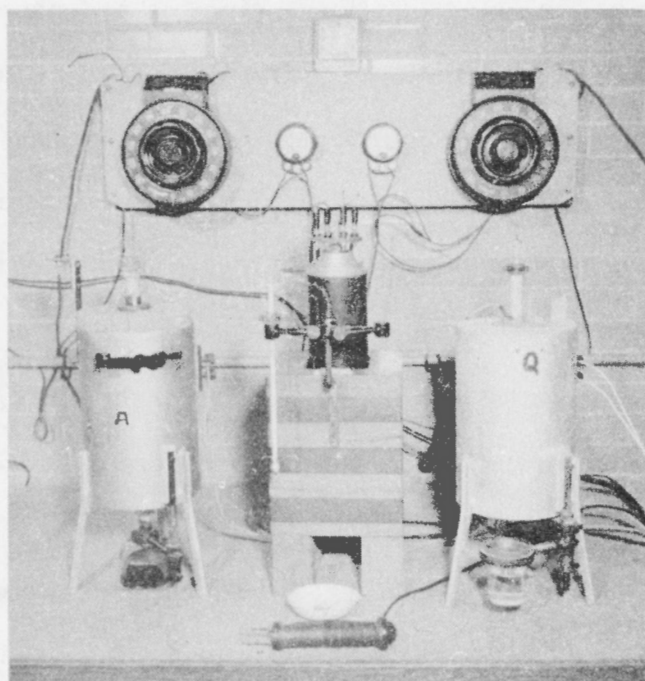
The Constitution of Bone China

An examination of the C_3P -A-S plane (See Figure 14, page 69) shows that tricalcium phosphate, anorthite and silica form a compatibility triangle, since their fields meet at a common point. This means that any melt whose total composition falls in the C_3P -CAS₂-S plane will ultimately yield on complete crystallization these three compounds in proportions dictated by the position of the composition in this plane. The quantities of the components may be determined readily by setting up a triangular coordinate lattice on the plane and reading the proportions in the usual way for such co-ordinate systems.

When the plastic model shown in Figure 15 is correctly oriented, it is possible to correlate to some extent the phase distribution on the C_3P -A-S plane with that on the base plane C-A-S. The plane

C_3P - CAS_2 -S falls between the two known planes just mentioned and it is possible therefore to speculate on probable phase distributions in this plane. Observations indicate that the system C_3P - CAS_2 -S is likely to be a simple ternary with a eutectic at approximately 30% C_3P , 40% CAS_2 and 30% S. It must be emphasized, however, that these figures are very approximate and are intended only to give a general indication of the eutectic point. More information on this point will be published when current studies on this system are completed.

The composition of most bone china, when calculated in terms of lime, alumina, silica and phosphorus pentoxide, falls below the C_3P -A-S plane, but slightly above the C_3P - CAS_2 -S plane. As a second approximation then, the thermal behaviour of bone china may be considered in terms of the C_3P - CAS_2 -S plane. Since bone china does not fall completely in this plane an accurate description of its constitution cannot be given unless a fourth component is also taken into account. Unfortunately there is insufficient information available on the phase distribution in the C-A-P-S tetrahedron to predict with certainty the composition of the required fourth component. If the fields of C_3P , CAS_2 , S and A_3S_2 come together at any point they would constitute a compatibility tetrahedron and mullite would be the required fourth component. Judging from the tendency for phase fields to sweep towards the C-P line, it seems likely that the aforementioned fields come together at



View of quench furnaces, cold junction, and quench rig.

some point above the suggested compatibility tetrahedron.

While the above condition seems to be the most probable, binary or ternary compounds of phosphorus pentoxide with silica and/or alumina as constituents of the compatibility tetrahedron cannot be dismissed entirely. Both AlPO_4 and SiP_2O_7 are known to be stable compounds, but the extent of their fields in the tetrahedron is unknown. No ternary compound of silica, alumina and phosphorus pentoxide has ever been reported. Until evidence to the contrary is brought forward it is not unreasonable to consider mullite (Al_2SiO_5) as being the fourth component in the quaternary subsystem.

The justification for studying the C_3P rather than the C_4P plane may now be appreciated better. Although the lime/phosphorus pentoxide ratio for bone china is frequently close to that of tetracalcium phosphate, this compound is not considered in discussions on bone china compositions because it falls outside the relevant compatibility tetrahedron. The phase diagram shows that any excess of lime over that required to form tricalcium phosphate reacts with silica and alumina to yield anorthite.

Since there is no indication of solid solutions in the $\text{C}_3\text{P-A-S}$ plane, it is probable that they are also absent in the relevant part of $\text{C}_3\text{P-Al}_2\text{SiO}_5\text{-SiO}_2\text{-S}$ tetrahedron. If the absence of solid solutions is assumed, the theoretical proportions of the four components in a bone china may be calculated in the manner

illustrated by the following example:-

Analysis²⁴ of Coalport Bone China

Component	Proportion
SiO ₂	42.88%
Al ₂ O ₃	15.06
CaO	23.16
F ₂ O ₅	16.30
N ₂ O, Na ₂ O, MgO, Fe ₂ O ₃ , etc.	2.60

a) Combine all P₂O₅ to form 3CaO.P₂O₅:-

142 units (weight) of P₂O₅ require 168 CaO.

therefore 16.3 P₂O₅ require $\frac{168 \times 16.3}{142} = 19.3$ CaO.

Thus, 3CaO.P₂O₅ formed = 16.3 + 19.3 = 35.6 3CaO.P₂O₅,

and CaO left = 23.16 - 19.30 = 3.86.

b) Use remaining CaO to form CaO.Al₂O₃.2SiO₂:-

56 CaO require 102 Al₂O₃ and 120 SiO₂

whence 3.86 CaO require $\frac{102 \times 3.86}{56} = 7.04$ Al₂O₃

and $\frac{120 \times 3.86}{56} = 8.28$ SiO₂

Thus, CaO.Al₂O₃.2SiO₂ formed =

3.86 + 7.04 + 8.28 = 19.18 CaO.Al₂O₃.2SiO₂

Al₂O₃ left = 15.06 - 7.04 = 8.02,

and SiO₂ left = 42.88 - 8.28 = 34.60.

c) Residual Al₂O₃ forms 3Al₂O₃.2SiO₂:-

306 Al₂O₃ require 120 SiO₂

whence $\frac{120 \times 8.02}{306} = 3.15$ SiO₂.

3Al₂O₃.2SiO₂ formed = 8.02 + 3.15 = 11.17 3Al₂O₃.2SiO₂

d) The silica remaining is left unreacted:-

$$34.60 - 3.15 = \underline{31.45 \text{ SiO}_2}$$

Summarizing:-	$3\text{CaO} \cdot \text{P}_2\text{O}_5$	= 35.60
	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	= 19.18
	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	= 11.17
	SiO_2	= 31.45
	Unaccounted	= 2.60

Interpretation of Results

From the foregoing discussion one might expect to find tricalcium phosphate, anorthite, mullite and one of the forms of silica in X-ray patterns of bone china. In actual fact only β tricalcium phosphate and anorthite were found in X-ray powder diagrams prepared from samples of Royal Doulton, Aynesly, Floral, Royal Grafton, Hammersley etc. This may be explained by considering the bone china to be in a non-equilibrium state. It must always be remembered that a phase diagram represents conditions in equilibrium, a state seldom completely achieved in most industrial processes. The calculation just made for the phase assemblage of a typical bone china shows that mullite and silica are to be expected in quantities which could easily be detected by X-rays. Now since the constituents of bone china bodies are very fine grained and well mixed it is reasonable to suppose that they would react readily on heating to 1300°C followed by slow cooling. It has already been noted that melts in the vicinity of the bone china composition precipitate

tricalcium phosphate first and then anorthite on cooling. Conversely on heating, anorthite and tricalcium phosphate would be the last phases to disappear. Thus, when a bone china body is heated, a viscous, highly siliceous liquid is formed first. Referring to the calculation it will be seen that free silica and mullite will form such a liquid. If the reaction went to completion the liquid would contain 81.25 per cent silica, and would be extremely slow to devitrify on cooling. Thus only tricalcium phosphate and anorthite would be found in a matured bone china body, because the mullite and silica would be in the glassy state. This reasoning leads to the hypothesis that bone china is made up essentially of an intimate mixture of tricalcium phosphate and anorthite bound together by a highly siliceous glass. In commercial bodies the presence of 1.5 per cent alkali metal oxides would promote the formation of the glass at temperatures lower than might be expected from phase equilibrium data.

A phase diagram gives no information on the kinetics of reaction between phases, therefore great care must be exercised when interpreting the behaviour of mixtures in systems that do not reach equilibrium rapidly. The system just discussed illustrates this point particularly well.

The results obtained from quenching runs on a commercial bone china are in accordance with predictions made from the theory outlined in the preceding paragraphs. Glaze-free samples of bone china were quenched from several different temperatures using the

technique applied to the phase systems studied in this work. The quenches were examined optically and by X-rays to determine the phases present. The primary phase was found to be β tricalcium phosphate, anorthite being observed as a secondary phase. Prolonged heating at lower temperatures failed to induce crystallization of other phases. Samples subjected to this long heat treatment of ten hours or more yielded a mixture of β tricalcium phosphate and anorthite in a siliceous glassy matrix. Being rich in phosphate the melts tended to solidify with a strained glass structure when quenched from temperatures near the liquidus (1450°C*).

Knowledge of the constitution derived from phase diagrams greatly aids in the interpretation of X-ray powder diagrams of bone china. All the samples of bone china that were examined gave an X-ray powder diagram similar to that shown in Figure 16a, page 81. This pattern appears to be that of tricalcium phosphate (Figure 16b) but the intensities of the principal lines are incorrect for this compound.

Examination of Figure 16c shows, however, that one of the principal lines (3.18) of anorthite is identical with one in the β tricalcium phosphate spectrum. The complex triclinic structure of anorthite causes it to reflect X-rays weakly, so that even under the best conditions it yields a weak powder pattern. In bone china where the anorthite present is very

* An average figure.

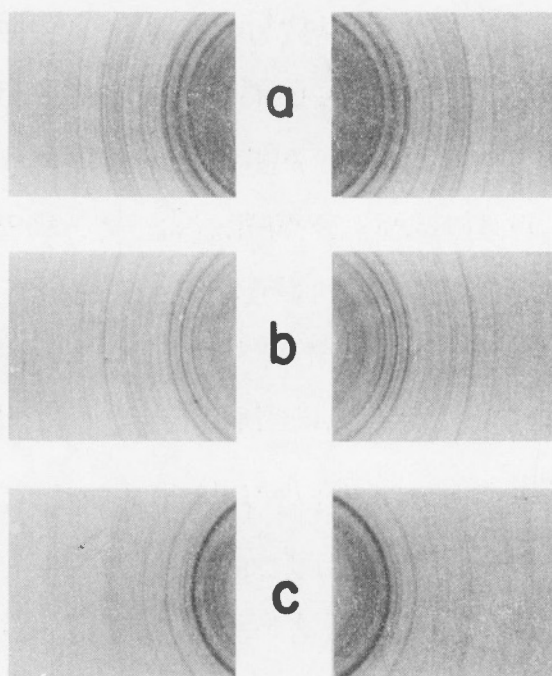


Figure 16. - X-ray powder diagrams:-
a) Bone china
b) β tricalcium phosphate
c) Anorthite

fine-grained and in relatively small quantities, only the strongest lines are likely to appear. Since these are close to, or identical with, those of β tricalcium phosphate, the pattern obtained is that of the phosphate with the single strong anorthite line (3.18) superimposed. If the bone china is quenched from a temperature at which all the anorthite is dissolved the normal β tricalcium phosphate pattern is obtained.

The quench work on commercial bone china substantiates the belief that the presence of small quantities of extraneous matter, such as soda and magnesia etc., has no appreciable effect on the phase relationships in the quarternary system. Their action seems to be one of fluxing, thereby facilitating vitrification and bringing about the formation of glass at a lower temperature. This experience is in agreement with that of other investigators in silicate chemistry. 25, 26, 27

Discussion of Results of Previous Investigations on Bone China

The scientific investigations^{1, 2, 3, 4, 5} on bone china made at the beginning of this century were mostly concerned with a) the action of bone ash on clay bodies, b) the constitution of the fired bone china body, and c) the tendency of the body to go "off colour". The latter subject is beyond the scope of the present work, but the first two points may be discussed profitably in the light of the new data.

a) The Role of Bone Ash in Bone China Bodies

An advantage of the phase equilibrium approach to the firing behaviour of ceramic bodies lies in the more detailed understanding of the role of the components used in the body. Frequently a substance is described as a Flux because it lowers the melting point of many well known ceramic bodies. That this behaviour is not necessarily general is revealed by an examination of many published phase diagrams, wherein it may be seen that a compound may flux some mixtures yet render other proportions of the same components more refractory. It is essential therefore that the significance of the word flux be adequately appreciated when considering the effect of additions to ceramic bodies.

One example of the difficulties caused by the unconditional labelling of a compound is to be found in the role of bone ash in bone china. Early investigators were divided into two schools of thought on the subject, viz. those who believed bone ash was a flux and those who considered it as a refractory. Figure 14, page 69, shows that both schools were partly correct, for initially tricalcium phosphate fluxes alumino-silicate mixtures (i.e. clays) but after reaching a minimal fusion point the bodies tend to become more refractory.

In many bone china bodies the alumina:silica ratio is 1:2.3 (see Table IV, page 9), and thus if a line be drawn from the C_3P corner of Figure 14 to the 1:2.3:: A:S ratio (i.e. 30% A) on the base line it will be seen that tricalcium phosphate acts as a flux

up to approximately 25 per cent but further additions increase refractoriness. The actual point at which the change-over occurs depends on the point of interception of the line from the C_3P corner with the mullite (A_3S_2) - silica eutectic line in the ternary system. Thus small quantities of tricalcium phosphate begin to increase the refractoriness of bodies rich in silica sooner than those containing less silica. It should be emphasized, however, that the above discussion relates to tendencies and not to absolute quantities. All alumina-silica mixtures whose melting points exceed $1730^{\circ}C$ are rendered less refractory by additions of tricalcium phosphate, but there is, however, an optimum percentage for maximum fusibility.

b) The Constitution of Bone China

The constitution of bone china has hitherto remained unknown, because of the difficulty of examining it by microscope. Examination of the fine-grained glassy body has failed to yield significant information.^{4, 7&8} It is interesting to note that Cronshaw⁴ observed in an experimental body the presence of crystals similar to mullite but differing in optical properties (e. g. extinction angle). He suggested that they might be a complex calcium alumino-silicate. It is evident from the C_3P -A-S phase diagram that the crystals he tentatively identified were anorthite.

In recent times, Weyl¹⁰ has speculated on the constitution of bone china. His work on bone ash opal glasses, taken in conjunction with that of the earlier workers previously mentioned,

led him to advance the hypothesis that bone china consists essentially of a lime-rich glassy phase with hydroxy- and/or fluor-apatite as the main crystalline phase and with mullite and quartz as minor constituents. The X-ray and phase equilibrium data prove this hypothesis to be incorrect.

The last scientific investigation on bone china described in the literature is that of Krause and Schlegelmilch⁸ published in 1932. While their particular interest lay in the development of a bone china body from German materials, some of their conclusions are worthy of comment. They confirmed the microscope observations of Cronshaw⁴, but like him were unable to identify what they saw. They took X-ray diffraction photographs of bodies at various stages of firing, but beyond stating that a change took place in the bone ash at 1275°C were unable to interpret the patterns. In common with the present investigator they found no mullite lines in the X-ray patterns. This, together with heating curve data, indicated to them that the usual decomposition products of burnt kaoline (viz. mullite and silica) were not formed. Results from density and compression strength determinations pointed to the formation of a eutectic at 900°C. Above 1000°C the development of eutectic was so rapid that the form of the ware being fired was endangered. Finally, they concluded that apart from quartz, the fired body was built up of the decomposition products of bone ash held together by a siliceous bond containing lime.

It will be appreciated, that although many of their conclusions are superficial they contain sufficient information to confirm the predictions made from the data derived from the present investigation on a model system.

General Observations

From the discussions in this and previous chapters the following observations may be made on the constitution and thermal characteristics of bone china:-

1. The system tricalcium phosphate-alumina-silica is not a true ternary, and therefore the crystallization sequences of mixtures occurring in or close to it cannot be described fully.

2. In spite of the above limitation, knowledge of this plane is important, since it enables the general phase relationships to be inferred of the part of the quaternary system in which bone china compositions fall.

3. A consideration of this quaternary system (lime-alumina-phosphorus pentoxide-silica) leads to the hypothesis that a fully crystallized bone china would consist of tricalcium phosphate, anorthite, mullite and silica.

4. Only tricalcium phosphate and anorthite are to be expected as crystallized phases in normal bodies, since mullite and silica along with small amounts of soda, potash, magnesia etc., form a stable glass. Free silica, however, may be present as an

unreacted constituent of the body or, for those bodies whose composition falls in the field of silica, it may be a primary phase. In either case the quantities will be small because, firstly, the normal fine grinding and thorough mixing applied to the bodies promotes interaction and, secondly, the location of those bone china bodies which lie in the silica field is such as to permit a minimum of primary silica formation.

5. The composition of bone china falls close to a eutectic between tricalcium phosphate, anorthite and silica. This condition accounts for its very short firing range, for as soon as bodies reach the eutectic temperature substantial quantities of liquid are formed rapidly which may cause the body to deform. From the calculation made in this section it can be seen that as much as 40 per cent of a body may liquefy quite rapidly on reaching the eutectic temperature. It is only the extremely viscous nature of this liquid that lessens the susceptibility of the body to deformation. The only way in which the quantity of liquid forming at the eutectic temperature can be reduced is to increase one of the components such that the composition of the body falls further away from the eutectic. If the essential character of bone china is to be preserved this means that the bone ash content must be increased. This however, may cause other difficulties in the manufacture of the ware. It is easy to envisage the difficulties likely to be encountered on reducing the clay

content of a body which already has little plasticity and poor working properties.

6. In view of the restrictions imposed by other requirements, such as plasticity during the fabrication of ware, it is unlikely that the suggested direction of compositional change can be made to full advantage for all bone china bodies. The value of phase equilibrium studies lies in the fact that they clearly show the inherent difficulties of processing this type of ceramic body. They are also extremely useful to persons wishing to make bone china with materials other than those traditionally or normally used, for the firing behaviour is analysed in terms of the final constituents of the body rather than of the raw ingredients. Krause and Schlegelmilch⁸ commented on the lack of such data during their investigations on the development of a bone china body from German materials.

7. A more detailed understanding of the thermal behaviour of bone china will be obtained when data is available on phase equilibrium relationships in the proposed compatibility tetrahedron, tricalcium phosphate-anorthite-mullite and silica. The study of a quaternary combination is a lengthy undertaking, but valuable information will be obtained most rapidly by investigating first the ternary system tricalcium phosphate-anorthite-silica, since its essential relations can be inferred from the data given in the present investigation. The study of the quaternary system could be developed from the ternary system by the investigation of the

10 per cent mullite plane. A complete study on the effect of higher concentrations of mullite would be unnecessary since it is the least abundant component.

APPENDIX I

Preparation of Tricalcium Phosphate

In phase studies as in all precise scientific investigation only pure compounds of constant composition may be used if accurate results are to be obtained. It was found in the present study, however, that although pure alumina and silica could be obtained commercially, pure tricalcium phosphate of stoichiometric composition was unprocurable. Several samples of alleged C. P. tricalcium phosphate were tested and found to be hydroxyapatite. Further to this, all of these salts contained notable quantities of sodium and frequently iron as well. The combination of non-stoichiometric composition and alkali impurity depressed the melting point from 1730°C (m. p. pure $\text{Ca}_3(\text{PO}_4)_2$) to as low as 1400°C .

Barrett and McCaughey¹⁴ met with the same difficulty in their investigation of the system $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$, but found that calcined dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was a good source of phosphorus for their mixtures. Contrary to Barrett and McCaughey's experience, tests made during the present investigation showed that the C. P. dicalcium phosphate

obtained commercially was as liable to compositional variation and alkali contamination as the tricalcium phosphate just mentioned. For instance, a sample of alleged C. P. dicalcium phosphate purchased from one of the most reputable chemical supply houses in North America was found to be nearer to tricalcium phosphate in composition and carried 0.5 per cent sodium. Alkali salts are common contaminants in so-called C. P. reagents, and because of their powerful fluxing action they render such materials useless for phase studies. The theoretical loss-on-ignition of dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) is 26.2 per cent, but samples obtained from commercial houses had loss-on-ignition values at 1000°C varying from 7 to 14 per cent only. This range of loss-on-ignition may be taken as some indication of the variability of the commercial salts.

Attempts to synthesize tricalcium phosphate in the laboratory using the method suggested by MacIntyre et al.²¹ met with no success. The basic principle of the method lay in the precipitation of $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ from chilled calcium sucrate solution by the addition of concentrated phosphoric acid in very slight excess. Although instructions were carefully followed the experimental results anticipated were not forthcoming. The gelatinous precipitate obtained was tested in the manner described by MacIntyre to distinguish between hydroxyapatite and tricalcium phosphate. This test involved the determination of the solubility

of 1 gm. of precipitate (dried at 105°C) leached for one hour in 100 cc. of 2 per cent aqueous citric acid solution at 20°C. If more than 85 per cent of the precipitate dissolved, it was to be described as tricalcium phosphate; if less dissolved it was to be called hydroxyapatite. The highest solubility found among several precipitates was 80 per cent and accordingly they were designated "Hydroxyapatites".

Melting point determinations were found to be more convenient in a laboratory equipped for phase equilibrium studies. It was quickly discovered that all the precipitates melted in the neighbourhood of 1400°C and that the refractive indices (approx. 1.595) of the fusions were too high for pure tricalcium phosphate (tricalcium phosphate $\alpha = 1.588$, $\gamma = 1.591$). This evidence of hydroxyapatite formation confirmed that derived from the citric acid solubility test, and as a result the synthesis of tricalcium phosphate by wet methods was abandoned. It is interesting to note in passing that X-ray powder diagrams are useless for detecting the apatite content of these precipitates, since the pattern for β $\text{Ca}_3(\text{PO}_4)_2$ is always obtained.

In the course of studying the wet preparation of tricalcium phosphate it was observed that when chilled calcium sucrose was added to dilute phosphoric acid, neutralization proceeded only to the displacement of the second hydrogen atom from the acid molecule. Further investigation indicated that this was an ideal method for the preparation of pure dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) of stoichiometric composition. The

dicalcium salt was easily converted to calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$) by ignition at 900°C and this latter compound was then used as a source of P_2O_5 throughout the phase investigation.

The preparation of these two compounds ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_2\text{P}_2\text{O}_7$) was carefully studied and the optimum conditions for their formation determined. The results of this investigation are now given in some detail.

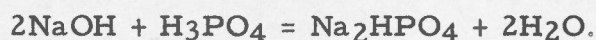
The Preparation of Dicalcium Phosphate Dihydrate and Calcium Pyrophosphate

Prior to making sufficient dicalcium phosphate for the entire phase investigation many preliminary experiments were undertaken. All of these runs showed that, provided the calcium succrate was added to chilled dilute phosphoric acid, the neutralization always stopped at the second stage of hydrogen replacement, even when a large excess of succrate was present. Thus, provided the additions were made correctly and the solutions kept chilled (10°C), a good product was obtained without any special attention being paid to the quantities mixed. For more certain results, however, it is recommended that the quantities of reactants be carefully measured and only a very slight excess of calcium succrate used.

The stock of dicalcium phosphate was prepared as follows: -
322.5 grams of C.P. calcium carbonate were calcined at 1000°C for one hour and the lime so obtained dissolved in 5 litres of 22.5% CO_2 -free aqueous sugar solution. Previous experience showed that,

if the freshly ignited lime was immediately added to the sugar solution, it dissolved easily and completely. The sucrate solution was chilled to 10°C and added to 190 cc. phosphoric acid (1.05 grams P₂O₅ per cc.) diluted to 3 litres with water.

The phosphoric acid had previously been assayed by titration with standard sodium hydroxide solution, using phenolphthalein as indicator and a little sodium chloride to sharpen the end point. The following equation indicates the reaction which takes place:-



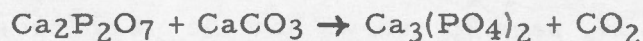
Addition of sodium chloride sharpens the end point by reducing the hydrolysis of the disodium phosphate.

The phosphoric acid was contained in a large stoneware vessel maintained at 10°C by an ice bath. The acid was vigorously stirred and the sucrate added slowly, in eleven stages. Samples for pH determinations were taken two minutes after each sucrate addition. Figure 17, page 95, shows how the pH changes as the acid is gradually neutralized. After stirring for one hour following neutralization the pH dropped to 8.2.

It will be noted that there is a slight inflexion in the neutralization curve at 2.5 litres calcium sucate, the point of formation of monocalcium phosphate. Completion of the reaction, however, is clearly shown by the rapid rise in pH once the second hydrogen atom has been displaced from the phosphoric acid.

The dicalcium phosphate prepared by this method settles readily and may be filtered easily. (Contrast with "tricalcium phosphate" made by MacIntyre's method²¹). After filtration the precipitate was washed with 10 litres of chilled distilled water. The small excess of calcium sucate was washed out easily since it is a very soluble compound. This was one reason for its use as a source of calcium in the preparation. Finally the precipitate was dried at 50°C for several days and stored ready for conversion to calcium pyrophosphate.

Since the ultimate aim was to produce tricalcium phosphate in the mixtures used in the phase study, it was found convenient to calcine the dicalcium salt at 900°C to obtain calcium pyrophosphate, $\text{Ca}_2\text{P}_2\text{O}_7$. Thus when tricalcium phosphate was required, calcium pyrophosphate and calcium carbonate were mixed in the proportions shown by the equation:-



and the required tricalcium salt formed in situ when the mixture was heated to 1600-1700°C.

Prior to converting all the dicalcium phosphate to pyrophosphate, samples were taken for loss-on-ignition determinations at 900°C. All samples were found to have a loss-on-ignition of 26.4 per cent, which is very close to the theoretical 26.2 per cent for the reaction:-



It was concluded therefore that the dihydrate of dicalcium phosphate had been made by the reaction between the phosphoric acid and

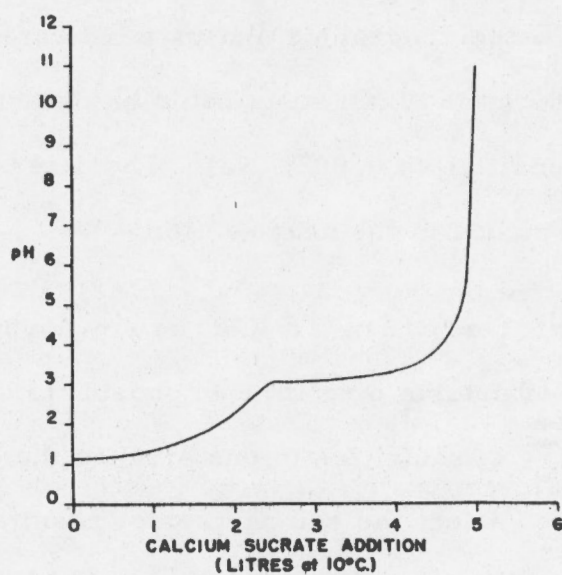


Figure 17. - pH vs. neutralization of phosphoric acid by calcium sucrate.

calcium succrate.

Since pyrophosphate was used as the source of P_2O_5 in the preparation of mixtures for the phase study, chemical analyses were made of this compound rather than of the initial precipitate. Accurate chemical analysis was found difficult and much time was spent checking methods of analysis before a thoroughly reliable scheme was evolved. Spectrographic analysis indicated high order or purity, and no sodium or alkali salts could be detected on a Beckman flame photometer (Sensitive to 0.002% Na). The determination of CaO and P_2O_5 is described in the next section.

Determination of Calcium in Calcium Pyrophosphate

Several methods of determining lime in phosphate were tried and even though there were similarities to one another the details were sufficiently different to affect the comparison of results. The method described below yielded the most consistent results and was adopted as the standard.

A dried sample weighing 0.625 grams was dissolved in a little hydrochloric acid and the volume of this solution made up to 250 cc. with distilled water in a volumetric flask. Duplicate analyses were then run on 0.25 gram samples obtained by withdrawing 100 cc. aliquots. The acidity of the aliquot was adjusted with hydrochloric acid until a few drops of brom phenol blue added to the solution turned yellow. Ten cc. of 0.5 Molar oxalic acid were added and the

solution was then boiled. 1M ammonia solution was added dropwise until the indicator turned green (pH 3). This caused calcium oxalate to be precipitated free from contaminating phosphate. After standing for three hours on a steam bath the precipitate was filtered on a fine sinter glass filter and washed with chilled 0.1M ammonia. The glass filter containing the precipitate was then transferred to a beaker containing 25 cc. of 1:8 sulphuric acid. After being warmed gently to dissolve the oxalate the solution was diluted to 100 cc. with distilled water, heated to 80°C, and titrated with 0.1N potassium permanganate. The permanganate had been previously standardized against United States Bureau of Standards sodium oxalate dissolved in a similar quantity of the same strength sulphuric acid and heated to 80°C. One cc. of 0.1N potassium permanganate is equivalent to 2.804 milligrams of calcium oxide (lime).

Some standard works suggest that the calcium oxalate precipitate be filtered on paper, ignited, and weighed as calcium oxide. However, it was found that the great activity of the freshly ignited lime made accurate weighing impossible. The samples continuously absorbed carbon dioxide and water from the air and increased in weight. Filtering on a tared sinter glass filter and weighing as calcium oxalate has also been recommended, but it was found that the alkaline filtrate noticeably dissolved the filter, thereby rendering the results less accurate.

The calcium pyrophosphate stock used in making the phase study mixtures was found to contain 44.1% CaO (Theoretical:44.12%).

Determination of Phosphorus in Calcium Pyrophosphate

As with the case of calcium, precise assaying was difficult and the well known standard methods were found wanting in accuracy. The methods based on the precipitation of phosphorus as phospho-molybdate were not at all satisfactory and the results obtained, most erratic. The best method²² found was to precipitate magnesium ammonium phosphate from the filtrate left after the removal of calcium oxalate in the lime assay, and after careful drying, to weigh it as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ on a tared sinter glass filter. The details of the method are given below:-

The filtrate and washings from the lime determination were evaporated to 100 cc. in volume and then acidified with hydrochloric acid until the solution turned red. Ten cc. of 0.5M magnesium chloride were then added and the solution neutralized with 9.0M ammonia until the indicator turned blue. After adding a 5 cc. excess of ammonia the bulk was made up to 125 cc. and the assay allowed to stand overnight. The precipitate obtained was filtered on fine sinter glass and then dissolved in 40 cc. of 1M hydrochloric acid. The bulk was made up to 100 cc., then 6 cc. of 0.5M magnesium chloride solution were added, together with sufficient 9.0M ammonia to turn yellow a few drops of methyl red added to the solution. Five cc. more ammonia were added, then the bulk was made up to 125 cc. and allowed to stand overnight. This second precipitate, which was more definite in composition was filtered, washed, and weighed on a tared sinter glass filter. Much care in treatment was required at this stage if accurate results were to be obtained. The sinter glass filter was

prepared by washing it successively with dilute hydrochloric acid, water, absolute alcohol and finally ether. The filter was then dried at 37°C and weighed. After filtration, the precipitate was washed with 0.04M ammonia in three lots of 5 cc. and then absolute alcohol and ether. Finally the precipitate was dried at 37°C and weighed. By these means a pure precipitate of strict stoichiometric composition was obtained. One milligram of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ represents 0.289 milligrams P_2O_5 .

The stock of calcium pyrophosphate was found to contain 55.5% P_2O_5 according to assays made by the above method.

Experiments on the Limitations of Application of the Sucrate Method of Preparing Dicalcium Phosphate Dihydrate

The success in making a stock of pure formula composition calcium pyrophosphate prompted further investigation on the sucrate method of synthesizing dicalcium phosphate dihydrate. Accordingly, runs were made to check the effect of a) temperature and b) great excess of calcium sucrate.

To study the above factors several runs were made in the manner described for the stock material, but varying appropriately the temperature or sucrate excess. Analyses were also made on the resulting products. The experimental results may be summarized as follows:-

1. At temperatures up to 25°C, the neutralization of phosphoric acid proceeds to the second stage of hydrogen displacement only.
2. Above 25°C neutralization begins to carry on to the third and final stage.
3. Dicalcium phosphate settles readily and is easily filtered. As soon as third stage neutralization commences the mixed precipitate becomes gelatinous and difficult to filter.
4. Below 25°C excess calcium sucate does not appear to react appreciably with the precipitated dicalcium phosphate, even after two hours stirring.
5. Although it is possible to prepare a satisfactory precipitate by simply adding calcium sucate solution to dilute phosphoric acid at room temperature until an indicator, such as phenolphthalein, turns red, it is recommended that the more rigorously controlled procedure outlined earlier be followed for best results.

APPENDIX II

The Properties of Calcium Pyrophosphate

In view of the purity of the calcium pyrophosphate obtained by the sucate method it was considered worthwhile to investigate quantitatively some of its physical properties in order to evaluate data given in the literature.

Melting Point

Tromel¹³, and Barrett and McCaughey¹⁴ both give a melting point of 1300°C, while Hill et al.²³ report a temperature of 1353°C. The "Handbook of Physics and Chemistry" (Chemical Rubber Publishing Co. Ed. 31) indicates a melting point of 1230°C.

Using the quench equipment described earlier in this study the melting point was found to be 1356°C. Since there is little difference in the atomic arrangement between the glass and crystalline pyrophosphate the quenching method is applied with difficulty. Using water as the quenching medium it was found that the first crystals formed at 1356°C and the last glass disappeared at 1352°C. Because of the possibility of supercooling, the liquidus temperature has been taken throughout the present work as the temperature at which crystal first appears in the quenched glass matrix. Hill et al.²³ preferred to consider liquidus as the point at which the last glass disappeared. This gave them liquidus at 1357°C. They preferred, however, to consider the result of 1352°C, yielded by a heating curve, as representing the true melting point of calcium pyrophosphate. In general, the agreement between their results and those given here must be regarded as very satisfactory.

It is stated in the literature²³ that calcium pyrophosphate exists in high (α) and low (β) temperature forms with a transition point at 1140°C. Checks were made by heating both allotropes at temperatures just above and below this temperature. The

results indicated that any change must be very sluggish, for if both α and β were heated at the same time for one hour neither one transformed. In view of the lengthy runs which would have been required to locate the transformation point accurately, it was decided to abandon this determination. However, it was observed that the β form will transform rapidly to α at 1250°C, but not at 1200°C. Thus, whatever the true transformation temperature is, it would appear that temperatures in the region of 1250°C are needed to bring about the transformation in a short period of, say, one hour.

It was also noted that molten pyrophosphate had a tendency to supercool and then freeze rapidly to form the low temperature or β modification. Samples of β calcium pyrophosphate were prepared in this way for optical and X-ray examination. The high temperature or α modification was obtained readily from the β form by heating the latter for one hour at 1250°C in a platinum crucible, and then quenching.

The high temperature modification was used for the optical and X-ray examinations described below.

Optical Properties

Samples of α and β calcium pyrophosphate prepared as described above were examined under the petrographic microscope. Refractive indices were found by immersion in various oils of known index. The optical constants found are summarized as follows:-

α $\text{Ca}_2\text{P}_2\text{O}_7$:- Biaxial negative, $\alpha = 1.584$, $\gamma = 1.605$

β $\text{Ca}_2\text{P}_2\text{O}_7$:- Uniaxial positive, $\omega = 1.630$, $\epsilon = 1.638$

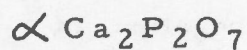
This data is in excellent agreement with that presented by Hill et al.²³

Density

The densities of the α and β forms were found by using a Berman torsion balance. The experimental results indicated that α calcium pyrophosphate has a density of 2.88 grams per cc. and β a density of 3.10 grams per cc., both taken at 25°C.

X-ray Data

X-ray powder diagrams of the samples were prepared using copper $\text{K}\alpha_1$ radiation ($\lambda = 1.5374$ kX, Siegbahn). The data obtained are tabulated below:-



d (kX)*	I+	d (kX)	I	d (kX)	I
7.00	vw	2.45	w	1.54	vw
6.31	vw	2.34	vw	1.52	vw
4.91	w	2.10	s	1.49	vw
4.26	w	2.04	m	1.38	vw
3.76	w	<u>1.98</u>	vs	1.33	m
3.52	w	1.90	vw	1.29	m
<u>3.32</u>	vs	1.83	vw	1.25	w
<u>3.20</u>	s	1.78	m	1.23	vw
3.07	s	1.70	vw	1.21	vw
2.77	m	1.67	vw	1.20	vw
2.64	m	1.63	m		
2.59	m	1.58	vw		

* Distance between parallel planes in the crystal lattice in Siegbahn units. The three strongest lines have been underlined. To convert kX units to Angstrom multiply by 1.00203.

+ Intensity of line recorded on film, vs = very strong, s = strong, m = medium, w = weak, and vw = very weak.

β Ca₂P₂O₇

d (kX)*	I+	d (kX)	I	d (kX)	I
6.49	vw	2.76	w	1.94	vw
5.20	vw	2.61	m	1.90	vw
4.43	vw	2.40	vw	1.77	vw
4.07	vw	2.34	vw	1.73	w
3.47	vw	2.26	vw	1.69	vw
3.34	vw	2.19	vw	1.55	vw
<u>3.22</u>	s	2.16	vw	1.47	vw
3.09	vw	2.09	vw	1.41	vw
<u>3.01</u>	m	2.03	vw	1.39	vw
<u>2.89</u>	vs	2.00	vw		

* Distance between parallel planes in the crystal lattice in Siegbahn units. The three strongest lines have been underlined. To convert kX units to Angstrom multiply by 1.00203.

+ Intensity of line recorded on film, vs = very strong, s = strong, m = medium, w = weak, and vw = very weak.

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1. The first part of the report is a general introduction to the subject of the study. It discusses the importance of the problem and the objectives of the research. It also mentions the scope of the study and the methods used.

2. The second part of the report is a detailed description of the experimental work. It includes a description of the apparatus used, the procedure followed, and the results obtained. It also discusses the errors and limitations of the experiment.

3. The third part of the report is a discussion of the results. It compares the results with the theoretical predictions and with the results of other experiments. It also discusses the implications of the results and the conclusions drawn from them.

4. The fourth part of the report is a summary of the work. It briefly reviews the main points of the report and states the conclusions.

5. The fifth part of the report is a list of references. It includes the names of the authors and the titles of the papers or books referred to in the report.

