THE PHYSICAL PROPERTIES
OF MODERN DENTAL PORCELAIN

Thesis submitted to the University of Sydney
as a requirement for admission to the
degree of Doctor of Philosophy.

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1968.
PREFACE.

Modern dental porcelain has been classified as a whiteware. Although not a typical whiteware, it has evolved from the traditional triaxial formula. To appreciate this material as an entity and its relationship to other conventional ceramic compositions, the peculiarities of its raw constituents and their mutual behaviour on sintering must be recognized.

Fine aesthetic qualities and relative ease of manipulation are undisputed characteristics of modern dental porcelain. Over the years, these special requirements have been instrumental in the development of today's highly translucent materials. They have become more glass-like. Consequently, their physical properties must be influenced, to a large extent, by this major vitreous phase.

Realizing this, there is no need to justify the inclusion of pertinent information about vitreous materials in the review of the literature. It would be a pity if we should fail to benefit from the experience gained in other fields when some relevance becomes apparent.

The manufacture of dental porcelain has always been a highly specialized and secretive industry; and comparatively little effort has been made by the dental profession to
(ii)

investigate its properties in a scientific way. It seems that any developmental progress has been based mostly on aesthetic requirements and empirical observations.

While of historical interest, much of the recorded information is not necessarily applicable to the modern materials. Also, few authors have presented their data in a descriptive and critical manner. Still fewer attempts have been made to relate testing to practical situations, or, at least, to standardize the testing procedures so that results from different sources could be compared.

There has existed an almost desperate need to establish some rationale for testing modern dental porcelain, and it has been the object of this research to develop methods of specimen manufacture and tests which might aid in improving our knowledge of the behaviour of these materials under some service conditions. All this was done in the light of a background awareness of the nature of related industrial ceramic materials.

Broadly, the physical properties studied in various brands of modern dental porcelain were: dimensional change on sintering, both linear and volumetric; density of the fired body; the transformation regions of the vitreous phases of two materials, and the effect of variables on strength.
In order to associate these characteristics with the individual porcelains more intimately, a study of their microstructures was included.

Except for a semi-quantitative spectrographic analysis for sodium and potassium in two brands of dental porcelain, all the experimental work described in this thesis was carried out by me in the Department of Operative Dentistry within the University of Sydney.

I am indebted to my supervisor, Professor J.S. Lyell, as he was directly responsible for engendering my interest in dental ceramic materials. To Miss J.M. Goldhawk I express appreciation for typing the thesis, and to Mr. B.J. Rumble for being very helpful in the preparation of photographic prints.
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PART A.
REVIEW OF LITERATURE

1. CERAMICS

Kingery (1963, p.3) defines ceramics as the art and science of making and using solid articles which have as their essential component inorganic, non-metallic materials. This is much broader than most traditional, more restrictive definitions, which in themselves tend to limit one's creative imagination.

Ceramics are better considered as a class of materials than the product of a special industry. Today, science and technology dictate composition. For example, compositions of triaxial whiteware porcelains are determined by: a) requirements for forming; b) requirements for successful firing; c) requirements for final properties; and d) economic considerations.

1.1 Triaxial Whiteware Compositions.

Abundance of the elements and their geochemical characteristics mainly control the types of minerals found in nature. Since oxygen, silicon, and aluminium together account for almost 90 per cent of the elements in the earth's crust, it is not surprising that the dominant minerals are quartz, silicates, and aluminosilicates.
These, together with other mineral compounds of oxygen, constitute the great bulk of naturally occurring ceramic raw materials.

Thus, the mineral raw materials used in the ceramic industry are mainly inorganic, non-metallic, crystalline solids formed by complex geological processes. Crystalline structure and chemical composition of the essential constituents and the nature and amounts of accessory minerals present largely determine ceramic properties. Consequently, these ceramic properties are subject to wide variation depending on the geological environment in which the mineral deposit was formed.

Traditional ceramic compositions, forming the basis for much of the whiteware industry, are mixtures of clay (the plastic or finely grained portion), feldspar (a flux or material which provides the glassy phase), and flint (the non-plastic or refractory crystalline portion). Such compositions include hard porcelain for artware, tableware, vitreous sanitary ware, electrical porcelain, semi-vitreous tableware, hotel china and dental porcelain. A typical composition could be considered, very roughly, as equal parts of kaolin, ball clay, feldspar, and flint (Norton and Hodgdon, 1931 & Johnson and Underhill, 1944).
2. THE RAW MATERIALS USED IN CLASSICAL CERAMICS

2.1 Silica and Silicate Minerals

Some form of silica is an almost invariable constituent of ceramic bodies (Bárti, 1965). In the earliest pottery it was no doubt present as a fortuitous impurity in the clay. In 1720, Astbury, an English potter, deliberately added ground calcined flint to his pottery for the purpose of increasing the whiteness (Hughan, 1951).

Pure quartz confers a high degree of translucency on the porcelain body, and for this reason it is greatly valued for best domestic porcelain.

The Naturally Occurring Forms of Silica.

These can be divided into three broad groups (Hughan, 1951).

(i) Macrocristalline Quartz: Distinct crystallinity characterizes this form and it is the most commonly used variety of silica for pottery bodies. Its mode of occurrence varies. The chief varieties are:

Detrital Sands: These have the advantage of a predominant grain size of between 0.1 - 0.3 mm, thus reducing the cost of grinding (Salmang, 1951, p.155). However, they are frequently contaminated by other detrital materials, which may detract from the fired colour.
Vein Quartz: By vein quartz is meant the hydrothermally produced quartz filling of veins in rocks. It does not constitute an economic source of silica.

Granitic Quartz: This accessory material in kaolinized granites and pegmatites is similar in type to vein quartz.

Quartzite: Recrystallization of sandstones forms this type of rock, and it consists almost wholly of silica. As a source of pottery silica the cost of mining and crushing is its chief disadvantage.

(ii) Microcrystalline or Chalcedonic Silica:

Such varieties of siliceous rock as flint, agate, hornstone, jasper, and chalcedony are classified under this heading. The grain size of these minerals is sub-microscopic and evidence of crystallinity rests largely on X-ray information (Hughan, 1951).

While some examples in this group are relatively easily ground, the content of undesirable impurities is in many cases too high for ceramic work.

(iii) Opaline or Amorphous Silica:

Opal is essentially an amorphous silica containing water and pigmentary material (e.g. iron oxide) in varying amounts. It is a widely distributed mineral gel but its impurities militate against its use as a ceramic raw material (Lee, 1961, p.14).
Kieselguhr or diatomaceous earth also falls into this class. It is found in deposits of the remains of prehistoric, microscopically small infusoria with silica skeletons. While this material is finely grained and relatively free of iron, it is generally reputed to cause a considerable loss in the plasticity of whiteware bodies. The clay bond is probably unable to cover the large surface area exposed by the minute irregularly-shaped grains.

(a) The modifications of silica.

Silica in the free state is usually found in the form of quartz, nevertheless there are two other independent crystalline species of silica, tridymite and cristobalite. These three crystalline forms may exist in several modifications, each of which is stable over a different temperature range.

Reversible (enantiotropic) transformations take place without reconstruction of the lattice, with a minor change in the crystal class and conservation of the external form, e.g.,

\[ \beta - \text{quartz (trigonal-trapezoidal)} \leftrightarrow \alpha - \text{quartz} \]

\[ \beta - \text{tridymite (orthorhombic)} \leftrightarrow \alpha - \text{tridymite} \]

\[ \beta - \text{cristobalite (tetragonal)} \leftrightarrow \alpha - \text{cristobalite} \]

(Salmang, 1961, p.7).
6.

The high-temperature (\( \alpha \)) forms usually have more open structures than the low-temperature (\( \beta \)) and (\( \gamma \)) forms; consequently, they have lower specific gravities than the latter.

On the other hand, the transformation of quartz into tridymite and cristobalite involves profound changes in the lattice structure and can therefore only take place slowly (Jones, 1967).

\[
\text{quartz} \xrightarrow{870^\circ C} \text{tridymite} \xrightarrow{1470^\circ C} \text{cristobalite} \xrightarrow{1728^\circ C} \text{melt}
\]

\[
\beta \xrightarrow{573^\circ C} \alpha, \quad \beta \xrightarrow{117^\circ C \text{ to } 163^\circ C} \alpha, \quad \beta \xrightarrow{230^\circ C} \alpha.
\]

Quartz, the stable form of silica at room temperature, upon heating, promptly inverts at about 573\(^\circ\)C to high quartz with considerable expansion, and on cooling, reverts instantly at the same temperature to the original form.

Above 870\(^\circ\)C quartz is unstable, but its conversion to the high-temperature modifications is so sluggish that it may survive considerable heat treatment above its stable range without change. The effect of heat on the macrocrystalline types of silica has been thoroughly studied (Hughan, 1951). In the absence of other minerals, quartz heated below 1100\(^\circ\)C for periods up to a few days shows no evidence of permanent change, other than some disintegration of large crystals. Above 1100\(^\circ\)C slow conversion to cristobalite occurs, while the transformation is completed in a few hours at 1400\(^\circ\)C.
7.

Since conversion to cristobalite is a process which commences at the grain boundaries, and continues towards the centre of the grains, the initial grain size of the material is an important factor controlling the rate of conversion at any temperature. While the above consideration is of prime importance in the choice of quartzite for silica bricks, it seems of little importance to the potter.

Impurities present in quartz undoubtedly influence the temperatures quoted and hence affect the likelihood of cristobalite formation (Jones, 1967). A roughly similar behaviour is shown by the opaline types of silica except that cristobalite formation is found at lower temperatures than those for quartz (Insley and Fréchette, 1955, p.60 & Salmang, 1961, p.166).

Besides the three main crystalline species and their modifications, there is also an amorphous variety, silica glass.

Tridymite, like cristobalite and silica glass, is unstable up to $870^\circ\text{C}$, even though its conversion to quartz below this temperature may not take place in finite time. At $117^\circ\text{C}$ ($100^\circ - 118^\circ\text{C}$) $\gamma$-tridymite inverts to $\beta$-tridymite, at $163^\circ\text{C}$ ($140^\circ - 165^\circ\text{C}$) to $\alpha$-tridymite. This is stable only up to $1470^\circ\text{C}$, at which point it converts to cristobalite.

Cristobalite has an inversion point at about $230^\circ\text{C}$
8.

(180° - 260°C), is stable above 1470°C and has the highest melting point of all crystalline forms of silica, 1728°C. Above this temperature only the melt is stable. If cooled rapidly below 1728°C it retains its amorphous condition and forms silica glass. Silica glass has the largest internal energy content of all forms of silica (Salmang, 1961, p.161).

The three crystalline forms of silica may exist in intimate mixtures for a long time, even though they are not in equilibrium and change form with temperature changes. A low temperature tridymite and cristobalite may exist for an indefinite period at room temperature. Microscopic examination of thin sections is a valuable aid in distinguishing these three main crystalline species of silica. Quartz differs from tridymite and cristobalite by its higher refractive index ($N_0 = 1.544$), its stronger birefringence (0.009) and the massive form of the individual crystals. At times it is not easy to distinguish quartz from feldspar.

In section tridymite appears microscopically, under polarization, as narrow wedges or needlelike. One would not expect to find tridymite in most products containing clay, as maintenance at 1300° - 1400°C for long periods is necessary.

Owing to their smallness and low birefringence, individual crystals of cristobalite may not be distinguished under the microscope (Insley and Fréchette, 1955, p.59 & Salmang, 1961, p.164).
9.

(b) Length changes on heating.

Remarkable differences in the thermal expansion of the different modifications of silica have been observed (Salmang, 1961, pp. 164 & 165). Quartz expands uniformly when heated up to its inversion at 573°C, when a sudden increase in length of about 0.2 per cent occurs. At 600°C the expansion ceases. This behaviour is reversible.

Tridymite undergoes two sudden changes in length at 117°C and 150°C. Together they amount to about 0.3 per cent, although the total increase in length up to 600°C is less than that of quartz.

The behaviour of cristobalite is quite different. At about 230°C it undergoes an increase in length of about 1.13 per cent. The total increase, which is completed by 500°C, is 50 per cent greater than for tridymite. Hence, cristobalite is dangerous in ceramic bodies intended to pass repeatedly through the temperature range from room temperature to red heat.

Tridymite should be the most suitable type of silica to have in ceramic bodies due to its small total length change and comparatively small increases associated with its inversions. However, although greater than that of tridymite, quartz's sudden length change is still relatively limited.
In unfired bodies quartz is to be regarded as a non-plastic constituent. The behaviour of silica during firing is characterized by its transformations and by solution effects with other body constituents. Grain size of quartz has a great influence on the thermal expansion and contraction of the ware. As a result of its more intimate association with the other ingredients, fine quartz has a greater effect than coarse (Russell and Weiss, 1944).
2.2 Feldspars and Feldspathoids.

The feldspars, widely used as raw materials in the whiteware, enamel, glass, and abrasives industries, are among the most important of the rock-forming minerals. They are a group of solid solutions of anhydrous aluminosilicates containing $\text{K}^+$, $\text{Na}^+$, $\text{Ca}^{2+}$ and $\text{Ba}^{2+}$ and are present in virtually all igneous rocks (Yoshiki and Matsumoto, 1951 & Kyonka and Cook, 1954). They are too often intimately mixed with other minerals so that their recovery in the pure state is expensive if not impossible.

The feldspars are used as fluxes, which provide the glassy phase, in ceramic bodies. As a melt, the liquid medium facilitates the diffusion process and aids the consolidation and formation of a non-porous body (Budnikov and Gevorkyan, 1953).

Commercial feldspars are found in pegmatite minerals along with quartz. They are frequently mixtures of several varieties of feldspars and vary in composition. The principal accessory minerals are quartz, mica and other silicates, while iron oxide and other impurities in small amounts are common (Geller and Creamer, 1931). Their variable composition may affect the physical properties and firing behaviour of the ceramic product in which they are used.
Isomorphous substitution in the crystal lattice of one cation for another gives rise to the several varieties. Those of major commercial interest are; potash feldspar (orthoclase and microcline), $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, soda feldspar (albite), $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$, and lime feldspar (anorthite), $CaO \cdot Al_2O_3 \cdot 2SiO_2$.

Potash feldspar crystallizes in the monoclinic form as orthoclase and in the triclinic as microcline.

Albite and anorthite crystallize in the triclinic form (Insley and Fröchette, 1955, p.61).

The three main varieties of feldspar seldom occur in pure form; mixed crystals are usually found. The mixed crystal series between soda and potash feldspar is known as orthoclase. A complete series of triclinic solid solutions between albite and anorthite are known as the plagioclases. Intermediate members of the plagioclase series have been given the mineral names oligoclase, andesine, labradorite, and bytownite in the order of increasing calcium content (Lee, 1961, p.17).

These mixed crystals are often disturbed by partial separation of the components in lamellar form, producing what is known as the perthite structure. This plaid-like "perthitic" intergrowth of plagioclase and orthoclase or
microcline evidently arises as a consequence of limited miscibility at low temperatures.

When considering sintering and melting behaviour, the structure of crystalline feldspar is just as important as the chemical composition.

Orthoclase melts incongruently with the breakdown into leucite, \( \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \), and melt. Decomposition of pure orthoclase begins at about 1160°C, but it is not complete until about 1290°C. At higher temperatures the leucite crystals grow and become less numerous; at about 1540°C they have redissolved (Salmang, 1961, p.173).

Pure albite melts at 1118°C. Albites have therefore been proposed as substitutes for orthoclase (Insley and Fréchette, 1955, p.64), but have not yet succeeded in replacing it.

Geller and Creamer (1931) have shown that refractoriness increases, and the softening range decreases with increasing \( \text{K}_2\text{O} \) content of the feldspars; at the same time the melt becomes more viscous and the body less likely to warp in the firing. Lime lowers the fusion point of orthoclase markedly, but not that of albite. The melting point is, however, not a measure of the solvent power of feldspars (Salmang, 1961, p.173).
Feldspar resembles quartz in that melting takes place without loss of shape. Due to its high viscosity at the melting point, only overheating causes the edges of the specimen to become rounded by flow. This melt is capable of dissolving appreciable amounts of quartz and clay substance. On cooling, it solidifies to a glass which forms the matrix of a porcelain body.

High grades of feldspars are produced in Europe, especially in Norway and Sweden. In the absence of rich native sources of potash feldspar in Great Britain, Cornish stone is used as a flux, while in North America, nepheline syenite is widely used for a similar reason. Hence, feldspar is by no means irreplaceable in ceramic bodies.

Cornish stone is composed of feldspar and talc. Nepheline syenite is an igneous rock, somewhat resembling granite. The rock contains little or no free quartz, but consists of about 50 per cent albite, 25 per cent microcline and 25 per cent of the feldspathoid, nephelite (Na₂O·Al₂O₃· 2SiO₂). Of the principal feldspathoid minerals, leucite and nephelite which are related to the feldspars in composition, occurrence and use, only nephelite occurs in deposits large enough to warrant economical exploitation (Lee, 1961, p.16). Nepheline syenite contains more Al₂O₃ and Na₂O than the
feldspars. Despite the fact that the melting point of pure nepheline is very high, \(1520^\circ C\), it is strongly depressed by albite and microcline.

For potassium–sodium feldspar, the eutectic at approximately 65 per cent potash feldspar and 35 per cent soda feldspar melts at \(1070^\circ C\). Since there is a similar mixture present in most natural potash feldspars, this temperature can usually be taken as the "melting point". Mixtures richer in potash yield a melt and solid leucite at high temperatures. As much as \(1540^\circ C\) is required to melt pure orthoclase completely (see p.13). The soda feldspars form a melt only.

If feldspar is melted at \(1400^\circ C\) under the conditions of porcelain manufacture, it is glassy and free from leucite. Feldspar melts solidify initially in the glassy state. They need many weeks to recrystallize. If the glassy feldspar is re-heated, it softens at \(930^\circ C\). This temperature may be \(40^\circ C\) higher in the case of feldspars rich in potassium and \(60^\circ C\) lower for those rich in sodium. Most commercial feldspar contains both a microcline or orthoclase constituent and a plagioclase, as well as quartz and other accessory minerals (Insley and Fréchette, 1955, p.62).
According to Amberg (1932), feldspars with a soda-lime (Na₂O/CaO) ratio above 5.25 are classed as albite; those with ratios between 5.25 and 1.35 as oligoclase and so on.

The fusion temperature of plagioclase increases rapidly with the decrease in soda and increase of lime. An oligoclase of a ratio of 1.35 starts to melt at about the same temperature as microcline (potash feldspar). Those with higher ratios have lower fusing temperatures. The plagioclase portion of commercial feldspars should always melt before microcline.

The differences in alkali content of feldspars and their perthitic structure are not the only factors governing their use in ceramics. Absence of accessory minerals such as quartz, mica, tourmaline, hornblende, titanite, etc., is still more important. The presence of quartz is particularly undesirable as it is difficult to distinguish visually from the crystalline feldspar. In amounts in excess of 10 per cent it raises the melting point but yields a more fluid melt. It is more effective in decreasing the vitrification range of ceramic bodies containing soda feldspar than those containing potash feldspar (Kingery, 1963, p.26). The amount of quartz present must be estimated.
Feldspar and/or nepheline syenite is used as the principal flux in almost all the classical bodies and also is used in glaze and glass compositions. The amount may be as low as 10 per cent in porous bodies and much higher in dense glassy bodies. Dental porcelain contains a very high percentage of feldspar or nepheline syenite.

Soda feldspar is preferred by glass manufacturers because of its lower melting point. Low iron content is their most critical requirement.

Pottery and enamel manufacturers usually prefer potash feldspar because of its longer vitrification range.

Nepheline syenite begins to sinter at 945°C and is vitreous at 1135°C (Lee, 1961, p.19). It deforms at 1190°C. It has a longer firing range and is a more active flux than the feldspars.
2.3 Clays.

Clays are the most widely distributed geological sediments. These minerals are finely particled hydrous aluminosilicates, which develop plasticity when mixed with water. Clays vary widely in mineral content, degree of purity and in physical characteristics. A common characteristic is their layer-lattice structure. They are all composed of electrically neutral or negative aluminosilicate layers which, when associated with water, provide for their plasticity (Lee, 1961, p.11 & Salmang, 1961, pp.26 & 58).

The mechanism of the process of clay formation is imperfectly understood. There are basically two views held, one preferred by geologists, the other by chemists. The older view, usually that of geologists, assumes that aging and weathering of rocks, such as granite and other igneous rocks containing feldspar mica and quartz, is responsible. The chemical view holds that clay is formed from solutions. Probably there is justification for both theories. The former would explain the formation of coarsely grained kaolin in primary deposits, the latter that of finely grained, colloidal, sedimentary clays.

Clays perform two important functions in ceramic bodies. Firstly, their characteristic plasticity is basic
to many of the forming processes commonly used. Secondly, dried clay wares lose their plasticity only to gain fair mechanical strength, enabling them to be fired into dense and strong articles without loss of shape.

On the basis of crystalline structure, the most common clay minerals may be classified into the kaolinite group, montmorillonite group, and the illite (hydrous mica) group.

The nature of a clay must be determined by the chemical composition of the parent rock and the physical and chemical environment in which the change takes place. Alkali feldspars tend to alter to kaolinite. The process is regarded as leaching out of alkali and expulsion of 4 SiO₂ (Kingery, 1963, p.19):

\[ \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \xrightarrow{\text{K}_2\text{O} - 4\text{SiO}_2} \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O} \]

orthoclase kaolinite

Ferromagnesian minerals, lime feldspars, and volcanic ash commonly alter to montmorillonite. The kaolinite structure accommodates only the hydrous aluminosilicate, whereas the structures of montmorillonite and illite always contain other elements, especially magnesium and iron.
20.

The clays used in the ceramics industry may be simply divided into kaolins, and other clays. The kaolins, which include china clay, are white and burn white. They have a grain size of about 0.5 – 2 microns and their mineralogical habit is described as that of pseudo-hexagonal scales (Insley and Fréchette, 1955, p.73). Other clays are mostly coloured and usually do not burn white. Their grain size varies from one micron down to fine colloidal dimensions.

For porcelain, kaolins only are of value since they alone produce the desired white fired colour.

Of the other clays, ball clays are used in all types of white wares, except in the finest chinaware. They are characterized by the presence of organic matter, high plasticity, high dry strength, long vitrification range, and a light colour when fired.

The fire clays are generally not white-burning, but are free from fluxes such as iron, alkaline earths, alkalies and excess silica.

Stoneware clays contain mineral impurities which bring about a partial melting of the body. Feldspar is a common ingredient. Terra cotta clays are buff-coloured after burning.
21.

Slip clays contain large proportions of fluxes and iron. They are used for glazes.

Very pure clays are refractory - impure clays fuse at some lower temperature.
The fact that quartz-clay-feldspar bodies are not sensitive to minor changes in composition, forming methods and firing temperature is one of their great advantages. The main differences between compositions are in the relative amounts and kinds of feldspar and clay used. As an increasing amount of feldspar is added, the amount of liquid formed at the eutectic temperature increases, vitrification proceeds at a lower temperature due to this extra amount of liquid present and greater vitrification and higher translucency are obtained. As feldspar is replaced by clay, higher temperatures are required for vitrification and the firing process becomes more difficult and expensive. However, the forming processes become easier, and the mechanical properties of the resulting body are improved (Kingery, 1963, p.418). Requirements relating to forming the ware mostly determine the amount and kinds of clay selected. As more difficult forming techniques are employed, a larger clay content is required.

Fired porcelain ware is usually white, always translucent and of very low porosity. The densification is due mostly to the use of feldspar as a flux. Other
fluxes can be used. The clay substance incorporated is nearly always in the form of kaolin, and quartz is almost never absent. The green composition of hard porcelain, the typical continental porcelain for domestic and laboratory ware, is nearly always about 50 per cent kaolin, 25 per cent quartz and 25 per cent feldspar (Salmang, 1961, p.329).

Dental porcelains require a higher translucency and are formed in small simple shapes so that high feldspar—low clay compositions are clearly indicated.

3.1 The Forming Process.

(a) Material preparation.

During the usual processing of ceramics, crystalline or non-crystalline powders are compacted and then fired at a temperature sufficient to develop useful properties. Naturally, the quality of the ceramic ware depends in part on the uniformity of the constituent raw materials. Absolute particle size and the particle size distribution of these constituents are of great importance.

In general, ball clays are the finest ingredients, (mostly below one micron), the china clays are intermediate, while the flint and feldspar are relatively coarse (mostly above 10 microns) (Kingery, 1963, p.33). The absolute level of particle size strongly affects the properties of each
constituent. The finely particled clay materials have high plasticity and high dry strength, but cause slow dewatering and have a high drying shrinkage. In the forming process, the feldspar and flint act essentially as fillers and contribute little to the plasticity or dry strength.

Particle size distribution strongly affects particle packing. Random packing of single-size particles leads to about 40 volume per cent porosity or void space. If an additional very fine material were added to fill the interstices, and this also had a 40 volume per cent void space, then the resulting porosity would be $0.4 \times 0.4 \times 100 = 16$ volume per cent void. In practice, this limit is not reached because we do not obtain a perfect distribution; we do not have the very large particle size ratios necessary, and for very fine particle sizes electrostatic surface forces of repulsion exist.

A minimum porosity occurs at a composition containing about 70 per cent coarse material. With a mixture of three individual particle sizes, better packing occurs and a fractional void space of about 25 per cent can be reached. (This porosity is equal to the firing shrinkage necessary to obtain a completely dense ceramic, 25 to 40 volume per cent or about 8 to 13 linear per cent (Kingery, 1963, p.35)).
Important as grain size is in ceramics, it should not be forgotten that only the surfaces of the grains take part initially in chemical reactions. Even after firing at high temperatures, true equilibria are never reached in ceramic bodies. For this reason, the surface area of the particles is of great importance.

(b) Drying.

The forming process of a ware is commonly assisted by a certain amount of moisture. Controlled drying is necessary before firing, otherwise defects such as warping, distortion and crack development may occur.

The initial drying rate is independent of water content in the ware and depends solely on the temperature, humidity, and rate of air movement over the surface. It is equal to the rate from a free water surface. When the water content drops such that the particles just come into contact, the rate of drying suddenly decreases. This is due to the resistance of the flow of liquid to the surface. Vaporization in the interior and diffusion of the vapour out to the surface must occur.

The major part of the drying shrinkage takes place prior to the stage of particle contact. A certain amount
of drying shrinkage is associated with each water film between particles. If the number of water films be reduced, the over-all drying shrinkage is reduced. Hence, coarse materials such as feldspar and quartz and other non-plastics can be added to reduce the drying shrinkage. However, as the drying shrinkage is decreased, the plasticity and ease of forming are also decreased.

(c) Firing.

During the firing process the development of either a viscous liquid or sufficient atomic mobility in the solid allows the forces of surface tension to consolidate the ware and reduce porosity. Firing shrinkage must be equivalent to the decrease in porosity. In ceramics in which nearly theoretical density is necessary, firing shrinkage is relatively high.

If the shrinkage proceeds at an uneven rate during firing, or a portion of the ware is restrained from shrinking by friction with the material on which it is set, stresses, warping, and cracking can develop. In setting the ware, excessive friction must be avoided. Control of temperature uniformity during the firing process is also of great importance. In addition, the time and temperature level of firing must be controlled to give a satisfactory and reproducible product.
Once the body composition and shape are chosen, thermal strains and hence cracking tendency can only be controlled by the thermal gradient through the piece. Thermal gradients are inescapable but can be minimized by slowing the heating or cooling rates. For quartz-containing bodies, cooling through the quartz inversion region is of particular importance (Mitoff and Pask, 1954).

A differential shrinkage of the fired ware is determined by particle shape in the green body. Generally, the more irregular the particles, the greater the differential shrinkage (Lamar, 1944). Particle size does not control differential shrinkage, as the relative shape of the particles is dependent on the natural cleavage characteristics of the mineral (White, 1944). Differential shrinkage is relatively higher in extruded bodies than in those that are dry-pressed. It increases with increased pressure in dry-pressed bodies. Particle alignment is undoubtedly the cause (Hampel and Cutler, 1953).

(d) Densification on firing.

Sintering and Vitrification:

During the firing process of a porous compact, there is a change in pore shape and in pore size. The result is
usually decreased porosity. Elimination of pores should increase strength and translucency of the ware.

The driving force for densification in all systems is surface energy (Weyl, 1952). The surface free energy is lowered by a decrease in surface area (Oel, 1960). Material transfer is affected by the pressure difference and changes in free energy across a curved surface (Kingery, 1963, pp. 195-198). If the particle size, and consequently the radius of curvature, is small, these effects can be very great. Of the possible mechanisms of material transfer, diffusion and viscous flow are important in the largest number of ceramic systems (Kingery, 1963, p. 370).

Densification, in solid-state sintering, or in systems sintered without the presence of a liquid phase, is mainly affected by the diffusion mechanism. The sintering rate is very sensitive to initial particle size and temperature.

While Lee (1961, p. 29) refers to vitrification of whitewares as the degree of densification on firing, I prefer Kingery's (1963, p. 380) usage of the term. He defines it as densification with the aid of a viscous liquid phase. Vitrification is the major firing process for the great majority of silicate systems. A viscous liquid silicate is formed at the firing temperature and serves as a bond for the body. The time required for densification is regulated by
the amount and viscosity of the liquid phase. This must be accomplished without slumping or warping of the ware under the force of gravity. The relative and absolute rates of densification and deformation determine, to a large extent, the temperature and compositions suitable for satisfactory firing.

The factors of most importance in determining the rate of vitrification are the surface tension, viscosity and particle size. That is, the initial rate of shrinkage is directly proportional to the surface tension, inversely proportional to the viscosity, and inversely proportional to the particle size (Oel, 1960).

For silicate materials surface tension is not a great variable. However, particle size, having a strong effect on the sintering rate, must be closely controlled. Even more important for control purposes is the viscosity and its rapid change with temperature. Consequently, temperature must be closely regulated. Also, viscosity can be varied greatly by composition. The rate of densification, then, can be increased by changing the composition to lower the viscosity of the glassy material.

The relative values of particle size and viscosity are also important. Viscosity must be such that appreciable deformation under gravitational forces during densification
does not occur. However, the particle size can be in such a range that the stresses due to surface tension are substantially greater than the stresses due to gravitational forces (Kingery, 1963, p. 383). Hence, the best means of obtaining densification without excessive deformation is to use very finely ground materials with uniform distribution.

Near the end of the sintering process, a major part of densification results from viscous flow under the pressure caused by fine, isolated, spherical pores (Mackenzie and Shuttleworth, 1949).

Naturally, the addition of small amounts of mineralizers to particular compositions can have a profound effect on the firing properties. Sane and Cook (1951) showed that fine grinding and intimate mixing of bodies were beneficial. Porosity and maturing temperature were decreased while the volumetric shrinkage increased.

As the maturing of a body is really a chemical reaction approaching an equilibrium condition, we might expect that it would follow the usual laws. These high-temperature reactions are not instantaneous but depend on both time and temperature. The rate of these reactions is also materially affected by the particle sizes of the constituents (Norton and Hodgdon, 1931 & Russell and Weisz, 1944).
Ware is commonly referred to as "overfired" if for any reason a higher firing temperature leads to poorer properties or a reduced shrinkage.

As already noted above, the amount of porosity in the green ware depends on the particle size, particle size distribution, and the forming method. The volumetric firing shrinkage is equal to the pore volume eliminated during firing. The addition of non-shrinking material to the mix can substantially reduce this firing shrinkage. This is one of the functions of flint in a porcelain body.

Non-uniform shrinking causes warping or distortion and can even cause cracks to open. Density variations in the green ware (and segregation of any non-shrinking material), temperature gradients during firing, flow under forces of gravity and frictional drag of the ware against its support, all cause non-uniform shrinking.
3.2 Constitution and Microstructure of Porcelain.

The properties of porcelains are regulated not only by the composition and structure of the phases present but also by their arrangement. Normal triaxial porcelain bodies consist essentially of the following microscopic phases: (a) a glassy groundmass intimately associated with minute mullite crystals and small included voids; (b) quartz grains which may show rounding and which may be bounded by clear solution rims; (c) glassy zones bearing the pseudomorphic outlines of feldspar grains (slender needles of mullite may appear in this glass); (d) fissures from the shrinkage of clay away from the non-plastics (these round out and decrease in size at the maturing temperatures); and (e) spherical blebs originating at higher temperatures in feldspar glass grains. These blebs grow in size in the overfiring range (Insley and Fréchette, 1955, p.93).

Of course, this structure represents a series of arrested reactions or failure to attain equilibrium. However, the attainment of equilibrium is not necessarily desirable.

(a) Changes during firing.

The earliest change in the maturation of a whiteware body is the shrinkage of the clay phase with the appearance of fissures. In the temperature range 500° - 600°C, kaolinite
dehydrates and becomes optically isotropic (Insley and Fréchette, 1955, p.96). Inversion of quartz to high quartz occurs at 573°C.

Microscopically, it is observed that feldspars in a whiteware body melt without at first changing shape. They lose their birefringence when fired to about 1200°C. The resulting extremely viscous liquid does not flow appreciably but reacts with other body constituents by diffusion. Its role as a solvent for quartz and kaolinite residue is limited (Buñnikov and Gevorkyan, 1953). Feldspar acts primarily as a liquid medium that facilitates the diffusion process. Depending on its composition, the melting of feldspar begins as low as 1100°C (Salmang, 1961, p.333).

As the temperature rises, ionic exchange by diffusion between body constituents becomes a more and more significant factor. Around 1250°C feldspar grains smaller than about 10 microns have disappeared by reacting with the clay (Kinger, 1963, p.420). It is generally believed (Norton, 1931; Fabianic, 1944; & Buñnikov and Gevorkyan, 1953) that the feldspar glass of the larger grains receives sufficient alumina by this transfer process to form first amorphous mullite (3Al₂O₃·2SiO₂) and silica glass. As the reaction continues, the amorphous mullite begins to
crystallize at the borders of the glassy grains, penetrating them as slender prisms, whose length is limited only by the size of the feldspar grains themselves. Alkali diffuses out of the feldspar.

Meanwhile, the clay, having dissociated into a multitude of minute, unresolved mullite crystals in a matrix of glassy silica, receives alkali from the feldspar and fuses to a more and more homogeneous glass in which the mullite nuclei continue to develop. Eventually, they may be distinguished as broad prismatic crystals up to about 0.01 mm long. They are seen mostly in random arrangement, but occasionally in a latticework outlining the original kaolinite crystals.

The source of mullite crystals in a porcelain is undoubtedly the clay, since it is the only constituent which contains a sufficient amount of alumina to develop these crystals (Morey, 1934 & Fabianic, 1944).

The slowest process is the solution of quartz. Receiving alkali and probably alumina from the feldspar, the quartz grains fuse first at the corners of the smallest particles and eventually around the whole borders of the largest grains. A clear solution rim of high silica-glass surrounding each grain increases in amount as the reaction
proceeds. By 1350°C quartz particles smaller than 20 microns are completely assimilated. Above 1425°C little quartz remains (Insley and Fréchette, 1955, p. 97). At this stage the porcelain would consist almost entirely of mullite and glass. Although mullite crystals grow larger at higher firing temperatures, according to Salmang (1961, p. 333), after many repeated firings they may redissolve in a homogeneous glass.

During these processes fissures formed by shrinking clay round out. Depending on freedom of enclosed air to escape from the ware, these rounded outlines could contract normally or expand. Also, the release of any dissolved gases in the original feldspar may form voids in the feldspathic glass if their escape is hindered. Now, the heterogeneous nature of porcelain, with a fine mullite-glass matrix harboring feldspar relics of glass and mullite, quartz grains with their solution rims and pores, can be readily visualized. Although mullite is the crystalline phase in both the original feldspar grains and in the clay matrix, the crystal size and development are quite different.

This failure to reach equilibrium is due to the high viscosity of the feldspathic glass (Bárta, 1965). It is not unlikely then, that the melt be inhomogeneous.
Around crystallites it would be enriched in respect of their constituent elements, and consequently it must have different properties in different regions.

(b) Effect of particle size.

Maturation of the body is accelerated and the firing range is increased when the particle size of the components is reduced. Smaller particles also reduce warpage, and increase translucency and mechanical strength (Sane and Cook, 1951).

The particle size effects of the flint are relatively more pronounced than those of the feldspar. The expansion and contraction of quartz grains in the matrix lead to stresses that may give rise to actual cracking. The stresses in individual grains can be reduced if the grain size is reduced. The properties of porcelains are improved if finely grained quartz is used rather than coarse material (Russell and Weisz, 1944).

The crystal size of the microcrystalline silicas is much smaller than the apparent grain size produced by grinding. The converse generally holds for the macrocrystalline types of silica. Thus at temperatures between 1000° and 1150°C an appreciable amount of cristobalite is formed from flint in a body, whereas little or none can be detected in a quartzose body below 1200°C (Hughan, 1951).
Both the alpha to beta and beta to alpha cristobalite changes occur over a relatively wide range of temperatures, and are therefore probably less potent causes of denting (cooling cracks) than the quartz conversions.

Finer grinding of the feldspar leads to greater glass development, reduced mullite occurrence in the feldspar pseudomorphs, fewer closed pores and improved translucency (Sane and Cook, 1951).

(c) Time - temperature.

A long soaking time at a given temperature may accomplish about the same degree of maturity in a body as a short soaking at a somewhat higher temperature. However, time is an important factor in the final crystalline texture. Norton (1931) found quartz solution and mullite development to be greater in the long-time runs than in the short ones.

Differences in crystalline texture make physical differences in the ware. Such variations include translucency and mechanical strength. Knowledge as to what service the ware is to be subjected determines the most satisfactory firing cycle. Of course, the most rapid rate of firing will be the most economical one.

(d) Résumé.

The over-all heterogeneous nature of porcelain has been depicted as a mullite-glass matrix containing feldspar.
relics of glass and mullite, quartz grains with their microfissures and solution rims, and pores.

The changes taking place during firing occur at a rate dependent on time, temperature and particle size.

In a whiteware body glass is formed from the melting of feldspar and the subsequent solution of clay and quartz into it (Johnson and Underhill, 1944).

At room temperature then, the amounts of the glass, mullite and quartz phases depend on the initial composition and conditions of firing treatment. A high feldspar content produces larger amounts of siliceous liquid at lower temperatures. Consequently, such a composition vitrifies at lower temperatures than porcelains with larger clay contents.

From the amount and properties of the glassy phase in porcelain, it must be concluded that it is an important constituent of the fired body.

The properties of porcelain are influenced by the inhomogeneity of its glassy phase and its crystalline inclusions. Salmang (1961, p.335) recommends soaking at top temperatures so as to achieve homogeneity. Paradoxically however, he suggests that a uniform, coherent framework of undissolved quartz enhances porcelain's mechanical properties.
Ceramic compounds without glass substance, or with only such a small glass content that the grains still in some fashion rest one upon the other, behave altogether differently from compounds in which the crystals are enclosed with glass or glassy basic material (Bárta, 1965). By replacing the potter's flint in whiteware bodies with a corresponding amount of No. A-2 calcined alumina, Austin et al (1946) increased their transverse strength to a marked degree. But, while the whiteness was increased, their translucency was reduced.
3.3 Translucency.

The ratio of transmitted to diffused light can be used to describe the translucency of an object. Since diffusion of light takes place at boundary surfaces or interfaces, it follows that anything which reduces such irregularities increases translucency.

The primary method by which translucency of porcelain can be increased is to increase the glass content. Maximum translucency was obtained by Chilcote (1934) when he used the ternary eutectic feldspar mixture (microcline 30 per cent, albite 60 per cent and andesine 10 per cent) in a typical porcelain body. Geller and Creamer (1931) found the translucency of vitreous bodies to increase (soda feldspar excepted) with increase in the $K_2O$ content of the feldspar used. The soda feldspar apparently produces a body equal in translucency to those bodies containing feldspars of intermediate $K_2O$ content. The translucency of the highest potash feldspar bodies is appreciably higher than that of the soda feldspar body. However, it must be remembered that increased $K_2O$ content increases refractoriness. Because it is convenient to attain a good result at a lower temperature, the use of a high soda feldspar should be encouraged.
Since mullite crystals are small and differ greatly in refractive index from the matrix, they opacify porcelain bodies most efficiently. The presence of the mullite phase must be discouraged if a highly translucent product is desirable. This is accomplished by increasing the ratio of feldspar to clay in the body formula. Fritted porcelains, such as dental porcelains, having a high feldspar content, are given high translucency by increasing the amount of glass at the expense of mullite development. However, since the presence of mullite strengthens the body, such a process is deleterious in this respect (Sane and Cook, 1951).

Provided that the composition of the glass remains unchanged, translucency increases with increasing grain size of quartz, but heat stability is reduced (Bárta, 1965). Since Salmang (1961, p.337) considers coarse quartz to reduce strength and to confer a grey cast on the fired porcelain, he regards fine grinding of the quartz to be essential. He has quoted a grain size of 10-25 microns for quartz and feldspar in the raw body to produce maximum translucency.

Any procedure which facilitates homogenization of the glass melt should increase light transmission. These procedures would include the addition of substances to lower
the viscosity at a certain temperature or the raising of the firing temperature. Naturally, prior fusion of the feldspar and quartz in the body recipe would also enhance this property. As the indices of refraction of the various phases present approach one another, so translucency is improved.

Internal voids reflect and diffuse light in porcelain bodies. Even in relatively low concentration they opacify markedly. The trapping of insoluble gases within closed pores imposes a limitation on the ultimate density that can be reached during firing in air. Theoretically, these can be reduced by minimizing the amount of any organic binder that may be present, using high compaction pressures, and vibrating selected particle sizes under vacuum. Prefusing the ingredients should also reduce gas evolution during sintering and promote maximum particle shrinkage before moulding. However, none of these approaches entirely eliminates porosity. The only significant improvement, in dental porcelain translucency before 1949, was secured by employing large-particle-size fritted ingredients with the fine particles, which normally would be present, removed (Vines et al, 1958).

Coarsely grained, fritted porcelains sintered in normal atmosphere produce relatively few large voids. Finely grained porcelains sintered under similar conditions
produce many small voids. Since the number and size of voids determine the effect on translucency, large particle sizes in air-firing produce less opacity because fewer voids are present. Unfortunately, the texture may suffer due to the large size of these voids (Vines and Semmelman, 1957 & Vines et al, 1958).

Densifying firing techniques.

Most vitrified ceramics have a dense, impervious surface, but still contain internal voids. However, depending on their fluidity at the maturing temperatures, almost complete density can be effected using densifying firing techniques. That is to say that porcelains with a high crystalline content, or those that are less crystalline, whose matured viscosity is high for any other reason, can impose serious limitations on these firing methods.

With amenable compositions, low-pressure or vacuum-firing, diffusable-gas-firing and pressure-cooling processes have been used to good effect (Vines et al, 1958).

In the vacuum-firing process, most of the air is removed from the interstitial spaces in the body. This provides less hindrance to the firing shrinkage. When air at atmospheric pressure enters the furnace, it compresses the dense vitrified surface of the specimen. Any low-pressure internal voids are then hydraulically compacted.
When the interstitial air is replaced by a furnace atmosphere of a diffusable gas, (e.g., helium, hydrogen or steam) then this gas is sealed in the interstitial spaces. On increasing the temperature the spaces decrease in size and disappear due to dissolution or diffusion of their contents into or through the porcelain.

The size of voids already formed can be reduced by pressure while the porcelain is in a flowable condition. The body itself acts as an hydraulic medium. It is obvious that any subsequent firing of this body must be followed by pressure cooling if the same translucency is to be attained.

A vacuum-sintered body, when reheated into its softening range and cooled under atmospheric pressure is in pressure equilibrium. No change in such a body should be expected.

Reheating a diffusible-gas-sintered porcelain under atmospheric pressure may still further the diffusion process. A higher density in the ware could be obtained.

While large particle sizes produce more translucent air-fired porcelains, small particle sizes give best translucency in vacuum-,diffusible-gas- or pressure-firing. The numerous, small voids so produced are readily made small enough so as not to interfere with light transmission (Vines et al, 1958).
3.4 Fritted Porcelain.

The structure of porcelain is largely determined by the solubility of the quartz, which increases with fineness, and by the reactivity of the glassy phase in dissolving the quartz and secondary mullite. This reactivity is much greater for soda than for potash feldspar (Schueller, 1966). The viscosity of silicate systems retards reactions. The heterogeneity of the substance, which is never desirable, can be controlled by suitable preparation of the raw batch mixture prior to sintering (Abramovici et al, 1966).

Fritted porcelain is used for the casting and vibration manufacturing processes. Fritted ingredients are also found in powdered ceramic porcelains (Lee, 1961, p.73). The raw batch constituents are melted to a glass and then quenched to a frit in water. The principal object of quenching the melt is to facilitate grinding (Andrews, 1961, p.321). It is clear that material treated in this way has many advantages over the unfritted variety. The firing temperature is lowered and sintering can be effected rapidly since further homogenization is unnecessary. A high translucency and smooth texture are readily accomplished.

Abramovici et al (1966) recommend the addition of premelted feldspar to the body mix for thin walled porcelain objects. They found less distortion and greater mechanical strength at lower firing temperatures.
COLOUR AND PIGMENTS.

The three primary attributes of colour are hue, saturation and brightness. "Hue" defines the spectral appearance. It is the quality that permits us to describe a colour in terms of the wavelength of monochromatic light which it matches. "Saturation" is a measure of the purity of a colour possessing hue. The terms pale or deep can be used to describe this characteristic. By "brightness" of a colour is meant the location of the equivalent neutral or achromatic colour in a scale ranging from black to white (McDevit, 1944).

A pigment is a colouring material which is insoluble in its vehicle. This definition excludes dyes which are soluble (Sawyer, 1942). A pigment need not necessarily have hue, as there are many white pigments.

The optical properties - colour, brightness, opacity, and light diffusion - are paramount in the preparation of pigments. These properties derive simply from the refractive index and light transmission or absorption peculiarities of the material and from its particle size (Sawyer, 1942 & Lindroth, 1953). Naturally, the net optical effect will also relate to the optical properties of the matrix and the geometry of the whole system. This geometry would involve the complete particle size distribution curve,
the volume ratio, and the evenness of distribution of the particles in the matrix (Robertson, 1942).

Even when particle size and shape are known, states of aggregation can complicate the picture. Groups of ultimate particles firmly stuck together from a hard aggregate. When they maintain their size and shape during manipulation, they constitute ultimate working units in the pigment suspension. Single particles also come under this classification (Green, 1942).

Ultimate particle interaction may take place when the pigment-vehicle ratio is sufficiently high to allow particle contact. When the pigment is rubbed or ground into the vehicle, especially when the vehicle wets the particles poorly, flocculation may occur. A flocculated pigment structure does not disperse readily into the surrounding vehicle (Green, 1942).

On passing through two different media, light is refracted and a portion of it is reflected at an interface. Throughout the length of each light path absorption also occurs. The amount of light reflection at the interface is governed by refractive indices. Nevertheless, even with an extremely large refractive index difference, only a small portion of light is reflected. At this rate, in order to
reflect substantially all light, a great number of interfaces would be required. A material, dispersed in a continuous medium of different refractive index, reflects more and more light as it is reduced to smaller fragments. Such reflected light would be well diffused.

Of course, for maximum reflection and scattering of light, a particle size about the wavelength of light would be optimal (Sawyer, 1942).

Good covering power, then, depends on suitable particle size and refractive index. However, reflection and scattering do not alter greatly the spectral composition of the incident light. But, absorption of light by the medium or pigment in a pigmented composition reduces the intensity of the reflected light and may alter the spectral distribution or colour of this light. Consequently, a white pigment must have a low and not particularly selective absorption. It must be transparent and colourless.

When the pigment is not transparent, absorption competes with reflection - scattering. If absorption is selective, the pigmented composition becomes coloured. A deep colour is produced by intense absorption of the wavelengths concerned. Then almost none of these wavelengths is returned from the pigmented composition by interfacial
reflection and scattering. A coloured pigment, therefore, has a very high absorption coefficient.

As for white pigments, covering power of a coloured pigment varies with refractive index and particle size. All things being equal, depth of shade varies more or less with particle size. This variation is great for materials of low absorption and small for materials of high absorption (Sawyer, 1942).

It can be readily understood that if a pigment dissolves in its vehicle, its particle size is reduced to molecular dimensions and its covering power is thereby lost.

Stability at elevated temperatures and inertness in silicate systems is required of pigments to be used in ceramics. This limits the palette of available colours. One of the most successful crystal structures for the development of a wide variety of stable colours is the spinel structure (Yamaguchi et al, 1954). The spinels are a family of minerals of the general chemical formula $R_0R_2O_3$, in which the divalent metal may be one or more of Mg, Fe, Cu, Zn, Ni, Co, or Mn and the trivalent metal may be one or more of Al, Fe, Mn, Ga, or Cr. They crystallize in the isometric system commonly as octahedra or dodecahedra. Simple spinels (consisting of a single divalent and a single
trivalent metal) rarely appear in nature, but they may be formed synthetically (Fréchette and Andrews, 1944).

Host lattices of ZrO₂ and ZrSiO₄ that can accommodate rare earth ions in solid solution have also been used as stable colours (King and Tesar, 1953). Spinels and other coloured crystals are usually formed by calcining finely divided and thoroughly mixed oxides at 1100° to 1400°C in a neutral or oxidizing atmosphere for one to eight hours (King and Tesar, 1953 & Yamaguchi et al, 1954).

Careful studies have established the existence of definite and quite stable compounds in some cases, and in others there is apparently the formation of solid solutions. Exact component ratios of compounds are not held in empirical compositions. An excess of one or more components is probably present most of the time, so that the net result is, more than likely, an intimate admixture of several types of coloured compounds (Robertson, 1942).

Mostly, colouring or opa quing glassy substances is done by means of solution, colloidal, or precipitation colours rather than by pigmentation in the ordinary sense. Generally speaking, the reason for the scant use of preformed pigments in solid glass is simply that molten glass at its firing temperature attacks almost every known substance. Attack and consequent destruction are exaggerated when pulverized pigments
are subjected to high temperatures for fairly long time cycles (Robertson, 1942).

Introduction of the pigmented material at a late stage in the glass making or fritting operation would improve this situation. When pigments are destroyed their disappearance may be due to pure thermal change, to oxidation, volatilization, double decomposition, or to solution.

Most of the factors governing the development of the colours in ceramic compositions are understood only in an empirical sense (McDevit, 1944 & Yamaguchi and Tomiura, 1954). Great variation in the destructive effect of molten glass on the pigment particles is experienced. Furthermore, this extent of reaction is not by any means a uniform characteristic of a given pigment. Even for a particular pigment, a wide range of variation depends upon the composition of the glassy matrix and the temperature and time in contact (Robertson, 1942). Generally speaking, the lower the temperature, the less the reactivity.

In consequence of these complexities, the study of pigmented systems has mostly been applied empirically (Sawyer, 1942). The selection of pigments, their proportions and their blending is approached on the basis of specialized performance tests purely by trial and error.
52.

5. DENTAL PORCELAIN.

5.1 History.

Porcelain was first made in China more than twelve hundred years ago. Pottery, or earthenware, is a much older material.

Most Chinese porcelain was made from kaolin and petuntse (pai-tun-tzü), a feldspar. Such a formula is termed hard-paste (or true) porcelain (Savage, 1963). This resonant and translucent ware was highly prized in Europe, even though soft-paste (or artificial) porcelains, such as maiolica from Italy and French faience, were flourishing. Not until shortly after 1700 was the nature of these Chinese materials recognized at Meissen, in Saxony (Savage, 1963). The middle of the eighteenth century saw porcelain production in France at Sèvres and later, in England, with Wedgwood and Derby. Bone china also originated about this time in England.

In 1774, Duchateau, a French apothecary, conceived the idea of a denture made from hard porcelain. He enlisted the aid of a porcelain manufacturer in Paris. However, the first attempts were disappointing. In 1788, Dubois de Chémant, a Paris dentist, improved the process and secured a patent for the sole rights to manufacture mineral teeth (Capon, 1927). These were apparently of one colour.
In 1808, Dubois Foucou published his results of an experimental study of the colour problem in porcelain. In the same year, Guiseppangelo Fonzi, an Italian dentist, invented platinum pins for anchorage (Capon, 1927).

Prior to 1838, dental porcelain was a relatively opaque, white material resembling other whitewares. At this time, Elias Wildman formulated a more translucent porcelain in colours approaching those of natural teeth (Clark, 1939).

Dental porcelain manufacture has always been a highly specialized industry. Manufacturers have jealously guarded any specific information about the field. Even today few details are widely known. There has been little attempt by the dental profession to investigate dental porcelain's properties in a scientific way. Over the years, development has continued as an art based on empirical observations.

Nevertheless, despite this attitude, remarkable achievements have been made in the aesthetic nature of the material. In 1949, the Dentists' Supply Company of New York invented vacuum-firing of porcelain teeth. This method produced dense, translucent pore-free porcelain. Claims of superior strength were also made (Vines and Semmelman, 1957).
For some time, there has been an obvious need for improvement in strength of dental porcelain. While modern porcelains provide biologically and aesthetically acceptable dental restorations, they require ideal situations to survive masticatory stresses. Because of this, the prospect of using enamelled metal crowns has been embraced enthusiastically by the profession. In 1965, McLean and Hughes suggested dispersion-strengthening dental porcelain with alumina crystals. While small alumina grains should increase strength, they also increase opacity. The authors claim to have produced a porcelain with the grain size of its reinforcing phase selected such that the translucency is acceptable, while the modulus of rupture is approximately double that of normal dental porcelains.

Today, a reawakening of interest in dental ceramic materials has begun. Needless to say, any work in this field will be stimulating to the investigator and rewarding to the profession.
5.2 Composition of Dental Porcelain.

As I have mentioned already, science and technology dictate composition. Requirements for forming, requirements for successful firing, requirements for final properties and economic considerations have undoubtedly been responsible for the evolution of today's dental porcelain compositions.

Only small and simple shapes are involved in the forming process. Hence, plasticity of the green ware is relatively unimportant and drying shrinkage is undesirable. These factors would allow for a considerable reduction in the proportion of the clay content. Added to this, the translucency that is demanded is enhanced by lowering or eliminating any mullite formation in the fired body.

Fritting dental ceramic materials simplifies the sintering process, while the product is rendered more homogeneous. Since colour matching is an important requisite of dental porcelains, low-temperature, short-time firing schedules are obviously desirable. Superimposed on this, colour rendition and translucency has been standardized by vacuum-sintering (Gatzka, 1953).

Having little or no dry strength when compacted, fritted ceramic powders may rely on selected particle sizes
and/or the inclusion of an organic binder as aids in the forming process. If the particle size distribution is selected carefully, the need for a binder would be obviated.

Like other ceramic compositions, the ingredients and their proportions used in dental porcelain vary according to the type needed. Although many differing classifications have been offered (Felcher, 1934; Clark, 1935 & Bartels, 1963), I prefer to think of dental porcelain as a specialized white-ware.

For over a century dental porcelains have been compounded with a feldspar base (Lee, 1955). Since the mid-forties the trend has been towards the lower fusing compositions (Bartels, 1963). For reasons already supplied, the demand for translucency precludes the incorporation of any significant quantity of kaolin. Also, if need be, the quartz content and its crystal size could be regulated to control translucency and thermal expansion compatibility. This leaves feldspar as the basic ingredient.

Hodson (1957, 1959(b)) confirmed this situation. She examined 12 porcelain powders including high-, medium- and low-firing varieties of the body, opaque, translucent, and enamel types. Apparently, two of the high-fusing porcelains consisted of raw minerals. The others contained
glassy particles, some of which were associated with mineral grains. Microcline, albite and quartz crystals were identified. However, Hodson (1959(b)) found quartz only in small quantity. In one low-fusing, body porcelain powder she noted mullite needles in feldspar pseudomorphs. This occurrence can only result from some kaolin content (see p.34). The most predominant phase found over all was glassy.

Thus, it is obvious that dental porcelain powders can be supplied in the unfritted or fritted forms. Mixtures of fritted and unfritted materials could also be made. The recommended firing temperatures of the different powders depend upon the percentages of ingredients used and their previous treatment. The high-fusing materials are mostly unfritted (Lee, 1961, p.73).

The following representative formula for a normal porcelain body for artificial teeth was supplied by Gatzka (1953):

- 70 - 80% albite (from Norway or Canada)
- 3 - 4% kaolin and the remainder quartz plus colouring additions.

Presumably, this is a European composition which is fritted. Potash feldspar and nepheline syenite are commonly used ingredients in the United States. Besides quartz and kaolin,
auxiliary materials include alumina, tin oxide and zirconium oxide when opacity is required. Borax, boric acid, sodium carbonate, fluorspar, lithium carbonate and zinc oxide are some of the fluxing materials (Lee, 1961, p.72 & Salmang, 1961, p.335). Manufactured pigments and metallic oxides of iron (Fe₂O₃), copper (CuO), titanium (TiO₂), nickel (NiO), cobalt (CoO) and uranium (U₃O₈) are used for colouring dental porcelains. Pigments used for shading porcelain teeth are concentrated colour frits, made of the enamel composition, and very finely ground (Lee, 1961, p.74). These highly pigmented frits are added to the enamel or body fritted compositions as required.

All modern dental porcelain powders are in the lower-fusing classes. Economics undoubtedly governed this trend. The effects of the various fluxing oxides differ considerably. Some increase opacity, e.g., TiO₂ (Salmang, 1961, p.132), others affect the coefficient of thermal expansion, e.g., K₂O, Na₂O (Geller and Creamer, 1931). Thermal shock resistance can be improved by substituting MgO for CaO and alkali in the body formula (Salmang, 1961, p.339). While it seems that, in the early days of lower-fusing compositions, fluxes appeared as free materials in the raw composition (Felcher, 1932, p.35), it is reasonable to assume
that such a practice has been discontinued by the manufacturers. Any fluxing materials used would undoubtedly be added before fritting.

The use of fluxing materials appears to be unnecessary if a high-albite or nepheline syenite composition were fritted before use in the dental laboratory.

Lee (1961, p.74) has supplied typical formulae for fritted enamel and body porcelain powders.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Enamel %</th>
<th>Body %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feldspar</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>Calcined Kaolin</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Silica</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

Presumably, these are representative of American dental porcelains. Where necessary, colour frits would be added.

The body composition is intended to have a slightly higher coefficient of thermal expansion than the enamel. This arrangement would produce a fired denture tooth in a state of compression. However, this condition may not necessarily be advantageous for a porcelain jacket crown.

Generally speaking, modern dental porcelains contain a glass frit as a batch constituent. Vitrification occurs through natural softening of the glass. They are materials that are self-glazing or that can be fire-polished.
Body vitrification would be directly related to the amount of glass present and inversely to its tendency to devitrify during firing (Goodyear and Russell, 1966).

While feldspathic porcelains are quite satisfactory in most respects, they are sensitive to rapid thermal change. In 1955, Lee reported the development of a porcelain using fused silica as a low-expansion basic material. These bodies would not check or crack as readily under localized heat development during grinding operations.

Recently, Hughes and McLean (1965) added 40 to 50 per cent alumina crystals to a low-fusing porcelain so as to produce a stronger, aluminous porcelain core material.
5.3 Physical Properties of Dental Porcelain.

(a) The forming process.

Matching the graduating shades displayed in natural teeth is a fundamental requirement of dental porcelain. It is for this reason that the forming process is unique and highly specialized. Deployment of the pigmented frits and the fired form are determined by individual demands.

The material is supplied as a dry powder. From this a slip is formed with distilled water. Although alcohol and glycol (Sayre, 1938) have been tried as vehicles, water, because of its low viscosity and high surface tension (Clark, 1935 & Klaffenbach, 1939), provides the most suitable medium. Soaking the particles in the vehicle, although apparently necessary for unfritted porcelains (Gill, 1932), does not appear of any value to the preparation of modern fritted slips. Air inclusion is conscientiously avoided, and the consistency of the thin paste is maintained (Clark, 1935).

These pigmented slips are moulded over a platinum matrix to form the crown, and the assembly is fired.

The methods used in condensing dental porcelain have been hand vibration without a mould, gravitation of the particles by absorption of the vehicle, spatulation or
ironing, whipping, hand vibration into a mould, and mechanical vibration into a mould. Wet vibration into a mould gives the most uniform results (Gill, 1932; Clark, 1935; Klaffenbach, 1939 & Baker, 1960). However, in experienced hands and with proper control of water content, an extremely well condensed porcelain crown build-up is possible using any combination of the other practices.

Many partial mould vibratory techniques have appeared in the literature. In 1946, Gill introduced a method where a full mould was made. When wet vibration is used, colour distribution is always a problem. The only way this can be overcome is to fire each colour application separately. Plainly, increasing the number of firings can overtax the stability of the pigments in the first layers.

(b) Test specimen formation.

Any test measures only the properties of the test piece, so it is important for the test piece to be prepared in a consistent and, as far as possible, reproducible manner. Even with the greatest care it is impossible to eliminate all variation in samples. In view of these facts, surely it is the duty of every investigator to simulate practical conditions in some way, while providing for relatively easy duplication of multiple specimens. Needless to say, having
made an effort in this direction, he must report the manufacture of his test samples in detail.

Many workers in the dental ceramic field have failed in this direction. In 1932, Gill used specimens 13 m m. X 10 m m. X 4 m m. without describing their formation. Felcher, in 1934, gave no dimensions for his split iridio-platinum ferrule. Skinner and Fitzgerald (1938) did take pains to describe the formation of their samples. Removable glass slabs set in a hydrocal block were used to form rectangular specimens, 19.88 m m. X 9.00 m m. X 3.96 m m. A standardized, wet vibration method of condensation produced bodies which were fired on platinum foil in a dental furnace. In the same year Sayre (1938) employed a cylindrical split mould 10 m m. high and 6 m m. in diameter, and a glass-lined mould with removable walls 31 m m. X 5 m m. X 5 m m. Both types of test pieces were fired on 0.001" platinum foil. A flat rectangular specimen was manufactured by Klaffenbach (1939) from a metal mould. In 1957, Sacchi and Paffenbarger employed a metal cylindrical mould 7 m m. X 4 m m. for measurement of volumetric shrinkage and compressive strength. Hodson (1959) produced discs from a mould 6.5 m m. in diameter and 3 m m. deep and bars, $1\frac{1}{2}''$ X $3/16''$ X $3/16''$, from a rubbery mould (1959(a)), and more recently, McLean and
Hughes (1965) described three types of specimens: rods, bars, and discs. Compaction of a weighed quantity of powder mixture was done with a punch into a 1/4" diameter hardened steel die at a pressure of 14.5 tons per square inch to produce the rods. Wet vibration into a square-section split steel mould, 30 m m. X 5 m m. X 5 m m., produced the bars. The discs were prepared by vibrating wet porcelain mixture into a circular mould whose dimensions were not provided. While Hodson (1959, 1959(a)) fired test specimens on platinum foil and on fine silex, McLean and Hughes (1965) used "1/4"-thick asbestos sheeting" impregnated with -20 micron calcined alumina as the tray.

From the above information, it is clear that there has been no attempt made at standardization. Few of the authors, if any, have tried to relate the volume of the fired specimens to approximate volumes involved in the field. It seems that firing schedules would be seriously affected by large variations in size. These schedules should show some relevance to porcelain crown manufacture. McLean and Hughes (1965) seem to have been the first investigators in dental porcelain to have considered seriously the variables involved in specimen manufacture. Nevertheless, the specimen sizes they used still seem to be arbitrary.
(c) Firing dental porcelain.

Modern fritted dental porcelain slip is condensed and carved into a crown shape on a platinum foil matrix and the assembly is then fired in a small electric furnace. The firing cycles are short and the temperatures involved are relatively low. These changes have made it possible to replace the expensive, platinum-wound muffles, which were required for unfritted compositions, with others wound with cheaper base metal alloys. A small fireclay crown stand placed under the platinum matrix is used to support the porcelain jacket crown during sintering.

Firing schedules relating to unfritted materials (Gill, 1931; Felcher, 1932; Clark, 1935; Argue, 1939; Klaffenbach, 1939 & Sayre, 1944), or indeed any property associated with these porcelains, must not be allowed to confuse the situation today. While these descriptions are of interest both physically and historically, they do not necessarily apply to modern fritted dental porcelains. Since a high degree of homogenization has been effected in the fritting process, firing the glassy, fritted powder is greatly simplified.

Before firing the green article, careful drying is essential. Particle sizes and the particle size
distribution will influence the rate of desiccation, all things being equal. With the small bulk involved, drying the ware is a relatively simple process.

In view of the rapid rate of sintering fritted powders, and the relatively simple process involved, I should very much like to see the classical, descriptive stages of firing applied only to those materials for which they were intended (Argue, 1939; Johnson et al, 1960 & Skinner and Phillips, 1960). Two stages would suffice in describing the sintering of modern dental porcelain, viz.,

(i) the absorbent stage and

(ii) the impervious or vitrified stage.

Such terms are applicable to both air- and low-pressure sintering. As the sintering rate would depend upon the bulk of the ware, the particle sizes in the powder, the composition of these particles, the degree of densification of the greenware, the temperature and the time, the adoption of such readily detectable stages of firing could be a distinct advantage. Whilst, traditionally in dentistry, "glazing" has occupied its place in the stages of firing, the rate of development of such a surface condition depends on one more factor, viz., surface smoothness of the ware.

Gloss and smoothness are terms (Russell and Rowlands, 1953(a))
which could be used to describe the degree of fire-finishing or "glazing".

Much attention has been focused on the development of gases from decomposition of the feldspars in the overfired ware (Clark, 1935; Sayre, 1944, & Hodson, 1959(a)). Today, both the careful selection of the raw feldspar mineral and its homogenization in the fritting process, would minimize this occurrence. However, colour stability and maintenance of form are still affected by overfiring modern dental porcelain.

Thermal expansion of dental porcelain would be affected by the Na₂O - K₂O ratio and by the percentage of uncombined silica (Geller and Creamer, 1931). High soda feldspar content provides a higher thermal expansion in vitreous bodies. Over the years great emphasis has been placed on slow cooling in order to relieve strain in the crown (Felcher, 1934; Skinner and Fitzgerald, 1938; Klaffenbach, 1939; Sartori, 1939; Gill, 1940 & Gill, 1946). Greater strength was the aim.

Today's dental porcelains are so formulated that relatively rapid removal of the article from the furnace after firing is possible. The size of the crown would militate against the setting up of large temperature
gradients. Aluminous dental porcelains are remarkably resistant to thermal shock on rapid cooling from furnace temperatures (McLean and Hughes, 1965).

(d) Condensation and firing shrinkage of dental porcelain.

Firing shrinkage is intimately related to condensation, and particle size affects both. A fractional void space of about 25 per cent can be reached when a selected particle size distribution provides optimal packing. However, even under these conditions one would expect a completely dense ceramic to be associated with a 25 to 40 volume per cent or about 8 to 13 linear percent firing shrinkage (Kingery, 1963, p.35). The porcelain with a high fraction of small particle sizes tends to shrink most (Clark, 1935).

The proportion of different particle sizes in the powder controls its working properties. Apart from packing solidly, such preparations with optimal particle size distribution interlock and obviate the need for a binder.

Despite serious attempts to increase densification by selection of particle sizes, reduction of organic binder, and pressure methods of condensation (Clark, 1935), before 1949, sealed porosity in the fired body was inevitable.
Greater translucency was effected in these porcelains by employing coarsely grained powders. This was a compromise (see p.42).

Vacuum-firing can produce almost complete densification. All things being equal, the firing shrinkage must be greater. Finely grained powders, while they are more manageable, aid the process (see p.44). Translucency is very high indeed. Mixed, selected particle sizes result in both maximum density and minimum firing shrinkage (Vines et al, 1958). Vines et al (1958) conducted microscopic porosity measurements on dental porcelain. They found:

<table>
<thead>
<tr>
<th></th>
<th>AIR-FIRED</th>
<th>VAC-FIRED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average number of bubbles per sq. mm.</td>
<td>73.7</td>
<td>8.1</td>
</tr>
<tr>
<td>Average maximum diameter (mm.)</td>
<td>0.055</td>
<td>0.022</td>
</tr>
<tr>
<td>Porosity (per cent)</td>
<td>4.50</td>
<td>0.08</td>
</tr>
</tbody>
</table>

These figures tally very closely with those published by Semmelman in 1957. Uniformity of colour is easier to achieve in vacuum-firing densifying techniques. Apart from the increased translucency, the fine powders involved allow for better dispersion of the pigments. The diffusible-gas-firing techniques have been mentioned (p.43). These densifying methods are comparable to vacuum-firing, but they are more costly. Hydrogen produces a reducing atmosphere which is
detrimental to the pigments. Helium is much safer while the colour is more stable (Lee, 1961, p.80). All things being equal, the apparent colour of the porcelain changes when it is vacuum-fired.

Internal voids have been attributed to (Vines et al., 1958):-

(i) the inclusion of air in the slip;
(ii) muffle atmosphere replacing binder or water in the interstices of the green ware;
(iii) evolution of gas from a variety of sources, and
(iv) overfiring.

Hodson (1959(b)) traced the development of bubbles in some air-fired porcelains to feldspar grains. Many were small when first formed, but they expanded with further heating. The largest voids ranged from 0.03 mm. to 0.22 mm. The composition of porcelain affects the firing shrinkage, e.g., fluxed, low-fusing powders, those containing binders, and fritted compositions. Under identical conditions, poorly condensed articles shrink most. Gill (1932), Sayre (1938) and Argue (1939) agree that the water/powder ratio in the slip should be kept to a workable minimum for optimal condensation.
Clark (1935), using fluxed and non-fluxed, presumably unfritted, porcelains, found "contraction" to vary from 9 to 20 per cent. These were air-fired porcelains, and he regarded all shrinkage above 10 per cent to be within the operator's control. These days gas evolution is minimal and careful handling can always avoid air inclusion in the slip.

Sayre (1944) found the volumetric firing shrinkage of high-fusing porcelains to vary as much as 10 per cent. This variation depended on the method of condensation. Vibratory condensation produced the greatest density and consequently the least shrinkage (Gill, 1932 & Clark, 1935). Moldal (1939) found an average volumetric shrinkage on the porcelains he fired to be about 34.6 per cent. Sartori (1939) quoted a similar value (viz., 34 per cent) up to four firings. Skinner and Fitzgerald (1938), testing high-, medium- and low-fusing porcelains, found the low-fusing porcelains to shrink more than the higher-fusing varieties, with one exception. These were air-fired and the volumetric shrinkage ranged from 31.7 to 39.5 per cent. In 1957, Sacchi and Paffenbergar recorded little difference in volumetric firing shrinkage between the low-fusing porcelains (38 per cent) and one high-fusing (37 per cent).
However, Hodson in 1959(a) showed low-fusing porcelain to have the highest shrinkage at all firings. The high-fusing bodies had least. At high temperatures, volumetric shrinkage decreased whereas linear shrinkage increased.

Using aluminous porcelain (40 per cent alumina), McLean and Hughes (1965) found the porosity of "green" compacts (bars condensed by wet vibration) to average 43.8 per cent. Air-fired specimens averaged 11.9 per cent porosity while vacuum-firing reduced it to 5.4 per cent.

These authors claim that the addition of alumina to dental porcelain decreases the firing shrinkage and markedly increases the resistance of the porcelain to pyroplastic flow.

(e) Specific gravity.

Moldal (1939) observed variations in specific gravity in different brands of opaque dental porcelain. The readings were higher than the specific gravity of translucent types. Sayre (1938) reported the variation in apparent specific gravity of high-fusing porcelains, regardless of the method of condensation or the consistency of the mix, to be so slight as to be of little practical importance. Skinner and Fitzgerald (1938) investigated porcelains from the high-, medium- and low-fusing varieties. Under
identical conditions of condensation, they found little difference in the apparent specific gravity of the various materials.

Hodson (1959(a)) showed that the true specific gravity of medium- and low-fusing porcelains underwent little change from the unfired to the fired powders. Both were fritted porcelains. Such was not the case for the unfritted high-fusing material. She found the apparent specific gravity to decrease in all specimens in an overfired state. The low-fusing had the greatest shrinkage and the lowest porosity.

A density or specific gravity reading does not measure porosity directly, but rather the effect which porosity has on weight. In different porcelain shades, the presence of different pigments can obscure the effects due to porosity (Semmelman, 1957). For a particular material, a measure of porosity can be gained when apparent specific gravity of the whole specimen is related to true specific gravity of the porcelain. Porous volume is expressed as a percentage of total volume.

Point counting, or the estimation of porosity from the population and size of the pores on the polished surface of a fired specimen, depends upon the assumption that the
pore distribution in the plane of measurement is representative of the whole body. Such is not the case. McLean and Hughes (1965) showed a range in the density which may occur in fragments of the same specimen. They found the weight method (apparent specific gravity in water) to be a satisfactory way of estimating porosity.

It is evident that much of the available, detailed information on condensation, firing shrinkage, and specific gravity is antiquated and possibly irrelevant to materials in use today.

(f) The strength of dental porcelain.

(i) Transverse strength or modulus of rupture.

In 1938, Skinner and Fitzgerald found the transverse strength of high-, medium- and low-fusing dental porcelains to be very similar. The specimens tested were made in a mould, 19.88 mm. X 9.00 mm. X 3.96 mm., from four different brands of porcelain. The values published ranged from 3,700 to 8,300 p.s.i. with an average of about 7,200 p.s.i.

Sartori (1939) tested a popular high-fusing material. The specimens were condensed into a rectangular, glass-lined mould, 20.63 mm. X 10.53 mm. X 7.17 mm., by vibration and spatulation. He found the transverse strength
to increase to 9,200 p.s.i. at the second firing only to
decrease to 6,900 p.s.i. on the eighth firing. Sartori
associated these results with inherent strains set up during
cooling. I feel this could be so, especially if one
relates it to the quartz content. In all cases the current
was shut off and the furnace allowed to cool to 537°C (1000°F),
when the door was opened to allow more rapid cooling to 260°C
(500°F), whereupon the specimen was removed from the furnace.
At least three tests were made for each firing method.

Veneer glazing with a lower firing ceramic coating
increased the strength to 10,400 p.s.i. Although Sartori
connected this finding with the relief of stresses by the
heat treatment involved, it seems that the development of a
compressed glaze layer would have more influence on this
strengthening (Russell and Rowlands, 1953(b)).

Moldal (1939), using a mould similar to that
described by Skinner and Fitzgerald (1938) with dimensions
20.340 mm. X 10.310 mm. X 5.082 mm., found some variation
in the transverse strength of early, opaque porcelain. He
tested two high-fusing, and one low-fusing, opaque porcelains
and recorded values ranging from 8,300 to 10,400 p.s.i.
These early, opaque porcelains appeared to be a little
stronger than the translucent types tested by Skinner and
Fitzgerald in 1938.
In 1944, Sayre regarded the modulus of rupture test to approximate forces acting during mastication. It is a good, relatively static test. On high-fusing specimens, 31 mm. X 5 mm. X 5 mm. before firing, Sayre (1938) found the greater the shrinkage, the less the transverse strength would tend to be. His results ranged from 4,200 to 8,400 p.s.i.

Seth, in 1948, reported the modulus of rupture of dental porcelain to be 7,100 to 8,300 p.s.i.

Hodson (1959(a)) made porcelain bars (2 of each porcelain), the shape and dimensions of which (viz., 1/2" X 3/16" X 3/16" before firing) were chosen specifically for testing transverse strength. She rejected individual values that exceeded the average by plus or minus 15 per cent. Removal of surface glaze reduced strength in two porcelains, but had no effect on the third. Although the porcelain with the greatest porosity was the weakest, strength appeared to be independent of porosity.

**AIR-FIRED PORCELAINS (GLAZE-FIRED) (Hodson, 1959(a)).**

<table>
<thead>
<tr>
<th>Porcelain Type</th>
<th>Strength (p.s.i)</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-fusing porcelain</td>
<td>8,290</td>
<td>5.9%</td>
</tr>
<tr>
<td>Medium-fusing porcelain</td>
<td>9,164</td>
<td>4.3%</td>
</tr>
<tr>
<td>Low-fusing porcelain</td>
<td>8,887</td>
<td>1.5%</td>
</tr>
</tbody>
</table>
Hodson found vitreous porcelains to be of similar strength as well as structure. The low- and medium-fusing porcelains appeared to be unaffected by overfiring, whereas the unfritted, high-fusing porcelain showed a loss of strength, which apparently is related to the increased porosity involved. Further controlled investigation into the effect that surface conditions and porosity have on strength are required.

The measured strength of dental porcelain must be limited by the most highly stressed flaw in the area under load. In 1958, Saklad suggested a visual technique for disclosure of gross surface imperfections using dye penetrants.

The liability dental porcelain has to fracture under low stress is its main disadvantage. On the basis of factors such as fusion temperature, resistance to thermal shock, mechanical strength in the fused state, thermal coefficient of expansion, bonding properties with dental porcelain, colour and aesthetic values, McLean and Hughes (1965) selected alumina to reinforce dental porcelains of similar thermal expansion. They quote the modulus of rupture of a typical porcelain to be 3,700 to 12,000 p.s.i., while that of recrystallized alumina is 55,000 p.s.i.
Also, the coefficient of expansion from 0 to 200°C for alumina is $6.2 \times 10^{-6}$ per degree C., while most porcelain varies from 6.4 to $7.8 \times 10^{-6}$ per degree C.

Bars, rods and discs were made as test specimens (see p.64). Discs were manufactured by a wet vibratory technique, and ground to one mm. thickness, and tested according to Timoshenko's (1959) method of determining the maximum breaking stress of a specimen disc. These authors regard this test as having a certain practical similarity to stresses which are likely to occur in a thin tooth section such as a jacket crown. Their results showed no significant difference between low- and medium-fusing porcelains, air- and vacuum-fired. Values ranged from 8,029 p.s.i. to 11,313 p.s.i.

When testing bars (30 mm. X 5 mm. X 5 mm., before firing) of aluminous porcelain (40 per cent alumina) they observed the modulus of rupture to increase with decrease in porosity. A general increase in strength with increasing specific surface or fineness of the alumina content was also claimed. No indication of the spread of the results was given.

Since an increase of specific surface area of the alumina crystals increases opacity, careful selection of the
alumina crystal size range is required to provide an acceptable compromise between translucency and strength. With vacuum-firing, McLean and Hughes (1965) claim to have produced a dental ceramic powder which will give a light transmission, on a one mm. thick disc, of the order of 20 per cent and with a modulus of rupture in excess of 18,500 p.s.i.

Rods of dental porcelain, which were compacted at a pressure of 14.5 tons per square inch and fired, showed a dramatic fall in strength when the surface glaze was removed by grinding. McLean and Hughes (1965) related this to the integrity of the surfaces of the pressed rods. Such conditions could not be achieved in dental ceramic practice. There was no significant difference in strength between the vacuum- and air-fired rods.

On the other hand, tests on ground bars showed vacuum-fired specimens, prepared by wet vibration, to give higher modulus of rupture values than those which were air-fired. However, these specimens were not made from the same porcelain.

McLean and Hughes (1965) illustrated that aluminous porcelain rods were not so dependent upon surface conditions as pure porcelain rods. Mild abrasion does not appear to
have such a marked effect on fall in strength. McLean and Hughes (1965) did not mention this point, but their results show that the aluminous rods (glazed) were not significantly stronger than the porcelain rods (glazed), while in the ground condition they were indeed.

In the bar specimens series, the results of nine tests on ground, air-fired, low-fusing porcelain were summarized as a mean of 10,291 p.s.i., with a standard deviation of 591 p.s.i., while ten ground, aluminous porcelain, low-fusing, air-fired samples appeared as 14,979 ± 876 p.s.i. From these results published by McLean and Hughes (1965), this relationship of the increased strength of aluminous porcelain (40 per cent alumina) over that of ordinary dental porcelain seems to me to be approach-ing one that is acceptable for all practical purposes.

(ii) Compressive strength.

In 1957, Sacchi and Paffenbarger carried out compressive tests on specimens about 7 mm. high and 4 mm. in diameter. An average of five readings for each test produced identical results of 48,000 p.s.i. for a low- and a high-fusing porcelain.
(iii) Impact strength.

It seems that the modulus of rupture test has been accepted by most to approximate the forces acting on porcelain crowns during mastication. Hodson (1959(a)) regards dental restorations to be subjected more to impact forces, but there are those who disagree (Pitt Roche, 1949).

There is no reliable method of measuring the impact strength of ceramic materials. However, Fox et al (1960) & Kulp et al (1961) developed a highly empirical impact test for dental porcelains. Weights of known hardness were dropped down a vertical chute from increasing elevations onto symmetrically shaped conical porcelain specimens. They found, under these very special conditions, that vacuum-fired porcelain consistently yielded 50 to 117 per cent higher impact strength readings than air-fired porcelain. They attributed this to the higher density, a diagnosis that is supported by Pettrow (1961). Air-fired specimens were usually shattered, while the average vacuum-fired samples suffered only minor chipping. These authors regard field reports on porcelain jacket crowns to support their findings. Air-fired, translucent porcelain was weaker than the air-fired, earlier, more opaque porcelain. McLean (1965) states that aluminous dental porcelains provide a
considerable increase in resistance to impact, thermal shock, and pyroplastic deformation over standard porcelains.

(g) Comment on strength of dental porcelain.

From the foregoing review it is clear that the strength of ordinary dental porcelain has a wide range. Realizing this situation, it is distressing that very few authors have presented their data in a critical and descriptive manner. Few attempts at standardization of the testing procedures have been made.

This confused situation needs to be corrected if intelligent use of these dental materials and progress towards a better understanding of them are to be made.

(h) Hardness.

The table below was compiled from information that was gleaned from the literature:

<table>
<thead>
<tr>
<th>TOOTH ENAMEL</th>
<th>FORCELAIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.H.N.</td>
<td>K.H.N.</td>
</tr>
<tr>
<td>415</td>
<td></td>
</tr>
<tr>
<td>420</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>343</td>
</tr>
</tbody>
</table>
It is obvious that the hardness of dental porcelains is more than sufficient to meet the demands. They resist attrition more than tooth enamel. To counteract this resistance to attrition, Pitt Roche (1949) has advised clinicians to roughen the porcelain areas of occlusal contact by grinding. This is intended to present an abrasive surface to wear opposing natural teeth so as to maintain the balance of occlusion.

(i) Coefficient of thermal expansion.

The thermal coefficient is a major factor in the ability of porcelain to resist thermal shock during fabrication or grinding. Thermal expansion is affected by the Na₂O - K₂O ratio, and by the percentage of uncombined silica present in the body (see p.36). The alkali content appears to be the dominating factor. The thermal expansion is governed by the glassy phase acting on the crystalline silica. Increases in the alkali content reduce the effect of quartz, thus tending to give a regular expansion (Rado and Edgar, 1960). It is possible to alter thermal expansion at will by changing the amount and viscosity of the glassy phase. Vitreous bodies containing high soda feldspars have the highest thermal expansion (Geller and Creamer, 1931). In predicting thermal expansion behaviour, the microscopic
examination of thin sections is not always a reliable guide (Rado and Edgar, 1960).

No relation is known to exist between the degree of strain in the quartz grains and its possible effect on mechanical strength, but two points seem to be established (Smothers, 1961): (1) wet grinding creates appreciably less strain in quartz grains enclosed in the glassy matrix than does dry grinding, and (2) refiring under these conditions does not seem to relieve all strain which may be created in quartz grains by dry grinding. The development of a material with better grinding characteristics has been recorded (Lee, 1955). The low-expansion basic constituent used was fused silica.

McLean and Hughes (1965) quote the coefficient of expansion of a typical porcelain (0 to 200°C) to be from 6.4 to 7.8 x 10⁻⁶/°C. This range coincides with results Sacchi and Paffenbarger (1957) determined from 30°C to 400°C, viz., 7.8 x 10⁻⁶/°C for a low-fusing and 6.4 x 10⁻⁶/°C for a high-fusing porcelain. Although Seth (1948) and others estimate 4.1 x 10⁻⁶/°C to approximate the thermal coefficient of expansion, this value appears to be too low.
(j) Solubility.

Sacchi and Paffenbarger (1957) tested the solubility of powdered, fused dental porcelain in boiling four per cent acetic acid. Although there were slight differences in the solubility of different porcelains, none of them showed sufficient to have any clinical significance.

(k) Tissue tolerance.

All things being equal, tissue tolerance of materials is related to surface characteristics and solubility. Allison and Bhatia (1958) and Pini (1958) demonstrated that oral tissues endure properly glazed and contoured porcelain very well. This acceptability of porcelain is well documented in the literature (Seth, 1948; Pitt Roche, 1949; Bastian, 1959 & Bartels, 1963).
6.

GLASS.

6.1 Physical Properties.

The development of porcelain is based on the formation of a highly viscous aluminosilicate glass from the feldspar. That is, glass provides the bond in porcelains.

The possibility that such matter may substantially influence the physical behaviour of dental porcelains is obvious. Claims that these materials are essentially glasses have been made (Lehman, 1961, 1963 & Hodson, 1959(b)). The matrix is a glass, and it is from this dominant phase the high translucency and relative homogeneity of modern dental porcelain is derived.

Bearing these thoughts in mind, it is logical to expect some gain from a brief review of the literature on the physical properties of glasses, particularly "massive" glass. To understand these characteristics of the vitreous state, one must be familiar with its structure and constitution.

* The term "massive" glass refers to samples of dimensions exceeding 0.1 cm. in any direction.
(a) The nature of the glassy state.

Glasses are described as supercooled liquids or as amorphous solids (Warren, 1934, 1937). The former term is justifiable from the point of view of physical chemistry, the latter from the theory of elasticity (Preston, 1942).

X-ray diffraction patterns for liquids imply that they are not structureless in the same sense as a gas. In liquids, structural units or arrangements of atoms exist as they do in crystalline solids. But, these units are not arranged in a regular manner. There is short-range order but not long-range order. Crystalline solids possess both short-range and long-range order leading to complete regularity throughout (Warren, 1937).

X-ray studies show that glass and liquids are similar in that both are amorphous forms of matter. However, their structures differ in one respect. In a glass, each atom has permanent neighbours at a fairly definite distance, while in a liquid the neighbours about any atom are continually changing (Warren, 1934).

Glass-forming materials form highly viscous melts. Sufficient transient bonding exists in the melt to produce this high viscosity. When the liquid is cooled to temperatures at which the free energy of the crystalline phase
would be lower than that of the randomly bonded structure, the atomic rearrangement necessary for crystallization is impeded (Warren, 1942).

Thus, a liquid structure persists even down to temperatures such that free long-range movement of atoms becomes impossible (Sun, 1947). A strong, but highly flexible scheme of bonding is the necessary condition for glass-forming ability. The glass passes through no sharp or definite transition in solidifying from the melt.

The definition proposed for glass as an inorganic product of fusion, which has cooled to a rigid condition without crystallizing (McMillan, 1964, p.7) appeals to me most. Many properties of glass, such as its transparency, X-ray diffraction pattern, and isotropy, confirm its liquid-like nature. Permeability to small particles such as sodium ions indicates its "open" liquid-like structure (Johnson et al, 1951).

Certain characteristics of the vitreous state of matter result from the high degree of polymerization and from the fact that the relaxation time of glasses is too high to allow the attainment of an internal thermodynamic equilibrium (Weyl, 1946). At room temperature glass has a "frozen-in" atomic configuration, possibly appropriate to some other,
higher, temperature. It may have a mixture of configurations, appropriate in part to several higher temperatures (Freston, 1942).

The energy barriers supporting the metastability of the glassy state are those that impede changes in the positions of molecules. In a glass certain internal degrees of freedom, characteristic of the liquid state, have not had time to come into equilibrium with their surroundings (Kauzmann, 1948). The properties of a glass of given composition may vary widely. These depend on its thermal history.

(b) Polarization.

Crystal structure deduced from X-ray analysis represents an ideal case which is far removed from reality. Thermal vibrations and especially mechanical effects may be sufficient to cause defects or holes in the lattice. Poulter and Wilson (1932) demonstrated the presence of holes in the structure of crystals and glass when they were able to force water, alcohol and ether into these materials under a pressure of 95 tons per square inch.

The co-ordination number of an atom or ion refers to the number of its immediate neighbours. Strong or weak bonds may exist between atoms. What is meant by "bond" is
the probability of the localized concentration of electron clouds in certain definite directions between these atoms (Sun, 1947). The ionic field strength is a measure of the electrostatic force which an ion can exert on neighbouring ions. The concept of field strength which considers ions to behave as incompressible spheres represents a simplified viewpoint (McMillan, 1964, p.16) which is not strictly true, since large ions of low charge are deformable. Size and polarization properties of ions determine the geometrical arrangement. According to Goldschmidt (1929), electrical polarization or deformability is due to the influence of the highly charged central ion on its larger neighbours. In the main, it is the ions of large radii such as O$_2^-$ that are polarizable or deformable. Electrostatically strong ions, or those that have small radii, are mutually repulsed with a force that can be derived from Coulomb's law (Weyl, 1952), rather than deformed.

Such a conception is required to explain the departure of some crystal structures from the strict geometry on which they are based. With the aid of this image of electrical polarization of ions, Goldschmidt (1929) was able to account for, not only the influence of temperature and pressure on the distances the ions were apart and the
consequential changes in co-ordination numbers, but also the polymorphism of the crystal types.

Isomorphism and mixed crystal formation arise through the substitution of ions by others of similar size and chemical behaviour. Thus Na\(^+\) can largely replace K\(^+\) in orthoclase feldspar.

The validity of rules based on the probable co-ordination, because of size and charge of the cations, and the cation to oxygen ratio, is limited to the anions of the rare gas type. The strongly deforming influence exerted by ions of incomplete electronic shells upon large anions leads to bonds which cannot be predicted by simple rules. The ionic radii of the deformed ions have lost their significance (Weyl, 1946).

When in crystals electrostatic valency rules are only approximate, in glass, where the structure is metastable, large departures from these rules are possible.

With the exception of sodium and potassium, the apparent relative sizes of the more important constituents of silicates may be regarded as being small in comparison with the oxygen atom (Bragg, 1929).

Often, the mutual deformation or the polarization of ions is neglected in crystal chemistry because, in the
interior of a crystal, each cation is surrounded by anions in a fairly symmetrical fashion so that the electrical field, to which it is exposed, is weak. However, polarization becomes very important if a polarizable ion participates in asymmetrical groups of ions where the environment leads to strong electrical fields. Since surfaces and interfaces are seats of strong electrical fields, the surface energy of a substance is a function of the polarization properties of its ions. This is particularly so for glasses. Their surface tensions depend on the polarizability of their cations (Weyl, 1952).

Thermal vibrations may lead to changes in the location of ions (diffusion) and increased reactivity at surfaces whose equilibrium has been disturbed. Weyl (1952) found that diffusion and sintering processes involve the formation of cation-cation-anion asymmetrical units. He regards these processes essentially to be due to the squeezing of a cation between two other cations and an anion. Hence, they are influenced by the polarizability of the ions.

In close proximity, the repulsion forces between polarized ions are only a fraction of the Coulomb forces between unpolarised ions. Repulsion of ions decreases with increasing polarizability because the dipoles, induced by
such deformation, produce ion-dipole attraction forces which are stronger than the dipole-dipole repulsion forces (Weyl, 1952).

Summarizing, processes which require a complete change in the geometry of a solid, such as diffusion and sintering, are governed by the repulsion forces which oppose the passing of the least polarizable ions. The magnitude of the repulsion forces between cations increases with decreasing anion to cation ratio, and with decreasing polarizability of all ions involved. This determines the activation energy of the reaction.

(c) Structure of silicate glasses.

As a rule glass represents a more spacious network than the corresponding crystal. Periodicity of a crystal should permit the most efficient packing of all ions, give the densest structure, and achieve electroneutrality in the smallest volume. The contrast of packing in vitreous silica and crystalline quartz is reflected in their densities: 
\[ \text{SiO}_2 \text{ glass} = 2.20 \text{ gm per cm}^3; \text{ quartz} = 2.65 \text{ gm per cm}^3 \]
(Norton, 1953).

Today's picture of the atomic arrangement in glass has developed from various kinds of information: the laws of crystal chemistry (Goldschmidt, 1929); the X-ray
diffracton study of glass (Warren, 1934); the various measured physical properties of glass; and the kinds of materials and ranges of composition in which glass-forming properties exist. Upon the basis of structural silicate chemistry, Zachariasen (1932(a), 1932(b)) predicted the three-dimensional random network structure of glass. Zachariasen's theory has received striking experimental confirmation from Warren's (1934, 1937) remarkable researches on the X-ray diffraction spectra of glasses.

Silicon in all silicates occurs only in the form of stable SiO\textsubscript{4} tetrahedra. The mutual repulsion of the cations is least when the SiO\textsubscript{4} tetrahedra touch at the corners only (Bragg, 1929). Silica (SiO\textsubscript{2}) is the prototype of the glass-forming oxides, for Si\textsuperscript{4+} is small, highly charged and just fills the space between four oxygen atoms. Owing to the high charge of the silicon ion, SiO\textsubscript{2} produces open structures.

A glass may be regarded as a collection of ions, some positively- and others negatively-charged (Ainsworth, 1954(b)). The valencies of the central ions, e.g., of Si\textsuperscript{4+} in SiO\textsubscript{4} tetrahedra, are completely saturated by their bonds to oxygen, but each oxygen has one valency free. Hence this radical may be regarded as a (SiO)\textsuperscript{4-} anion (Weyl, 1946 & Johnson and Bristow, 1951). The residual oxygen valencies
must satisfy themselves somewhere externally. Thus a SiO$_4$ tetrahedron is able to attach itself through free oxygen valencies to another SiO$_4$ tetrahedron.

The attainment of equilibrium is rapid in melts of low viscosity, but it is very slow in those that are highly viscous. The remarkable glass-forming properties of silica are due to features which result from the co-ordination scheme. A strong tendency for each silicon to surround itself by four oxygens exists even in the melt. Hence, each oxygen tends to form a bond between two silicones (Warren, 1937). Such bonding, although continually forming and breaking, stiffens the melt. This high viscosity prevents crystallization on cooling. Thus, the glass is a form of matter in which the co-ordination scheme is the same as in the crystalline phase, but which cooled too rapidly from its viscous melt to allow the orderly building up of a regularly repeating structure to any appreciable extent. The fact that each oxygen is bonded to only two silicones puts such flexibility into the structural scheme that the random network is almost as stable as the crystalline configuration and can therefore continue to exist (Warren, 1937).

Figure 1 illustrates schematically in two dimensions the regularly repeating structure of a crystal as distinguished
Fig. 1.

Schematic two-dimensional figures to illustrate the difference between the regularly repeating structure of a crystal (a) and the random network of a glass (b).
from the irregular structure of a glass. In the orderless vitreous lattice there are many larger "holes" formed than occur in the uniform crystalline structure. This absence of symmetry and periodicity in the atomic structure of glasses is the cause of their optical isotropy. The transparency of glasses is explained by the existence of extended networks in just the same manner as the transparency of crystals is accounted for.

Only small cations can form glasses, since only these have a low co-ordination number and a high charge, both of which are essential for the formation of open structures. These glass-forming cations are: $\text{Si}^{4+}$, $\text{B}^{3+}$, $\text{P}^{3+}$, $\text{P}^{5+}$, $\text{As}^{3+}$, $\text{As}^{5+}$, $\text{Ge}^{4+}$, and possibly also $\text{V}^{5+}$, $\text{Sb}^{5+}$, $\text{Cd}^{5+}$ and $\text{Ta}^{5+}$.

While alumina ($\text{Al}_2\text{O}_3$) alone cannot form glass, $\text{Al}^{3+}$ is capable of replacing $\text{Si}^{4+}$ isomorphously (Zachariasen, 1932(b)).

Vitreous silica is probably the simplest glass. Warren (1942) showed the Si – Si distance to be nearly twice the Si – O value of 1.62 Å. This indicates that the Si – O – Si bond angle is nearly 180°. The orientation of one tetrahedral group with respect to a neighbour group about the connecting Si – O – Si bond is indefinite. Hence, it is a random three-dimensional network which is built up.
The fact that these small, glass-forming cations of high charge surround themselves with oxygen ions has already been demonstrated. Tetrahedral groups are particularly favourable to glass formation. If the chemical composition of the melt does not provide sufficient oxygen ions to permit the formation of independent $SiO_4$ groups, the tetrahedra must share oxygens. This sharing of oxygens is the main reason why silicate melts polymerize. On cooling, this polymerization increases the viscosity of the melt very rapidly and finally leads to a rigid three-dimensional network (Weyl, 1946). If there were sufficient oxygen ions provided in the melt to form independent $SiO_4$ tetrahedra as in the case of sodium orthosilicate, $Na_4SiO_4$, there would be no more necessity for sharing the oxygens and with it for polymerization. Such melts are fluid and can crystallize easily on cooling. Therefore, whether or not a melt forms a glass depends upon the size and the charge of the strongest cations, and on their numerical relationship with oxygen anions.

While the crystalline forms of silica - quartz, tridymite, and cristobalite - have normal values for thermal expansion, the thermal expansion coefficient of vitreous silica we know to be extremely small. Expansion can take place by two processes; 1) change in average interatomic
Fig. 2.

(a) and (b) are schematic, two-dimensional figures representing certain crystalline modifications of silica. Although the interatomic distance is the same, (b) represents a smaller volume than (a).

(c) represents, in two dimensions, the random network of vitreous silica. There is a definite structure in vitreous silica, but it is a structure with regard to immediate neighbours rather than the regularly repeating crystalline structure.
distances, and 2) configurational alteration, such as a change in bond angles. Since the Si - O bond is very strong in silica, it is reasonable to presume the large expansion of quartz to be due mainly to the second process. Then, if the Si - O - Si bond angle be temperature dependent, a thermal expansion of crystalline silica can result from a change in bond angle. A regularly repeating crystalline structure demands a co-operative manoeuvre, while the lack of an orderly structure in vitreous silica precludes the possibility of such a co-operative alteration (Fig. 2 a, b, & c)(Warren, 1942). Rotations which will increase a particular Si - Si distance will in general cause a decrease in other Si - Si distances. The net change in volume due to rotations of the groups will tend to cancel out because of the randomness of the structure. Hence, vitreous silica's very small expansion coefficient relative to quartz could be a direct result of its random structure. Also, since the Si - O - Si bond is nearly equal to 180°, any small change in the angle will produce an extremely small change in the Si - Si distance.

Glass is not a chemical compound in the ordinary sense of the word. Its unit cell is infinitely large and consequently there are no restrictions with regard to the
relative numbers of chemically different atoms, provided, of course, that the valencies be balanced. Zachariasen (1932(a), 1932(b)) considered commercial glasses to be formed as a result of the accommodation of non-glass-forming cations (network modifiers) in holes in the SiO$_4$ network, whereby the properties of pure vitreous silica are not altered fundamentally but merely altered quantitatively. The fact that these network-modifying cations find themselves in the holes of the network which are bounded by oxygen atoms, is in agreement with the requirement that they should not cause a great increase of potential energy. The dimensions of the holes are determined by the size of the cations occupying them (Zachariasen, 1932(b)). Since the framework itself is without periodicity and symmetry, the holes must be statistically distributed and there will be no restriction on behalf of symmetry as to which and how many of these holes are to be filled by cations.

The introduction of basic oxides (Na$_2$O is a good example) into silica glass results in reduction of the viscosity and an increase in the thermal expansion coefficient (McMillan, 1964, p.12). Both these effects can be attributed to weakening of the bonds in the vitreous lattice. Gaps are produced in the continuous network structure. Two non-
bridging oxygens, one of which has been contributed by the basic oxide, replace the bridging oxygen ions which formed the link between two SiO₄ tetrahedra. These oxygen atoms derived from the basic oxide act as bridge breakers (Warren, 1942). In the actual structure of say soda-silica-glasses, each silicon is surrounded by four oxygens; some of the oxygens are bonded between two silicons and some to only one silicon. The sodium ions are held rather loosely in the various holes in the Si - O network. They are surrounded on an average by about six oxygen ions (Ainsworth, 1954(b)). Other alkali metal oxides, such as lithium or potassium oxides, take part in the glass structure in a similar manner. Lithium ions, on the average, will be accommodated in smaller structural interstices than the sodium ions and the potassium ions in larger ones. Divalent cations also can act as network-modifying ions. Whereas in the case of the univalent cations (Li⁺, Na⁺, K⁺) two cations are present for each pair of non-bridging oxygens, one divalent cation (Ca²⁺, Pb²⁺, Ba²⁺) only is required for each pair of non-bridging oxygen ions (McMillan, 1964, p.14).

Figure 3 is a two-dimensional schematic representation of a soda-silica glass. This model can also be considered to represent, in a simplified fashion, the
Fig. 3.

A two-dimensional model of the atomic arrangement in a soda glass. The oxygen-silicon ratio is greater than two, due to the oxygen introduced by the Na$_2$O. It is impossible for every oxygen ion to be bonded to two silicons. Hence, there are two kinds of oxygens; those bonded to two silicons, and those bonded to only one silicon.
Fig. 3.
structure of the multi-component glasses. The large atom labelled Na might be partly Na, K, Ca, Pb, or Mg. The small network-forming atom labelled Si might be B, P, or partly Al (Warren, 1942).

The distinction between network-forming and network-modifying cations is based on the different strengths of their electric fields (Weyl, 1946). Apparently, monovalent network-modifying ions do not make the same demands for single-bonded oxygen ions as do the divalent ions, and fit into the structure as best they can.

The X-ray work of Warren (1937) ruled out the possibility of there being discrete molecules in glass. It did not rule out the possibility of compositional changes from one region to another. Warren's method gave no indication of the distribution of sodium ions. They may find themselves in varying situations according to chance, the number of surrounding oxygen atoms and their type, (that is, whether "single" or "double" bonded) changing within limits from one sodium atom to another. The number of "single" bonded oxygens equals the number of sodium atoms present (Warren, 1940). These facts provide only the barest outline of the vitreous structure.
While in a crystal the co-ordination number of individual cations is constant throughout the structure, in glass this is not so. As we have seen above, some of the cations have more surrounding oxygens than the natural co-ordination number, and others have less. However, the mean value corresponds closely to the crystalline case. In glasses, then, only mean values of interatomic distances can be quoted. For those cations contained in interstices bounded by more oxygens than their natural co-ordination number, the principle of increasing binding-energy with decreasing ionic size does not hold. It would be less than anticipated (Ainsworth, 1954(b)). For cations of slightly different size, but with the same natural co-ordination number, the effect must be to lessen the difference to be expected from their different sizes. When there is a large disparity in ionic radius, which involves unequal preferred co-ordination numbers, the smaller ion would then be expected to exert a much larger binding force. Large size and small charge is demanded of network-modifying cations as small and highly charged cations will tend to produce devitrification (Zachariasen, 1932(b)).
(d) Aluminosilicate glasses.

A group of glasses termed aluminosilicates comprise alumina usually to the extent of about 20 to 25 per cent (Skinner and Wilson, 1934). They contain major percentages of silica, and are characterized by their high softening temperatures.

In crystals, the aluminium ion can be four or six co-ordinated with oxygen, giving rise to tetrahedral $\text{AlO}_4$ or octahedral $\text{AlO}_6$ groups. The tetrahedral groups can replace $\text{SiO}_4$ tetrahedra in silicate lattices (Warren, 1942). Although aluminium oxide is not capable of forming a glass, it can take part in the glassy network. It is what is known as an intermediate oxide (Weyl, 1946). Hence, in moderate amounts, $\text{Al}^{3+}$ can replace $\text{Si}^{4+}$ in vitreous structures (Safford and Silverman, 1947).

$\text{Al}^{3+}$ ions form $\text{AlO}_4$ tetrahedra with similar dimensions to $\text{SiO}_4$ tetrahedra, and these $\left[\text{Al}^{3+}\left(\frac{0^2}{2}\right)_{4}\right]$ groups are the characteristic structural elements in aluminosilicate glasses. The $\text{AlO}_4$ tetrahedra have negative charges which neutralize the charges of univalent cations that are accommodated in the interstices between tetrahedra (McMillan, 1964, p. 14). Consequently, the addition of equivalent amounts of $\text{Na}_2\text{O}$ and $\text{Al}_2\text{O}_3$ to silica will not produce non-
bridging $O^{2-}$ ions and the network structure will remain continuous. The resulting sodium aluminosilicate has a more stabilized glassy state than softer sodium silicates, and its higher viscosity is accompanied by a lower rate of devitrification (Taylor and Rindone, 1966). Due to the strong bridging-oxygen network, the thermal expansion is lower than for other sodium silicates (Stevels, 1954). An increased chemical durability exists in an aluminosilicate glass, since the most polarizable, non-bridging $O^{2-}$ ions are changed into less polarizable, bridging Al $- O - Si$ oxygens (Weyl and Marboe, 1962).

In sodium silicate glasses the strongest bond between the $Na^+$ ion and the network is through the non-bridging, polarizable $O^{2-}$ ion:

$$Na^+ O^{2-} Si^{4+} \left( \frac{O^{2-}}{2} \right)_3$$

The bond between a $Na^+$ ion and the surrounding bridging $O^{2-}$ ions in a sodium aluminosilicate glass is much weaker. This binding force between a $Na^+$ ion and the network is represented by the whole tetrahedron:

$$Na^+ \left[ Al^{3+} \left( \frac{O^{2-}}{2} \right)_4 \right]^-$$

This means that the $Na^+$ ion in a sodium aluminosilicate glass is more mobile when under the influence of an electric field (Weyland and Marboe, 1962).
Very simply then, we can regard sodium and potassium aluminosilicates as three-dimensional networks of $\text{AlO}_4^{-} - \text{SiO}_4^{-}$ tetrahedra. Since the alkali ions interact only with bridging $\text{O}^{2-}$ ions, their field strengths can be correlated with the melting points of crystalline alkali aluminosilicates, and with the viscosities of alkali aluminosilicate glasses. By attracting electron density away from the binding region, i.e., from the bridging oxygen ions between Si - Si, Al - Si, or Al - Al cores, the alkali ions facilitate viscous flow. The small $\text{Li}^+$ ion polarizes the bridging $\text{O}^{2-}$ ions much more than a $\text{Na}^+$ ion and the latter more than a relatively large $\text{K}^+$ ion. A clear-cut relationship exists between field strengths of the alkali ions and the major binding forces within the glass. The viscosity of albite is less than orthoclase; and lithium aluminosilicates form rather fluid melts.

The foregoing discussion has been based on the random network theory of vitreous structure, and this provides an extremely useful concept in understanding the nature of glass. However, there is evidence that suggests that glass is not as homogeneous on the submicroscopic scale as the random network theory might imply (Hoffman and Statton, 1955).
(e) Structural changes of glass on heating and cooling.

Since no two atoms in glass are structurally equivalent, the energy required to detach an atom from the network will vary for each atom. Therefore, the breakdown of the network, with increasing temperature, is a continuous rather than an abrupt phenomenon.

With a rising temperature, network-modifying cations begin to migrate without any appreciable breakdown of the vitreous framework proper (Johnson and Bristow, 1951). Of course, univalent cations migrate through the framework more easily than divalent cations, and smaller cations more easily than large cations with the same charge. Alkali ion migration increases with temperature.

At still higher temperatures the vitreous network proper begins to break down, and large parts of the framework may start migrating. Indeed, the degree of polymerization is a function of temperature, as is the viscosity of the melt.

When the temperature of a simple crystal is changed, only the amplitudes of the oscillations of the atoms and molecules making up the lattice are affected. There is no affect on the thermodynamic properties of the crystal. However, as the temperature of a liquid is changed, its
structure changes in a relatively drastic way. For any glass, the structure is thermodynamically unstable below the liquidus temperature, and a tendency towards crystallization (or "devitrification") exists. The rate of crystallization is temperature dependent, and if the glass has been cooled rapidly through this dangerous range of temperature it will remain reasonably stable. Such a product displays properties which are continuous with those above the liquidus temperature (Jones, 1948-49).

Now, the degree of configurational order in a liquid is a function of the temperature, decreasing with increasing temperature. Part of the heat supplied must be engaged in changing the configuration to one of greater disorder. There is thus a configurational contribution to the specific heat of liquids in addition to the contribution required to increase the vibrational energy (Kauzmann, 1948). This is probably the main reason for the increased specific heat of a liquid near its melting point as compared with that of a solid. For a particular supercooled liquid or amorphous solid, below a certain temperature, the equilibrium times of configurational changes may become so long that they would not occur during ordinary measurements (Jones, 1948-49). Accordingly, the measured specific heat would be smaller by a corresponding amount.