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DEPARTMENT OF MINES AND TECHNICAL SURVEYS  
MINES BRANCH

# THE CONSTITUTION OF BONE CHINA

PART II

Reactions in Bone China Bodies

by

P. D. S. St. Pierre

MINERAL DRESSING AND PROCESS METALLURGY DIVISION



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Technical Paper No. 7

1954

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# THE CONSTITUTION OF BONE CHINA

## II. Reactions in Bone China Bodies

by

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### INTRODUCTION

In the first paper<sup>1</sup> of this series it was shown that a normally fired bone china consists of interlocking crystals of  $\beta$  tricalcium phosphate and anorthite in a siliceous glassy matrix. It appeared from a consideration of the composition of bone china bodies in terms of the system, lime-alumina-phosphorus pentoxide-silica, that the high temperature behaviour of the china might be interpreted by reference to the compatibility tetrahedron tricalcium phosphate-anorthite-mullite-silica. It should be noted, however, that other combinations are possible.<sup>1</sup>

The green body, however, is compounded from natural materials whose mineralogical make-up is very complex. Thus, although the final number of components in the sub-system is small, their formation depends on the complex mineralogical interactions caused by the heating of the body. The extent to which phase data may be applied depends therefore, on the ease with which such reactions take place. Previous experience with synthetic mixtures indicated that these re-

actions took place rapidly, but no information was obtained on the path they followed.

The primary purpose of the investigation covered in the present report was then, to obtain data on the complex interim interactions caused by heating a typical, green, bone china body, and to verify that the reactions proceed rapidly. A second purpose of the investigation was to assess the advisability of further phase studies. It is anticipated that the information obtained will also be of value in supplementing data on coefficient of expansion, porosity and density, etc., obtained in detailed investigations on firing procedure.

#### EXPERIMENTAL METHOD AND EQUIPMENT

The studies described in this report were all carried out on bodies kindly supplied by two of England's leading manufacturers of bone china.

The reactions which take place on heating a china body were studied by two techniques, namely, Differential Thermal Analysis and X-ray Diffraction. Differential thermal analysis was applied to determine approximately the temperatures at which major reactions took place on heating the body. The sample for thermal analysis was placed in a cell in a palladium block centred in a horizontal, electrically heated tube furnace. An inert reference substance, alumina, was similarly placed in an adjacent cell. Heating at a rate of 12°C per minute to 1100°C was

effected by a Leeds and Northrup programme controller. Differences in temperature between the sample and the reference caused by reactions in the body, were recorded by a platinum-platinrhodium differential thermocouple placed in the two cells. The temperature of the palladium block was recorded by means of a platinum thermocouple in conjunction with a Leeds and Northrup Micromax recorder. The signal from the differential couple was amplified and recorded on a Leeds and Northrup Speedomax differential recorder.

In the X-ray diffraction technique a Philips X-ray Geiger counter goniometer was used as described below to study the mineralogical changes caused by heating the green china body to various temperatures. The fundamental principles of operation of this instrument are essentially the same as those involved in X-ray diffraction by the well known Debye-Scherrer powder technique, but a Geiger counter is used instead of film to record the X-ray reflections. This has the advantage of recording not only the Bragg angle, but also the intensity of the diffracted beam. The basic operation of the apparatus may be briefly described as follows:-

A small flat area (approximately 2 cm. x 1 cm.) of finely powdered sample is irradiated with an accurately collimated beam of X-rays. The sample is rotated about an axis in the plane of the specimen and at right angles to the beam of X-rays. Since the sample is composed of

randomly oriented particles, X-ray reflections are obtained from the various crystallographic planes of the constituents. The presence and intensity of such diffracted beams are detected by a Geiger counter set on an arm that scans radially about the same axis as the specimen and is in the same plane as the X-ray beam. By rotating both specimen and scanning arm, diffracted beams are obtained from the same set of particles throughout the operation. In this way the correct relative intensity values are obtained for the reflections from the various crystallographic planes. It will be appreciated, from a consideration of the ordinary laws of reflection, that the scanning arm must make twice the angular displacement per unit time of the rotating specimen in order to be in position to receive any possible diffracted beams. Thus the scanning arm records a value twice that of the Bragg angle. The pulses from the counter are applied to a rate meter whose signal is recorded logarithmically on a potentiometric recorder. Tracings of the recorder charts are shown in the figures in the Results Section of this paper.

Powdered samples were prepared in the following way:- a fresh sample of the green body was placed in a 10 cc platinum crucible for each run, and heated in air in an electric furnace for 20 minutes at a predetermined temperature. Runs were made at 600, 800, 1000, 1200, 1300 and 1370°C. The fired samples were then air cooled, finely ground and examined on the X-ray diffractometer. The diffractometer data

relevant to this investigation were as follows:-

|   |                       |
|---|-----------------------|
| Geiger Counter Scan (2 $\theta$ )       | 7-70°                 |
| Speed of Scan                           | 2° per minute         |
| Collimating Slits                       | 1°                    |
| Target                                  | Copper                |
| Filter                                  | Nickel                |
| Time Constant                           | 3 seconds             |
| Sensitivity (10" full scale deflection) | 100 counts per second |
| Plot                                    | Logarithmic           |

Experiments were carried out on two bodies from different manufacturers, but the results were identical. Table I shows the chemical analyses of these bodies after drying at 110°C for 24 hours. In view of the similarity of results, only body "A" is considered in the rest of this paper.



TABLE I

Analyses of Two Bone China Bodies\*

|                                | A     | B     |
|--------------------------------|-------|-------|
| SiO <sub>2</sub>               | 30.42 | 32.88 |
| Al <sub>2</sub> O <sub>3</sub> | 13.12 | 14.35 |
| Fe <sub>2</sub> O <sub>3</sub> | 0.30  | 0.25  |
| TiO <sub>2</sub>               | 0.02  | 0.02  |
| CaO                            | 27.69 | 25.48 |
| MgO                            | 0.05  | 0.03  |
| P <sub>2</sub> O <sub>5</sub>  | 20.86 | 18.76 |
| F                              | 0.16  | 0.20  |
| Na <sub>2</sub> O              | 0.74  | 0.97  |
| K <sub>2</sub> O               | 1.62  | 1.37  |
| SO <sub>3</sub>                | 0.08  | 0.08  |
| Cl                             | Trace | Trace |
| L. o. I.                       | 4.74  | 5.36  |
| Total                          | 99.80 | 99.73 |

\* Carried out by W. L. Chase, Mines Branch Chemical Laboratory.

## RESULTS

The differential thermal analysis plot revealed only the reactions of the clay in the body. Thus, the only features observed were the normal kaolin endothermic evolution of combined water at ca. 580°C, and the exothermic decomposition of the dehydrated kaolinite at ca. 980°C. Although apparatus was used which could reveal a 1/2°C temperature differential as a 5" peak on the plot, it was not possible to interpret the data other than in terms of kaolin reactions.

The X-ray diffractograms indicating the chemical changes that take place on heating a bone china body are given in Figure 1. In Figure 2, diffractograms are presented of the individual constituents found in unfired bone china. Of these, Cornish stone is the most complex mineralogically and the diffractograms of its components are shown in Figure 3. The diffractograms of the phases present in fully matured china are reproduced in Figure 4. For convenience in marking the Figures, the names of the various constituents have been abbreviated according to the following legend:- A = anorthite, C = clay, F = feldspar, G = gehlenite, H = hydroxyapatite, M = mica, Q = quartz, T =  $\beta$  tricalcium phosphate.

It will be noted that the X-ray method revealed changes a great deal more successfully than the differential thermal analysis. The sensitivity of X-rays, however, depends considerably on the chemical

nature and structure of the mineral being sought. It is reasonable to assume generally that the limit of detection is about 5% by weight of substance sought, though it may be considerably better than this on occasion. Generally the microscope is a much more sensitive means of detecting chemical changes, but could not be used in this study because the crystals in the fine-grained china body were too small to be examined optically.

In interpreting the X-ray diffractograms, it should be noted that lines from the various body constituents frequently overlap. In important cases this has been noted on the diffractogram; in less important circumstances the lines have been assigned to the major constituent. This situation is most common in the diffraction patterns of the unfired and lower temperature specimens, and is due to the complexity of the X-ray diffractograms of the raw constituents of the body. The identification of the various constituents found in the series of fired bodies was based on a direct comparison of the diffractograms shown in Figures 1 to 4. The  $2\theta^\circ$  scale under the diffractograms is intended for guide purposes only and not for quantitative measurement. Table II shows a compilation of observations made on the diffractograms in Figure I.

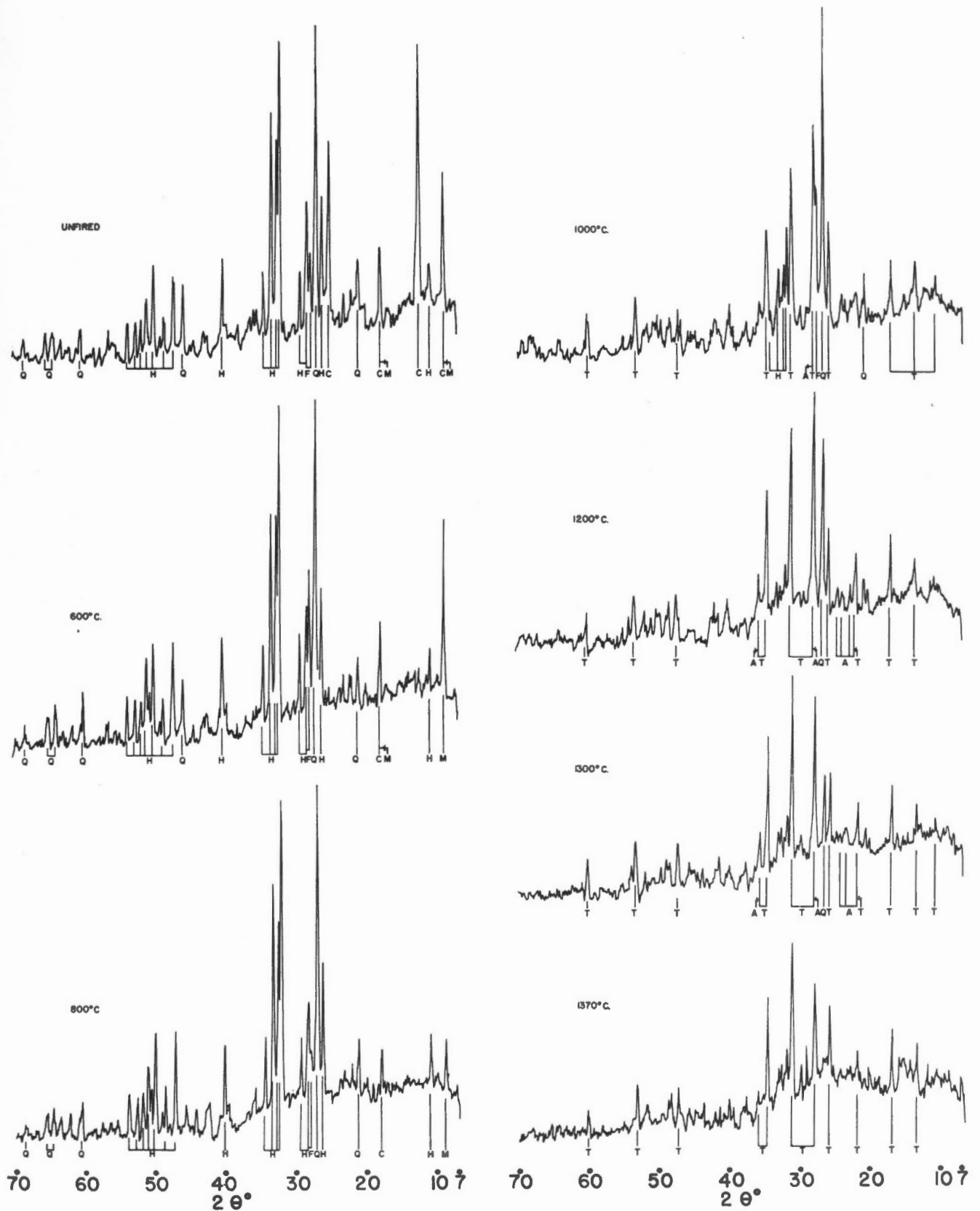
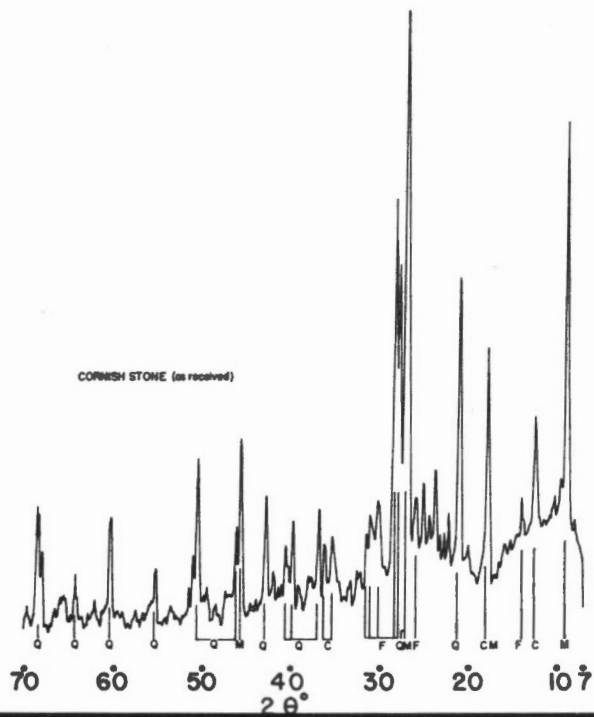
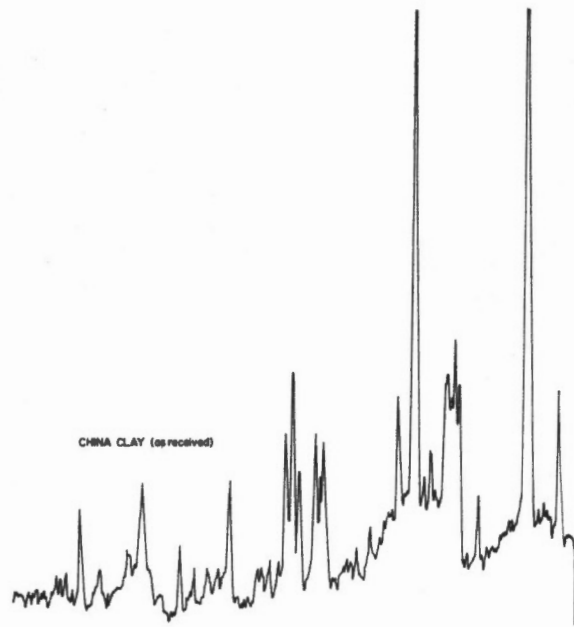
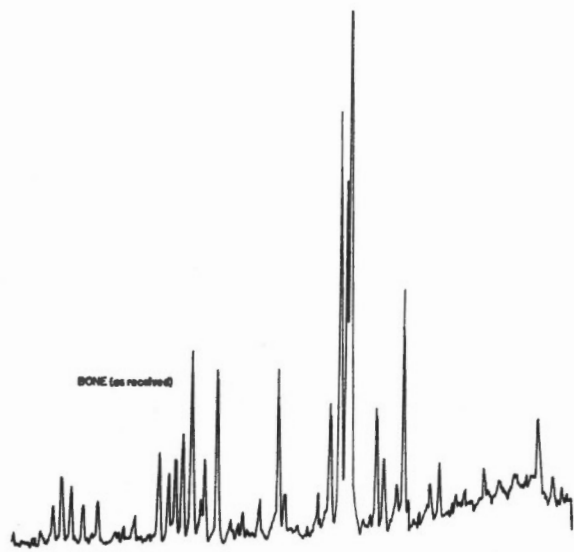


Figure 1. - X-ray diffractograms of bone china body "A" heated to various temperatures for 20 minutes.



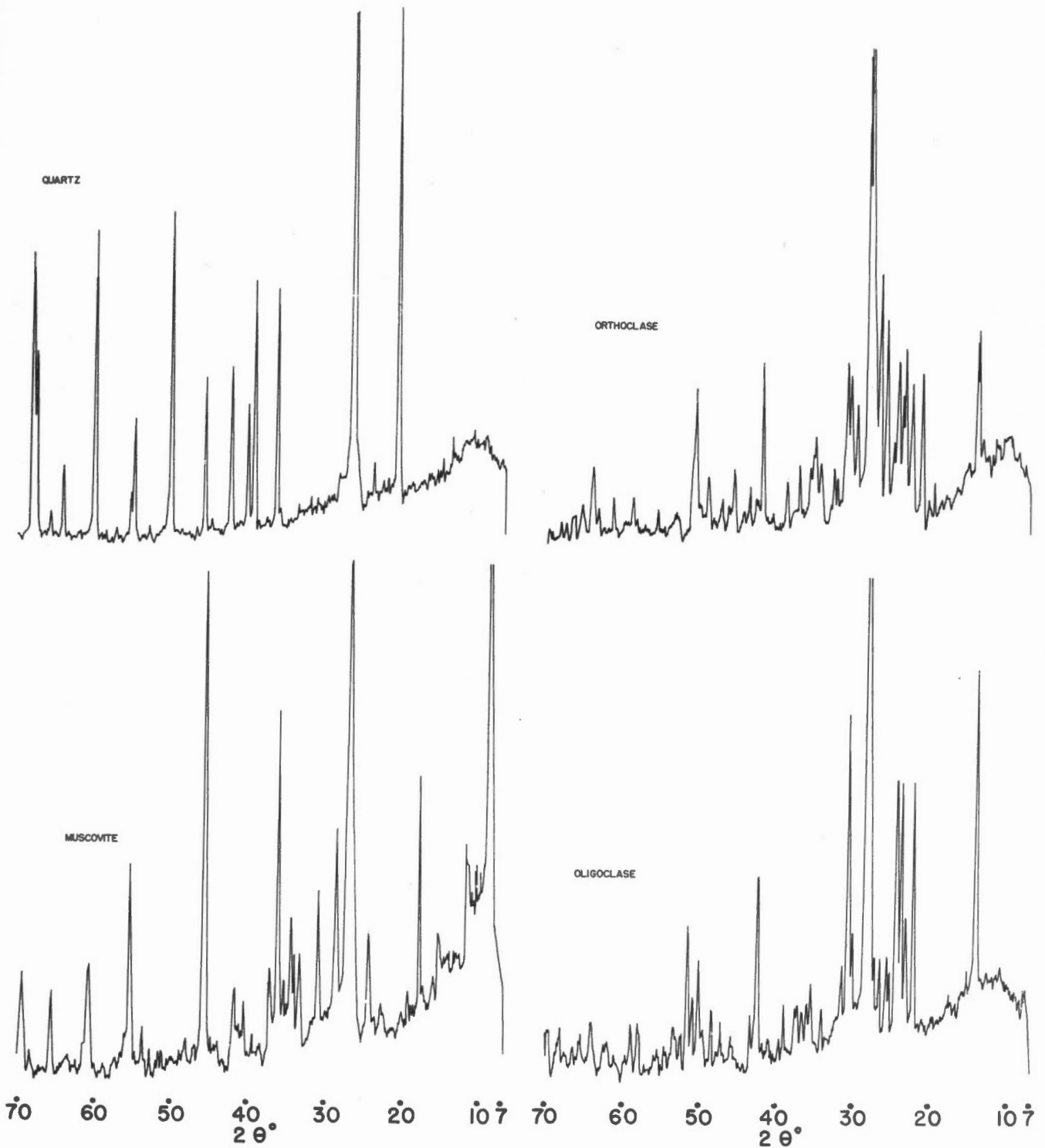


Figure 3. - X-ray diffractograms of the principal constituents of Cornish stone.

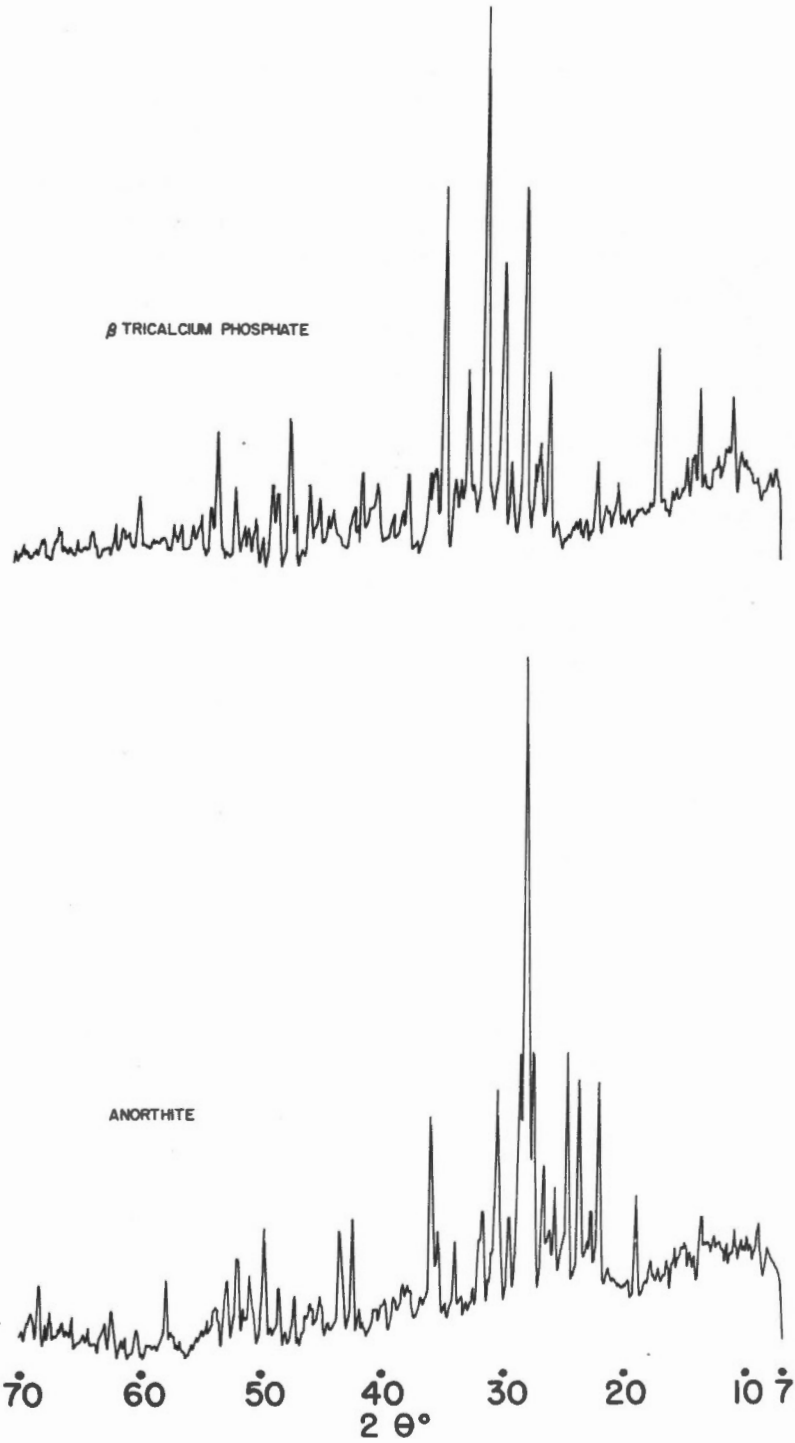


Figure 4. - X-ray diffractograms of the principal crystalline phases found in a matured bone china.

TABLE II

Constituents of a Bone China Body

Fired to Various Temperatures for 20 Minutes\*

| Temperature °C | Notes on Constituents   |
|----------------|---|
| Unfired        | Bone ash - Hydroxyapatite (H)<br>China clay - Kaolin (C)<br>Cornish stone - Feldspars (F) (Orthoclase and Oligoclase)<br>- Quartz (Q)<br>- Mica (M)   |
| 600            | Hydroxyapatite, quartz, kaolin, feldspar and mica. Strong clay line at ca. $12.5^{\circ} 2\theta$ seen in first diffractogram has now practically disappeared, probably due to loss of water from structure. It would now appear that the line marked C and M at ca. $18^{\circ} 2\theta$ in the first diffractogram must be attributed mostly to mica. Apart from this, structure as before.   |
| 800            | Hydroxyapatite, quartz, kaolin, feldspar and mica. Mica line much weaker, feldspar line diminished. Hydroxyapatite and quartz lines undiminished.   |
| 1000           | $\beta$ tricalcium phosphate (T), hydroxyapatite, feldspar and quartz.<br>Hydroxyapatite decomposing to yield $\beta$ tricalcium phosphate. Suspect lime released from hydroxyapatite has reacted with some clay to form anorthite (A). Intensity sequence of tricalcium phosphate lines abnormal and probably due to reinforcement by anorthite line at ca. $28^{\circ} 2\theta$ . This effect is commonly observed in normally matured china <sup>1</sup> . |
| 1200           | $\beta$ tricalcium phosphate, anorthite and quartz.<br>The hydroxyapatite has completely decomposed. The strength of the quartz lines has diminished notably (see especially quartz line at $27^{\circ} 2\theta$ ).   |

\* Based on diffractograms of Figure I.



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| Temperature °C | Notes on Constituents   |
|----------------|---|
| 1300           | $\beta$ tricalcium phosphate, anorthite and quartz.<br>The quartz line ( $27^{\circ} 2\theta$ ) has continued to diminish indicating further solution of silica. The intensity sequence of the principal lines of $\beta$ tricalcium phosphate now more nearly normal. Presumably the anorthite is dissolving and not reinforcing the $28^{\circ} 2\theta$ line of the phosphate. |
| 1370           | $\beta$ tricalcium phosphate.<br>All constituents apart from the phosphate have dissolved.  |

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#### DISCUSSION OF RESULTS

The observations noted in Table II suggest that, apart from the slow solution of the quartz in the liquid formed during the rapid firing, reactions take place quite readily on heating a bone china body. Each sample was placed in the furnace in the green state, and therefore those heated to the higher temperatures underwent several changes during the twenty minute heating period.

Up to  $1000^{\circ}\text{C}$ , the nature of the changes taking place were observed to be somewhat similar to those known to occur in earthenware and related bodies. Such reactions have been discussed in detail by Weymouth and Williamson<sup>2</sup>, Tuttle and Cook<sup>3</sup>, Dale and Francis<sup>4</sup>, McVay<sup>5</sup>, Austin<sup>6</sup>, Norton and Hodgdon<sup>7</sup>, Norton<sup>8</sup>, and others. The work of these authors indicates that initially the reactions are limited to the decom-

position of the individual green body ingredients, but at the higher temperatures interactions commence.

At first there is a loss of mechanically entrapped water from the body, and later the chemically combined water from the clay is evolved (500 - 600°C). The oxidation of any carbonaceous matter may also commence about this time. Free quartz present in the body undergoes a volume change at 573°C due to an enantiomorphic atomic rearrangement. At ca. 980°C the dehydrated kaolinite breaks down further. The exact nature of the decomposition seems to depend on the extent of crystallization of the original kaolinite<sup>9</sup>. The changes involve the formation of  $\gamma$  alumina, and mullite with silica. It is said that in some cases  $\gamma$  alumina is formed first and mullite with silica later, while in others the  $\gamma$  alumina formation is absent altogether. However, prolonged heating is necessary to induce sufficient crystal growth for these compounds to be detected by X-rays, and further to this it has been suggested that in practical bodies the feldspar reacts with the decomposing clay to form a viscous liquid at these temperatures. Unfortunately X-ray analysis offers no conclusive evidence on this point in connection with the short heating cycles used in the present investigation. The diffractogram of the product obtained by heating Cornish stone and clay together for 30 minutes at 1000°C was found to be essentially that of the Cornish stone heated alone at the same temperature. This pat-

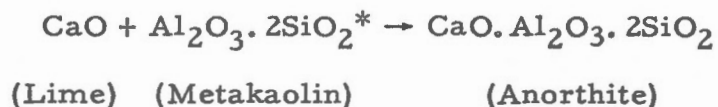
tern in turn was similar to that of the unfired material except for the disappearance of the mica and clay lines.

The special features of bone china reactions commence at ca. 1000°C when the bone ash begins to decompose. The hydroxyapatite gradually breaks down into  $\beta$  tricalcium phosphate and also releases lime and water, as indicated by the equation:-



The water shown in the equation is probably released across a considerable range of temperature since it has been claimed that hydroxyapatite will retain traces of water up to temperatures as high as 1400°C. The change in the intensity sequence of the principal X-ray diffraction lines of  $\beta$  tricalcium phosphate at 1000°C suggests that one of them ( $d = 3.18 \text{ \AA}$ ) is being reinforced by the only very strong line in the anorthite pattern which also has the 3.18  $\text{\AA}$  spacing. It might be argued that such reinforcement is to be expected because of the presence of oligoclase in the Cornish stone; the spacing of the strongest line of this soda-lime feldspar being identical with that of anorthite. However, subsidiary experiments indicated that when only bone and clay were heated together at 1000°C the 3.18 (i. e.,  $28^\circ 2\theta$ )  $\beta$  tricalcium phosphate line was again reinforced. The reinforcement was insufficient, however, to cause a complete change in intensity sequence of the principal  $\beta$  tricalcium phosphate lines.

It is unfortunate that evidence for this reaction must be based on changes in one diffraction line only, but this is an intrinsic difficulty since the anorthite pattern has only one really strong line. However, the synthesis of anorthite at relatively low temperatures (ca. 1000°C) is disclosed by the X-ray examination of the product obtained by heating lime and clay together at 1000°C. In this experiment lime and dehydrated clay (metakaolin), in the proportions indicated by the equation below, were heated for 2-1/2 hours at 1000°C and then examined by X-ray diffraction.



The diffractogram of the heated product indicated the presence of gehlenite ( $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) as well as the anticipated anorthite. A consideration of the lime-metakaolin join in the lime-alumina-silica phase diagram shows that this condition may be expected in the course of the reaction. It may further be predicted from the phase diagram that in the very early stages of reaction even dicalcium silicate may be formed. Further experiment showed that very prolonged heating at 1000°C was necessary to bring about the decomposition of the gehlenite and hence the completion of the reaction noted above.

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\* This formula is used to indicate proportions only; no definite structure is implied.

Above 1000°C the reactions are characteristic of bone china alone, since the predominating constituent, bone ash, decomposes completely and reacts, bringing about the formation of  $\beta$  tricalcium phosphate and anorthite as already noted. From 1000 - 1370°C the solution of quartz proceeds rapidly until none is detected at 1370°C. It should be noted, however, that at temperatures much above 1250°C the body is overfired and quite useless commercially. The solution of quartz is also a function of time, so that in commercial practice the solution is completed at a lower temperature. Quartz has not been detected in X-ray examinations of several normally matured bodies.

Soon after its formation, anorthite begins to dissolve in the liquid until it is completely dissolved at 1322°C\*. The X-ray data confirm the phase studies in showing that  $\beta$  tricalcium phosphate is the primary phase of the body, and anorthite the secondary phase.

It is not surprising that the high temperature reactions proceed very rapidly, since it is almost certain that part of the phosphatic fraction dissolves in the siliceous liquid formed at lower temperatures rendering it more fluid and therefore more reactive. The exact temperature at which this occurs is not known, but in view of the beginning of rapid solution of quartz between 1000 and 1200°C, it seems likely

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\* Determined for these particular samples by the Geophysical Laboratory quench method.

that the phosphatic solution commences in this temperature region. Reactions in china are also promoted by the fine grinding and intimate mixing received during the preparation of the body.

### CONCLUSIONS

1. The results of this preliminary investigation suggest that at temperatures below 1000°C the reactions taking place in bone china are similar to those observed in earthenware and are probably governed by the same mechanisms.
2. At approximately 1000°C the bone ash begins to decompose yielding  $\beta$  tricalcium phosphate, lime, and water. The lime probably reacts immediately with surrounding materials, while the water escapes as a gas.
3. At temperatures above this decomposition point the ensuing reactions are characteristic of bone china alone.
4. Although a detailed kinetic study was not attempted, the notable changes obtained at temperatures above 1000°C with a 20 minute heating cycle indicate that reactions proceed rapidly in the later stages of firing bone china bodies.
5. It follows from conclusion 4 that phase diagrams may be used profitably in interpreting the behaviour of bone china bodies at elevated temperatures since equilibrium should be readily obtained.

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