

*Some physical properties of raw and calcined flint.*

(With Plate XIV.)

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*Introduction.*

**F**LINT from the chalk of north-western Europe has long been an ingredient of ceramic 'bodies'. It is still widely used by British pottery manufacturers in glazed tiles and in certain types of tableware. Continental manufacturers also have made some use of it.

Flint is more readily converted to cristobalite than are the coarser-grained varieties of quartzose silica. The presence of an adequate amount of cristobalite in the 'body' ensures that, at room-temperature, the glaze-film on the ware shall be under a compressive stress. Thus the development of 'crazing', i.e. of minute tension-fissures in the glaze, tends to be avoided. The compressive stress arises because, during the cooling of the glazed ware in the kiln, the diminution of volume which accompanies the change high-cristobalite  $\rightarrow$  low-cristobalite produces an accelerated thermal contraction of the body. This temporarily accelerated contraction puts the more slowly shrinking glaze under compression and the resulting strain is not easily released at the low temperatures involved (Webb, 1939; Simpson and Webb, 1939).

Before flint is added to a pottery body it is calcined. Calcination serves essentially to make the flint easier to grind and, incidentally, to change the colour of the flint from black or greyish-black by incident light to white. The industrial calcination of flint has been practised for over two centuries, but only since 1900 have acceptable explanations been advanced of the more obvious phenomena which accompany it. Certain phenomena are still neglected or only inadequately explained. It is hoped in the present contribution to extend our knowledge of them.

*The nature of flint.*

It is probable that flint and other forms of chalcedonic silica are essentially cryptocrystalline quartz. Imperfection or distortion of the quartz lattice (Shishacow, 1936) may cause certain properties of these minerals to differ from those of more coarsely crystallized quartz. Correns and Nagelschmidt (1933) have, however, explained the peculiar optical properties of chalcedony by considering the arrangement and crystallographic orientation of the quartz fibres of which, according to their X-ray studies, it is composed. X-ray investigation by A. W. Hull (see Washburn and Navias, 1922) has proved that both chalcedony and European flint contain considerable amounts of quartz.

Thermal expansion curves have demonstrated the existence of the low-quartz  $\rightleftharpoons$  high-quartz transition in flint (Houldsworth and Cobb, 1922; Holdridge, Nancarrow, and Francis, 1942), and in chalcedony (Le Chatelier, 1914). Thermal analysis, however, has not always produced evidence of this transition in chalcedony and flint (Fenner, 1913, but cf. Sosman, 1927, p. 177; Pressler and Shearer, 1926; White, 1927) or in chert (Tuttle, 1949); despite the negative result for chert, X-ray photography showed quartz to be present therein.

H. V. Thompson made two analyses of European flint for Mellor and Campbell (1916) in which slightly over 1 % of water was reported; our own figure is similar. Holdridge et al. (1942) suggested that the water might be present as a monomolecular film binding together aggregates of silica molecules. Their hypothesis, though over-simplified, was significant because it implied an adsorption of water by the flint material as a whole. Alternatively, water may be regarded as associated more particularly with the opal which has been reported by some investigators. Tarr (1926) and Bosazza (1937) identified opal in English flint microscopically; indeed, Bosazza reported 76 % of it in a water-ground sample. Such material is invariably calcined prior to grinding and identification of opal therein must be discredited.

The heating of flint with caustic soda solutions causes preferential attack (cf. Oakley, 1939). This attack is not specifically on opal because fine-grained quartz is appreciably affected (cf. Correns and Nagelschmidt, 1933).

The presence of well-distributed opal could explain the fact that the density and refractive index of chalcedony or flint are both less than those of quartz. The hypothesis of a minute porosity is an acceptable alternative (see below); adsorbed water also could influence the two properties cited.

*Some reported effects of heat on flint and chalcedony.*

*Density.*—Mellor and Campbell (1916) showed that the density of flint decreased to 2.22 after repeated calcinations at temperatures of presumably between 1250° and 1300° C. The range of densities listed for cristobalite by Sosman (1927, p. 303) is 2.310–2.320. Rieke (see Robson, 1922), Hirsch (see Simpson and Webb, 1939), and Holdridge et al. (1942) also obtained anomalously low densities for calcined flint. The same was true of Washburn and Navias (1922) whose very careful determinations gave:  $d_{25}^{25}$  2.251 for flint which had been heated for 2 hours at 1430–1460° C. Chalcedony similarly treated gave  $d_{25}^{25}$  2.175. Calcined chalcedony had frequently been described as having a peculiarly low density although dilatometric evidence suggested that it was cristobalite (cf. Endell and Rieke, 1913, and refs. there cit.; Le Chatelier, 1890, 1914).

Houldsworth and Cobb (1922) recorded the presence of cristobalite in calcined flint and based their conclusion on both dilatometry and refractive index measurement; they made the novel claim that tridymite appeared in some circumstances (cf. Sosman, 1927, p. 85).

A distinct advance in our knowledge was made when Hull demonstrated to Washburn and Navias (1922) by X-ray powder photography that cristobalite was the only crystalline phase detectable in strongly calcined flint or chalcedony.

The apparently low densities of calcined cryptocrystalline silica may depend on the existence in its structure of fine cracks or pores not readily accessible to a liquid (Endell and Rieke, 1913; Le Chatelier, 1914). Washburn and Navias (1922) showed that when calcined chalcedony was very finely ground its measured density increased by 2%. This result was thought by the investigators to indicate the presence of many minute pores. The interpretation is well founded, for the density of very finely ground quartz normally appears to be greater, not less, than that of coarser material. This phenomenon has been attributed to the formation of amorphous silica (e.g. by Martin, 1927), but adsorption effects, involving the liquid used in the determinations of density, provide complicating factors (Culbertson and Weber, 1938).

Simpson and Webb (1939) assumed the existence of micro-capillary air spaces, impenetrable by liquids, between the quartz fibres of calcined flint. Heating induced a thrust of the fibres and an escape of water which tended to increase the number of these spaces. Thus the density of the flint appeared to fall before there was any conversion to cristobalite, and the cristobalite which finally appeared was itself of

anomalously low density (cf. Sosman, 1927, pp. 273 and 388; Holdridge et al., 1942).

There is thus general agreement among investigators that the measured densities of calcined flint or chalcedony are affected in some degree by the presence of minute pores inaccessible to liquids. Other suggestions have been made, but on slender evidence. Sosman (1927, p. 273) mentioned the possibility that the fall in density of cryptocrystalline silica, which supervenes at low temperatures, might depend on some rearrangement of molecules to give a cristobalite-type of structure. This rearrangement was promoted by the water present in such silica and ceased when it had been evolved. There is, indeed, experimental evidence that water may promote the formation of cristobalite, but here the initial silica was amorphous (Cohn and Kolthoff, 1948). Washburn and Navias (1922) thought that states intermediate in crystallinity, and thus in density, between those represented by silica-glass and by eucrystalline cristobalite might be possible. This idea receives some support from the claim of Endell (1948) that appropriate thermal treatment of kieselguhr produced a material of a degree of crystallinity intermediate between that represented in amorphous silica and in low-cristobalite; X-ray evidence was used to support this thesis.

*Refractive index.*—Flint is known to show a decreased refractive index after calcination, but no systematic study of the phenomenon has yet been published. Washburn and Navias (1922) and Williamson (1941) found that the refractive indices, determined by immersion, of some samples of calcined flint were distinctly above the values for the mean refractive indices of low-cristobalite or low-tridymite tabulated by Sosman (1927, pp. 599–600), but below those of quartz. Sosman (1927, p. 273) was aware that the refractive index of calcined cryptocrystalline silica could be affected by the presence of pores. Ostwald (1924) and Dunham, Claringbull, and Bannister (1948) have mentioned comparable phenomena.

*Colour.*—The flints used in the European ceramic industries are frequently obtained from sea-beaches as pebbles or boulders; sometimes they are taken directly from the chalk. The British potter has been wont to recognize two types of flint among the material from beaches, namely 'black' and 'grey'. Grey flints are said to shatter more readily than black flints during calcination (Mellor and Campbell, 1916; Heath and Leese, 1923). The essential differences, if any, between the two types remain undetermined.

Raw flint is predominantly black or greyish-black unless it has been stained or altered. Some investigators have agreed that carbonaceous matter contributes to the production of the colour or is even its sole cause (cf. Tarr, 1926; Washburn and Navias, 1922). Alternatively the finely particulate structure of the rock may be assumed to prevent most of the incident light from being reflected to the eye (Tarr, 1926; Oakley, 1939). Indeed, if a minutely fibrous structure be ascribed to the chalcedony in the flint, an effect may be expected comparable to the dark appearance of needle-points bunched closely together and facing the observer (cf. Woods, 1934, p. 106, for a discussion of this and similar optical phenomena).

Adequate calcination of flint causes it to become white by incident, though not by transmitted, light. This whitening may not depend entirely on the oxidation of carbonaceous matter, for it can be ascribed also to reflection from the planes along which the flint has fractured during heating (Oakley, 1939; Holdridge et al., 1942).

Calcined flint, although white by incident light, shows an unexplained brownish colour by transmitted light even in sections only 30–40 microns thick (Williamson, 1941, 1949). The existence of this brownish colour can be inferred from photomicrographs of partially fused felspar-flint mixtures provided by Heath and Mellor (1914), and of flint serving as a constituent of silica-bricks (Hugill and Rees, 1931). None of these authors comments on the colour. The classical paper by Klein (1916) on the micro-structure of porcelain suggests that he was deceived by the brownish colour of the flint in an English tableware body into confusing flint with calcined clay.

#### *The flint of the present experiments.*

This flint was in the form of boulders obtained, through commercial sources, from English sea-beaches. It was of the type termed 'grey' by potters. When examined microscopically, it was found to have a fine-grained siliceous matrix in which there were many coarser areas of calcareous or siliceous material. A few of these areas were manifestly sections of organic structures, but it is likely that many of them occupied the sites of former structures of this kind. Obvious also were numerous separate or aggregated thin annuli of chalcedony which gave the initial impression of having replaced the shells of foraminifera. Most, or all, of them were probably of inorganic origin. Some of these annuli enclosed a brownish material, existing also in a few irregular areas outside them, which showed an aggregate polarization like that of the matrix. There

was no good reason for identifying the material as opal rather than as chalcedony; indeed, no satisfactory examples of opal were encountered. Further, no opal was obtained by centrifuging finely powdered flint with liquids of appropriate density.

Only a single specimen could be confidently recognized as a foraminifer. The more interior parts of its shell were still calcareous but the remainder had been replaced by chalcedony. This mineral had commonly developed as negatively elongated fibres traversing the thickness of the shell (pl. XIV, fig. 1). Similar processes of silicification had affected other structures, elsewhere in the flints, identified as fragments of lamellibranch (or brachiopod) shells. Usually replacement had been by fibres of chalcedony arranged in the manner just described, but occasionally by a mosaic of chalcedony grains without obvious structure. A few radiolaria were noticed and there were some fragments which appeared to be sponge remains.

Sporadic spherulites of chalcedony had diameters up to 0.2 mm. Related bodies were apparent in which elongation sometimes sufficed to produce rectangular or tapering areas in which parallel fibres sprang from both sides of the central axis (pl. XIV, fig. 2). Some of these rectangular structures may have been sponge spicules. It is, of course, possible that certain 'spherulites' are merely cross-sections of the rectangular structures. Fan-like growths of chalcedony were common and some formed aggregates. In certain aggregates the fibres diverged from points on the boundary between the aggregate and the fine-grained matrix which surrounded it (pl. XIV, fig. 3). This arrangement suggests growth into a cavity which initially was empty or, more probably, occupied by calcareous material presumably of organic origin. A rare type of spherulite had a wide core of radiating chalcedony fibres and a discontinuous outer shell of calcitic material into which the spherulitic structure sometimes continued.

The fine-grained matrix of the flint was not a mosaic of equidimensional grains. High magnifications revealed it as crenulated or interlocked units grading downwards in size until they were no longer distinguishable. Each unit showed undulose extinction of a type which suggested the presence of minute fibres with a fan-wise disposition. In the coarser units such a structure was actually detectable. Indeed, there was a gradation in size between the units of the matrix and the coarser chalcedonic structures already described.

Chalcedony fibres of all lengths and arrangements had the usual negative elongation; positive elongation was rarely found.

Certain regions of extensive silicification appeared to occupy the sites of coherent sponge remains and in some of these regions were seen collections of granules which were probably carbonaceous.

The flint matrix contained rhombohedral carbonate as specks or as small crenulate units interlocked with the silica. The distribution of this fine calcitic material was not uniform and was unrelated to that of the larger patches of carbonate; a few of these patches were clearly the remains of fossils.

One section contained an interesting inclusion (pl. XIV, fig. 4). This appeared as a crudely rectangular area with approximately parallel longer sides and irregular ends. Its dimensions were about  $2.5 \times 1.5$  mm. It contained a broad axial belt of contiguous crystals of carbonate which were dominantly hexagonal in outline. This belt was flanked on both sides by zones of silica. The silica consisted of quartz units which had replaced the euhedra of carbonate and had usually preserved their shape. Sometimes a discrete quartz crystal had replaced a particular euhedron of carbonate; some pseudomorphs, however, consisted of several quartz crystals. Mechanical extraction yielded sufficient carbonate for spectrographic examination. The carbonate was distinctly ferriferous and had some Mg and Ca, with traces of Na and P. The process of silicification to which it had been subjected would appear to be that which affected also the more obviously organic structures, still partially preserved in calcareous material, seen elsewhere in the sections.

Wells (1947) described the replacement by silica of carbonate rhombs contained in chert. Further, he directed attention to occurrences of rhomb-bearing cherts in limestones free from rhombs. The association of a rhomb-bearing flint with the chalk would resemble such occurrences. However, the aggregated euhedra first described may well be a section cut from the prismatic layer of a large lamellibranch (or brachiopod) shell. The rhombs discussed by Wells appear to have been of inorganic origin.

The mean refractive index of the siliceous material of the flint matrix was 1.538 for sodium-light; the corresponding density was 2.622. These figures are below those commonly recorded for quartz, although only quartz was identified in the sample by X-ray powder photography. If opal were present it was in an amount too small to show the X-ray diffraction effects to be expected from a silica gel. Much of the quartz was, however, very fine-grained. Further, thermal expansion curves, obtained from test pieces made of crushed flint bonded with a little

bentonite, revealed the volume change which accompanies the low-quartz  $\rightleftharpoons$  high-quartz transition.

Cristobalite, if present, was in an amount too small to be detected by the X-ray powder photographs. This possibility was considered because low- or high-cristobalite has been reported in association with opal (Greig, 1932; Levin and Ott, 1933).

An analysis of the raw flint is shown in table I. The preponderance of Na<sub>2</sub>O over K<sub>2</sub>O is found also in other analyses of flints from sea-beaches (Mellor and Campbell, 1916; Holdridge et al., 1942). Consequently it may indicate something other than vagaries of analytical technique. Exchange or other reactions, or adsorption effects, involving sea-water may be responsible for it. The trace of chloride also suggests interaction with sea-water.

TABLE I. Analysis of raw flint. (Analyst, Miss B. C. Terrell.)

SiO <sub>2</sub>	...	98.19	H <sub>2</sub> O—	...	0.33
Al <sub>2</sub> O <sub>3</sub>	...	nil	CO <sub>2</sub>	...	0.24
*Fe <sub>2</sub> O <sub>3</sub>	...	0.02	TiO <sub>2</sub>	...	nil
MgO	...	0.21	P <sub>2</sub> O <sub>5</sub>	...	0.03
CaO	...	0.30	Cl	...	trace
Na <sub>2</sub> O	...	0.08	SO <sub>3</sub>	...	nil
K <sub>2</sub> O	...	0.03			
H <sub>2</sub> O+	...	1.11			
					100.54

\* State of oxidation not determined.

The loss in weight of flint on ignition is caused almost entirely by the evolution of water and the decomposition of carbonates. Water tends to be expelled at lower, and carbon dioxide at higher, temperatures. An investigation was made by using an apparatus devised by Mr. A. J. Gaskin. This apparatus plots automatically a continuous isobaric curve of weight-loss against temperature. It is designed in such a way that the sample is maintained in an approximate equilibrium over the whole temperature range; a determination occupies some 50 hours. The resulting curve for flint is shown in text-fig. 1. The pronounced upward inflection between 300° and 400° C. accords with the marked loss in weight found at 350° C. by Holdridge et al. (1942). These investigators used a technique differing from that here described and the two sets of results are not quantitatively comparable. The sudden inflection between 600° and 700° C. can be ascribed to the loss of CO<sub>2</sub> from carbonates.



*Experimental.*

*Density.*—To avoid the extensive contamination likely to accompany the fine-grinding of the tough flint, the material was broken merely into chips prior to calcination. These chips were  $\frac{1}{2}$ – $\frac{3}{4}$  inch long and their greatest thickness did not exceed  $\frac{1}{4}$  inch. The calcined flint was readily friable, except when it had been produced at temperatures below 400° C. It was pulverized in an alumina mortar.

In preliminary experiments the flint was heated for 9 and for 18 hours at some of the lower calcination temperatures to be employed. As the longer period of heating caused little or no further reduction in density a standard time of 9 hours calcination was adopted, but it is not claimed that the densities reported are equilibrium values.

Calcination was performed in electrical resistance furnaces equipped with temperature-controlling mechanisms and recording pyrometers. It was, however, necessary to employ a gas-fired pot furnace for the highest temperature attained. Here the atmosphere was distinctly reducing. The temperature in this furnace was determined by an optical pyrometer and was somewhat above 1500° C.; a more accurate estimate was not practicable.

The calcined material was ground to pass a 200-mesh B.S. sieve and its density was determined in water at 25° C. by the use of a pycnometer. Despite the addition to the water of a small amount of a wetting agent, it was noticed that any ultra-fine material produced in grinding floated persistently. Although the production of such material was minimized as far as possible, it was necessary to remove the material by washing. We are aware that Washburn and Navias (1922) recorded that the density of very finely ground calcined flint was 2 % greater than that of coarser material. However, our measured values are in any case only the average given by mixtures of particles of slightly differing densities. This follows from the somewhat varied thermal behaviour to be expected from parts of the flint which differ in degree of crystalline perfection or development, e.g. the coarser spherulitic and other structures and the fine-grained matrix. The existence of such a phenomenon was confirmed by suspending samples of powdered calcined flint in liquid diffusion columns; most particles had similar densities, but a few had slightly aberrant densities. It can be accepted, however, that the densities measured pycnometrically are dependent chiefly on the thermal behaviour of the material termed 'matrix' in the microscopical description (see above) as this material predominates in the flints.

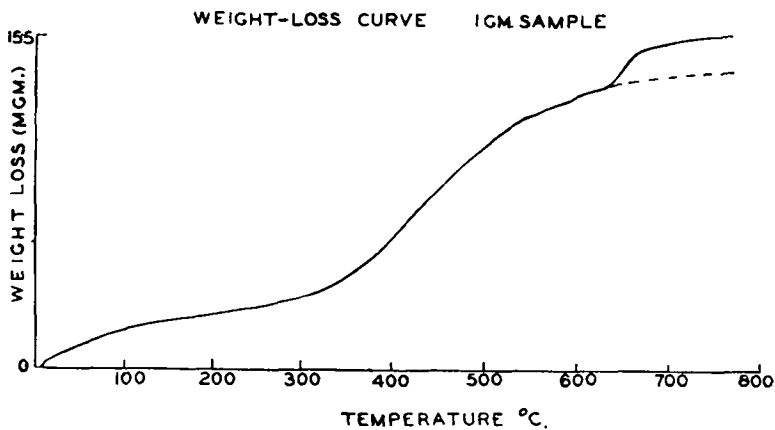


FIG. 1. Weight-loss versus temperature curve for flint. A 1 gm. sample lost a total of 15.5 mgm.

TABLE II. Effect of calcination on some properties of flint.

Calcination temperature.	Density.	Porosity (Calculated).	Refractive index Found.	Refractive index Calc.	Phases identified by X-rays.
Uncalcined	2.622	1.03 %	1.538	1.543	quartz
200° C.	2.612	1.42	1.536	1.541	—
300	2.611	1.44	1.534	1.541	—
400	2.593	2.12	1.530	1.538	—
500	2.553	3.64	1.520	1.529	—
600	2.499	5.66	1.515	1.519	—
700	2.493	5.90	1.514	1.516	—
800	2.490	6.01	1.512	1.516	—
900	2.485	6.17	1.512	1.515	quartz
1000	2.489	6.03	1.512	1.515	quartz
1050	2.495	5.81	1.511	1.517	—
1100	2.506	5.42	1.510	1.519	quartz
1200	2.472	6.67	1.508	1.512	quartz + some cristobalite
1300	2.268	2.21	1.476	1.474	—
1400	2.224	4.08	1.469	1.465	cristobalite
1400° C. (recrystd. Na <sub>2</sub> CO <sub>3</sub> )	2.283	1.55	1.479	1.478	cristobalite
1000° C.					
1400° C. (recrystd. 1500° C. ÷)	2.319	nil	1.485	—	cristobalite

The results are summarized in table II and fig. 2. A decrease in density begins at the lowest temperatures of calcination and becomes

more pronounced at 300° C. At this latter temperature the dehydration curve (fig. 1) displays an upward trend. The decrease in density continues to 600° C.; a flattening of the dehydration curve has already become apparent somewhat below this temperature. This flattening is

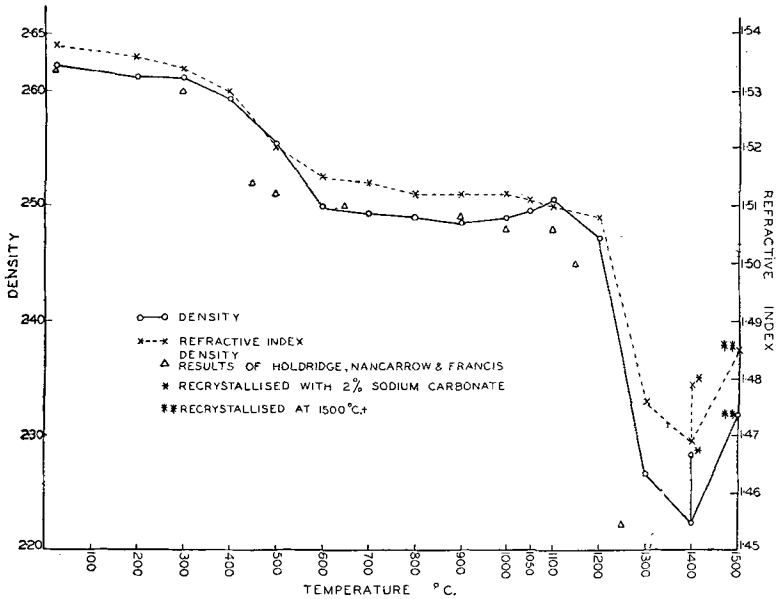


Fig. 2. Density/temperature and refractive index/temperature curves for flint.

now continued in sympathy with the near-horizontal portion of the density curve, and is seen particularly in the extrapolated portion of the dehydration curve (represented in fig. 1 by a broken line). The sharp upward inflection in the weight-loss curve between 600° and 700° C. can be ignored because it was produced by the loss of CO<sub>2</sub> from carbonates.

The density curve tends to be horizontal between 600° and 1000° C. A slight upward trend then supervenes and continues to 1100° C. From this temperature the decrease in density, now marking the formation of cristobalite, becomes very noticeable. Cristobalite was first detected in material calcined at 1200° C.; this temperature is close to the 1150° C. determined by Holdridge et al. (1942). Hitherto, despite apparent changes in density, the flint has consisted entirely or predominantly of quartz.

The temperature-density curve agrees approximately in shape with

the generalized curve depicted by Simpson and Webb (1939), but its initial descent ceases at 600° C., not 300° C., and the later descent, accompanying the formation of cristobalite, begins at 1100° C., not about 950° C.

The reason for the slight rise in density between 1000° and 1100° C. has not yet been elucidated; indeed, elucidation is likely to prove difficult. Factors which could promote an increase in density include one or both of the following:

- (a) A sintering or other process which, without forming a new phase, produced a more compact structure.
- (b) The formation of quartz from amorphous material in the flint.

Schulman, Claffy, and Ginther (1949), and Bailey (1949) showed that amorphous silica or silicic acid were converted to quartz in the presence of lime. Not only does flint contain lime, but the increased density appears at temperatures where these investigators found that quartz was effectively produced.

At 1400° C. the flint, though now converted to cristobalite, has a density considerably below that quoted for this material. The phenomenon presumably results from the persistence of minute pores. Attempts were therefore made to increase the density by recrystallization. Two methods were used:

- (1) The material was reheated with 2% of sodium carbonate for 9 hours at 1000° C. This caused a distinct increase in density. The resulting solid was still cristobalite.
- (2) The material was reheated for 6 hours at temperatures somewhat greater than 1500° C. The product was cristobalite of normal density (table II; fig. 2).

The density figures obtained by Holdridge et al. (1942) have been plotted with ours in fig. 2. There is a considerable measure of accord along the near-horizontal portion of the curve. Presumably the structure of calcined flint attains a certain stability at about 600° C. and maintains it throughout the temperature range represented by this portion of the curve. In regions where drastic structural changes are occurring, i.e. below 600° and above 1000° C., the densities obtained by various investigators may well be expected to differ.

*Refractive index.*—The material which had been used to study the effect of heat-treatment on density was employed also for determinations of refractive index in sodium-light by immersion technique. The fact that a scatter of density values had been found in individual samples

led naturally to the supposition that a scatter of refractive indices would be found also. This was, in fact, true; commonly there were some grains of refractive index slightly higher than that of the mass of the material. Presumably the more robust structural units in the flint are apt to maintain rather higher densities or refractive indices than does the fine-grained matrix when both receive the same thermal treatment. Differences in density or refractive index within the same sample tended to diminish as the temperature of calcination increased and to be annulled where there had been an extensive development of cristobalite. Further, the grains commonly showed an aggregate polarization in shades of grey which was marked in the quartz-containing specimens. However, the mean refractive indices of that part of the flint previously termed the 'matrix' were determined and showed a remarkable correlation with the corresponding densities (fig. 2).

An anomalously low refractive index may be exhibited by material which is still quartz and not cristobalite; this effect can be ascribed to the presence of minute pores. The peculiarly low refractive index of the cristobalite prepared from flint at 1400° C. is similarly explicable.

Recrystallization of the cristobalite to give a less porous structure should be accompanied, not only by the rise in density which has already been demonstrated, but by a rise in refractive index. The data in table II and fig. 2 show that this is so. In particular, the recrystallization of cristobalite at temperatures slightly greater than 1500° C. yielded a product not only with a normal density but with a normal refractive index (cf. values listed by Sosman, 1927, p. 599). Some results described by Robson (1922) appear to be comparable; he reheated industrially calcined flint at temperatures which were probably about 1400° C. and obtained a product with the refractive index of cristobalite.

Ostwald (1924) cited investigations which showed that the measured refractive indices of hydrophane or of tabashir depended on the particular liquid with which these materials were soaked. In calcined flint the pores are filled, not by liquid, but by gas (presumably air, water-vapour, and carbon dioxide, although some pores may be empty), but a similar phenomenon arises. In contrast to the behaviour of hydrophane or tabashir, it is not possible to replace any substantial proportion of the contained gas by a liquid.

Some of the investigators cited by Ostwald showed further that an approximation to the measured apparent refractive index of soaked siliceous material can be calculated by using an appropriate mixture-

formula involving the refractive index of the solid silica and of the soaking liquid.

A similar calculation for flint has been made on the basis of the following assumptions:

- (1) The raw flint consists of quartz.
- (2) Flint calcined up to and including 1200° C. is exclusively quartz.
- (3) Samples calcined above 1200° C. are exclusively cristobalite.
- (4) The density of quartz is 2.649 and its mean refractive index is 1.549.
- (5) The density and refractive index of cristobalite are those recorded for the sample recrystallized at temperatures somewhat greater than 1500° C. (table II).

The porosities and refractive indices of the samples were calculated from the formulae:

$$P = 100 \left( 1 - \frac{Da}{Dt} \right) \quad \text{and} \quad N = \frac{V_s \cdot N_s + V_p \cdot N_p}{V_s + V_p},$$

where  $P$  is the percentage true porosity of the solid,  $Da$  its apparent and  $Dt$  its true density,  $N$  its apparent and  $N_s$  its true refractive index,  $V_s$  and  $V_p$  the volumes of solid and pore-space respectively in a given volume of porous solid, and  $N_p$  the refractive index of air.

The results of both calculations appear in table II. There is some correspondence between the determined and calculated refractive indices of the quartz-rich material; this is more marked from 600° to 1000° C., i.e. along the near-horizontal portion of the temperature-density curve. The cristobalite-rich material also shows correspondence which is particularly close for the cristobalite recrystallized at 1000° C. with 2% of sodium carbonate.

*Colour.*—An endeavour was made to oxidize the carbonaceous matter in the flint without employing elevated temperatures. This was done by soaking small chips in 100 volume hydrogen peroxide for six months. The supernatant liquid was replaced by fresh hydrogen peroxide about every week. At the end of the treatment the flint had become distinctly paler by incident light. This effect may arise, however, merely by the soaking of liquid into a porous structure; it may be comparable, for instance, with the transparency caused by steeping air-dried hydrophane or tabashir in water (cf. Ostwald, 1924). Such an explanation of the results is, however, unlikely, because prolonged boiling of flint chips in water containing a wetting agent, under a reflux condenser, produced no obvious fading of the colour seen by incident light.

The whitening of flint which accompanies calcination became significant at 400° C. and was especially obvious in the range 500–600° C.

Holdridge et al. noticed that flint shattered markedly at about 365° C., i.e. near the critical temperature of water; our own experience has been similar.

Of some interest is the peculiar patchy brownish colour which calcined flint exhibits by transmitted light even in sections or grains only 30–40 microns thick. The colour was incipient at 400° C., marked at 500° C., and strong at 600° C. and upwards to 1400° C., irrespective of whether the particles were quartz or cristobalite. The observations were made on particles which had passed a 200-mesh B.S. sieve. Thin sections even of raw flint may be found to transmit a very pale straw colour if they are examined microscopically with a low-powered objective.

The colour may depend on the presence of foreign material, probably iron, or, alternatively, it may be caused by peculiarities in the fine structure of the calcined flint itself. That iron may be involved is suggested especially by the results of Hedvall and Sjöman (1931). They found that, if the changes low-quartz → high-quartz or low-cristobalite → high-cristobalite occurred in the presence of ferric oxide, there was definite interaction between the silica and the iron compound. In particular the change quartz → cristobalite led to the formation of a reddish product which was presumably a ferriferous solid solution.

An attempt was therefore made to remove iron from the flint and to decide if such removal weakened the brownish colour of the calcined material. Flint was calcined at 500° C. and then finely powdered; the grains of powder transmitted a strong brownish colour. The powder was heated in streams of chlorine at temperatures up to 550° C. or of carbon tetrachloride vapour (i.e. probably chlorine and phosgene) at temperatures up to 700° C. Such treatment was maintained for six hours; by this time water through which the issuing gases had bubbled gave no further reactions for iron. The flint from several experiments showed no fading of the initial brownish colour (contrast the bleaching of the rutile similarly treated by Williamson, 1940).

The second hypothesis, i.e. that the brown colour depends on the structure of the solid, must be considered the more probable. The brown colour may be equated with the yellowish-red colours which, as Ostwald (1924, p. 391) remarked, are transmitted by many dispersions.

In these laboratories brownish colours, visible in transmitted light, have been produced by a variety of processes:

(a) The 'smoking' of glass by the fumes from burning magnesium.

- (b) The acidification of solutions of sodium thiosulphate (cf. Bancroft and Gurchot, 1932).
- (c) The dehydration of silica-gel; the colour disappears when the gel is rehydrated.
- (d) The incipient devitrification of glass by appropriate heat-treatment.

All the examples cited by Ostwald or by ourselves involve a phase which is finely dispersed through or on another phase. The example most directly comparable with calcined flint is dry silica-gel which presumably contains gas-filled pores in a solid medium. A behaviour like that of flint has been noticed in topaz by Bradley, Schroeder, and Keller (1940). On calcination this mineral acquired a tan or light-brown colour which appeared to depend mainly on the presence of submicroscopic pores and cracks caused by the loss of volatiles. Endell and Rieke (1913) had stated that the internal cracking of heated silica produced an optical effect which gave the impression of isotropism when the material was examined with the microscope; they did not mention specifically the brownish colour here described. It has been noticed in the present investigation that this colour interferes appreciably with the recognition of birefringence. Williamson (1941) has already discussed some factors which may cause the appearance of a real or apparent isotropism in calcined flint.

Calcined flint is a solid which contains gas-filled or empty pores. Thus the brownish transmitted colour is not caused by the Christiansen effect (Ostwald, 1924; Raman and Ramaseshan, 1949; Woods, 1934), because this requires, among other prerequisites, two phases of different dispersive power but having a common refractive index in some part of the spectrum.

If the brownish colour can be regarded as an impure yellow-orange, produced because the pores in the flint vary somewhat in dimensions, a comparison with the well-known findings of Rayleigh is invited. Rayleigh's mathematical thesis indicated that the light transmitted through a heterogeneous system of appropriate granularity is richer in the radiation of longer wave-lengths; that scattered is richer in the radiation of shorter wave-lengths. The light scattered by the pores in flint should thus be richer in blue, but this was not demonstrable in the few simple experiments which were made; cracks in the flint appeared to reflect sufficient white light from their walls to conceal any blueness from the eye. Bancroft and Gurchot (1932), however, have cited heterogeneous systems in which a change in the size of the dispersed phase has caused



a systematic alteration in the colours transmitted. This would be expected from Rayleigh's findings, but the colours may arrange themselves in successive series which, furthermore, may show a repetition which is nearly regular. Brown colours (cf. flint, &c.) may be represented in these series. It does not seem possible to deduce such colour series from Rayleigh's equations which, in their present form, apply only to a limited range of sizes. Shoulejkin (1924) has now extended Rayleigh's mathematical treatment to the study of particles of any size (see also Sinclair and La Mer, 1949, for a bibliography of light-scattering phenomena). We, however, do not feel competent to pursue this discussion further.

It was mentioned earlier that the brown colour persisted even in flint calcined at 1400° C., i.e. in cristobalite. If the colour depends on the presence of minute pores, the recrystallization processes, which convert this cristobalite to material of higher density and refractive index, should lead to a disappearance of the colour. This was confirmed. Recrystallization in the presence of 2 % of sodium carbonate (see above) gave a colourless cristobalite although the process, as indicated by the somewhat low density of the material, was incomplete. It could, of course, be argued that a foreign tinctorial agent had left the crystals and had become concentrated in the small amount of soda-rich phase produced. However, similar results followed the recrystallization, at temperatures somewhat greater than 1500° C., of flint with no added fluxes. The recrystallized material was often clear although there were many turbid grains. The turbidity depended on the presence of collections of obvious cavities. The typical brown colour had, however, disappeared.

In conclusion, the possibility may be noted that the brownish colours seen in thin sections of some natural or artificial products may result from an optical phenomenon of the type discussed above, e.g. certain opals, volcanic glasses, and feldspars (MacGregor 1931, p. 525) and the fine-textured partially glassy matrix of many whiteware and other ceramic 'bodies'. Further, it may be significant that the colophane described by Dunham, Claringbull, and Bannister (1948) as having a low refractive index, dependent on porosity, is brown in thin section.

#### *Summary.*

(1) Cretaceous flint from the sea-beaches of England was shown by X-ray powder photography to consist of quartz of which much was very fine-grained. Opal or cristobalite, if present, were in amounts

too small for detection. The flint had the microscopical characteristics of chalcedony.

(2) Included calcareous matter, of which some was the undoubted remains of fossils, had been partially replaced by silica. This was well displayed by an aggregate of eumorphic carbonate, with Fe, Mg, and Ca, of which part had been converted to pseudomorphs of quartz.

(3) A chemical analysis and a continuous weight-loss versus temperature curve are presented for the flint. The obstinate retention of water at elevated temperatures does not in itself imply the presence of opal; adsorption and occlusion in a fine-grained system could suffice to give this effect.

(4) In the raw state the flint was blackish by incident light. Prolonged treatment with hydrogen peroxide caused a fading of this colour. After adequate calcination the flint was white by incident light, but brown by transmitted light even at thicknesses of 30–40 microns.

(5) Calcination caused also a decrease in density and refractive index. The density-temperature curve declined steeply from 300° to 600° C. and then much more slowly to 1000° C. A further sharp fall succeeded from 1100° to 1400° C. This second fall was caused by the formation of cristobalite; below 1200° C. quartz alone was detected by X-ray powder photography.

(6) The density-temperature and refractive index-temperature curves showed a general similarity of shape.

(7) The cristobalite formed at 1400° C. was of anomalously low density and refractive index.

(8) Anomalously low densities and refractive indices were shown by flint calcined at various temperatures irrespective of whether quartz or cristobalite was present. These properties were attributed to the presence of minute pores.

(9) To the pores was ascribed also the brown colour by transmitted light which accompanied the anomalous properties mentioned and appeared in both quartz-rich and cristobalite-rich preparations. Recrystallization of the cristobalite prepared at 1400° C. increased the density and refractive index and discharged the brown colour; these effects are explicable by the removal of minute pores. Comparable examples of the production of brownish colours in dispersions are enumerated; some are of geological interest.

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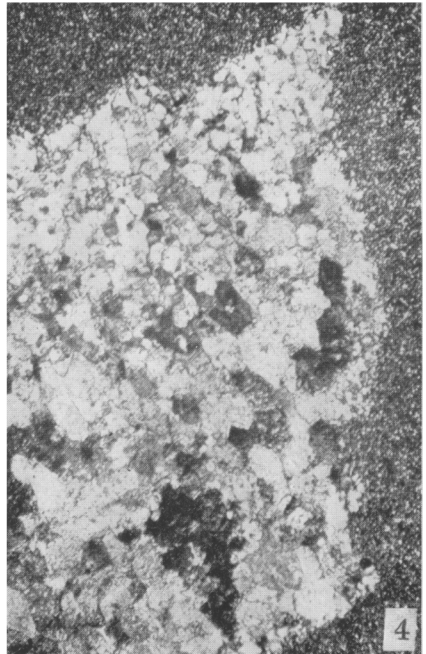
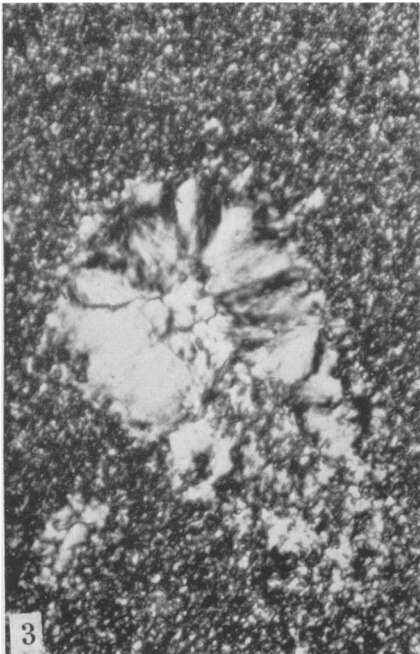
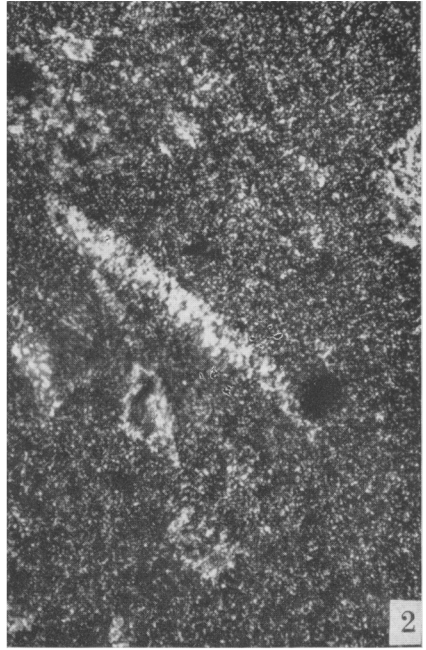
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## EXPLANATION OF PLATE XIV.

## Photomicrographs of flint.

- FIG. 1. Foraminiferal shell in flint. The central portion is still calcareous, the rest siliceous.  $\times 153$ .
- FIG. 2. Elongated body consisting of fibrous chalcedony. Some of the coarser areas elsewhere contain rhombohedral carbonate.  $\times 80$ .
- FIG. 3. Chalcedony fibres diverging from the boundary between the 'matrix' and coarser aggregate.  $\times 130$ .
- FIG. 4. Inclusion in flint. Eumorphic rhombohedral carbonate partially replaced by quartz near the boundary with the 'matrix'.  $\times 51\frac{1}{2}$ .
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