XIV.—*Studies in Ancient Glasses and Glassmaking Processes. Part V. Raw Materials and Melting Processes*

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Abstract

The recipes recorded from 1700 B.C. to the seventeenth century A.D. for making non-lead-containing glasses all prescribe crushed silica rock or sand and ash (or glassmakers' salts) as the major, or as the only, constituents. Yet all analyses disclose the presence in the ancient glasses of from 2–3 per cent up to more than 20 per cent of lime; 0·2–0·5 per cent up to 7 per cent of magnesia and somewhat similar amounts of alumina and iron oxide; and phosphoric and other oxides (see Part IV).

Analyses are now given of seven sands from possible ancient Egyptian glassmaking sites; and one Syrian, from the mouth of the River Belus. In only one (Assouan) is the lime less than 1 per cent whilst in four it exceeds 10 per cent. Alumina, magnesia, and iron oxide are also present in considerable amount, the lowest iron oxide being that in the samples of Belus sand (0·15 per cent).

Soda could have been derived from the natron lakes of Egypt or (less likely) from Nile water; soda and potash by burning coastal or desert plants, or inland plants and trees. The coastal or desert plants yield both sodium and potassium salts but with a much greater proportion of the sodium salts in a reactive form (e.g. carbonate). On the other hand, ash from inland plants contains much more of potassium than of sodium salts. Both types also contain lime and magnesia in amount greater, in some plants, such as beechwood, than the potassium and sodium salts; and also phosphoric oxide and silica.

Accordingly, apart from solution of material from the melting pots, ancient glasses owe their complex compositions to iron oxide, alumina, lime and (frequently) magnesia derived from the sand, and soda, potash, lime, magnesia, and phosphoric oxide, as well as residues of sulphate and chloride, from the ash.

The presence of substantial amounts of non-reactive sulphate and chloride in all the possible sources of soda or potash necessitated prolonged melting and heavy labour to make clear, homogeneous glass.

The present paper is devoted to the dominant non-lead-containing ancient glasses. Those containing lead will be discussed in Part VI.

It will serve as a useful introduction to the consideration of the raw materials used by the ancient glassmakers to set out the most important statements which have been made during the 3000–3300 years under review about the composition and preparation of glass.

The first, to which reference has already been made in Part III, is the Babylonian chemical text of 1700 B.C. or earlier, translated and published by C. J. Gadd & R. Campbell Thompson (1936). It contains four recipes for glazes in each of which the major constituent is zukû-glass, but no indication of its composition or preparation is given. There are several other recipes in which these glazes serve as the basis of others by the fusion of prescribed amounts of them with stated quantities of colouring materials; but there is no point in quoting them since we are here concerned only with the major materials. A thousand years later in age, the Nineveh tablets translated by R. C. Thompson (1925, 1936) record a considerable number of glass recipes, unfortunately lacking in several cases the name or quantity of some ingredient, as is the case in the record of the composition of zukû-glass. The most complete and clear of the recipes is for sirşu-glass, referred to as follows:

> To make sirşu-glass:
> 20 mana of sand, 1 talent (60 mana) of salicornia-alkali, 1⅔ mana of saltpetre, ⅔ mana of lime.

The recipe for dušû (crystal), somewhat less complete, in that the translator does not appear to have found simple renderings for two minor ingredients, also has as its chief components, 20 mana of sand and 60 mana of salicornia-alkali, together with 2 mana of saltpetre and 10 shekels (1/6 mana) of lime.

Some seven hundred years later, that is, in the first century A.D., Pliny, after recounting the legend about the discovery of glass by the action of heat on lumps of nitre and the sand at the mouth of the River Belus, proceeds, in the following chapter, to say:

> In process of time, as human industry is ingenious in discovering, it was not content with the combination of nitre, but magnet-stone began to be added as well; from the impression that it attracts liquefied glass as well as iron. In a similar manner, too, brilliant stones of various descriptions came to be added in the melting, and, at last, shells and fossil* sand. Some authors tell us that the glass of India is made of broken crystal† and that, in consequence, there is none that can be compared to it.

The above, according to Pliny, was the ancient procedure. In his own time, he states, a very white sand for the purpose (that is, for glassmaking) was found at the mouth of the River Volturnus in Italy. This, he says,

> is prepared for use by pounding it with a pestle and mortar; which done it is mixed with three parts of nitre, either by weight or measure, and when fused is transferred to another furnace.

In the tenth century A.D. the complete batch composition prescribed by Theophilus was 'two parts of the ashes of which we have spoken' (i.e. beechwood ashes) 'and a third of sand, carefully purified from earth and stones, which sand you shall have taken out of water, mix them together in a clean place'. In the sixteenth century the prescription was essentially the same. In his book dated 1540, V. Biringuccio says:

> The method of composing glass. . . . First one takes ashes made from the saltwort that comes from Syria. . . . Now some say that this ash is made from fern and some from lichen; which of these it does not matter here . . . some of those sparkling white

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* i.e. 'excavated', as from a mine or quarry, in contrast to a beach.

† Some commentators (see e.g. M. L. Trowbridge, *Philological Studies in Ancient Glass*, Univ. of Illinois, 1930) have imagined that this phrase 'broken crystal' implied broken crystal vessels, and have supposed that Pliny must have been misinformed. There are, however, in various parts of India extensive outcrops of massive quartz (or quartzite) of such high purity that pieces of it look like broken crystal. Such an outcrop near Hyderabad city is calcined and then crushed for glassmaking. With reasonable care in selection and treatment it yields a crushed product containing less than 0·01 per cent Fe_2O_3 and is one of the purest glassmaking sands which have been commercially used in the twentieth century.

> river stones that are called pebbles and that are clear and breakable and have a certain resemblance to glass. When it is impossible to have these, take in their place a certain white mine sand that has a certain rough harshness. Of whichever of these is taken, two parts are put to one of the said salt (ashes) and a certain quantity of manganese according to your discretion.

Likewise in the sixteenth century, Georgius Agricola gives the following instructions:

> One part of coarse or fine sand made from fusible stones should be mixed with two parts of soda or of rock salt or of herb salts, to which are added minute particles of *magnes*.

Alternatively,

> two parts of the ashes of oak or holmoak, or of hard oak or Turkey oak, or, if these be not available, of beech or pine, are mixed with one part of coarse or fine sand, and a small quantity of salt is added, made from salt water or sea water, and a small particle of magnes.

Essentially the same mixture of finely powdered pure siliceous rock or of sand plus ash is the prescription of Antonio Neri in 1612 and remained the basis for glassmaking in many factories right up to the early part of the nineteenth century. Except for the very small amounts which appear in the Assyrian recipes and perhaps, as mentioned by Pliny, in the form of shells, lime, as pointed out in Part III, was not knowingly added by the glassmaker.

POSSIBLE SANDS EMPLOYED IN ANCIENT GLASSMAKING

The only two sands for glassmaking which are specifically mentioned by location in classical writings are that at the mouth of the River Belus on the Syrian coast, and the seashore deposit mentioned by Pliny near the mouth of the River Volturnus between Cumae and Liternum, north-west of the ancient harbour of Pozzuoli and of Naples.

The Belus sand enjoyed a reputation over many centuries. R. C. Thompson has suggested (1936) that it may even have been purchased by the Sumerians for making their glazes. It is specifically mentioned by Strabo (born 63 B.C.) as being used for glassmaking and its use for the same purpose is referred to by Pliny, Josephus, Tacitus, and several other classical writers of the first century A.D. Presumably it served the glassmakers who established and operated factories along the Syrian coast for many centuries, and was also extensively exported.

The sources of sand employed in ancient Egypt are unknown. Flinders-Petrie (1894 and 1925) considered that quartz pebbles, calcined and ground, were used by the glassmakers of the eighteenth Egyptian Dynasty in order to obtain glasses practically free from iron oxide. This surmise cannot survive examination of the facts derived from analysis, as A. Lucas (1948) has pointed out. It is obvious from the data assembled in Part IV of this paper (1956) that the iron oxide content of all the Tell-el-Amarna glasses is substantial and it is almost certain that only sands such as the impure sands of the desert could have supplied most of it. Lucas states of such sands that they contain not only iron oxide and alumina but also lime and magnesia and frequently small amounts of manganese; but he reproduces no analyses. The massive two-volume work by W. F. Hume entitled *The Geology of Egypt* contains no sand analyses but there are several items of useful information. Thus he states (1925) that sea sands near Alexandria and those of the Red Sea and the Gulf of Suez are calcareous. Also in this volume is embodied an interesting report by J. Ball (1907) on the character of the minerals to be found along the Nile at the first Assouan cataract. The river sand at that point was highly angular, with quartz fragments associated with felspars, hornblende, and magnetite. In some locations of the river, water washing had produced concentrations of magnetite and in others hornblende. At Assouan, sands of pure snowy white silica were found with occasional grains of felspar and calcium carbonate. The sands north of Assouan differed in mineral content. On the western bank of the Nile opposite Luxor the sand glittered with mica and the micaceous sand extends up to Cairo. Where wind-borne sand had swept for long distances over limestone desert floors, the latter constituent became more conspicuous.

Being unable to obtain precise analyses of sands, either from published works then known to me, or through any agency in Cairo, when on a visit to that city in 1953–4, I collected samples from Tell-el-Amarna, probably the best known eighteenth Dynasty site of glassmaking, and also a sample of river silt from the Theban shore of the Nile, opposite Luxor, about a hundred yards away from the low-water level of the river. It may be noted that the Tell-el-Amarna sands, although on the eastern side of the Nile, were golden yellow and the Thebes river silt grey. The sample from Tell-el-Amarna selected for analysis was collected near the site of the workmen's houses, in the ancient city.

As to the sands at the mouth of the River Belus, Palestine, I was fortunate at Haifa, through the good offices of Mr. A. Weiss, Engineer to the Palestine Glass Works Ltd., to obtain access to some analyses which had been made by Drs. Heimann* and Berl in 1935. They showed that not only, as pointed out by Hume, are the seashore sands of Alexandria, the Gulf of Suez and the Red Sea calcareous, but so also are those of the Mediterranean coast at Haifa. Since the analyses of Heimann and Berl contained no reference to magnesia I thought it desirable to make an independent check and accordingly collected a sample. Its partial analysis, and the fuller analysis of the two Egyptian sands, were carried out for me by the Glass Works Laboratory of the General Electric Co., Wembley. I acknowledge, with thanks, the courteous help in this connection of Dr. E. Preston, Messrs. A. C. Jeffkins, and G. W. Warr.

Subsequent to the carrying out of these analyses I was able to get access to a copy of H. D. Parodi's *La Verrerie en Égypte* (1908), a University thesis not readily available, and found that it contained three analyses of sands by himself and three others by A. Lucas, although I cannot discover that Lucas himself published them. Achmounein is near Beni Hassan. The

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* Now Professor of Chemistry in the Technical High School, Haifa.

other locations are readily identified. The various analyses are given in Tables I, II, and III.

TABLE I

Composition of Desert Sands from Ancient Egyptian Glassmaking Regions

	A. After H. D. Parodi			B. After A. Lucas		
	Karnak	Fayoum	Achmounein	Pyramids	Assouan	Alexandria
SiO_2	83·61	95·22	96·74	82·35	93·78	32·0
Al_2O_3 Fe_2O_3	1·32	1·86	0·62	1·45	3·59	0·70
CaO	12·01	1·85	1·91	8·40	0·67	34·98
MgO	1·23	0·09	0·57	tr	tr	2·20
NaCl	—	—	—	0·19	tr	0·38
SO_3	—	—	—	0·22	nil	nil
Moisture	1·57	1·02	0·11	1·15	0·37	0·64
Loss on ignition	—	—	—	6·56	1·12	29·56

TABLE II

Composition of Sand from Three Sites in Bay of Acre (Mouth of Belus, Haifa) June–July 1935

(After Drs. Heimann and Berl)

Site	1	2	3
SiO_2	80·98	80·8	80·16
Al_2O_3	3·58	3·92	5·27
Fe_2O_3	0·12	0·12	0·15
CaO	9·0	8·82	8·6
Loss on ign.	6·3	6·6	5·8

Note: As a test of constancy of Fe_2O_3, samples were taken at 60 cm. and 120 cm. depth at each of six sites. The range of Fe_2O_3 was 0·07% to 0·21%.

TABLE III

Composition of Sands from Ancient Sites

	Egypt		Syria (Haifa)
	Tell-el-Amarna	Nile bank opposite Luxor	
	March 1954	March 1954	December 1953
SiO_2	60·46	72·69	76·40
Al_2O_3	2·25	8·18	n.d.
Fe_2O_3	1·73	5·60	n.d.
TiO_2	0·44	1·20	n.d.
P_2O_5	0·08	0·12	n.d.
CaO	18·86	4·86	10·73
MgO	0·83	2·44	0·75
BaO	nil	0·18	n.d.
Na_2O	0·30	1·21	n.d.
K_2O	0·74	1·10	n.d.
MnO	0·02	0·09	n.d.
SO_3	0·05	0·06	n.d.
Total moisture	0·42	1·04	0·40
Loss on ign. at 900°	13·90	1·60	7·80

NOTES

Mineral Contents

Mr. A. C. Jeffkins kindly supplied the following notes on the mineral content based on microscopic examination of the above three sands.

1. *Tell-el-Amarna Sand.* A quartz-calcite deposit, some of the calcite appearing as fossiliferous shell detritus. Much of the quartz was iron-stained and associated with dolorite. Approximate mineral content: quartz 50–55%, calcite 30–33%, felspar 5%, pyroxenes 5%, ilmenite 1%.
2. *Silt, Thebes.* Unevenly graded and the heavy mineral content suggests porphyry or syenite as the source. Approximate mineral content: quartz 55%, orthoclase and plagioclase felspars 16–18%, amphiboles and pyroxenes, mainly hornblende, 16–20%, ilmenite 2–3%, calcite and barite 4%, clay and mica 2–3%.
3. *Sand from mouth of Belus, Haifa Bay.* A quartz-calcite deposit, much calcite being fossiliferous shell detritus. Approximate mineral content: quartz 70–75%, calcite 16–18%, plagioclase felspars 4%, pyroxenes 4%, ilmenite 1%.

The material taken from the Nile Bank at Thebes (Table II) can probably be ruled out as unlikely ever to be used as a normal source of glassmaking sand. It has all the characteristics of a river silt, that is of rock material in the process of undergoing disintegration. The striking fact about the sands from Tell-el-Amarna and Karnak is their high lime content. Both these areas are adjacent to the long limestone bluffs, some hundreds of miles in length, which run parallel to and not far from the Nile from just south of Cairo down to Luxor and Thebes; and no one who has seen a sandstorm raging, as I myself witnessed from Luxor, could doubt that much lime must come from wind-driven material scoured from the limestone bluffs. The amount of this constituent would, from the nature of its source, be likely to vary from point to point. The sand from near the Pyramids, at Gizeh, also has a substantial lime content. Those from the Fayoum, from Achmounein and from Assouan contain much less limestone and have the highest silica content, ranging from approximately 94 to 97 per cent. The Alexandrian sand quoted in Table I has a calcium oxide content of approximately 35 per cent, equivalent to about 65 per cent of calcium carbonate, and the silica is only 32 per cent. There is no information as to the precise locality from which the sample was taken. The dunes along the north coast of Africa west of Alexandria are also known to be heavily charged with limestone shell detritus. It is possible that the Alexandrian sample was wind-blown, whereby the platy shell detritus, despite a slightly higher density than the quartz grains, would be winnowed out and therefore in greater concentration on the dunes than in the material on the beach or under the sea. Whether or not such sample was really representative of Alexandrian sands, it could not possibly have been used for glassmaking purposes without heavy dilution by a nearly pure silica sand.

Similar calcareous sands are not unknown on the coasts of the British Isles. One such deposit in which quartz grains are mixed with a large proportion of shell detritus is to be found in the sand dunes at Hayle in Cornwall, and another, of lower shell content, at Elie on the coast of Fife, Scotland. Both were tried for glassmaking in the early 1920's, and in both cases the glass underwent extensive devitrification in the tank furnace with the deposition of what was then diagnosed as wollastonite ($CaO.SiO_2$). We are left guessing, therefore, as to the source and composition of the sand employed by the glassmakers of Alexandria.

The sand at the mouth of the Belus also contains lime equivalent to from 14·5 to 18 per cent of calcium carbonate and, from our independent check, about 1·5 per cent of magnesium carbonate. When mixed with alkali, from whatever source obtained (see below), the lime content of the mixture might well fall within safe limits in the glass.

The six analyses recorded by Parodi (Table I) do not give separate values for the alumina and iron oxide in the sands but only the combined totals, a fact which prevents any conclusion being drawn about their suitability based on the iron oxide content. Judged by this same criterion, the Belus sand, with much the lowest iron oxide of the sands quoted, does not bear favourable comparison with the sands used by the modern glassmaker and could not be expected to yield truly colourless glass. The alumina content is also substantial (3·5 to 5·2 per cent).

THE SOURCES OF ALKALI

The possible sources of alkaline salts open to the ancient glassmaker were at least four in number: large-scale deposits resulting from the evaporation and drying up of former land-locked seas and lakes; local evaporation in pans or pits of sea or river water; leaching out of salts from soils; and the ashes of vegetable matter. Deposits from former seas or lakes of interest to the glassmaker are illustrated by the impure carbonate and bicarbonate at Wadi Natrûn and at El Kab in Egypt and at Magadi in East Africa; of sodium sulphate at Wadi Natrûn and at various places in Europe, U.S.S.R., Turkey, Canada, and India; and of potash, borax and other salts at Trona, California. The Dead Sea and the Great Salt Lake of Utah are examples of deposits undergoing development. All seas and oceans are saline owing to the presence of numerous salts, particularly chlorides and sulphates.

It is a natural conjecture that natron from Wadi Natrûn or other of the lakes containing sodium carbonate and bicarbonate may have been used for glassmaking. It had already been used from very early times as a detergent, in medicine, and in the process of embalming. Specimens of it have been found in ancient Egyptian tombs and analyses of it and also of modern soda obtained from the Wadi Natrûn are given in Table IV. This natural soda is reputed to have been exported from very ancient times. H. E. Benrath (1875) stated that the export of this raw soda had continued until 'present times' and he quoted an analysis by M. H. Klaproth which applied to the beginning of the nineteenth century. The sample contained sodium carbonate 22·4 per cent, sulphate 18·3 per cent, chloride 38·6 per cent, water 14·0 per cent, and insoluble matter 6·7 per cent. The features of the material, in both ancient and modern samples, are complexity and variability of composition, the proportion of carbonate, bicarbonate, chloride, and sulphate varying widely. As to its use for glassmaking, H. D.

Parodi has pointed out (1908) that all the ancient Egyptian glasses contain much more potash than can be derived from natron or natural soda.

In regard to the nature of the salt obtained by artificial evaporation, it would vary with the source, whether sea or river. One case to which reference may be made is to the saline content of Nile water. Pliny (first century A.D.), in describing the various ways in which nitrum was obtained, says that in Egypt it was prepared from Nile water and mentioned Naucratis, in the Nile delta, and Memphis, some twenty miles south of the present city of Cairo, as sources, the nitrum from Memphis being of inferior quality. In the long account of processes for preparing various salts which Agricola describes in his *De Re Metallica* of 1556, he refers to one in use on the banks of the Nile, according to which Nile water was led through sluices and by channels into pits or pans where it evaporated and yielded 'salt'. A woodcut of the supposed operations illustrates the account.

TABLE IV

Range of % Composition of Samples of Natron

(after A. Lucas)

	Ancient Samples from eighteenth Dynasty Tombs (7 samples)	Modern Natron from Wadi Natrûn (14 samples)
Sodium carbonate	15·5–94·0	22·4–75·00
Sodium bicarbonate		5·0–32·4
Sodium chloride	0·5–39·5	2·2–26·8
Sodium sulphate	5·5–27·8	2·3–29·9
Water, free and combined	5·6–19·8	1·9–20·0
Matter insol. in water	5·4–27·0	tr–31·1

It is of interest that A. Popp (1870) made an investigation both of the sediment and of the salts in solution in the Nile at a point described as two hours distant from Cairo, southwards. Special arrangements were made to carry out precise analyses in Egypt in order to avoid any changes due to time and transport to Germany. The matter in solution, when evaporated in platinum and dried at 100°C., amounted on the average to 0·142 grams per litre (quite modest in comparison with some drinking waters of Western Europe) and had a composition returned as:

TABLE V

Na_2CO_3	25·15%	$CaSO_4$	4·68%
K_2CO_3	5·40	NaCl	3·91
$CaCO_3$	24·21	Fe_2O_3	2·23
$MgCO_3$	21·70	$Ca_3(PO_4)_2$	0·53

Organic matter, ammonia, silica, 12·12%.

Points of special interest are the relative proportions of soda and potash and the high proportions of calcium and magnesium carbonates. If a salt, or nitrum, were indeed prepared from Nile water, as Pliny stated, the labour involved would be very heavy in proportion to the result obtained, for 7000 parts of water would have to be evaporated in order to yield a single part of the salt. Whether or not the salt or nitrum was so prepared, the annual inundations of the Nile would naturally leave the submerged sands, after subsidence and evaporation of the water, richer in the constituents normal in glassmaking materials.

Finally, in regard to salts derived from plant ash, it is clear that alkali derived from this source has a long tradition in glassmaking. The alkali referred to in the tablets of Assur-bani-pal of the seventh century B.C. is in all instances derived from the plant salicornia; and the traditional glassmaking mixture, namely, sand plus ash, whatever minor constituents might be added, continued basically the same until early in the nineteenth century. Indeed, on reference to the succeeding tables which set out the compositions of the ashes of different plants, it could be a legitimate deduction that glazes on pottery might have originated at an early date when the primitive methods of firing were used in which the pots were stacked in, and covered by, the fuel: chaff, straw, reeds, or wood, the ash from which reacted with the clay or siliceous material of the pot. The discovery that a crude glaze was produced by this means might have given the natural impetus to further experimentation and so set on foot the long course of development which ultimately led to the isolation of the glaze, or glass, as an independent material.

I propose to discuss at some length this derivation of alkali from plant ash and its employment in glassmaking, for its proper understanding has a very important bearing on the problems of glassmaking over many centuries.

PLANT ASH AS THE SOURCE OF GLASSMAKING CONSTITUENTS

The ash from plants has been employed for many centuries for medicines, detergents, and as the source of alkalis for manufacturing operations such as soap making and glass manufacture. Ultimately, in the eighteenth century, it became established that two kinds of alkali existed, namely, soda and potash; and, with the further progress of chemistry, that plants which were grown near the sea or on salt desert land were associated with a relatively high soda content whilst those of inland regions were relatively rich in potash. What has been all too little appreciated is that all plant ashes contain many other constituents besides the compounds of sodium and potassium, and that the alkali in coastal and marine plant ash is not wholly soda nor that in inland plant ash wholly potash.

The earliest plant recorded as a source of alkali for glassmaking is that on the Nineveh Tablets translated by R. Campbell Thompson as salicornia, which he stated was the name of two species of chenopodiaceae abounding in soda.* Pliny refers to the production of 'nitrum' from the

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* Löw, in *Flora der Juden*, Vienna, 1924–8, says that the soda-producing plant salicornia herbacea is very common in Egypt, Syria, Judaea, and Arabia.

ash of the oak (quercus) as no longer in use in his day. About a thousand years later Theophilus strongly recommended beechwood ash, and this material remained in favour in many regions of Western Europe for several hundred years, being mentioned by Heraclius and Agricola. Biringuccio (1540) referred to the saltwort from Syria and also to ash from ferns, whilst Agricola (1556) mentioned, in addition, various kinds of oak and pinewood ash as suitable for glassmaking. Neri (1612) wrote of polverine or rochetta, the plant ash exported from the Levant, Syria, and Egypt; and the early chapters of his book are devoted to the further purification of polverine and of ashes derived from a number of plants recommended, particularly fern, cods and stalks of beans, bramble berry bushes, millet stalks and rushes and reeds. His translator and commentator, Christopher Merret (1662), mentioned four types of plant from which the Alexandrians prepared polverine, namely (in the classification of the second half of the seventeenth century) kali geniculatum, kali secunda, kali Egyptiacum, and kali spinosum. The last-named he identified from a specimen which happened to be in a bag of imported polverine and he stated that the species also grew on our own coasts and on the banks of the Thames, but the British-grown plants yielded practically no ash compared with that to be derived from samples of the same plants brought from the Levant and burnt under identical experimental conditions. Merret also added his quota to the list of useful plants for making ash and concluded that 'the best and strongest of all English ashes are made of the common way thistle'.

By the end of the sixteenth century another source of ash known as barilla had become established. It was prepared from coastal plants near Alicante, Spain, and was exported extensively. Its hold on the alkali trade of England by the beginning of the nineteenth century was such that when Muspratt established the first factory in England in 1823 to work the Leblanc process, the objective, as stated by Partington (1918), was to be the production of 'British barilla'.

Neri expressed a preference for polverine (and rochetta) over barilla. There is no direct information about the composition of polverine, but according to H. Leng (1835) barilla might contain up to 30 per cent of sodium carbonate. By the courtesy of Imperial Chemical Industries Limited I have obtained access to a report dealing with one of the activities of the Economic Section of the Spears Mission to Syria in 1943. In reviewing possible schemes for new industries or for the development of existing native small-scale efforts, information was put before the Mission about the composition of a product locally known as 'Keli', the residuary ash from a plant called 'Chinane' which grows in the Syrian desert.* The dried plant was said to yield one fourth of its weight of ash, and, based on some fifty different samples of Keli, its composition was as given in Table VI.

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* Mr. D. G. Emerson has informed me that in 1951 he visited in Aleppo a native soap factory at which a proportion of Keli was used among the ingredients of the mixture to be boiled.

TABLE VI

Composition of Keli or Ash from the Syrian Desert Plant 'Chinane'

Parts per 1000

Part Soluble in Water:	600	Part Insoluble in Water:	400
Sodium carbonate	450	Calcium carbonate	340
Sodium hydroxide	25	Calcium phosphate	40
Potassium chloride	45	Magnesium carbonate	10
Potassium sulphide	30	Carbon	10
Silicates, phosphates, and other inorganic matter and water	50		

The Keli, as represented by the above analysis, is so exceptionally rich in sodium carbonate that one could wish for further investigation of 'chinane' and other coastal and desert plants in the Levant and Egypt.

TABLE VII

Composition of Kelp from the Orkneys

(From N. Graeger, *Die Glasfabrikation*, 1868)

100 parts contain 6·8 of water, 63·4 soluble material, 29·7 insoluble

Soluble Material		Insoluble Material	
Potassium sulphate	4·5	Calcium carbonate	6·4
Sodium sulphate	3·6	Calcium phosphate	10·5
Calcium sulphate	0·3	Calcium sulphate	1·1
Magnesium sulphate	0·9	Magnesium carbonate	6·8
Sodium sulphite	0·8	Sand	1·6
Sodium hyposulphite	0·5	Alumina	0·1
Sodium carbonate	5·3	Organic matter	2·87
Sodium chloride	26·5		
Potassium chloride	19·3		
Calcium chloride	0·2		
Magnesium iodide	0·3		
Sodium sulphide	1·6		
Sodium phosphate	0·5		

TABLE VIII

Range of % Composition of (Four) Samples of nineteenth-century Varec

(from N. Graeger, *Die Glasfabrikation*, 1868)

Sodium carbonate	0– 9·5	Potassium carbonate	nil
Sodium sulphate	0–30·9	Potassium sulphate	18·6–41·5
Sodium sulphite	0–14·9	Potassium sulphite	nil
Sodium chloride	29–50·7	Potassium chloride	4·1–20·0
		Potassium iodide	tr

The burning of marine plants to yield a crude alkali was practised on the western shores of the British Isles and of France, the product from seaweed being known as kelp in the United Kingdom and varec in France. Analyses of samples of each are recorded in Tables VII and VIII. The composition of the varec is presumably that of the soluble part of the ash and both kelp and varec will be seen to yield poor supplies of sodium carbonate.

All the analyses in Tables VI to VIII reveal the complex character of the ash derived from both the coastal and the marine plants. But before further discussion of the characteristics of the types of ash disclosed it will be advantageous to deal with those obtained from inland plants. This last-named type appears in Germany, France, and England in the early Middle Ages, certainly by the tenth century A.D., since it is Theophilus, whose work has now been assigned to that century, who made known the use of ash from beechwood. Its introduction brought about a major change in glass composition, since in ash from inland plants the potash greatly predominates over the soda, so much so that from the analyses of ancient glasses of European origin, in medieval and Renaissance times, it is easy to determine which were made from the ashes of beechwood, oak, fern, etc., and those derived from polverine or barilla. Our knowledge of the ashes from inland trees and plants is far more extensive than that which relates to the vegetation of the coasts, the deserts, and the sea, because of the importance which agricultural chemistry has attained since Liebig's work at the middle of the nineteenth century. The data in Table IX are derived from the table forming part of the article 'Ash' in T. E. Thorpe's *Dictionary of Applied Chemistry* (1937), the table having been collated mainly from the numerous determinations of E. Wolff (1871). As here produced the data selected from Thorpe have been recalculated so as to show the percentage of each constituent present in the total ash. Approximations have been used but any variations are too slight to modify the general conclusions.

For a fuller appreciation of the composition of the various types of ash the article in Thorpe's *Dictionary* should be read, but one or two points of special interest may be noted. First, the list of elements present to different extents in plant ash is a long one. It includes a number of the trace elements, such as Li, B, Ag, Zn, Co, which have been detected and recently determined spectrographically in ancient glasses. Like the major constituents of ashes they were taken up from the soil through solution, that is, in saline solution from river or sea water.* Aluminium and iron are only

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* H. U. Sverdup, M. W. Johnson & R. H. Fleming, in *The Oceans: Their Physics, Chemistry and General Biology*, New York, 1942, Table 36, pp. 176–7, give a list of the average sea water content of some forty elements. The amounts, in terms of mg./Kg. of elements with which we have largely to do in glassmaking, are as follows:

Cl	18980	S	884	Sr	65
Na	10561	Ca	400	C	28
Mg	1272	K	380	Sr	13
		B	4·6	Rb	0·2
		Si	0·02–4·0	Al	0·5
		F	1·4	Fe	0·002–0·02
		N	0·01–0·7	P	0·001–0·10
		Li	0·1		

The dominant elements are the two alkali-forming elements, sodium and potassium, and the two alkaline earth elements, calcium and magnesia combined with chlorine or sulphur, the latter mainly as sulphate. The saline content is of importance to the composition of the ash of plants which grow on the coast or on areas formerly inundated by the sea and in the sea itself. The authors point out that the content of some of the elements appears low because it is kept under continual control by rapid removal by living agencies. Thus calcium is removed to build up the skeletons and shells of marine organisms and phosphorus is essential to plankton and to marine plants, as is also nitrogen.

minor, though necessary, constituents, varying greatly with the plant. Manganese occurs in ash from beechwood, particularly in the leaves, which in different specimens have yielded MnO to the extent of 1 to 11 per cent of the ash. W. Geilmann, K. Beyermann, Th. Brückbauer & H. Jeneman (1955) have recently corroborated this fact by new data indicating a range of Mn_3O_4 content in beechwood ash from different sources of 0·2 to 13 per cent.

TABLE IX

Percentage Ash Content and Composition from Various Air-Dried Vegetable Materials

(Calculated from data in Thorpe's *Dictionary of Applied Chemistry*, 1937, Vol. I, pp. 508–9)

Substance	%	% Composition of Ash								
	Total Ash	SiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	S	Cl
Wheat straw	4·26	66·2	6·1	2·5	2·8	11·5	5·4	2·8	3·8	—
Barley straw	4·39	53·8	7·5	2·5	4·6	21·2	4·3	3·6	2·9	—
Heather	3·61	35·2	18·8	8·3	5·3	13·3	5·0	4·4	—	2·2
Fern	5·89	6·1	14·1	7·6	4·6	42·8	9·7	5·1	—	10·2
Reeds	3·85	71·4	6·0	1·3	0·26	8·6	2·1	2·8	—	—
Sedge	6·95	31·4	5·3	4·2	7·3	33·2	6·7	3·3	—	5·6
Rush	4·56	11·0	9·4	6·3	6·6	36·6	6·3	8·8	—	14·2
Wheat (grain)	1·77	1·7	3·3	12·4	3·3	31·1	46·3	2·2	—	8·4
Beech (leaves)	3·05	33·8	44·9	5·9	0·7	5·2	4·7	3·6	—	0·3
Beechwood, trunk	0·55	5·4	56·4	10·9	3·6	16·4	5·4	1·8	—	—
Beech brushwood	1·23	9·8	48·0	10·6	2·4	13·8	12·2	0·8	—	—
Oak	0·51	2·0	72·5	3·9	3·9	9·5	5·8	2·0	—	—
Apple	1·10	2·7	70·9	5·5	1·9	11·8	4·5	2·7	—	—
Mulberry	1·37	3·6	57·0	5·8	6·6	36·6	6·3	8·8	—	14·2

This extraordinary occurrence of manganese in beechwood ash is most interesting as throwing light on the methods of Theophilus (tenth century A.D.) to produce yellow, flesh colour, and purple tints in glass intended for window glass for church decoration. He noted that it was a matter of time of standing in the pot what colour was obtained, as, indeed, one might expect with manganese.*

Returning to the consideration of Table IX the representation of the amounts of the constituents as percentages of the total, adopted for the purpose of this paper, makes more clearly discernible the possibility that, even allowing for the presence of sulphates and chlorides, the ash from some plant sources might itself produce a glass when heated at high glass melting temperatures. This might be true, for example, of wheat straw and barley straw.† The composition of the sample of ash from reeds also does

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* Heraclius also relied on ash from beechwood to produce the flesh-coloured and purple colour required, and J. Fowler (1880) commented on this same interesting observation, associating it with the presence of manganese.

† A Swedish architect, when visiting London in 1778, had the opportunity of looking over a glassworks situated in Southwark and reported that the glassmaking mixture was composed of one part of sand and three parts of ash. The kind of ash most favoured was that obtained from a neighbouring bakehouse where straw was used for firing the baking ovens. (A. Baeckström, Y. W. Anderberg & B. Simmingsköld, *Glastekn. Tidskr.*, 1947, **2** (5), 76–80.)

not depart very much from that of a potash–lime–magnesia–silica glass. These facts are indeed suggestive, particularly in the case of straw either from wheat or barley, that some primitive glass might have had its origin in a fierce fire in which straw was burned. The silica content of the ash varies greatly and in some plants the potash content is much greater than the soda and reaches high levels in fern, sedge, rush, wheat grain, and mulberry. Due largely to the potash the total alkali salts exceed 40 per cent in the ash of these plants except wheat grain, where it is 34 per cent; but in all five plants the proportion of the ash which exists as chloride and sulphate is high.

TABLE X

Variability of Composition of Beechwood Ash Revealed in Different Samples

(from H. E. Benrath, *Die Glasfabrikation*, 1878)

	Analyst: Hartwig	Henneberg (1)	Henneberg (2)
K_2CO_3	11·7	6·7	4·7
Na_2CO_3	12·4	11·0	3·2
K_2SO_4	3·5	4·4	23·3
NaCl	—	0·7	5·0
$CaCO_3$	49·5	27·4	25·1
$MgCO_3$	7·7	17·7	12·6
Phosphates	10·1	15·6	10·9
SiO_2	2·5	16·9	12·4

What is most important, and one of the central points, in fact, to an understanding of the composition of ancient glasses, is the high proportion of calcium oxide and the substantial proportion of magnesia. In the case of ash from well-grown wood, such as that of the beech, oak, apple, and mulberry, the combined lime and magnesia range from about two-thirds to three-quarters of the total ash, and in seven of the fourteen plants the combined lime and magnesia in the ash exceeds that of the potash and soda. The proportion of magnesium carbonate in the Syrian desert plant ash (Table VI) is but one per cent of the total and there are no other data known to the author concerning the ash from Mediterranean coastal plants by which a desirable check on Table VI could be effected. Of the importance of magnesium salts in kelp and in the ashes of land plants there is no doubt. The P_2O_5 content is also of interest; and it is significant that Geilmann found P_2O_5 to be present in every one of the seventy-five ancient glasses examined by him, ranging over nearly three thousand years. It will be noted from Tables VI, VII, IX, and X that P_2O_5 is a substantial constituent of all the coastal, marine, and inland plant ashes quoted. Of the fourteen land plants included in Table IX, nine contained more P_2O_5 than Na_2O. The amount of sulphate and of chloride in the ash is also substantial and these constituents usually appear in the precise analyses of ancient glasses.

The next fact of importance is the great variability in the relative proportions of the constituents present in ashes from different plants. Considering, for example, two of the largest constituents, namely, lime and magnesia, their ratios in different plants vary widely. In grasses and straws the ratio CaO : MgO is generally at least 2 : 1 and in some 4 : 1 or 5 : 1. In autumn leaves, from seven common European trees, the ratios found ranged from 9 : 1 to 5 : 1, whilst in nine varieties of air-dried wood the ratio was from 1 : 1 for larch to 13 : 1 for apple. In broom, however, it is 8 : 7, in sedge 9 : 7, and rush 3 : 2.

Variability, however, is not confined to that between different kinds of plant. Since a plant must draw all its mineral content from the soil, if the latter becomes impoverished or its composition changed, then the mineral content of the plants grown in that location will undergo modification. It may certainly be anticipated—and indeed is a fact—that the ash from any particular plant has a different composition according to the locality in which it is grown. This has been thoroughly well demonstrated in the case of beechwood ash, by the examples which are quoted in Table X from data compiled by Benrath and confirmed in more recent examples by Geilmann and his associates.

The high content of chloride and sulphate of the alkali from all available sources, the varying composition of the ash from different plants, and the inconsistency of the composition from any one source, posed problems for the ancient glassmaker in his attempts to make clear, bright, homogeneous glass, problems from which the modern glassmaker for several decades has been protected. I propose now to examine these problems and the attempts to solve them.

THE VARIABILITY IN COMPOSITION OF THE GLASS COMPONENTS AND THE PROBLEM OF MELTING

Whichever of the three typical sources of soda or potash referred to in the preceding section was used, the ancient glassmaker would be faced by the fact that part of his material, varying from 5 to 80 per cent, could not be incorporated into glass. The only components readily reactive with sand or quartz are the carbonates and bicarbonates, the sulphites and sulphides. The chlorides are practically non-reactive, NaCl and KCl being so stable that they melt and volatilise without decomposition; whilst the sulphates are only reactive very slowly unless reduced by carbonaceous or other reducing agents, to sulphites or sulphides. The reaction $SiO_2+2NaCl+H_2O=Na_2SiO_3+HCl$ in moist air was shown by F. Clews and H. V. Thompson (1922) to be just discernible at 600°C. but still very small up to 1000°C., and the dissociation or decomposition of sodium sulphate requires a temperature of not less than about 1200°C. in the absence of reducing material. In the natron or soda derived from soda lakes in Egypt, sodium chloride and sulphate were often present in large amounts. The samples found in eighteenth Dynasty tombs (Table IV) contained combined chloride and sulphate ranging from 6 to 53 per cent, six out of the eight having more than 25 per cent; of the fourteen modern samples from Wadi Natrûn, eight contained more than 10 per cent and five more than 25 per cent. In three modern samples from another Egyptian lake at El Kab,

A. Lucas found from 66 to 87 per cent of sodium chloride and sulphate. The material obtained from Nile water (Table V) was a laboratory sample resulting from evaporation in platinum, and contained chloride (NaCl) and sulphate ($CaSO_4$) totalling about 8·5 per cent.

Of the plant ashes, 'Keli' (Table VI) contained only 4·5 per cent of potassium chloride; but the kelp of Table VII consisted of various chlorides and sulphates to the extent of 56·5 per cent, whilst varec (or at least the soluble part, Table VIII) was mainly chlorides and sulphates with only a little carbonate. The analyses of the inland plant ashes (Tables IX and X) reveal the presence of considerable amounts of chlorides and sulphates.

Neri, and subsequent well-informed writers on glassmaking, recognised the variability of the quality of the ash they might have to employ. He and Merret referred to the 'strength' of the ash and indicated that preliminary essays of its strength might be advisable. Even as late as 1835 H. Leng commended the system of testing advocated by Daudenet Bastenaire in which seven numbered small crucibles were charged with sand and ash in proportions increasing from 1 : 1 to 1 of sand and 7 of ash, and observing the results of heating the mixtures in the furnace. If it was not until the time of Neri that we learned of the laborious operations involved in the preparation of glass, it is partly due to the new outlook engendered by the Renaissance towards the complete recording of scientific and technical operations and partly to the fact that the majority of the earlier commentators on glassmaking were reporters only and had no practical experience. The problem of making and reproducing workable glass from two supposedly simple materials, sand and nitrum or sand and ash, materials which in fact were usually complex and variable in composition, must always have been difficult and inescapable.

The removal of impurities or undesired constituents could be accomplished by a succession of operations: purification of the raw materials by selection and, in the case of ash, by solution, filtration, and evaporation; by fritting the glassmaking mixture; and by the subsequent conversion of the frit into glass, the prolonged heating of the latter to remove volatile material and its treatment by quenching in water or, by mechanical means, to remove the unincorporated residue.

Neri devoted the earliest chapters of his Book I to the preparation of a 'salt of polverine' which was the product from the purification of the ash (polverine) by solution, filtration, and evaporation. He claimed that by using this salt rather than the crude original he could make a fine crystal glass. There was one disadvantage, for he noted that the glass he made with this refined salt was less durable than that obtained from unrefined polverine. The reason, unappreciated by him, was that the stabilising calcium and magnesium carbonates and phosphates had been partly or wholly removed by the purification. This was the lesson which P. D. Deslandes also had to learn some 150 years later at St. Gobain when he began to use purified soda, but, as stated in Part III of these studies (1956), he went on to discover that stability could be restored by the addition of ime.

The presence of phosphate in many types of glass through the medieval period and until the eighteenth century indicates that, whatever the practice in making crystal glass, purification of the ash was not carried out as a general rule.

The melting process was carried out in two stages, first a comparatively low temperature operation whereby the sand and the ash (or soda) were converted into a frit, the second in which the frit was converted to glass in crucibles in the melting furnace. Flinders-Petrie (1894) considered that this two-stage process was carried out in eighteenth Dynasty Egypt. From Pliny's obscure account the process in his time would seem to have involved three stages: 'one part of [sand] so prepared was mixed with three parts of nitre, either by weight or measure, and when fused is transferred to another furnace. Here it forms a mass of what is called "hammonitrum", which is again submitted to fusion and becomes a mass of pure, white glass.'

Theophilus (tenth century A.D.) is more explicit. The two parts of (beechwood) ash and one part of (washed) sand are subjected to prolonged and careful mixing and then heated in the special part of the furnace intended for fritting. 'When they have begun to grow hot, immediately stir them lest they chance to melt by the heat of the fire and run into balls. Do this for the space of a day and a night.'

Neri (1612) does not insist on so long a period of fritting. He directs that the mixture of sand and ash shall be heated in the fritting furnace (known as the calcar), that it be spread well and kept stirred by an iron rake until the fine powder grows into lumps as big as small nuts. 'The fritt will be well and perfectly wrought in the space of 5 hours, being stirred all that time and a sufficient fire continued.'

What took place precisely in the fritting furnace would depend on several factors: the purity of the sand, the composition of the ash, the temperature, the duration of the fritting treatment, and whether the furnace conditions were reducing or oxidising (i.e. smoky or clear). We have to bear in mind that if the ash had been well purified it would still contain chlorides and sulphates, whilst if used unpurified there would be calcium and magnesium carbonates and phosphates. Alumina, iron oxide, lime, and magnesia, present as impurities in the sand, would complicate the problem of composition. In all these circumstances comments on the changes in the fritting furnace are bound to be speculative; but there are some guiding posts. First there are the following physical and chemical data:

	M.Pt. (°C.)	B.Pt. (°C.)	Incipient Decomposition or Dissociation Temp. (°C.)
Na_2CO_3	851°	—	—
K_2CO_3	891	—	—
NaCl	801	1413	—
KCl	776	1500	—
Na_2SO_4	884	—	1200°
K_2SO_4	1076	—	—
$CaCO_3$	—	—	*ca.* 400
$MgCO_3$	—	—	below 400

We also know from the work done by Howarth, Sykes & Turner (1934), that with a mixture of good sand, pure limestone, and sodium carbonate in proportions to yield a glass of commercial type, of composition 75 per cent SiO_2, 10 CaO, and 15 Na_2O, reactions, consisting of gradual decomposition of $CaCO_3$ to produce CaO and slow chemical action of the sodium carbonate on the sand grains, take place below 600°C., that is, long before any melting occurs; but they are not even moderately rapid until the temperature reaches 800° to 900°C. Moreover, the solid product remains as a powder below 700°C. and only assumes a sintered or fritted condition above 750°C.

Further, it may be anticipated that the sodium and potassium chlorides will form with one another and the other salts eutectics which melt at temperatures considerably below the melting point of either, and such melting would stimulate fritting. In view of the injunction of Theophilus, of Neri, and of still later commentators, that the mixture must not be allowed to liquefy,* we can assume that the temperature of the frit would probably not reach 750°C. Two obvious disadvantages of permitting melting to occur at this stage would be the greater difficulty in handling the product, and the attack on the fritting floor with its resultant corrosion of the refractory material and the absorption of further impurity.

If the upper limit of temperature in the frit was about 750°C., very little loss of sodium chloride by volatilisation could be expected and the frit would pass over to the glass-melting crucible with most of this impurity retained.

As to the sulphate, very slow reaction takes place with carbon or carbonaceous matter at temperatures below 750°C., but the time allocated to the fritting process would almost certainly be inadequate to bring about extensive reduction to sulphite or sulphide and thus open the way to reaction with sand. The fritting furnace may have been of the reverberatory type in which the flames passed over the mixture undergoing fritting; but if the injunction to use only dry wood were obeyed, an injunction which repeatedly occurs in the accounts of glassmaking processes from the date of the Babylonian text on glazes and of the Nineveh tablets on glasses onwards through the centuries, there would be little carbonaceous matter in the flame to reduce the sulphate.

In the final conversion of the frit into glass in the melting crucible the alkali salts would melt, dissolve in one another and also take calcium and magnesium carbonates into solution. Decomposition of the alkaline earth carbonates would proceed rapidly, as also would the reaction between the alkaline carbonates and the sand.† Eventually the lime and magnesia would also combine with sand. The chlorides and sulphates have only a limited solubility in molten silicate glass. In a glass of percentage composition SiO_2 75, CaO 9·2, Na_2O 15·8, the solubility of sodium chloride at

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* Lardner, however, in *The Manufacture of Porcelain and Glass*, London, 1832, allows of the frit becoming pasty so that it can be raked out and broken up into small cakes.

† A convenient general reference on the chemical reactions in glassmaking is 'The Scientific Basis of Glassmaking', W. E. S. Turner, this *J.*, 1930, **14**, 368–424 T.

1400° was found by H. M. Bateson & W. E. S. Turner (1939) to be 2·34 per cent. The highest amounts of Cl found by analysis of ancient glasses by Geilmann and associates (1955) were 1·17 per cent in an Egyptian eighteenth Dynasty glass and 1·18 per cent in a Roman specimen from the Saalburg, Germany, these values being equivalent to 1·93 and 1·95 per cent respectively of NaCl. As to the sulphate content the highest SO_3 found by these workers was 0·66 per cent.

From our knowledge of the construction and operation of glass-melting furnaces it is highly doubtful if temperatures as high as 1200°C. were normally attained before the second half of the eighteenth century. In Part I of these studies (1954) I have shown that the upper limit of temperature used by the Egyptian glassmakers at 1370 B.C. was 1100°C. with a probable practical limit nearer 1050°C. The diagrams available of tenth to sixteenth-century A.D. furnaces, in conjunction with observations on wood-fired furnaces seen at Murano, would not lead me to anticipate the likelihood of exceeding 1200°C. In such circumstances the removal of excess chloride by volatilisation would be impracticable. Decomposition of sulphate would also be slow.

The removal of excess chloride and sulphate and the attainment of glass of satisfactory quality called for treatment other than prolonged heating. Neri's procedure, after the frit had been well melted with its first dose of manganese in the melting furnace, was to cast the glass into 'great earthern pans or clean bowlsful of clean water' so that the 'water may take from it a sort of salt called sandever which hurteth the Crystall and maketh it obscure and cloudy, and whilst it is a working still casteth forth sandever'. The quenched glass (presumably after being dried) was then to be put into a clean pot, remelted and recast into water, these operations to be repeated until the founder was satisfied. After the final purification the glass was melted with such further quantity of manganese as was deemed necessary. All this labour, it should be stated, was involved despite the fact that the ash for making this crystal glass was the purified ash or 'salt or polverine'.

Merret (1662), commenting on Neri's method, explained first that 'Sandever' originated from the French 'Suin de Verre', or fat of the glass, because it formed a fluid layer floating on the surface of the glass. Writing of English practice (mid-seventeenth century), he said, the founders did not get rid of the sandever by casting the glass into water but by a ladle. Unless it be all scummed off ' 'twill make the glass unfit for working, very brittle, and in no way plyable'. The 'best metall', he says, meaning presumably glass prepared from purified materials, 'will yield in a pot of two hundred weight a quarter or half a hundred of sandever'. 'For green glasses, when the ashes are bad', he says, 'they are compell'd to fill the pot four or five times with more fresh ashes . . . before the pot will be filled with metall.'

The sandever must have been available in substantial quantity in England by the middle of the seventeenth century because it was a recognised article of commerce, finding use as a flux for metals and being exported to France for seasoning meat and to destroy weeds and vermin in gardens.

The need to scum the surface of the molten glass before working it continued throughout the nineteenth century and into the twentieth, but the scum or gall of later years was mainly solid impurities made porous and scummy by gas bubbles. A liquid salt layer on the glass was frequently experienced when the source of the soda in the glass was wholly or in substantial proportion sodium sulphate which, for many years in the nineteenth and twentieth centuries, had extensive use, partly because it could be obtained purer than soda ash, and partly on account of lower price.

Finally, in connection with this problem of the complex composition of the alkali, reference must be made to the dominant proportions of the soda over the potash present in the ancient glasses of all periods except those of the medieval and Renaissance times in Western Europe after the adoption there of beechwood and other inland plant ash. I have pointed out earlier (p. 285) in this paper that there is no such clear-cut difference between coastal and marine plant ashes on the one hand and those from inland plants on the other, as to enable one to say that the former contain sodium and the latter potassium salts only. Both alkalies can be present, as is evident from Tables VII and VIII, which show analyses of varec and of kelp. The latter contained 31 per cent of potassium compared with 32 per cent of sodium compounds. The composition of the resultant glass will depend, however, not on the total of the salts but on the amount of each available, that is, capable of reaction with the sand; and reaction is confined to the carbonates and bicarbonates, sulphites and sulphides. Whereas both the varec and the kelp contained sodium carbonate and sulphite, the potassium was wholly in the form of chloride and sulphate, of which the chloride would supply no potash to the glass and the sulphate only a limited amount dependent on the presence of carbonaceous material and on the furnace conditions, as already discussed.

Thus far, this discussion of the purity of the two major constituents of the glassmaking mixture on the melting processes and the composition of the glass has been confined mainly to the alkali sources. This much can be said in regard to the source of the silica, that the remedy against impurities introduced by the sand was recognised at an early date. Thus, Pliny reported on the fine quality of the glass made by using Indian rock crystal (or massive quartzite) and the writers of the medieval and Renaissance times advocated the use of quartz pebbles or pure silica rock as preferable to sand. In making artificial gems Neri insisted on quartz pebbles or silica rock heated and quenched and then ground on porphyry.

General Conclusions

The quotations with which this paper began showed that over a period of more than 3000 years the basic constituents from which glass was made were two in number: powdered quartz or silica rock or sand, and 'nitrum' or soda or plant ash. Colouring agents such as manganese, copper, and cobalt compounds were usually incorporated at later stages of the melting. Only very small amounts of lime appear in the receipts on the Nineveh tablets, a little through the agency of shells according to Pliny, and none in any later instructions before the end of the seventeenth century A.D. Yet analysis shows that all the ancient glasses (except a small number containing much lead) had lime as a major constituent and were usually of complex composition. The many constituents could only be derived from the sand and the soda or ash, together with impurities from the refractory materials arising through corrosive attack during the fritting and melting operations. From the tables of analyses of possible raw materials it is evident that the sands were the probable sources of considerable alumina, varying amounts of iron oxide, lime, in several cases in large amounts, and magnesia. Manganese was frequently present in Egyptian sands. Natural soda from lakes supplied the soda but also much chloride and sulphate. The salt from evaporated Nile water could yield sodium and potassium carbonates, with chloride and sulphate, and calcium and magnesium carbonates. Plant ash, without differentiating here between coastal and inland plants, could furnish sodium and potassium carbonates, much chloride and sulphate, much calcium and magnesium carbonates and phosphates. If powdered quartz were used instead of sand, any alumina and iron oxide in the glass would presumably be furnished by corrosion of the refractory material, which would also yield some silica, and much smaller amounts of lime, magnesia, and alkaline oxides; for the ancient alkaline materials appear to have been free from alumina and iron oxide except in very small amounts. These facts explain why it was possible for the ancient glassmakers over many centuries to be making soda–lime–magnesia–silica glass and yet be unaware that they were so doing until the second half of the eighteenth century. Moreover it is now clear that not only was each of the two basic raw materials complex in character, but each was liable to variation in composition.

We may find in this situation a possible explanation of the variations in the proportions of the basic constituents in the glassmaking mixture as prescribed by different ancient authorities. These proportions ranged from 1 of sand to 3 of ash, or nitrum (Nineveh tablets and Pliny), through 1 : 2 (Theophilus, Heraclius, and Agricola) and 2 : 1·3 (Neri) to 2 : 1 (Biringuccio). Mental gymnastics have been performed by commentators in trying to explain what seemed to them discrepancies or departures from practical facts in these old formulas. I have directed attention, in Part III of this paper (1956), to the extraordinary explanation offered by R. C. Thompson for the high ratio of the alkali of salicornia to sand (3 : 1) prescribed in the Nineveh tablets. The same ratio as recorded by Pliny is explained by E. Dillon (1907) as meaning probably three parts in twelve or ten; and W. Froehner (1879) by basing a theory on the supposition that the duodecimal system may have been used, converts Pliny's 3 of nitrum to 1 of sand, to 3 of nitrum to 9 of sand. Without holding any brief for Pliny's information, which is at times obscure if not incorrect, it is possible, in the light of the data in this paper, to say that, with one possible exception (Biringuccio's) any and all of the ratios might, dependent on the source of the materials, be workable. Neri's ratio was based, not on sand and crude ash, but on pure silica in the form of ground quartz or pure siliceous rock, and purified ash, that is, salt of polverine. Biringuccio may possibly have had purified materials in mind but we leave his instruction as doubtful.

Glassmaking has, until well past the middle of the nineteenth century, been generally rated as a precarious and secretive business. It is clear why, over so many centuries, it was precarious. In 1689, even J. Kunckel, foremost German chemist of his day, could not bring himself to admit the value of lime in glass; and in connection with his production of gold ruby glass he wrote of the immense trouble involved and the inconsistency of the results. More than a century later, P. Guinand, the Swiss cabinet-maker who succeeded in making good quality optical glasses where several distinguished scientific men had failed, referred to the difficulty of reproducing good glass from raw materials lacking in purity (M. von Rohr, 1926). The day of a chemical industry making standardised products had yet to come. And if, after many trials and errors, when using available materials, an ancient glassmaker succeeded in working out procedures for making good glass, is it surprising that he should be secretive? Who shall say that he was not justified?

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Addendum

Since this paper was submitted for publication, the author has had the opportunity of visiting Egypt again, of inspecting the soda lakes at Wadi Natrûn and learning of other sites of sands possibly suitable for glassmaking purposes. The following information may be of interest; but it should be emphasised that none of it affects the author's conclusions set out in the main body of the paper.

The lakes at Wadi Natrûn are still being used as a commercial source of sodium sulphate and chloride although their commercial importance has been rapidly declining. The geological formation below the lakes is complex. One or more of the lakes contains relatively sweet water, and borings in various places have also tapped sources of sweet water by means of which farms have recently been created from the desert for growing citrus fruit, grapes, cereals, beans and other agricultural products. In some of the lakes one or other of the salts, namely, sodium sulphate, carbonate or chloride, is predominant. A concise account of the lakes is given by W. F. Hume in his *Geology of Egypt*, Vol. I, 1925.

For the information about three Egyptian sands I am indebted to Messrs. Verreries et Vitreries Yassin, Cairo, and Dr. Abou el Azm, of the National Research Council, Cairo. The site of the Maadi sand, which I visited, lies some twenty miles S.E. of Cairo. Here a bed of white to grey-coloured sand of considerable depth has been disclosed after stripping off the overlying three or four feet of brown sand. After being sieved and washed it finds a limited use in making light green glass. The second sand was obtained from a locality near the middle of the north shore of Lake Moeris, in the Fayoum, where, there is reason to suppose, glassmaking took place during the first to third centuries. In composition it is generally similar to the Fayoum sand examined by Lucas (Table I, p. 281). The third sand was derived from Sinai and has a lower iron oxide content than any other of Egyptian origin thus far discovered. Its disadvantages are a high proportion of fine material and transport cost.

Enquiries failed to elicit any clue to sources of sand possibly used by the Alexandrian glassmakers.

Additional Egyptian Sands which have been Tested for Modern Glassmaking

	1	2	3
	Maadi (sifted and washed)	Fayoum	Sinai
SiO_2	97·88	97·83 (by diff.)	99·2
Al_2O_3	1·40	1·02	0·5
Fe_2O_3	0·20	0·32	0·05
TiO_2		0·22	
CaO	0·20	0·41	0·3
MgO		0·07	
MnO		tr	
Loss on ignition		0·13	

The author has also had the opportunity of visiting the Italian coastal stretch between Cuma and Liturno from which, according to Pliny, the glassmakers of his day obtained a white sand for glassmaking. Nothing but grey-brown sand was seen throughout a several mile stretch of coast. Independently, through the courtesy of Prince G. Ginori Conti and of his friend, Professor Carobbi, samples of sand were collected by the geological staff of the University of Naples from six locations on the coastal strip between Cuma and the outlet from Lake Patria. They were also subjected to qualitative mineral analysis under the microscope. It seemed evident from the colour and mineral content of the samples that whatever were the characteristics of the sand in Pliny's day they had probably been changed by volcanic action which was not only very vigorous in A.D. 79 but also at intervals from the sixteenth century onwards. This activity was displayed not only by Vesuvius but also in the neighbourhood of Cuma itself. Two minerals which were present in all six samples (in addition to quartz) were augite and calcite. The former is associated with volcanic activity whilst the latter is due to shell detritus, as is the case with many Mediterranean sands. It is highly probable that calcite was present in the sand of Pliny's day. It is also conceivable that by exploring the layers of sand deeply enough below that now contaminated by volcanic detritus the sand of which Pliny wrote might be reached.

11 October 1956.