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RAW MATERIALS

RESEARCH AND DEVELOPMENT

DOSSIERS

IV. PHOSPHATE

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DOSSIER ON PHOSPHATE

A report
by

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PREFACE

This "dossier" on phosphate is part of a series of technico-economic studies that have been prepared under the sponsorship of the "Commission of the European Communities" (Directorate-General for Research, Science and Education) on some of the most critical mineral commodities.

The decision to carry out those studies, as well as other work to be published under the general heading "Raw Materials Research and Development", results from current concern about prospects of supplying the European Community with raw materials in sufficient quantities and at acceptable costs in the mid- to long-term. An essential part in defining the purpose and scope of the dossiers was played by a Sub-Committee of CREST (1), established to investigate on-going activities in the member states, both in the areas of primary and secondary raw materials, in order to determine what R & D actions, if any, should be undertaken by the Community to alleviate its supply problems.

This report has been prepared by the Institute of Geological Sciences, London, in collaboration with the Bureau de Recherches Géologiques et Minières, Orléans, under contract no. 260/261 ECI F-UK with the European Economic Community. It was first submitted in November 1977 with the title: "Phosphate resources of the European Economic Community", and slightly revised later.

The primary aim of the study is to bring together all the relevant data concerning the phosphate resources of the EEC, much of which is scattered in the literature and not always readily available. The study aims to provide an up-to-date assessment of phosphate deposits and occurrences in each of the EEC countries, in the light of modern mining and beneficiation techniques and prevailing market conditions, and to make recommendations for further research, if appropriate, into those geological environments which hold out some promise of current or future economic potential.

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(1) "Comité de la Recherche Scientifique et Technique". Set up by the Resolution of the Council of Ministers of the European Communities of 14 January 1974, the Scientific and Technical Research Committee (CREST) is responsible for assisting the Community Institutions in the field of scientific research and technological development.

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SUMMARY

1 Phosphate rock is widely distributed within the EEC, both geographically and geologically, occurring chiefly as phosphatic nodule beds and as formations of phosphatic chalk or phosphatic limestone, the latter being primarily of Upper Cretaceous and Miocene age. With only a few notable exceptions, the more important occurrences are of sedimentary origin.

2 Individual phosphate nodules tend to have a relatively high phosphate content but generally occur in beds which are too thin to be amenable to modern, large-scale mining methods. Many such occurrences were formerly extensively worked, however, in Belgium, France, the Federal Republic of Germany and the United Kingdom, particularly during the latter half of the 19th century and in the early part of the present century. In most cases mining eventually became uneconomic in the face of competition from cheaper, higher grade sources of supply overseas, chiefly North Africa and the USA.

3 At present phosphate rock production in the EEC is on a very limited scale, total output in 1976 amounting to only 113,000 tonnes. None of this production is suitable for the manufacture of phosphoric acid and phosphate fertilisers. Phosphatic chalk is mined in the Somme Valley of northern France for direct applications as a soil conditioner, and in the Federal Republic of Germany phosphate nodules recovered as a by-product of iron ore mining near Braunschweig are used as a source of phosphate in basic slag manufacture. However, the latter operation is due to cease at the end of 1977 because of exhaustion of reserves. Phosphatic chalk was also obtained until 1968 from washer rejects associated with former phosphate working in Belgium near Ciply.

4 It is estimated that total production of phosphate rock in the EEC to date has been about 43 million tonnes, of which nearly 50 per cent has been produced in France and a further 41 per cent in Belgium. Nearly 70 per cent of the total output has consisted of phosphatic chalk. By comparison EEC imports of high grade phosphate rock during the period 1967-1976 amounted to 142.5 million tonnes.

5 For the manufacture of phosphate fertilisers, apart from basic slag, and most phosphate chemicals, the EEC is entirely dependent upon imports of phosphate rock, principally from Morocco, to satisfy the needs of its large and well-established fertiliser and chemical industries. The countries of the Community have for many years been a major, traditional market for phosphate rock and the dependence on imports is expected to continue, with perhaps increasing quantities being delivered as phosphoric acid instead of rock. EEC imports of phosphate rock totalled 13.5 million tonnes in 1976, containing an estimated equivalent P_2O_5 content of 4.5 million tonnes.

6 Basic slag has been of particular importance in the EEC as a phosphate fertiliser, representing also the most important indigenous source of phosphate within the Community. Although still significant, output of basic slag is declining. Production amounted to 0.8 million tonnes of equivalent P_2O_5 in 1976.

7 Although phosphate rock occurrences are widely distributed, known resources in beds of sufficient thickness and extent to be commercially attractive are extremely small, particularly when compared with those of the principal producing and exporting countries. Nevertheless, the information available at present is such that further discoveries of phosphate rock may be found within the Community and that, therefore, research and exploration is justified.

8 Main recommendations include: systematic exploratory work, under the aegis of a working party with available phosphate expertise, on the phosphate potential of major sedimentary basins in EC countries; full-scale investigation of phosphate-bearing sediments of Upper Cretaceous age; research on such specific topics as the Lower Carboniferous of southern France, the Upper Carboniferous phosphate beds of western Ireland, the Tertiary phosphate limestones of southern Italy, the apatite-bearing rocks of the Loch Borralan igneous complex in Scotland, and some of the Lower Palaeozoic sequences in Wales and elsewhere in the United Kingdom; beneficiation studies, accompanied by work on phosphate rock characterisation; and, finally, an assessment of the possible economic benefit which might result from the commercial extraction of uranium during phosphoric acid manufacture".

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1. INTRODUCTION

Phosphorus (P), a universal constituent of protoplasm, is required for growth, health and reproduction in all forms of plants and animals. This important role in life processes is shared with other elements such as nitrogen, oxygen, hydrogen, carbon and sulphur but, unlike the majority of these elements, phosphorus is available only in the lithosphere in the form of phosphate minerals.

As a commercial source of phosphorus, phosphate rock is the basis of a major industry of world wide importance. Its economic value resides in the fact that there is no substitute for phosphate rock in the manufacture of phosphate fertilisers and phosphorus-based chemicals.

Since 1972 marketable production of phosphate rock has exceeded 100 million tonnes a year, to which the EEC countries (France and the Federal Republic of Germany) have contributed only negligible amounts in the form of phosphatic nodules and phosphatic chalk. However, phosphorus removed as an impurity during steelmaking is recovered in basic slag, the production of which within the EEC makes a substantial, although declining, contribution to total phosphate requirements. The EEC is therefore dependent on imports for virtually all the phosphate rock supplies required for its large domestic fertiliser and phosphate chemical industries (Fig 1).

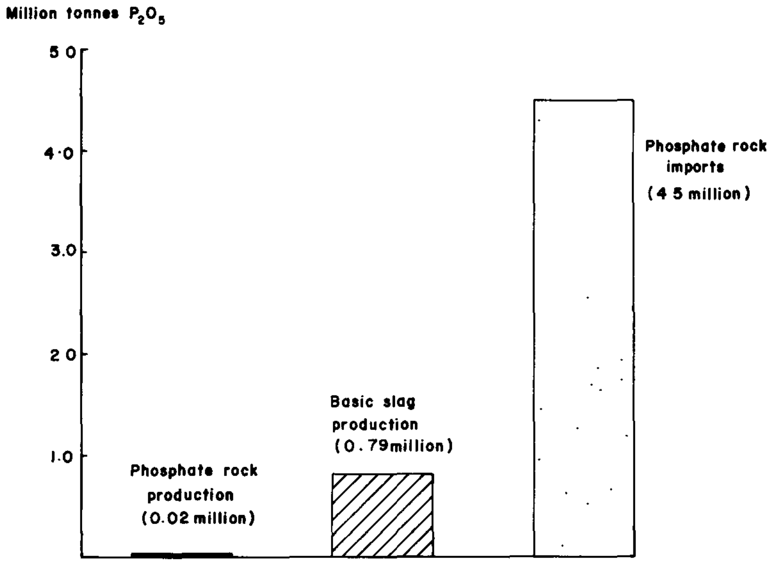


Fig 1 EEC sources of phosphate, 1976

1.1. TERMINOLOGY

Phosphate rock is essentially a trade name used to describe naturally-occurring material containing one or more phosphate minerals and possessing a chemical and physical composition suitable for its commercial use. As such, the term embraces a wide variety of rock types of diverse origin, character and mode of occurrence.

Phosphate rock is referred to also as rock phosphate, phosphorite and apatite rock. The term phosphorite, although originally used in 1794 to describe a massive form of apatite, tends to be restricted to sedimentary deposits of marine origin, principally those which are of commercial or potentially commercial importance. In the strict geological sense, phosphorite should be regarded as a rock which contains more than 50 per cent phosphate minerals, rocks with less than this amount being described merely as phosphatic, but this restricted use of the term phosphorite has not gained popularity, principally because of the extremely low grades of phosphate rock now being worked commercially. Apatite rock denotes phosphate rock of igneous origin or, in some minor instances, sedimentary phosphate rock which has become metamorphosed.

The phosphate content of phosphate rock, as mined, is commonly reported as phosphorus pentoxide, P_2O_5, which is arrived at by chemical analysis, or as calcium phosphate, $Ca_3(PO_4)_2$, since this is the chemical form in which it exists in almost all commercial supplies of phosphate rock. The calcium phosphate content has traditionally been referred to as bone phosphate of lime (BPL), although in recent years there have been largely unsuccessful attempts to introduce the expression TPL (triphosphate of lime) and TCP (tricalcium phosphate) as alternatives.

Commercial phosphate rock generally contains between about 60 and 83 per cent BPL (28 and 38 per cent P_2O_5),the marketable material entering international trade usually containing more than 65 per cent BPL (30 per cent P_2O_5). Phosphate rock with as little as 5 per cent P_2O_5 is mined and processed on a commercial scale.

The phosphate content of phosphate intermediates such as phosphoric acid, and of phosphate fertilisers generally, is also expressed in terms of percentage P_2O_5. The elemental phosphorus content, P, is normally given only in reference to elemental phosphorus manufacture or to indicate the phosphate content of iron ores.

The following conversion factors indicate the relationships between P_2O_5, BPL and P:

per cent P_2O_5	x 2.1853 = per cent BPL
	x 0.4364 = per cent P
per cent BPL	x 0.4576 = per cent P_2O_5
	x 0.1997 = per cent P
per cent P	x 5.0073 = per cent BPL
	x 2.2914 = per cent P_2O_5

Among the essential plant nutrients, phosphorus is one of the less abundant in most soils and its availability is one of the most critical factors controlling plant growth. A large proportion, but not all, of the phosphate present in fertilisers is 'available' as a nutrient to plants. The available P_2O_5 is determined on the basis of 1) per cent water solubility, and 2) per cent solubility in ammonium citrate. Phosphate insoluble in either water or ammonium is considered unavailable.

Phosphate rock identification

Phosphate rock is not very distincitive and frequently resembles limestone or other common rocks in appearance. It is therefore easily overlooked or incorrectly identified during prospecting, particularly in those areas which are relatively unknown geologically or have not previously been considered likely to be phosphate bearing. In the hand specimen it varies very widely in appearance, although within any particular phosphate field its features are generally fairly consistent so that a lithology identified as phosphatic can usually be recognised without much difficulty. In addition exploration parties are invariably equipped with simple apparatus for the determination of the P_2O_5 content of samples suspected of being phosphatic.

Pelletal textures, when present, are a distinct feature common to many deposits of sedimentary phosphate rock in various parts of the world. The term pellet denotes a syngenetic sedimentary phosphate particle having a spherical, oval or elliptical shape. Pellets generally range from 0.06 mm to 4.0 mm in diameter and include those having a marked concentric structure (ooliths). Any rock sample showing pelletal textures may therefore be suspected of being phosphatic and worthy of more detailed examination, particularly when the rock has a resinous lustre and is accompanied by a bluish-grey coating or 'phosphate bloom' on weathered surfaces.

Positive identification of samples becomes much more difficult with lower grades of phosphate rock, particularly where it passes imperceptibly into siltstone, shale or limestone, for example with decreasing P_2O_5 content. In such cases the presence of phosphate can generally be determined only by geochemical field tests such as the one developed by the U.S. Geological Survey for the rapid and semi-quantitative determination of the phosphate content of phosphate rock. This method, which is now being widely used in phosphate exploration, involves the reaction of a vanadomolybdate reagent with phosphatic material to give a precipitate of phosphovanadomolybdate, the yellow colour of which is then compared with that of reference solutions. The test has been found capable of giving results to the nearest 5 per cent of P_2O_5. Under controlled conditions this colorimetric method can be accurate to within one per cent P_2O_5.

Petrographical descriptions show that colour is of little value in recognising phosphate rock, particularly the higher grades. Most samples collected in the field are also moist or wet and have appreciably darker colours than when dried; those dark-grey to black in colour are often rich in organic matter, which may also account for the foetid odour of some samples when broken. Specific gravity may in certain instances be useful in distinguishing between black, compact phosphate rock and coal or carbonaceous shale.

PHOSPHATE MINERALS

The element phosphorus is widely distributed in the earth's crust, but because of its great affinity for oxygen is not found in nature in a free or uncombined state. In the form of orthophosphate, (PO_4), phosphorus also combines readily with a number of cations, chiefly calcium, to form numerous phosphate minerals. There is known to be more than 150 phosphate minerals but only the calcium phosphates, mainly those of the apatite group, and, to a very limited extent the aluminium phosphates, are generally found in phosphate deposits of commercial importance. Members of the apatite group are particularly widely distributed, occurring as common accessory minerals in many igneous, regionally and thermally metamorphosed rocks, and in sedimentary rocks where they are frequently found as detrital or primary minerals. Apatite occurs also in various residual deposits, including those produced by intensive weathering of carbonatites, and as replacements of limestone or coral rock by phosphatic solutions derived by the leaching of guano deposits. An isomorphous series exists between individual apatite minerals, with four prominent pure end-members, the chemical formulae of which are given below:

Fluorapatite	$Ca_5(PO_4)_3F$
Chlorapatite	$Ca_5(PO_4)_3Cl$
Hydroxyapatite	$Ca_5(PO_4)_3OH$
Carbonate-apatite	$Ca_5(PO_4,CO_3OH)_3(F,OH)$

Fluorapatite, containing theoretically about 42 per cent P_2O_5, is usually used synonymously with the term apatite. It is by far the most common mineral of the group in crustal rocks. In igneous and metamorphic rocks, the apatite is generally coarsely crystalline. However, the precise composition of apatite in phosphate rock varies considerably depending on the origin and the degree of substitution of other elements. This is particularly true of sedimentary apatites which may show marked departures from the theoretical fluorapatite composition. In most sedimentary phosphate deposits apatite occurs as complex aggregates composed of microscopic or submicroscopic crystallites, the satisfactory identification of which can be effected only by X-ray and chemical examination. In most cases it has been found to be carbonate-apatite, principally within the varietal range assigned to francolite, which has been used as a suitable name for apatite containing appreciable percentages of CO_2 and more than 1 per cent F. The name collophane, originally introduced for the stratified, opal-like substance found on the Caribbean Island of Sombrero, has been frequently applied to the cryptocrystalline phosphate mineral. If the name is to be retained it should be used only when the identity of the apatite-like mineral cannot be established with certainty.

The mineralogy of the apatite group of minerals is made complex by the fact that apatite is host to many substitutions by cations and anions. For example, mutual replacements can take place between the F, Cl and OH ions, although the appreciable difference in size between those of F and Cl involve a structural rearrangement in chlorapatite and may account for the comparive rarity of this mineral in crustal rocks. Replacement of calcium by U, Sr and rare-earth elements is common. Compared with fluorapatite, carbonate-apatite (francolite) contains theoretically only about 34 per cent P_2O_5.

Aluminium and iron phosphates

Phosphate minerals containing significant amounts of either aluminium or iron, and in some cases both, are to be found chiefly in tropical or subtropical regions where they are formed by intensive lateritisation of phosphatic bedrock. In the residual deposits worked as a source of phosphate in western Senegal augelite ($Al_2PO_4(OH)_3$) and crandallite $[CaAl_3(PO_4)_2(OH)_5.H_2O]$ are predominant, while in Florida in the so-called aluminium phosphate zone removed as part of the overburden in the landpebble mining district, the principal minerals in addition to fine-grained carbonate fluorapatite and crandallite, are millisite $[(Na,K)CaAl_6(PO_4)_4(OH)_9.3H_2O]$ and wavellite $[Al_6(PO_4)_4(OH)_6.9H_2O]$ of which crandallite and wavellite are the most typical. Similar assemblages of aluminium and iron phosphates have been described from Christmas Island in the Indian Ocean and from a number of islands of volcanic origin in the Caribbean and the western Pacific. In Senegal an earthy zone of finely crystalline augelite is underlain by nodules bearing crandallite and cryptocrystalline pallite $\left[Ca_3Al_{13}(PO_4)_8OH_{18}.6H_2O\right]$, the latter apparently having been produced by the leaching of phosphatic clays in the sedimentary succession.

1.2. ORIGIN AND MODE OF OCCURRENCE

Few minerals rival phosphate rock in the wide variety of rock types in which it appears in nature, reflecting the correspondingly diverse geological environments in which phosphate deposits can be found. The principal kinds of phosphate deposits may be classified according to the processes primarily responsible for their mode of occurrence.

IGNEOUS DEPOSITS

In igneous rocks, in which phosphorus is the eleventh most abundant element, apatite tends to become concentrated during the early part of the main or magmatic stage of crystallisation. In intrusive alkaline igneous rocks, in nepheline-syenite and particularly in basic alkaline varieties, phosphorus in the form of apatite may even be present as a main constituent. Striking examples of such complexes occur in eastern and southern Africa, Brazil and the USSR. In addition to nepheline-syenite, ijolite and carbonatite are common members of the rock assemblage. The largest apatite deposits of igneous origin are in the Khibiny nepheline-syenite massif in the USSR, a circular pluton about 40 km in diameter. These sheet-like masses of apatite-nepheline bearing rock, averaging about 100 m in thickness, have been traced 12 km along the surface and more than 2 km down the dip near the southern boundary of the complex.

Apatite has a long range of crystallisation, however, and forms also in the later or pegmatitic stages, the products of which are commonly segregated into dykes and veins in, for example, Norway and Canada. One of the best known disseminated deposits (nelsonite) occurs in the USA in Virginia.

Phosphate deposits of igneous origin have the distinction of being among the lowest grade to be worked on a commercial scale. The Jacupiranga carbonatite in Brazil contains, for example, an average of only 5 per cent P_2O_5.

Apatite occurs as an accessory mineral in many igneous rocks within the EEC. A notable occurrence of igneous apatite is in the Loch Borralan alkaline complex, in Scotland, in which variable amounts of the mineral have been identified. Small intrusive bodies of apatite-bearing carbonatite occur in the central part of the Kaiserstuhl volcanic complex near Freiburg in the Federal Republic of Germany.

SEDIMENTARY DEPOSITS

Most of the world's production of phosphate rock is derived from marine, sedimentary rocks. Typically these form bedded or stratified deposits associated with either dark carbonaceous shale, chert and carbonate rock or with cherty carbonate, sandstone and shale, depending on the regional depositional environments. Individual beds may be up to 6m in thickness as mined, and contain up to 35 per cent P_2O_5. One of the largest accumulations of phosphate rock is the Western Phosphate Field in the western United States, within which the well-known Phosphoria formation is distributed over an area of about 140,000 km^2.

Within the EEC the most common occurrence of sedimentary phosphate rock is as thin beds of phosphate nodules of widely ranging geological age. These phosphatic beds represent very slow or intermittent depositional conditions which allowed the phosphatisation of pebbles and fossils to take place, with current action having the effect of winnowing away finer sediment and thus concentrating the phosphatic debris. Reworked phosphatic nodules and fossils are also commonly concentrated on eroded surfaces. Although formerly of considerable economic importance as a source of phosphate, thin phosphatic nodule beds are of little commercial interest today.

The phosphatic chalk deposits of the Paris Basin of France and the Mons Basin in Belgium have been the most important sources of sedimentary phosphate rock within the EEC and have contributed the major part of former output. Although not in a readily usable form, phosphate is also widely distributed in small amounts in the Mesozoic sedimentary iron ores of France, the Federal Republic of Germany, the United Kingdom, Luxembourg and Belgium, the Lorraine iron ore field being the most important.

Theories devoted to the formation of sedimentary phosphate deposits of marine origin are among the most controversial. Each has its merits but none accounts satisfactorily for the many and varied geological features exhibited by phosphate rock.

Sea-water is nearly saturated with phosphate and, because of the high influx rate from the continents by rivers, there must therefore be an effective mechanism whereby the phosphorus content is constantly precipitated. Recognising this fact, theories on the origin of marine phosphate rock have been concerned chiefly with establishing how sufficient quantities of phosphate in solution could be concentrated in any one place to provide the enormous amounts now available as phosphate deposits.

The theory advanced by A.V. Kazakov in 1938 for the inorganic or physical-chemical precipitation of phosphate from cold, upwelling oceanic currents has become widely accepted, although several authorities have questioned the validity of upwelling of ocean water as an effective mechanism for carrying comparatively high concentrations of phosphate from the deeper portions of the ocean onto continental shelf areas. According to this concept the deposition of marine phosphate is controlled mainly by the temperature and acidity (pH) of the sea-water. Phosphate is precipitated on shelving sea floors between depths of about 50 m and 200 m where the pH of upwelling cold oceanic waters rises with increasing temperature and decreasing partial pressure of CO_2. It cannot be precipitated within the zone of photosynthesis, where the available phosphorus is vigorously consumed by phytoplankton, nor below about 200 m, where conditions of phosphate supersaturation are prevented because of the high CO_2 content and the resulting low pH. Deep cold waters in the ocean contain nearly 0.3 ppm PO_4, whereas surface waters contain only 0.01 ppm PO_4 or less. There is no complete agreement on the nature of the stable phosphate mineral in sea-water, but most investigations indicate that it is carbonate-fluorapatite.

Another inorganic theory suggests that the origin of phosphate rock may be linked with submarine volcanism. Marine phosphorites have been found associated with volcanic igneous rocks in only a relatively small number of countries, but no direct genetic relationship between phosphate deposition and volcanism has yet been established and the association can generally be shown to be fortuitous.

There is considerable evidence to suggest that the conditions necessary for the precipitation of phosphate from sea-water cannot be explained solely by the inorganic chemical theory and that, instead, various marine organisms play an important role in creating environments favourable to the precipitation of carbonate-fluorapatite. Theories involving a biochemical origin for phosphorite are based on the assumption that phosphorus in sea-water is first concentrated by organisms, chiefly plankton, which use it to form skeletons and the soft parts of their bodies and on death fall to the sea floor, where the organisms then decompose and set free their phosphorus content. Geological evidence has been presented in support of a biochemical origin.

Before the First World War most of the known marine phosphate deposits were believed to be exclusively of organic origin and formed by the accumulation and subsequent burial of animal or vegetable debris. Concentrations of phosphate are found in the bones of vertebrates and in the shells of some invertebrates, chiefly certain brachiopods and crustacea, while a number of other marine invertebrates secrete slightly phosphatic skeletons. Thus may organisms contribute a relatively significant amount of phosphate to the accumulating sediments. The pelletal or granular structure shown by many marine phosphorites is believed by some authorities to be due to the presence of coprolites or faecal pellets of invertebrate animals. The term coprolite has often been mistakenly applied to nodular or pebbly phosphorite occurrences, since true coprolitic deposits must contain high proportions of faecal material. Such organic phosphate deposits, including bone beds and fish beds, 'coquina' phosphate (the name applicable to relatively coarse-grained friable deposits consisting chiefly of shell fragments) may be present locally in sufficient quantity to be of commercial importance. Such deposits are invariably thin and of low grade, however, and organic theories have now been generally abandoned in favour of biochemical concepts capable of accounting much more adequately for the immense size and high grade of many marine phosphate deposits.

Some field and laboratory investigations have suggested that replacement of calcium carbonate by phosphate solutions is a much more important mode of formation of bedded marine phosphorite deposits than has hitherto been realised. Limestone is an especially favourable host rock for such replacement, the process being in most cases a diagenetic one, i.e. involving chemical and physical changes that take place in sediments during and after their deposition, but before consolidation and in general similar to the formation of many of the so-called primary dolomites. Replacement of calcite by apatite has been demonstrated experimentally, apparently taking place more readily with decreasing grain size of the carbonate mineral, but evidence for its operation on a large scale appears to be lacking in most deposits. Quantitatively, interstitial accretion is probably a much more important diagenetic process and may be one of the ways in which phosphate pellets and similar aggregates common in many phosphate deposits are first formed. It has been suggested that phosphate released by diagenetic processes under reducing conditions in marine basins may reach concentrations one hundred times greater than in the overlying surface waters.

Numerous instances of phosphatisation of calcium carbonate in a marine environment have been described in the geological literature, chiefly of a wide variety of organic materials including shells, wood, faecal pellets, as well as bones and teeth of vertebrates. Geologically very recent examples are the phosphatised foraminifera found on the sea floor off the coast of California and the occurrence of phosphatised Globigerina ooze, phosphatised limestone, as well as partially or completely phosphatised calcitic fossils, on a number of seamounts ('guyots') situated in the central Pacific.

RESIDUAL DEPOSITS

Weathering processes play an important part in the formation of enriched residual and replacement deposits from phosphate rock of either igneous or sedimentary origin. For example, the leaching of carbonate and sulphide minerals, together with the oxidation of carbonaceous matter, has raised the P_2O_5 content of the deposits of the Phosphoria formation from about 27 to 30 per cent at depths of a few hundred metres to 35 per cent near the surface. In many instances weathering has accounted for the formation of deposits from phosphatic beds which would otherwise not been proved mineable. The 'brown-rock' residual deposits in Tennessee, for example, have been derived from poorly phosphatic limestones of Ordovician age. Similar deposits were formerly worked in the Federal Republic of Germany and in central France.

Weathering of carbonatite at Sukulu in Uganda involving the removal of calcite, dolomite and other more soluble minerals has produced a thick, apatite-rich soil containing an average of 12 per cent P_2O_5. This type of deposit was formerly regarded as characteristic only of intense weathering under hot, tropical climatic conditions but similar deposits have evidently formed also in cold, glacial environments in Finland and Canada.

Residual deposits of igneous origin have not been found in any of the EEC countries.

1.3. EXPLORATION

The significant discoveries of phosphate rock which have been made since the Second World War and have been primarily responsible for greatly augmenting known phosphate resources,have amply demonstrated the importance of systematically applying basic geological principles to the complex problem of locating new phosphate deposits. In the case of marine sedimentary phosphates, the problem is often one of palaeogeography and as such involves the detection of marine sedimentary sequences and the delineation of associated geographical areas likely to reflect an environment favourable to phosphate deposition. Exploration for marine phosphate deposits are thus dependent primarily on a knowledge of the stratigraphy and structure of the region under investigation,obtained as a result of detailed geological mapping, in contrast to many metalliferous ores which may be indicated by reconnaissance geochemical or geophysical prospecting techniques. In areas already well-known geologically, most of the preliminary and time-consuming work can be eliminated by a study of established stratigraphical sequences, followed by field examination of selected critical sections. Geological information obtained also from oil and water drilling operations has proved particularly successful in some areas in detecting phosphate-bearing formations.

The chemical analysis of borehole or well cuttings is a particularly promising technique in the exploration for phosphate where a search for oil or water is being carried out in sediments likely to be phosphate bearing. For example, during an evaluation of the phosphate possibilities of the south-eastern coastal plain of the USA, cuttings from numerous water wells in southern Georgia and northern Florida were analysed and the results plotted on large scale regional maps. Sediments containing more than 5 per cent P_2O_5 were considered to represent phosphate anomalies. This technique led to the delineation of a phosphate-bearing belt extending from central Florida northwards to Georgia and then north-eastwards to the Atlantic Ocean and containing 6 or 8 marked phosphate anomalies. Drilling subsequently showed that some of them possessed reserves of between 50 to 75 million tonnes of marketable phosphate rock.

Geochemical methods designed primarily for phosphate prospecting have not been developed, although sampling appears to be one technique which could be used to outline a potential phosphorite-bearing area. Unusually high dissolved phosphorus contents have been found, for example, in the acid streams and lakes which drain the extensive phosphate deposits in Florida. Similarly, geophysical methods have been relatively little used as a means of detecting phosphate deposits, with the notable exception of radiometric surveys which have proved particularly useful. It depends on the presence of uranium, which in many submarine phosphorites ranges from 0.005 to 0.02 per cent. Phosphate rock, together with certain black shales, is thus significantly radioactive compared with most other sedimentary rocks.

In general if the response sample being examined is four or more times the normal 'background' reading, the sample should be retained for quantitative laboratory analysis. Aerial radiometric reconnaissance over large areas, in certain cases by helicopter, can also assist in detecting uranium-bearing phosphate deposits, but generally only under favourable circumstances.

Gamma-ray logs made in the course of test drilling provide a most convenient and rapid method of detecting beds of phosphorite within thick sedimentary sequences, particularly in areas not well known geologically. The technique has been used successfully in Turkey, where deposits of Upper Cretaceous age were discovered in 1962; in delineating phosphatic zones in the relatively unconsolidated water-bearing Miocene sediments of North Carolina; and in correlating phosphate beds during prospecting operations, such as those carried out, for example, in the Western Sahara, Syria and Queensland, Australia. Gamma-ray logging of drill holes in the exploration and development of phosphate reserves is standard practice in Florida.

PHOSPHATE FACIES

Phosphate rock is frequently associated with black, carbonaceous or bituminous shales or mudstones and cherts (or other siliceous sediments), as well as certain carbonate rocks. Such an assemblage is called the phosphate facies, a term which was apparently first used by Russian geologists during the early 1930s and is a most effective indirect aid to phosphate exploration. Its recognition in various countries has led to the successful discovery of several promising deposits. The facies reflects a very slow rate of deposition, so that it therefore has a greatly reduced thickness compared with sedimentary sequences deposited elsewhere during the same time interval. ~~The~~ recognition ~~of 'condensed' sequences can be very important~~ in delineating sedimentary sequences likely to be phosphate bearing.

A relatively thick sequence composed of, say, limestone, clays or shales, and chert, and containing only thin, low grade phosphate can pass laterally into a much reduced sequence with thicker, higher grade phosphate beds. The stratigraphical position of any occurrence of phosphate, however insignificant, should be noted and investigated in detail, therefore, with a view to finding deposits which may be possibly of commercial interest. Stratigraphical studies based in part on the use of lithofacies and isopachyte maps are important in identifying 'condensed' sequences and in establishing facies variations. Many condensed phosphate-bearing sequences also show a transgressive relationship to the older rocks.

STRUCTURAL CONTROL

Geological studies of sedimentary marine phosphate deposits have hitherto largely ignored or minimised the effect of local or regional tectonic activity. However, there is now considerable evidence available to show that the tectonic environment can greatly influence the character and geographical distribution of phosphate deposits.

For example, most of the well-known Mesozoic and Tertiary phosphate deposits of the ancient Russian platform are associated with depressions or downwarps ('syneclises') in which favourable bathymetric conditions were created for the deposition of phosphate.

Comparable phosphate deposits have been found in many other parts of the world and include those situated along northern and western margins of the African platform and on the Coastal Atlantic Plain of the USA. In Israel the most favourable conditions for phosphate formation appear to exist only in the 'synclinal facies', that is, in depressed areas of the basin floor which formed before or simultaneously with the deposition of phosphate. Similar conditions may have been operative during the deposition of the phosphatic chalk formations in northern France and Belgium. In other cases, the character and distribution of phosphate deposits may be greatly affected by the development of submarine, sometimes emergent, ridges, domes or other structural 'highs'.

EXPLORATION IN THE EEC

Very limited phosphate exploration has been carried out in the EEC, except in France where a systematic national inventory of phosphate rock resources was begun in 1975 by the Bureau de Recherches Géologiques et Minières (BRGM). To date much of the work has been confined to the Paris Basin, Brittany, and the Pyrenean and Montagne Noire areas of southern France. Zonation of known occurrences of Senonian phosphatic chalk has been made on the basis of micropalaeontology, the microfauna, essentially of benthonic character, becoming increasingly rich in pelagic forms where phosphate occurs. This appears to be a promising line of research. An aerial scintillometer survey carried out in the Paris Basin in 1961 gave effective results only where the overburden did not exceed 1 m. Rapid drilling of favourable horizons has also been carried out using gamma-ray logging for the *in situ* estimation of P_2O_5 contents.

In County Clare, Irish Republic, where phosphate rock was first discovered in 1924, exploratory drilling was first carried out between 1944 and 1946 and more recently between 1974 and 1977. Phosphate rock of varying thickness has been encountered in each of the 77 boreholes drilled to date, and in the recent work precise correlation between boreholes has been achieved on the basis of macrolithological units, such as goniatite bands, thin pyritic horizons, thin phosphate bands and nodular horizons, which are all traceable over a large area and have enabled a detailed interpretation of the stratigraphy to be made. As a result it proved necessary to core only the phosphate-bearing sequence, thus making possible considerable savings on drilling costs. The average depth of the holes drilled was 43 m with a maximum of 60 m. Gamma and resistivity logging has been carried out and has confirmed normal core logging results.

Exploration of the phosphate deposits of the southern Salentino Peninsula in Italy was performed by the French Société d'Etudes et de Recherches (SODEREC) between 1968 and 1970. The initial work in delineating the distribution of phosphate was based on a radiometric survey using a vehicle mounted and hand-held scintillometer. Using a standard of 12μrh (micro-Roentgen per hour) it was shown that a fossiliferous limestone containing abundant phosphate nodules gave readings of 150 to 200μrh. The phosphate bed was detected radiometrically under thin Pliocene limestone cover up to a maximum thickness of 18 cm. Apart from some sampling of the phosphate nodule bed and beneficiation trials no further work was carried out. Recent proposals for further exploration work have been made by another commercial organisation.

Radiometric surveys were carried out by the Comitato Nazionale per l'Energia Nucleare in 1965 and proved successful in locating phosphate-bearing beds in southeastern Sicily.

1.4. MINING AND BENEFICIATION

Phosphate rock is mined by both openpit and underground methods, the specific techniques adopted varying to a large extent with the nature and depth of the deposit. At present, approximately four-fifths of the total world production is obtained from openpit operations.

The phenomenal increase in demand for phosphate rock since the last World War has brought about considerable changes in the phosphate mining industry. Of particular significance has been the use of large earth-moving equipment such as draglines and power shovels as well as the introduction of the bucket-wheel excavator of a type originally designed for the openpit mining of lignite in the Federal Republic of Germany which, although involving substantial capital investment, has been eminently successful in providing large tonnages of phosphate ore from regular, flat or gently dipping deposits.

The most extensive openpit phosphate operations are in the USA in Florida, where all the major phosphate producing companies employ walking draglines, usually electrically driven, to handle large tonnages of unconsolidated rock. Bucket capacities are variable, one of the largest to remove overburden was installed in 1966 with a capacity of 49 cu.yd (37 m^3) equivalent to about 75 tonnes of rock. Machines in common use carry buckets of 35 to 40 cu.yd (27 to 30 m^3) capacity, with boom lengths ranging from 68 to 76 m. Sedimentary phosphate rock is mined underground extensively in Morocco and on a much more limited scale in Tunisia, Jordan and Egypt. Igneous apatite deposits are worked underground only in the USSR.

The methods of treating various phosphate ores, particularly those of low grade and complex mineralogy, have presented a considerable challenge to metallurgical skill and resourcefulness. Depending on the source and quality of the rock, the various operations used in beneficiating the crude ore include washing and screening, desliming with cyclones or hydroseparators, magnetic separation, flotation, calcination and drying. Of these, flotation has become perhaps the most important stage in phosphate rock beneficiation.

Most phosphate ores require beneficiation, with the notable exception of Moroccan rock, which contains 31 to 33 per cent P_2O_5 and requires only screening and drying before being marketed, as does the output from Nauru, for example, which contains some 38 per cent P_2O_5. Very low grade phosphate ores can now be beneficiated on a commercial scale, those from the Palabora Complex (South Africa) with an average of 7 per cent P_2O_5 and the Jacupiranga Carbonatite (Brazil) averaging 5 per cent P_2O_5 affording striking examples. It is reported that in the USSR, laboratory tests have indicated that diorite containing an average of only 4.7 per cent P_2O_5 can be upgraded by flotation to yield a concentrate with 35 per cent P_2O_5, the process achieving a phosphate recovery of 94 per cent.

Most siliceous ores consisting largely of quartz are amenable to economic beneficiation and even quite low grade feeds can be accommodated.In Florida, for example, the average grade of phosphate rock mined is about 11 per cent P_2O_5, quartz sand constituting about one-third of the crude ore. Much more challenging is the as yet largely unresolved problem of obtaining a satisfactory commercial phosphate concentrate from carbonate ores, in which calcite, dolomite or ankerite are the principal gangue minerals. Efficient separation of apatite, calcite or dolomite, has proved difficult. The problem becomes even more acute where the carbonate minerals and apatite are intimately admixed. However, if soft and relatively unconsolidated (as in the case of some phosphatic chalks), carbonate gangue minerals may be separated by scrubbing in some cases. Although separation by flotation is feasible, most of the commercial procedures resort to calcination followed by wet chemical separation or slaking. Even in such cases, the process may be regarded as too expensive if the ore contains less than about 25 per cent P_2O_5. The only commercial beneficiation plant which successfully separates apatite from calcite by flotation is operated near Jacupiranga in Brazil.

MINING IN THE EEC

Phosphate rock, in the form of phosphatic chalk, is mined in northern France near Nurlu, 14 km east of Péronne, and near Hallencourt, some 16 km SSE of Abbeville. It is recovered also as phosphate nodules as a by-product of iron ore mining at Broistedt, 16 km south-west of Braunschweig in the Federal Republic of Germany (Fig 2). Total production from these three sources amounted to 113,000 tonnes in 1976, of which the bulk, amounting to 85,000 tonnes averaging 18 per cent P_2O_5, was produced at Broistedt.

Broistedt

Detrital Upper Cretaceous ores consisting of clay ironstones and phosphate nodules reworked and enriched from argillaceous Albian sediments are worked at Broistedt by both conventional underground and openpit mining methods. Phosphate nodules make up about 6 to 10 per cent of the limonitic iron ore, which contains on average 38 to 39 per cent Fe_2O_3, 1.8 per cent P (about 4 per cent P_2O_5) and 0.5 per cent Mn. The thickness of the conglomerate is variable, reaching a maximum of 15 m, the section worked at the Mathilde mine by Stahlwerke Peine Salzgitter AG ranging from 3 to 7 m in thickness. The shaft reaches the deposits at a depth of approximately 100 m. On the northern side of the mining area, where the conglomerate reaches its maximum thickness, openpit operations have penetrated the underground workings. Overburden and ore are removed by means of 28-tonne Caterpillar tractor-scrapers. The mine produced 1.5 million tonnes of iron ore in 1976.

The iron ore deposits at Broistedt are, however, approaching exhaustion and mining ceased there at the end of 1977. To date the phosphate concentrate obtained by beneficiation has been used in the manufacture of basic slag at a nearby plant.

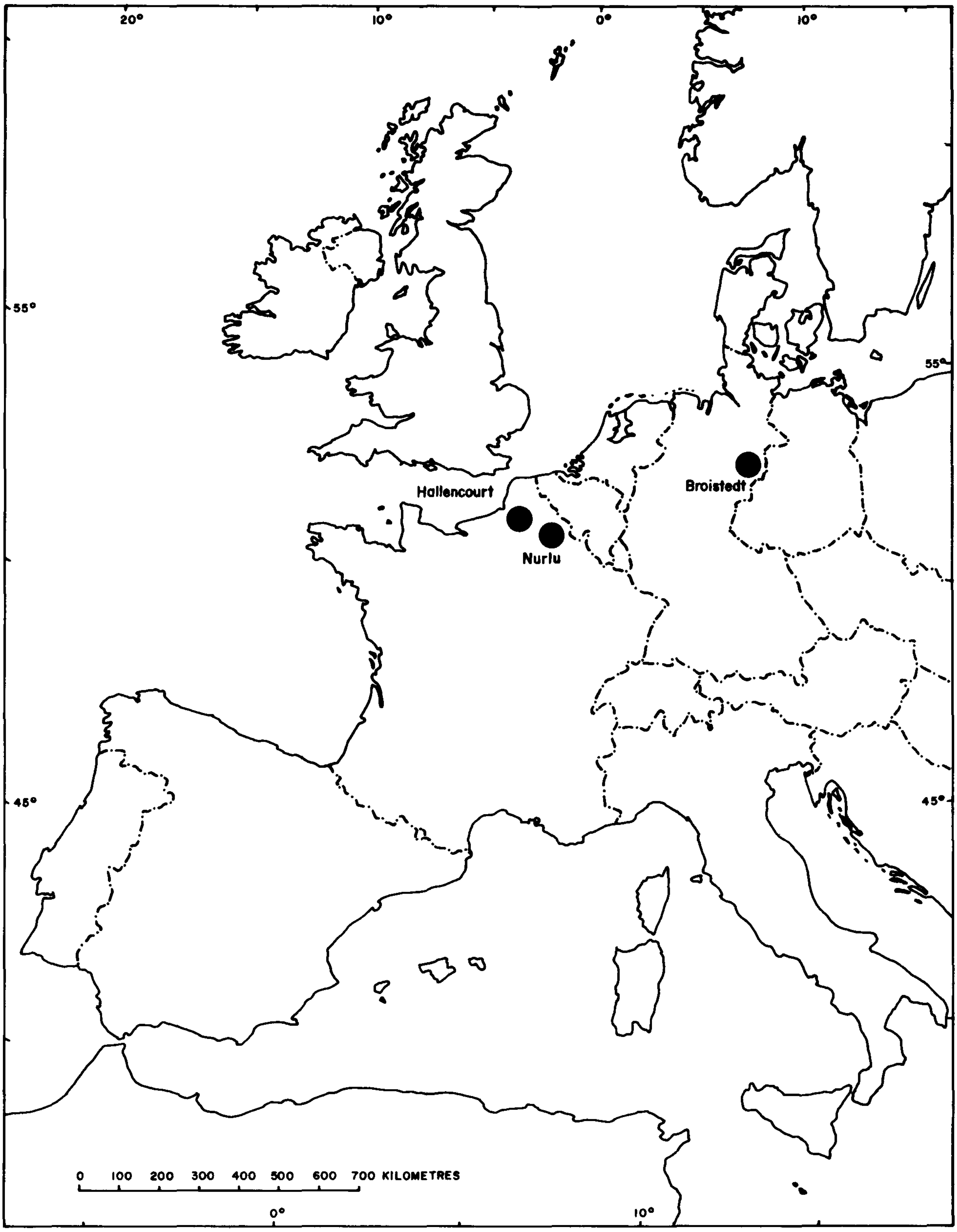


Fig 2. Location of phosphate rock production within the EEC, 1976.

Hallencourt

Deposits of Santonian - Campanian phosphatic chalk are worked near Hallencourt by underground room-and-pillar techniques. Three phosphatic chalk horizons occur, as shown below, but only the upper, thicker bed is presently worked although the other two beds have been worked in the past.

	Depth	Thickness	Average P_2O_5
	metres		Per cent
Upper Bed	38	7-8	10
Lower Bed	51	2-3	10
Third Bed	62	2	5-6

The beds occur as lenses orientated in a roughly NE-SW direction, the mine shaft being situated at the southwestern end of the Upper Bed and the northeastern end of the Lower Bed.

The mine, which is operated on behalf of the fertiliser producer Compagnie Française de l'Azote (COFAZ), produces annually between 20,000 and 25,000 tonnes of phosphatic chalk averaging 10 per cent P_2O_5. A section some 5 m thick is mined. After blasting, the phosphate rock is removed by front-end loaders with 0.65 m^3 buckets and transferred to rail cars of the same capacity for transfer to the shaft bottom. There are some 27 km of tunnels in the mine which has been worked since 1942. Workings extend some 600 m NNE of the shaft and the limit of the deposit has apparently been reached. Remaining reserves of phosphatic chalk in the Upper Bed have been placed at 250,000 tonnes, but there are plans also to mine the Lower Bed.

Nurlu

A bed of Santonian phosphatic chalk about 6 to 7 m thick is also quarried at Nurlu by a private contractor on behalf of COFAZ, although it was formerly mined by room-and-pillar methods until underground operations ceased some 20 or 30 years ago. Mine galleries have been revealed by excavating backfilled waste. Quarrying equipment includes a RH 4LC shovel and a Caterpillar D4D bulldozer-scraper. Present output is about 10,000 to 14,000 tonnes per annum of phosphatic chalk averaging about 15 per cent P_2O_5. The deposit, which has been worked since the First World War, is lenticular in shape and varies considerably in thickness.

As at Hallencourt, the output from Nurlu is transported to a nearby plant, where it is crushed, dried in rotary kilns to reduce the moisture content from 20 to 1 per cent, screened to remove hard lumps of chalk and flint and then finely ground. The product is marketed as 'phoscalcine' (Phosphates de Chaux Agricòle des Craies phosphatées de la Somme) containing 10 per cent insoluble P_2O_5, this average content being maintained by blending with lower grade phosphatic chalk or imported Florida rock (36 per cent P_2O_5). It is sold for direct application to acid soils in Picardie, the Ardennes and the Loire Valley, generally within a range of 500 km from the point of production.

PHOSPHATE ROCK BENEFICIATION IN THE EEC

Phosphatic chalk at present being produced in northern France is merely crushed, dried and screened before being finely ground. The detrital iron ore containing phosphatic nodules mined at Broistedt in the Federal Republic of Germany, however, is classified and subjected to heavy media separation (Fig 3). Three marketable concentrates are produced:

Feinerz concentrate (1-4mm) : 43 to 44 per cent Fe_2O_3
1.3 to 1.4 per cent P

Grosserz concentrate (4-35mm) : 52 to 53 per cent Fe_2O_3
1.3 per cent P

Phosphate concentrate (4-35mm) : 8 to 9 per cent Fe_2O_3
9 to 10 per cent P

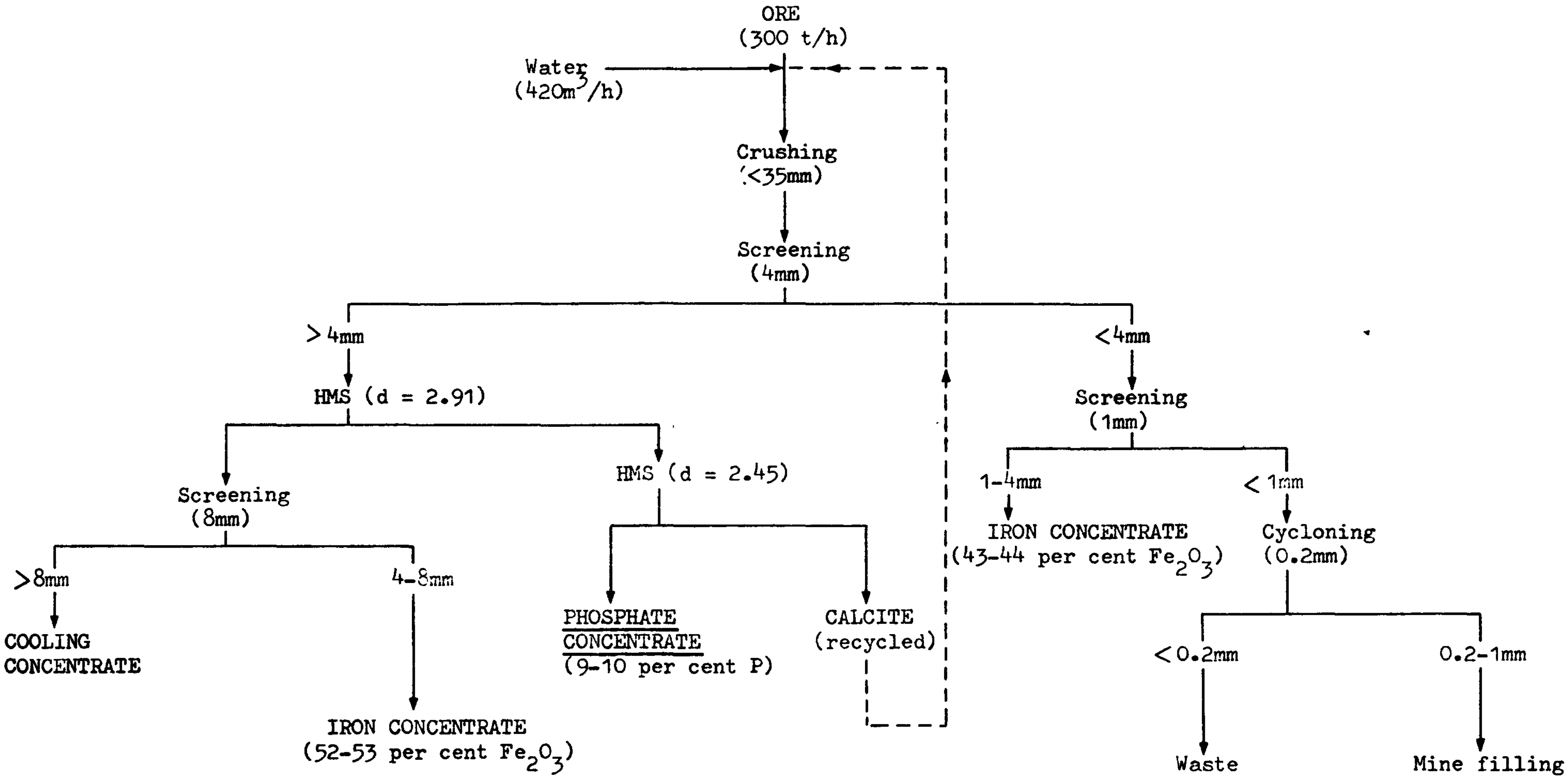


Fig 3 Production flowsheet of phosphate concentrate at Broistedt, Federal Republic of Germany

The phosphate concentrate, containing 21 to 23 per cent P_2O_5, represents about 7 per cent by weight of the ore feed. The beneficiation plant is capable of treating ore at the rate of 6,000 tonnes per day. A phosphate concentrate has been produced at Broistedt since heavy media separation facilities were installed there in 1956.

ENVIRONMENTAL CONSIDERATIONS

Phosphate mining within the EEC has a negligible impact on the environment because of the very limited scale of the present workings. Any possible future extraction of phosphates would inevitably have a local impact, but since total demand for phosphate rock within the EEC (13.5 million tonnes in 1976) is substantially less than the production of many other minerals such as coal, iron ore, sand and gravel and other construction raw materials, the total effect on the environment would be correspondingly smaller.

The extent of the impact on the environment of phosphate working would depend on the nature of the deposit, its size and geology, whether it could be worked by opencast or underground methods, and the rate of output. The nature, grade and mineralogy of the phosphatic ore would also be significant, since the type of processing facilities required to produce a marketable product may have a marked environmental impact. Large quantities of water may be required for processing, either for washing the ore and/or for flotation purposes. In addition, large quantities of slimes and tailings may be produced presenting waste disposal problems. There is no evidence to suggest, however, that these problems could not be overcome with a well-planned reclamation policy for the restoration of worked out areas and the disposal of waste, and the normal recycling of water to conserve water resources.

1.5. USES AND SPECIFICATIONS

The number of uses of phosphate rock is comparatively limited, although the chemicals obtained from the processing of this raw material have a wide variety of applications. An estimated 80 to 90 per cent of world phosphate rock supply goes into fertiliser manufacture, for which purpose phosphate rock has no substitute as a source of phosphorus. This percentage has not changed significantly in recent years.

The consumption of phosphate as fertiliser has been concentrated in the developed or industrialised countries where, in addition, other non-fertiliser uses of phosphate rock are developed to a high technological level. Non-fertiliser products are numerous, the most prominent in terms of tonnage being sodium triphosphate (STP), a major component of heavy duty laundry detergents. However, the use of phosphates for detergents has for some years been threatened by new pollution laws. Because of this, it is possible that detergents and other non-fertiliser applications may be susceptible to substitution in the longer term.

Within the last 15 years fertiliser technology has changed radically, with the emergence of new, high grade products containing greater proportions of plant nutrients. The main trend has been the transition from low grade 'straight' phosphate fertilisers, such as the once popular single superphosphate and basic slag, to more highly concentrated, multi-nutrient (NPK) formulations, based on ammonium phosphates, and triple superphosphate systems. These are derived from phosphoric acid and it is significant that world-wide use of phosphate rock for phosphoric acid manufacture quadrupled during the 1960-1970 period, for example, whereas overall phosphate rock consumption only doubled. The production of such fertilisers now accounts for more than one-half of the total world consumption of phosphate rock for fertiliser manufacture.

Another important use of phosphate rock is as a component in the manufacture of animal feed supplements, mainly calcium and sodium phosphates, the former providing also an important source of calcium and phosphorus in foods and restoratives. This end use is important as it requires phosphate rock with a very low or negligible fluorine content, such as that produced on the Caribbean island of Curaçao and exported mostly to the USA. Another important source of fluorine-free phosphorus compounds is defluorinated phosphate rock produced by thermo-chemical means. Phosphate rock for direct application to the soil, when finely ground, has been an important end use for many years. More than 50 per cent of the world consumption of ground rock is accounted for by the USSR and in certain tropical countries, such as Malaysia and Sri Lanka, there has been a long tradition of using ground phosphate rock as fertiliser on predominantly acid soils. In Europe, the important consumers are France, the United Kingdom, the Federal Republic of Germany and Austria.

Aluminium phosphate

The potential commercial use of aluminium phosphate has been investigated in several west European countries following the discovery and development shortly after the Second World War of substantial deposits of calcium-aluminium phosphate rock in western Senegal. Methods of extracting P_2O_5 and Al_2O_3 have been developed in France but not adopted commercially and at present the entire output of calcium-aluminium phosphate in Senegal is calcined and used as fertiliser. Tests have shown that heat treatment can convert to a suitable fertiliser the so-called 'C' grade phosphate rock at present removed as part of the overburden on Christmas Island, which has proved particularly troublesome in fertiliser processing because of the high contents of aluminium and other impurities. Similar material forming the 'leached' or aluminium phosphate zone occurs in central Florida but is not used commercially at present.

SPECIFICATIONS

There are no precise or standard trade specifications for phosphate rock and in most cases sales are based on average chemical composition and general physical properties as agreed between seller and buyer. Phosphatic raw materials are valued primarily for their BPL content and in general the most desirable material to use will be that which has a maximum phosphate content and minimum impurities and which can be delivered and processed at the lowest cost per unit of phosphate. Such factors as transport costs, international policies and currency restrictions may be more decisive in certain instances. In addition, the commercial value of a particular grade or type of phosphate rock is affected by the presence of admixed impurities such as silica, carbonates, iron, aluminium and organic matter and for these certain permissible limits are normally stipulated. Recent trends in the fertiliser industry have been towards the use of lower grade and more troublesome rock in phosphate processing, chiefly as a result of the expansion of phosphoric acid production in countries processing phosphate rock deposits of poorer quality.

Chemical composition

In terms of BPL or tricalcium phosphate content the requirements may vary considerably depending on the ultimate use of the raw material. For the manufacture of superphosphate, particularly triple superphosphate, as well as elemental phosphorus and phosphoric acid, relatively high grades are desired, most phosphate concentrates for such purposes containing more than 60 per cent BPL (28 per cent P_2O_5). Similarly, ground phosphate rock for direct application to the soil as fertiliser normally needs to contain at least 60 per cent BPL, especially if it is to be mixed with potash and sold in competition with other fertilisers.

Physical composition

In the manufacture of both superphosphate and 'wet-process' phosphoric acid, finely ground phosphate rock is required to ensure complete acidulation. The speed of reaction increases with fineness of grind, resulting in a reduction of processing time and the size of the equipment required. Conversely, however, finer grinding usually means added investment and operating costs. For example, phosphate concentrates that consist of hard, coarsely textured particles or highly crystalline apatite, as in some deposits of igneous origin, are often too unreactive for wet-process phosphoric acid and also superphosphate manufacture. These may require additional grinding to some acceptable particle size. The degree of fineness selected for rock grinding depends on the reactivity of the rock, the handling method used and the type of process employed. It may range from about 50 per cent through a 100-mesh Tyler screen to 95 per cent through 200-mesh. Some of the newer techniques have concentrated on reducing the fineness of grind without affecting efficiency. In general, the optimum textures of phosphate rock concentrates for acidulation with acid are soft, porous, pelletal or sand-size phosphate particles that are easily handled and can be ground without difficulty.

Calcined phosphate may have low reactivity because of changes in basic chemical structure, as well as agglomeration and loss of porosity, for example, which tend to drastically reduce surface area. In addition, much of the carbonate which may originally have been present is lost during calcination. The production of elemental phosphorus in an electric furnace requires a phosphate charge in lump form since fine material tends to block the passage of the phosphorus and gasses evolved. For this reason finely divided phosphate such as may be recovered by flotation is unsuitable for direct use in the furnace processes, while in other cases run-of-mine phosphate and lower grade phosphatic shales, though having a suitable chemical composition, also contain relatively high amounts of fine material. Feed size is normally 5 to 8 cm in diameter and for full and economic operation part or all of the phosphate fines present may have to be treated by various methods, including pelletising or nodulising, sintering and briquetting, before it enters the furnace.

IMPURITIES IN PHOSPHATE ROCK

Apart from important variations in the composition of the apatite mineral itself, there are equally important differences in the kinds and amounts of accessory mineral impurities that may be present, as well as in the manner in which these impurities may be distributed, all of which can greatly affect the performance of phosphate rock during processing.

Commercial concentrates from different sources may therefore frequently not be interchangeable in a particular manufacturing process, in spite of their apparent equality indicated by the conventional comparisons of P_2O_5 or gross chemical composition. Moderate amounts of calcium carbonate can enhance reactivity and up to 4 or 5 per cent CO_2 is generally considered acceptable, particularly in superphosphate manufacture. The gas liberated from the carbonates on acidulation renders the product porous and spongy and consequently facilitates drying. However, relatively high amounts cause effervescence which leads to foaming in phosphoric acid reactors, particularly if organic materials are also present. Thus, one of the most important chemical factors affecting the economics of acidulation grade rock is the CaO : P_2O_5 weight ratio since this determines acid consumption per tonne of P_2O_5 produced and, in phosphoric acid manufacture, the amount of calcium sulphate which has to be filtered. A typical range for the CaO : P_2O_5 ratio is 1.4 to 1.6, beyond which excessive quantities of process acid are required. The presence of magnesium is never desirable since it creates high viscosity in phosphoric acid manufacture and reduces the solubility of products after ammoniation. Usually most of the magnesium in phosphate rock occurs in apatite, in which up to 0.7 per cent MgO may be present. Ores high in organic matter generally have to be calcined to avoid the problem of foaming in phosphoric acid manufacture.

Two impurities which are particularly troublesome in wet-process phosphoric acid and ammonium phosphate manufacture are iron and aluminium (R_2O_3). In elemental phosphorus production also, iron may cause significant amounts of phosphorus to be lost as ferrophosphorus. Phosphate concentrates with more than 3-5 per cent R_2O_3 are unattractive for phosphoric acid manufacture, although suitable for superphosphate processes. Some nitrophosphate processes can tolerate high R_2O_3 contents. Too high a fluorine (F) content is undesirable since, in the form of hydrofluoric acid (HF), it is very corrosive. For most processes the F content should not normally exceed about 3 or 4 per cent. The corrosion caused is related to the F : Active silica (SiO_2) ratio in the rock which determines the concentration of fluoride ions in the phosphoric acid produced. There are fewer examples of this type of corrosion compared with those caused by chloride. In general, a content exceeding 0.1 per cent chlorine (Cl) cannot be tolerated when conventional stainless steels are used for plant construction. While active silica aids in removing F, unreactive silica can pose processing problems.

The grindability of phosphate rock concentrates is affected by the moisture (H_2O) content, which is also a very important element in freight costs. Usually the moisture content is about 3 to 4 per cent and should not exceed 5 per cent. Recently wet grinding techniques (involving ball-and ring-roll mills) have come into vogue at some phosphoric acid plants at or close to mine site. In the USA, for example, wet rock may contain about 8 to 12 per cent H_2O on delivery to wet grinding units. Wet grinding has proved more efficient and cheaper provided rock transportation costs are small.

1.6. MARKETING AND PRICES

Phosphate rock is marketed primarily on its BPL or phosphate content and sold on an f.a.s./f.o.b. basis, with freighting handled by buyer (or seller) in a seperate transaction. Contracts with North and West African suppliers normally provide for a guaranteed minimum grade as well as maximum contents of moisture and of the combined iron and aluminium oxides, allowing for a reduction in the price to the buyer if these limits are exceeded. Improved methods of mining, beneficiation and drying techniques have made it possible to regulate the grade and physical condition of the marketable material to within such narrow limits that a relatively simple selling system has also come into use in the USA, the products being sold at a given price per tonne on a dry basis. For example, Florida land-pebble phosphate of, say, 75/74 per cent grade for export is sold on the basis of 75 per cent BPL with an allowance for a fall to 74 per cent minimum. Fractions above and below the basis call for an adjustment in price. The chemical composition of the principal grades of phosphate rock imported into the EEC countries is shown in Table 1. The system is in contrast to the somewhat complicated calculations of value needed to protect the buyer earlier this century because of the varying contents of BPL, moisture and impurities of the phosphate rock marketed.

For superphosphate manufacture there is little or no export market for phosphate rock containing less than about 65 per cent BPL, while much of the 58/63 per cent BPL material is shipped chiefly as ground phosphatic fertiliser for direct application to the soil. The minimum grade for wet-process phosphoric acid manufacture is around 65 per cent BPL (30 per cent P_2O_5). In general the higher grades of phosphate rock are more attractive and the premium payable for higher quality rock increases rapidly with increasing phosphate content.

TABLE 1 CHEMICAL COMPOSITION OF PHOSPHATE ROCK CONCENTRATES IMPORTED INTO THE EEC

	FLORIDA 72 per cent BPL	SENEGAL 80-82 per cent BPL	MOROCCO 70-72 per cent BPL	TUNISIA 65-68 per cent BPL	TOGO 79-81 per cent BPL	USSR 86 per cent BPL
	per cent (dry basis)					
P_2O_5	33.12	37.68	32.89	30.23	36.85	39.5
CaO	48.26	51.08	50.89	48.92	51.69	50.0
Fe_2O_3	1.29	1.02	0.30	0.37	1.30	0.45
Al_2O_3	1.11	1.15	0.47	0.77	1.00	0.71
MgO	0.28	0.04	0.35	0.76	0.03	0.11
Na_2O	0.243	0.17	0.7	1.50	0.27	0.13
K_2O	0.126	0.03	0.08	0.08	0.05	0.11
SiO_2	6.10	2.95	4.15	3.12	2.99	2.04
CO_2	3.20	1.45	4.61	5.18	-	-
SO_3	0.76	0.25	1.92	3.42	-	-
F	3.81	3.32	3.17	3.26	3.75	3.00
Cl	0.009	0.03	-	0.09	0.12	-
Combined water (H_2O)	2.17	1.70	1.82	3.46	1.44	-
Organic matter	0.65					-
TOTAL	101.28 (a)	100.87	101.04	101.16	99.49	100.26 (b)

(a) Total includes 0.038 per cent MnO
0.0146 per cent Cr_2O_3
0.236 per cent TiO_2
0.0091 per cent V_2O_5
0.0114 per cent As_2O_3
0.04 per cent sulphide as S.

(b) Total includes: 0.34 per cent FeO
2.14 per cent SrO
0.85 per cent RE_2O_3
0.42 per cent MnO
0.42 per cent TiO_2
0.01 per cent V_2O_5.

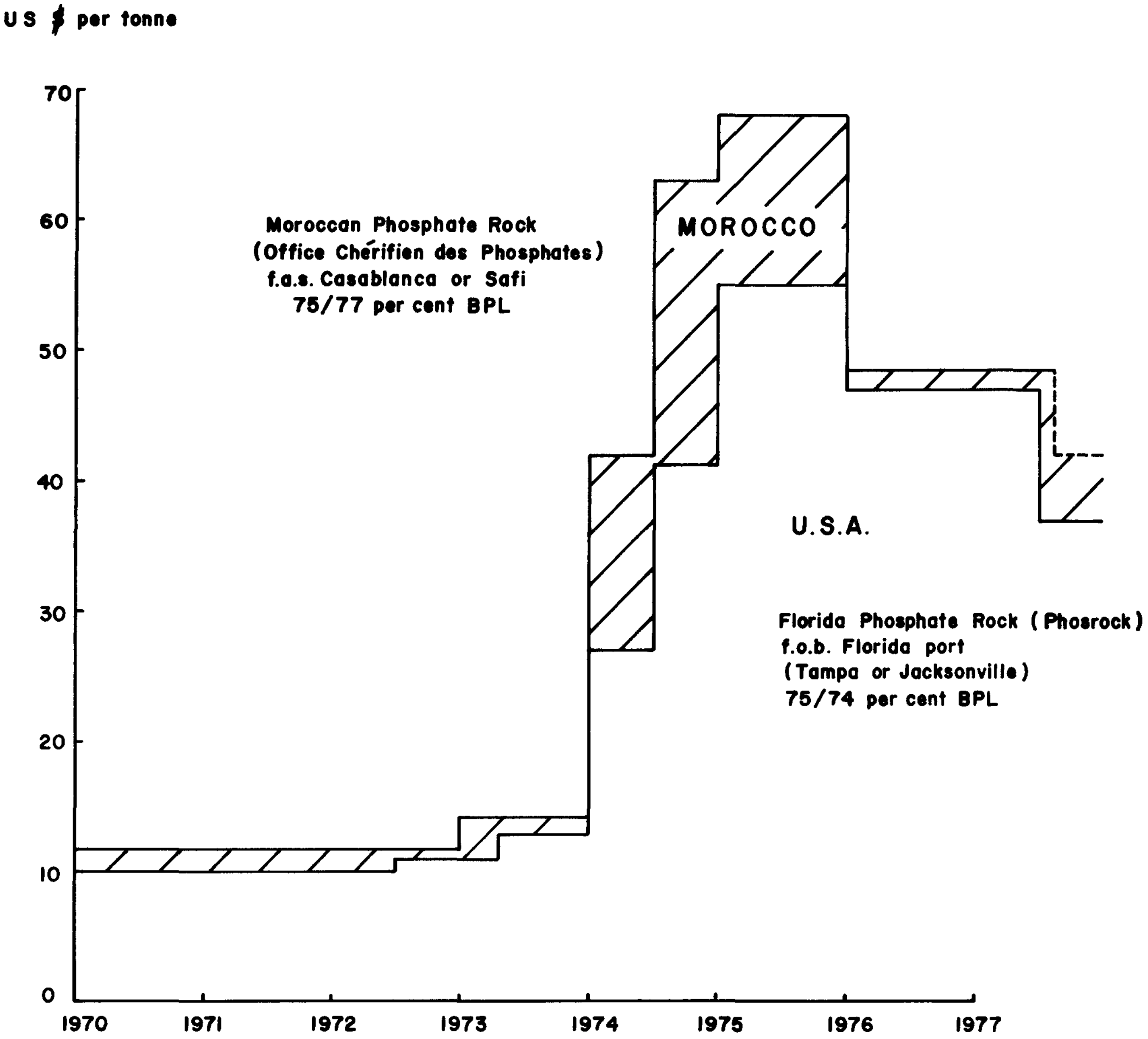


Fig 4 Listed export prices of phosphate rock, 1970-1977

PRICES

Phosphate rock has recently joined many other raw material commodities by moving into a succession of cyclical price changes which instinctively follow corresponding changes in world demand and supply (Fig 4).

Price levels for phosphate rock were comparatively stable during and after the Second World War until about 1964 when significant increases, generally by as much as 10 per cent., were put into effect by most of the major suppliers, although in some cases becoming operative only after existing contracts expired. These increases as well as the firm prices quoted for phosphate rock for some years subsequently reflected largely the considerable rise in world demand for phosphate rock. Supplies of new sources of high-grade rock brought into production early in the 1960s, principally those from Senegal and Togo, tended to be more competitively priced especially where freight differentials have had to be taken into account. Prices again remained relatively stable during the late 1960s, Moroccan phosphate rock, 70/72 per cent BPL grade, for example, being quoted at US $ 12.10 per tonne f.a.s. Moroccan port. Price increases in Moroccan rock which took place between 1971 and 1973 were in general linked with the devaluation of the US dollar and inflation running at some 5 per cent.

Particularly dramatic price increases for all grades of Moroccan phosphate rock were announced in October 1973, followed by revised increases in respect of Florida rock exports. Further substantial increases were imposed in 1974. The various listed price levels which have become effective since 1973 are shown in the accompanying table. Other major producers announced comparable export price increases. In 1975, however, there was a substantial decline in demand for phosphate rock and the rebuilding of producer stockpiles became increasingly evident. The resulting oversupply situation has led Morocco to cut prices and give discounts.

TABLE 2 MOROCCAN AND US EXPORT LISTED PRICES, 1974-1977

Morocco (OCP)

Grade Per cent BPL	Price US $ per tonne f.a.s. Casablanca, Safi or El Aaiun			
	January 1974	July 1974	January 1975	January 1976
80	50.00	75.00	Withdrawn	54.00
77/79 (calcined)	47.25	71.00	76.50	51.50
75/77	42.00	63.00	68.00	48.50
70/72 (Khouribga)	40.00	60.00	65.00	46.00
70/72 (Youssoufia)	37.50	56.25	60.75	43.50

USA (Phosrock)

Grade Per cent BPL	Price US $ per tonne f.o.b. Florida port (Tampa or Jacksonville)				
	January 1974	July 1974	January 1975	January 1976	July 1977
77/76	29.53	46.75	62.00	53.00	39.00
75/74	27.07	41.3	55.00	47.00	37.00
72/70	23.62	35.43	48.00	41.00	34.00
70/68	21.65	32.48	43.00	37.00	32.00
68/66	19.68	29.53	39.00	33.00	30.00
66/64	17.72	27.07	36.00	30.00	28.00

Price reductions of up to 29 per cent came into effect in January 1976, so that the listed price of 75/77 per cent BPL rock, for example, has reduced from $ 68 per tonne f.a.s. Moroccan port to $ 41-43 per tonne. Phosrock, the US phosphate export association, subsequently cut its prices also, by some 14 per cent, in order to maintain a competitive position. It has been reported that Moroccan export prices, f.a.s. Casablanca or Safi, averaged from $ 35 to $ 37 per tonne during 1976 and declined towards the end of the year to between $ 30 and $ 32 per tonne for 70/72 per cent BPL rock. The price of US exports of similar grade is reported to have ranged from $ 27 to $ 34 per tonne, f.o.b. Tampa, Florida.

The price increases in phosphate rock were reflected in the price of manufactured fertilisers and consumer resistance has become more pronounced than was considered probable. As a result, world fertiliser stocks have reached unexpectedly high levels.

TRANSPORTATION

Transportation costs are an extremely important item in the economic evaluation of phosphate deposits, due primarily to the relatively low unit value of phosphate rock. Most commercial deposits competing successfully in world markets at present are situated considerably less than 100 km from deepwater port facilities.

Phosphate rock freight rates vary considerably and depend on many factors, with a complex pattern of imports and exports covering most of the trade routes of the world. During the latter half of 1977, for example, rates of $ 16.35 per tonne were reported for bulk shipments from Dakar (Senegal) to the west coast of India, $ 11.00 per tonne Jacksonville (Florida) to Brake (Federal Republic of Germany) and $ 5.65 Tampa (Florida) to Antwerp.

Seaborne phosphate rock shipments are somewhat less than the world trade in rock, the difference being accounted for largely in trade between the USSR and eastern Europe, which is mainly overland by rail and barge, and between the USA and Canada and Mexico, although North American coastal shipments by barge and ocean-going vessels amount to over 10 million tonnes annually and are much larger than comparable overland trade. Phosphate rock shipments represent only a relatively small percentage of the seaborne trade in the main bulk commodities but nevertheless ranks fourth after iron ore, coal and grain. Shipping distances are relatively short due to the proximity of north and west African producers to their main market, Europe.

Most phosphate rock shipments are in bulk, bagged shipments being now relatively rare, although Christmas Island 'dust' continues to be shipped to Malaysia in this way. The vessels employed in the phosphate rock trade range from conventional bulk carriers to 'tweendeck' tramps or cargo liners of 12,000 to 15,000 dwt, the bulk carriers of 20,000 to 25,000 dwt size being ideally suited and increasingly employed in the medium-to long-haul trades to reduce freight rates. There is significant employment also of 30,000 to 40,000 tonne carriers.

PHOSPHATE ROCK MARKET TRENDS

Phosphate rock demand, reflecting the dependence on fertiliser markets, can be related in a general way to the demand for food which in turn is determined to a large extent by population growth and agricultural progress, as well as the ability of countries or regions to produce, pay for and apply fertilisers. Industrial i.e. non-fertiliser, consumption of phosphate rock will be confined mainly to industrialised countries, the overall increase in demand being roughly commensurate with economic growth, even allowing for substitution in detergents. Technical and feed-grade phosphates may eventually be produced in the developing countries but this is unlikely to have much impact, even in the long term, on the total supply-demand balance, which is determined primarily by anticipated fertiliser usage.

At present, the main markets for phosphate rock are the developed countries, with nearly one-third of the total world consumption accounted for by North American and about one-quarter by western Europe, where consumption is concentrated in the EEC countries, notably France. It has been estimated that in western Europe, phosphate rock demand, and hence imports, may reach 25.5 million tonnes by 1980, representing an average annual growth of 2 to 3 per cent during the 1970-1980 period.

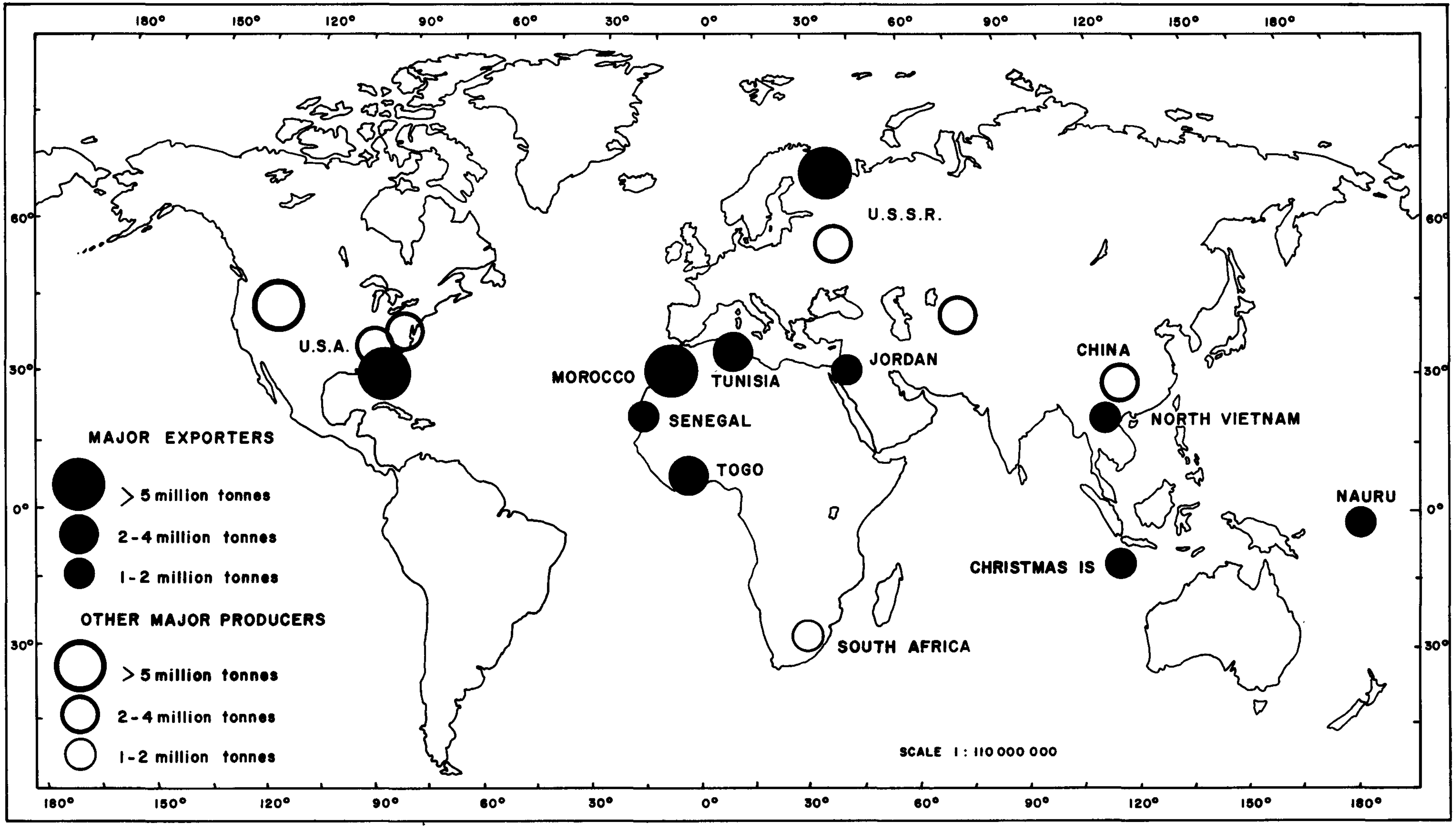


Fig 5 Major world suppliers of phosphate rock, 1976

2. WORLD PRODUCTION AND TRADE

Phosphate rock forms the basis of a large industry of world-wide importance, primarily as a result of the phenomenal development since the Second World War of the phosphate fertiliser industry, for which phosphate rock is the only suitable raw material.
World production of marketable phosphate rock reached a record total of some 133 million tonnes in 1975, more than double the output in 1960 and about 10 times that achieved just before the Second World War. There was, however, a marked decline in total world output in 1976 to some 107 million tonnes. The compound growth rate throughout the 20-year period, 1956-1975, was 7 per cent per annum. It is estimated that since recorded production began in 1847, in Suffolk in England, a total of about 2,000 million tonnes of phosphate rock has been produced.

2.1. MAJOR SOURCES OF SUPPLY

The bulk of the world's production comes from the USA, the USSR and Morocco, which together provided about 79 per cent of the world total in 1976. A further 16 per cent is derived from some 9 countries, each of which has a marketable production of around 1 million tonnes or more. The quantities of marketable phosphate rock produced by major sources of supply during the period 1972-1976 are shown in Table 3. Except for the USA, the USSR and South Africa, the principal producing countries export most or all of their output (Fig. 5).

USA

The United States, for many years the principal source of world supply, produced an estimated total of 44.6 million tonnes of marketable rock in 1976, a quantity equivalent to about 42 per cent of total world output. By far the most important commercially are the mines situated in central Florida which, together with North Carolina, accounted for 81 per cent of domestic production;

TABLE 3. PRODUCTION OF PHOSPHATE ROCK, BY MAJOR PRODUCERS, 1972-1976

	1972	1973	1974	1975	1976
			Thousand tonnes		
USA	36,087	37,613	40,458	44,301	44,571
USSR	19,722	21,250	22,505	24,150	24,200
MOROCCO	14,468	16,564	19,327	13,548	15,293
TUNISIA	3,297	3,473	3,884	3,481	3,294
NAURU	1,337	2,323	2,288	1,534	755
SOUTH AFRICA	1,252	1,365	1,304	1,774	1,639
TOGO	1,928	2,272	2,480	1,161	2,067
SENEGAL	2,419	1,693	1,878	1,871	1,786
CHINA (a)	2,600	3,000	3,000	3,400	3,400
CHRISTMAS ISLAND	1,151	1,538	1,764	1,391	1,033
JORDAN	694	2,211	1,595	1,353	1,717
VIETNAM, NORTH (a)	280	500	1,200	1,400	1,500
TOTAL	84,235	93,802	101,683	99,364	101,255
WORLD TOTAL	88,912	97,359	109,092	133,190	106,820

(a) Estimate

Source: ISMA Limited, Paris.

those in the Western Phosphate Field, chiefly in Idaho and Montana, and Tennessee supplied the remaining 13 per cent and 6 per cent respectively. Most of the marketable output, which generally contains between 44 and 77 per cent BPL, is consumed domestically but the U.S.A. also maintains a substantial export trade in rock averaging more than 66 per cent BPL, in spite of considerable competition from North and West African phosphate producers. Exports exceeding 9.1 million tonnes in 1976 were made to many countries but chiefly to Canada, Japan and Western Europe, particularly the Federal Republic of Germany.

For many years Florida has been the largest phosphate-producing area in the USA as well as one of the most productive in the world. At present roughly two-thirds of the annual output is destined for the domestic agricultural market; relatively small quantities are used for direct application to the soil, as well as for the manufacture of animal feed supplements and elemental phosphorus. As many as 11 individual companies are mining phosphate rock in Florida. Phosphate rock for export or domestic water shipments is transported mainly by rail to one of several port terminals, notably at Tampa, the largest of which has a loading capacity of about 4 million tonnes per annum. In northern Florida a mine is operated near White Springs about 40 km west of Jacksonville, through which commercial shipments are made.

About 80 per cent of the phosphate rock produced in the Western Phosphate Field, amounting to some 5.8 million tonnes in 1976, is produced in southeastern Idaho. It is estimated that more than one-half of this production is consumed in phosphorus manufacture. Montana, the nearest source of supply to Canada, thereby enjoys a substantial advantage in freight costs compared with producers in Idaho, Wyoming and Utah. A large proportion of the phosphate exported to Canada as rock is returned to the USA in the form of high-analysis fertilisers, notably ammonium phosphate. All the marketable phosphate rock produced in Tennessee is consumed domestically in the manufacture of elemental phosphorus.

USSR

The USSR is the world's second largest producer of phosphate rock, with an estimated marketable output in 1976 of 24 million tonnes, more than one-half of which was in the form of apatite concentrate. Apatite is produced from the remarkable Khibiny alkaline igneous complex, in the Kola Peninsula where four large mines: Kukisvumchorr (S.M. Kirov) and Yukspor, Rasvumchorr, Tsentralny (Apatite Circus) have been in operation since 1964 and provide the basis of phosphate fertiliser production in the USSR. Mining of deposits on the neighbouring Mount Koashva is reported to have begun in 1973. Most of the output is in the form of a flotation concentrate, averaging 34 per cent P_2O_5 but small quantities of apatite or crude apatite are also produced and used for metallurgical purposes. Exports are entirely of Khibiny apatite, amounting to an estimated 5.5 million tonnes in 1976, equivalent to approximately one-half of the total estimated production of apatite, chiefly to East Germany and other eastern European countries and to the Federal Republic of Germany. Apatite concentrate and apatite ore are transported by rail either 60 km to the ice-free Arctic port of Murmansk, north of Kirovsk, or some 400 km to Leningrad.

Important sources of sedimentary phosphate rock are the deposits situated in southern Kazakhstan in the Lesser Karatau Mountains, north-west of Dzhambul, which have been worked since 1946 and are used in the manufacture of elemental phosphorus and superphosphate; most of the remaining tonnage of phosphate rock is obtained from the European part of the USSR, particularly in the Bryansk, Kirov, Kursk, Leningrad and Moscow regions. These mines are essentially opencast operations. Much of the output is used as ground rock or 'phosphorite meal' for direct application to the soil.

Morocco

Phosphate mining began in Morocco in 1921 and has since grown at a remarkably rapid rate, due chiefly to the high grade and soft, friable nature of the deposits, as well as to the large capital investment in the industry. The country has for many years been one of the world's major phosphate rock producers and also the largest exporter. Production amounted to 15.3 million tonnes in 1976. Phosphate mining in Morocco is in the hands of the Office Chérifien des Phosphates (OCP), the organisation formed by the Moroccan Government in 1921.

Domestic consumption of phosphate rock is small, in spite of the fact that Morocco is a predominantly agricultural country, so that nearly all the production is exported, chiefly to Europe, the principal consuming countries being France, Belgium, the United Kingdom, the Federal Republic of Germany and Spain. Morocco shipped over 14.6 million tonnes in 1976 of which 8.4 million tonnes was destined for western Europe. Sales of Moroccan phosphate rock in the last decade have accounted for over 40 per cent of deliveries by all suppliers to world phosphate markets.

About three-quarters of the annual output is obtained from deposits situated along the northeastern margin of Oulad Plateau or "Plateau des Phosphates", near Khouribga, about 54 km south-east of Casablanca. The remainder is produced near the village of Youssoufia (formerly known as Louis Gentil), about 30 km ESE of the port of Safi, where mining began in 1931. Four distinct phosphate beds have been designated by OCP, of which one (Bed I) containing 31 to 35 per cent P_2O_5 has provided virtually all the output to date. Except for rock sufficiently high in grade to be transported direct to Casablanca, the production from the Khouribga area is sent to Khouribga for further treatment. From there the dried phosphate is carried by rail to Casablanca. Phosphate exports represent about 80 per cent of total shipments from this port which is one of the largest in Africa, an illustration of the importance of phosphate to the Moroccan economy. Phosphate rock produced at Youssoufia is carried by rail to Safi.

Tunisia

Production of phosphate rock has been the most important sector of Tunisia's mineral industry for many years, the value of output greatly exceeding that of all other minerals produced. Marketable production amounted to nearly 3.3 million tonnes in 1976 and most of this was derived from the famous Metlaoui, Redeyef, Ain Moularès and Djebel M'Dilla mines situated in southern Tunisia near Gafsa. All these mines are operated by the State owned Compagnie des Phosphates et du Chemin de Fer de Gafsa, which also owns the railway from the mines to the shipping port of Sfax, approximately 250 km to the east. The remainder is produced by Société Tunisienne d'Exploitations Phosphatières (STEPHOS) at Kalaa-Djerda in the western part of central Tunisia. Phosphate rock from this mine is carried by rail some 400 km to the port of La Goulette (Tunis).

About 1.7 million tonnes was exported in 1976, Tunisia being a major supplier of finely ground rock marketed under the trade name of Hyperphosphate. Deliveries to western Europe, particularly France, Federal Republic of Germany and Italy, accounted for more than 70 per cent of total exports until 1965, but since then shipments to eastern European and eastern Mediterranean countries have increased considerably, notably to Poland, Yugoslavia and Greece. Exports consist chiefly of 65/68 per cent BPL rock.

Togo

Togo is a major producer of high grade phosphate rock, estimated output in 1976 of concentrates averaging 81 per cent BPL amounting to 2 million tonnes, almost all of which was exported, chiefly to France which received 885,000 tonnes. Deposits situated in southern Togo near the village of Akoumapé have been worked since 1960, exports beginning in 1961 with shipments to Japan and the USA. Most of the output however, has been exported to western Europe. A major recent development has been the completion in 1973 of a new mine at Kpogamé, just west of the existing operations, which is capable of providing an additional 600,000 tonnes. Phosphate mining in Togo is in the hands of Compagnie Togolaise des Mines du Bénin (COTOMIB), a company which was founded in 1957 and nationalised in 1974. From the mines the phosphate rock is carried by rail across Lake Togo to a washing plant at Kpémé situated on the coast, a total distance of some 25 km.

Nauru

Deposits of very high grade phosphate rock have been worked on the raised coral atoll of Nauru in the Central Pacific since 1906. Output reached 2.3 million tonnes in 1973, but has since declined to 775,000 in 1976. Prior to the creation of the Nauru Republic in 1968, practically the entire output of rock averaging 83 per cent BPL was shipped to the traditional markets of Australia and New Zealand with relatively small quantities exported periodically to the United Kingdom. Since 1968, new markets have been established, notably in Japan. The deposits on Nauru are worked by the Nauru Phosphate Corporation, which was formed in 1969 to take over the management of the industry that for many years had been in the hands of the British Phosphate Commissioners. There are no exports to any of the EEC countries.

South Africa

South Africa has become a substantial producer of phosphate rock since the early 1960s, marketable output amounting to some 1.6 million tonnes in 1976. Most of the total output is produced in Transvaal Province, almost entirely from the famous Palabora Igneous Complex worked by the State-owned Phosphate Development Corporation (Pty) Limited (FOSKOR) which was formed in 1951. Apatite concentrates containing a minimum of 36.4 per cent P_2O_5 (80 per cent BPL) have been produced from the complex since 1955. Mining is based on a pyroxenite orebody containing an average of only about 7.5 per cent P_2O_5. To date nearly all the output has been consumed domestically but in the last year or so trial shipments of apatite concentrate have been made to a number of overseas countries, including western Europe.

Senegal

Deposits of phosphate rock have been worked in western Senegal since 1960 near Taïba, on the Thiès Plateau about 7 km NNW of Tivaouane. Estimated production amounted in 1976 to 1.8 million tonnes averaging 82 per cent BPL. Most of the output is exported, chiefly to the Federal Republic of Germany, the United Kingdom and Japan. Small quantities of finely ground phosphate rock are also sold locally as fertiliser under the trade name of "Baylifos". The deposits are worked by Compagnie Sénégalaise des Phosphates de Taïba, phosphate concentrates being transported by rail via Tivaouane to Dakar, a distance of about 41 km.

Also on Thiès Plateau near Thiès are aluminium phosphate deposits of secondary origin which are worked by Société Sénégalaise des Phosphates de Thiès, a subsidiary of the Rhône-Poulenc group. The deposits have been worked since 1949, most of the output being exported, chiefly to France, where it is calcined, ground and marketed as a fertiliser ("Phospal") containing 34 per cent P_2O_5. Small tonnages of "phospal" are also manufactured in Senegal for local use.

Jordan

Phosphate rock occurs extensively in Jordan and has been mined on a commercial scale since 1942 near Er Ruseifa NNE of Amman and, since 1961, to the east of El Hasa, some 200 km north of the deep water port of Aqaba. Production amounted to 1.7 million tonnes in 1976, nearly all of which was exported either from Aqaba or, to a much lesser extent, transported by truck or rail via Syria to Beirut in Lebanon. India has traditionally been Jordan's principal customer, but in recent years substantial deliveries have been made also to eastern and western Europe. In 1976, 1.7 million tonnes were exported, chiefly to Roumania and Bulgaria.

Phosphate rock is mined in Jordan by the Jordan Phosphate Mines Company, Limited, a government controlled concern incorporated in Jordan in 1953. Phosphate concentrate averaging 70/72 per cent BPL was the standard product until 1967, when marketable rock with 73 per cent BPL and 75/77 per cent BPL began to be shipped from El Hasa. In addition, phosphate fines extracted by air separation during the drying stage are made available as ground rock, "Jorphos", which contains 66 per cent BPL and is sold for direct application to the soil, notably to Sri Lanka.

Christmas Island

High grade phosphate deposits on Christmas Island in the Indian Ocean approximately 130 km off Java have been worked since 1899, and since 1948 by the Christmas Island Phosphate Commission, the British Phosphate Commissioners acting as managing agents. Production in 1976 amounted to about 1.1 million tonnes of rock containing 82 per cent BPL, all of which was exported, notably to Australia.
Since the Second World War the Australian and New Zealand superphosphate industries have consumed nearly all the phosphate rock produced on the island. There are no exports to the EEC countries.

Phosphate dust recovered from the treatment process is bagged and shipped for direct application to the soil, chiefly to Malaysia and Singapore, and also to Indonesia; small quantities have been exported to Australia for use in stock foods and for experimental purposes.

China

China is a major producer of phosphate rock in the Far East, with an output in 1976 estimated to be 3.4 million tonnes. Most of the deposits are believed to be of low grade and are worked in various parts of the country to supply local fertiliser plants. Part of the output is also used for direct application to the soil as fertiliser. The best known deposits are in the southwestern China in the Yunnan and Kweichow provinces. There are no exports, as far as is known, and imports chiefly from North Vietnam and Egypt, amounted to 1.3 million tonnes in 1976.

Vietnam

Deposits of phosphate rock occur near Laokay in the northern part of Vietnam close to the Chinese border and have been worked on a large scale since 1957 by the Vietnam National Minerals Export and Import Corporation. Production in 1976 amounted to an estimated 1.5 million tonnes of phosphate rock averaging 33 to 35 per cent P_2O_5. Exports, estimated at 1.1 million tonnes, have been directed to China and eastern Europe, notably Roumania, which provided financial aid and technical assistance for the reconstruction of the Laokay mine. Since 1966, however, shipments to Europe have been negligible.

2.2. POTENTIAL SUPPLIERS

The marked shortage of phosphate rock supplies in both 1973 and 1974, together with the very high rock prices which prevailed briefly as a result, stimulated exploration for new phosphate deposits as well as reassessment of a number of deposits hitherto believed to be uneconomic. Several phosphate development projects are under consideration or are being undertaken, notably in northern Europe, which could conceivably be capable of providing the EEC with at least part of its anticipated phosphate rock requirements. A supplier of growing importance to western Europe was the Western (formerly Spanish) Sahara from which, however, there have been no exports since the early part of 1977.

Sweden

Prospects of a potential source of supply of phosphate rock to the EEC are offered by the high-phosphorus magnetitic iron ore deposits situated around Kiruna and Gällivare in northern Sweden and at Grängesberg in central Sweden, which contain appreciable amounts of apatite as the principal non-iron mineral. These well-known iron ores have contributed substantial quantities of phosphorus to the European basic slag industry. Some 77 per cent of the iron ore reserves, amounting to 5,344 million tonnes, are contained in apatitic ores.

Recent changes in steelmaking technology and a consequent decline in demand for phosphoric iron ores has led to the development of processing facilities at Grängesberg for the production of dephosphorised ore which also yield a high grade apatite concentrate as a by-product. At Grängesberg, fine grinding, magnetic separation and froth flotation yield an apatite concentrate with 16.8 per cent P (38.5 per cent P_2O_5), a maximum of about 1.5 per cent Fe, about 2 per cent SiO_2 and 0.3 per cent Na_2O+K_2O. Production of apatite concentrate amounted to 30,000 tonnes in 1975 and is expected to reach 160,000 tonnes of apatite (61,500 tonnes P_2O_5) in 1978.

It is envisaged that the greater part of the output will be exported. There are also plans to produce apatite from Kiruna iron ore. The iron ores of the Kiruna area are classified as low phosphorus ($<0.1\%$ P) and high phosphorus ($>1\%$ P), although some of the latter ores may assay between 2 and 5 per cent P. At Malmberget (Gällivare orefield) the distribution of phosphorus is fairly regular at about 0.4 per cent P and at Grängesberg the phosphorus content of the ore raised is about 0.7 per cent P. During the period 1938 to 1945, when overseas supplies were curtailed, some 515,500 tonnes of apatite concentrates were produced at Malmberget and 81,700 tonnes at Grängesberg. Magnetite and hematite were removed by magnetic and gravity separation respectively, and the residue was subjected to froth flotation to produce an apatite concentrate with 27 to 30 per cent P_2O_5 and about 7 per cent Fe. The superphosphate produced during the war from this raw material contained about 15 per cent P_2O_5 of which only 7 per cent was water soluble because of the high iron content. Freight and concentration costs were said to be high.

Apatite is an important constituent also of some of the sövite (carbonatite) breccias which occur as steeply dipping ring dykes in an alkaline igneous complex on Alnö Island, situated off Sundsvall in southern Vasternörrland. Proved resources of apatite-sövite containing between 4 to 15 per cent apatite have been estimated at 2.15 million tonnes to a depth of 50 m. Drilling has indicated that sövite breccias continue to greater depths without significant variations in size, so that total reserves of sövite above sea-level may be estimated at about 60 million tonnes.

During the Second World War the possibility of exploiting the deposits was investigated, but no flotation method was developed which could produce satisfactory apatite concentrate from sövite. However, from 1941 until the late 1950s about 50,000 tonnes of finely ground sövite were produced annually for direction application to the soil. Improvement of beneficiation techniques in recent years could perhaps lead to a renewal of interest in the Alnö carbonatite complex as a possible commercial source of phosphate.

Finland

Apatite deposits situated in northern Finland north-east of Savukoski, Lappi Department, and in the southern part of the country near Siilinjärvi, Kuopio Department, have attracted commercial interest in recent years and are to be brought into production on a limited scale during the late 1970s.

Near Siilinjärvi, about 24 km north of Kuopio, steeply dipping zones of apatite bearing rock up to 10 m thick occur in mica-gneiss of Precambrian age. Drilling carried out during the late 1950s over an area of about 6 km^2 has shown that the zone of apatite mineralisation extends from just north-east of Siilinjärvi for a distance of at least 11 km and is up to 700 m wide with reserves to a depth of about 100 m estimated at about 460 million tonnes of rock averaging 10 per cent apatite (4.2 per cent P_2O_5). A mine at Siilinjärvi is planned to come into production in 1978 to supply phosphate rock to a nearby fertiliser plant operated by Kemira Oy. Mining of a trial quantity of ore was begun in 1975 and a pilot plant is currently in operation.

North-east of Savukoski deposits of secondary, ferruginous phosphate rock overlie the Sokli carbonatite which was discovered in 1967 close to the Finnish-Russian border. Drilling carried out on behalf of the steel and vanadium producer, Rautaruuki Oy, has proved over 50 million tonnes of rock averaging 18.3 per cent P_2O_5, with an indicated quantity of the order of 50 million to 100 million tonnes of rock of lower grade. On average the phosphate rock contains at least 20 per cent Fe, but tests have shown that a marketable concentrate can be produced. However, the deposits are situated in a remote part of the country and considerable investment in infrastructure will be required.

Norway

In southeastern Norway the Kodal apatite-ilmeno-magnetite deposits north of Larvik have been investigated by Norsk Hydro SA since the late 1950s. The deposits could perhaps be mined at the rate of 1 to 2 million tonnes per annum to yield a magnetite concentrate and, as a by-product, perhaps 170,000 to 340,000 tonnes of apatite concentrate averaging about 39 per cent P_2O_5 (85 per cent BPL). There are no plans to develop a mine at Kodal in the immediate future. Drilling has indicated a reserve of nearly 100 million tonnes containing 15 to 25 per cent apatite (approximately 6 to 10 per cent P_2O_5) of which some 22 million tonnes are considered proved.

Greece

Deposits of sedimentary phosphate rock were discovered in 1976 in the Delvinaki area of Epirus, close to the Greek-Albanian border by the Institute of Geological Research. Preliminary investigations have indicated the presence of at least 10 million tonnes of phosphate rock averaging 15 per cent P_2O_5, individual beds ranging from 2 to 10 m in thickness. The phosphate bearing series has been found to outcrop over a distance of 50 to 60 km, of which a continuous strip of 15 km occurs near Delvinaki. The possibility of developing a mine is being investigated but it is doubtful whether any phosphate rock will be available for export. Greece currently imports about 650,000 tonnes per annum, exclusively from North African producers.

Spain

Phosphate deposits of igneous and sedimentary origin occur in various parts of Spain, the most important being the igneous apatite deposits in Caceres Province which are regarded as a continuation of the occurrences found in the neighbouring part of eastern Portugal. The deposits were worked during the latter part of the 19th century and again between 1916 and 1921 and during the Second World War. Individual deposits contain up to 1.5 million tonnes of rock averaging less than 18 per cent P_2O_5, but no up-to-date assessment of resources and likely reserves has been made. Resources of sedimentary phosphate rock of Upper Cretaceous age in southeastern Spain (Murcia Province) have not been evaluated.

Egypt

Very large deposits underlying Abu Tartur Plateau in the western desert of Egypt northwest of El Kharga are awaiting development. These deposits estimated to contain about 800 million tonnes of rock averaging 25 per cent P_2O_5, have been investigated since 1968 and a project has been considered which involves the production of perhaps some 7 million tonnes per annum of marketable concentrate with 68 to 70 per cent BPL, to be exported via a Red Sea port. An underground mine will have to be developed, and a railway constructed to connect the deposits with the Red Sea, a total distance of some 520 km. Feasibility studies are currently being undertaken; should plans to develop the Abu Tartur deposits on the scale envisaged come to fruition, the existing Egyptian phosphate industry, which is not large by international standards, will be transformed to rival in size those in neighbouring North African and Middle Eastern countries.

2.3. EEC PRODUCTION AND TRADE

Production of phosphate rock within the Community is extremely limited and is confined to a very small output of phosphatic chalk from deposits in the Somme Valley of northern France and to the recovery of phosphate nodules from iron ore mined at Broistedt in the eastern part of the Federal Republic of Germany. Total output from these sources amounted to 113,000 tonnes in 1976, of which 85,000 tonnes averaging 18 per cent P_2O_5 was produced in Germany and 28,000 tonnes averaging 10 per cent P_2O_5 in northern France (Table 4). Phosphatic chalk was also produced near Mons in Belgium until 1968.

IMPORTS

Western Europe has been for many years the major world market outlet for phosphate rock, accounting for nearly one third (17.3 million tonnes) of total world trade in phosphate rock in 1976. The EEC accounted for about 24 per cent (13.5 million tonnes) of this total. Morocco is by far the largest single supplier, followed by the USA, Togo, the USSR and Senegal. Over the last 10 years, 1967-1976, about 142.5 million tonnes of phosphate rock of varying grades have been exported to the EEC from the major producers (Table 5) of which Morocco supplied 45.1 per cent and the USA a further 23.6 per cent (Fig 6). The largest proportion of the phosphate rock produced in Togo and Senegal has been destined for the EEC area.

France is the principal world importer of phosphate rock, with deliveries from the major producers amounting to over 4 million tonnes in 1976, followed by Poland, Japan, the Federal Republic of Germany, Canada, Roumania and the United Kingdom. Imports into the EEC in 1976 are shown in Table 6 and Fig 7.

TABLE 4. PRODUCTION OF PHOSPHATE ROCK IN THE EEC, 1952-1976

	Belgium[1]	France[2]	Federal Republic of Germany[3]
		Thousand tonnes	
1952	87	102	n.a.
1953	56	87	"
1954	35	118	"
1955	20	102	"
1956	14	91	"
1957	16	93	"
1958	18	103	"
1959	13	77	"
1960	8	58	"
1961	14	66	"
1962	12	67	"
1963	14	50	"
1964	22	43	"
1965	20	35	"
1966	25	37	"
1967	27	64	63
1968	30	32	70
1969	-	33	86
1970	-	26	69
1971	-	19	60
1972	-	25	75
1973	-	29	93
1974	-	40	85
1975	-	18	75
1976	-	28	85

n.a. = not available

Sources:

1 1952-1968. Statistical Summary of the Mineral Industry. Institute of Geological Sciences.

2 1952-1969 Statistical Summary of the Mineral Industry. Institute of Geological Sciences.

1970-1976. Annales des Mines.

3 1967-1976 Der Bergbau in der Bundesrepublik Deutschland.

TABLE 5. WORLD EXPORTS OF PHOSPHATE ROCK : CUMULATIVE TOTALS 1967-1976

Thousand tonnes

Importing Country:	Morocco	USA	USSR	Togo	Tunisia	Senegal	Jordan	Others (1)	Total of importing country
Belgium-Luxembourg	11,077	4,129	1,865	1,225	289	26		13	18,624
Denmark	2,032	11	790		206				3,039
France	16,606	3,142	11	8,631	4,796	3,686	125	1,112	38,109
Germany, Federal Rep.	3,524	12,144	7,981	681	770	385		53	25,538
Irish Republic	3,367						10	52	3,429
Italy	8,540	8,056	272	125	780	346	332	317	18,768
Netherlands	6,828	4,844	314	4,175	126	1,602		40	17,929
United Kingdom	12,225	1,279	599	24	721	1,944	5	307	17,104
TOTAL EEC IMPORTS	64,199	33,605	11,832	14,861	7,688	7,989	472	1,894	142,540
% from each exporting country	45.1	23.6	8.3	10.4	5.4	5.6	0.3	1.3	100.0
TOTAL EXPORTS from each exporting country	129,246	112,157	45,770	16,828	21,508	11,971	10,437	30,562	378,479
% dependence of exporting country on EEC	49.7	30.0	25.9	88.3	35.7	66.7	4.5	6.2	37.7

(1) Other exporters include Israel, Egypt, Syria, Nauru, Ocean & Christmas Islands, N. Vietnam, Sweden, Australia, Western Sahara, South Africa, Curaçao and Mexico.

Source: Institute of Geological Sciences, London.

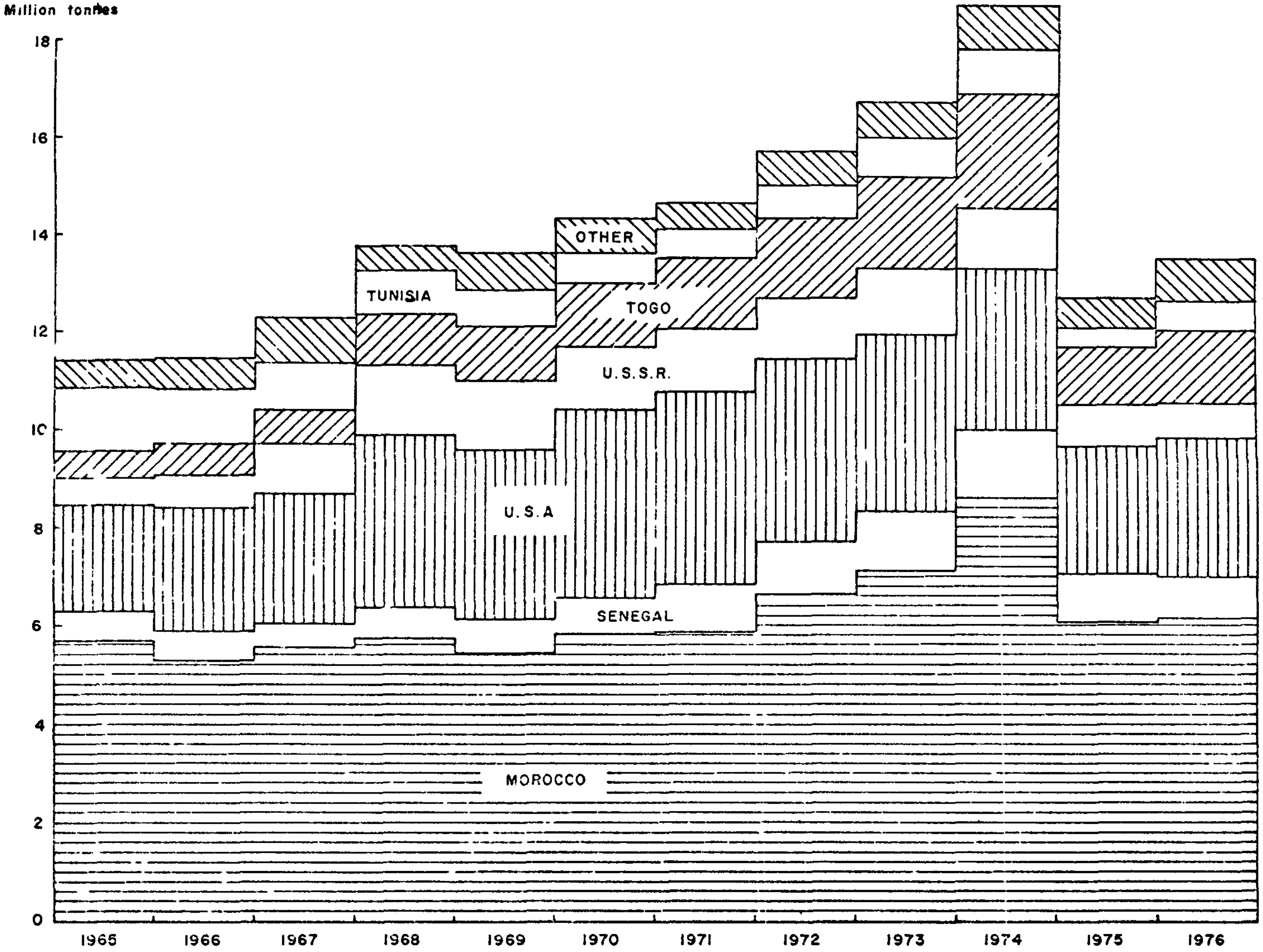


Fig 6 EEC imports of phosphate rock by major suppliers, 1965-1976

TABLE 6. EEC IMPORTS OF PHOSPHATE ROCK, BY GRADES, 1976

Importing country	65 and less	66-68	69-72	73-77	78 and more	Total(a)
		Per cent BPL				
		Thousand tonnes				
Belgium	14.0	-	1018.1	224.0	216.6	1472.8
Denmark	-	-	154.4	25.9	73.0	253.2
France	767.9	365.1	814.6	819.7	1273.6	4040.8
Germany, Federal Rep.	37.8	508.3	894.5	380.7	718.8	2540.0
Irish Republic	-	-	101.2	62.5	-	163.7
Italy	67.7	30.5	1271.8	160.9	38.0	1568.8
Netherlands	83.9	320.9	251.2	363.9	571.0	1600.8
United Kingdom	14.3	49.6	307.8	1094.7	269.4	1735.8
Total	987.6	1,274.4	4,813.6	3,132.3	3,160.4	13,375.9

(a) Totals may not add because of rounding

Source: ISMA Limited,Paris.

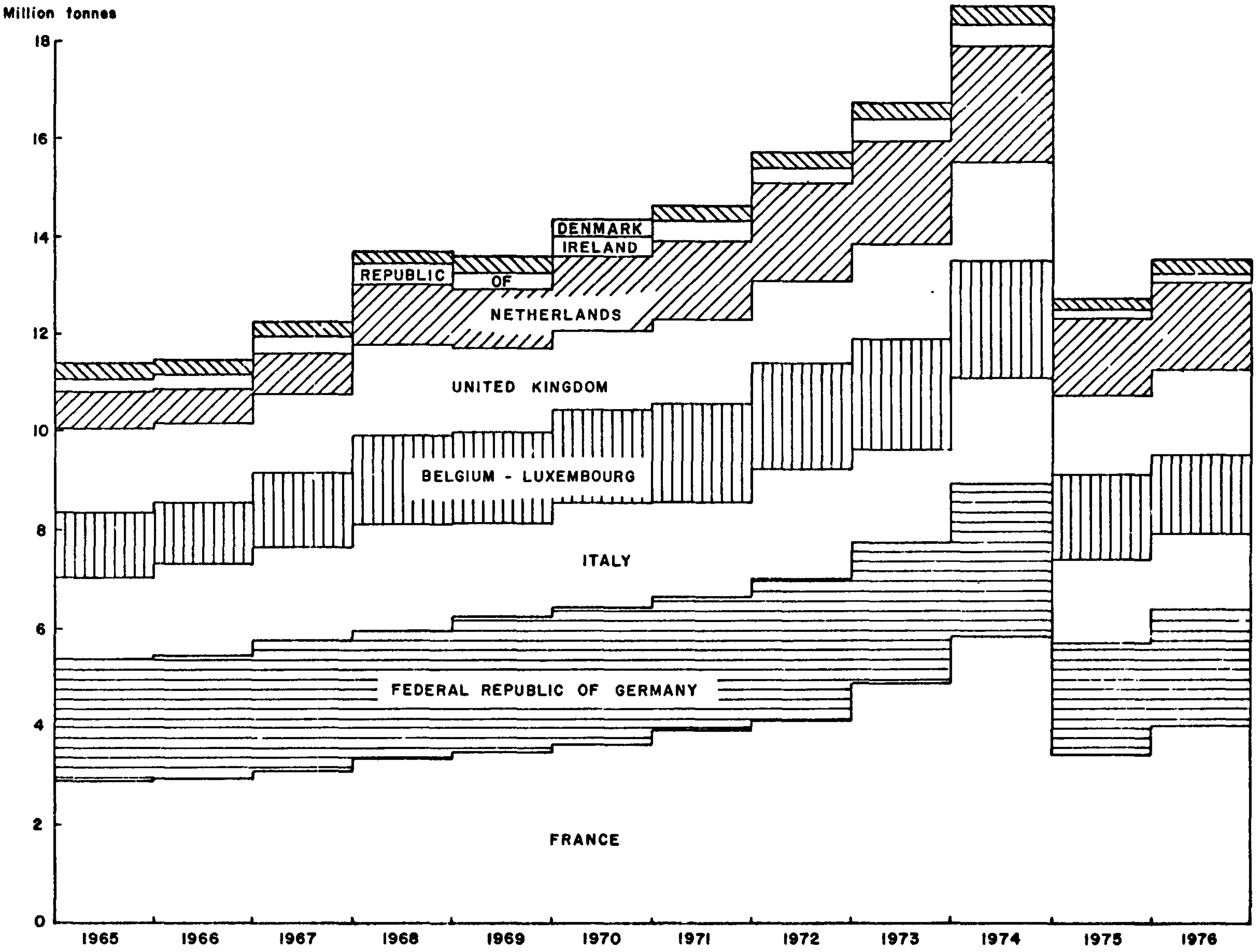


Fig 7. EEC imports of phosphate rock by country of destination, 1965 - 1976

TRADE WITHIN THE EEC

There is a small trade in what may be described as re-exports of phosphate rock originally imported from other countries and most of this takes place within the EEC. Belgium, the Federal Republic of Germany and the Netherlands all re-export phosphate rock, chiefly to neighbouring European countries, apparently in finely ground form for direct application to the soil as fertiliser. Total shipments of phosphate rock within the EEC countries amounted to some 22,000 tonnes in 1976.

FORMER EEC PRODUCTION

During the latter half of the 19th century, deposits of phosphate rock occurring in various parts of western Europe were extensively worked and for a brief period accounted for the bulk of the world production. However, the rapid development of higher grade deposits in the USA and North Africa at the beginning of the present century had a serious effect on the European phosphate mining industry and after the First World War production was intermittent and on a much reduced scale.

Commercial recorded production of phosphate rock began in Suffolk, England, in 1847, when about 500 tonnes of so-called coprolites were produced and used in the manufacture of superphosphate. The United Kingdom had a virtual monopoly in the production of this fertiliser until about 1905 and consequently most of the output from deposits opened up during the latter half of the 19th century was imported into the United Kingdom. In the United Kingdom, phosphate nodules ('coprolites') were also mined chiefly in Cambridgeshire, where working began in 1857, and which soon became the principal source of supply. Deposits were also mined to a very limited extent in Wales and Yorkshire. The last reported production was in 1909, except for a small output during the First World War and it is estimated that nearly 2 million tonnes of phosphate rock were produced during the life of the phosphate mining industry in the United Kingdom. Annual output reached a maximum of some 262,000 tonnes in 1876.

Phosphate rock was subsequently discovered in France, near Lille, in 1853, and the important Boulonnais (Pas-de-Calais) deposits opened up in 1860, eventually to achieve a regular annual output of around 20,000 tonnes. It was not until the discovery of the Beauval deposits of phosphatic chalk in 1886 that the Somme Valley became a major source of supply. Between 1886 and the First World War, the Somme deposits were actively exploited, production exceeding 300,000 tonnes in 1899, but after the war mining was on a greatly reduced scale. It is estimated that the Senonian Chalk formations have yielded around 16 million tonnes since these were first worked in 1886, of which 9 million tonnes were produced in Somme Department. Deposits have been worked also in parts of eastern and southern France, including those near Cierp in the Pyrénées from which there was a limited production until 1930.

Phosphate in the form of phosphate nodules was first reported in Belgium in 1856 but mining did not begin until ten years later, a large output being rapidly attained. In spite of the advent of North African rock, average production continued to exceed 200,000 tonnes until 1913. During the Second World War production was increased from about 20,000 tonnes in 1940 to some 428,000 tonnes in 1943.

Most of the output was in the form of phosphatic chalk obtained from the Mons Basin. Production ceased in 1968.
The phosphate mining industry in the Federal Republic of Germany has followed a somewhat similar course. Significant tonnages of Lahn phosphate were produced in Hessen from 1867, output reaching a maximum of about 53,800 tonnes in 1884. Mining after 1893 was sporadic and on a very reduced scale, chiefly during and shortly after the First World War to provide raw material for Rhenania phosphate manufacture. Deposits were briefly worked also in parts of Lower Saxony during the early part of the century.

Production of phosphate rock in the other EEC countries has been on a very limited scale. Deposits in western Ireland were worked between 1927 and 1939 and during the Second World War, producing a total of about 105,000 tonnes. In the eastern Netherlands, deposits near Hengelo yielded about 10,000 tonnes in 1919-1920.

It has been estimated that approximately 43 million tonnes of phosphate rock have been produced within the EEC up to the present day, of which some 30 million tonnes has consisted of phosphatic chalk. Estimated phosphate rock production, by Member States, is shown below:

Belgium	18 million tonnes, of which 13.5 million tonnes was phosphatic chalk.
Denmark	0.002 million tonnes
France	21 million tonnes, of which 16 million tonnes was phosphatic chalk.
Federal Republic of Germany	2 million tonnes
Luxembourg	Nil
Irish Republic	0.1 million tonnes
Italy	Nil
Netherlands	0.01 million tonnes
United Kingdom	2 million tonnes

2.4. REGIONAL SUPPLY AND DEMAND

About 85 per cent of the world phosphate rock production is consumed by the fertiliser industry and this percentage has not changed significantly in recent years. Demand for phosphate rock is therefore governed largely by growth in fertiliser consumption. About 5 per cent of total phosphate rock production is used in the manufacture of feedstuff and a further 2 per cent in insecticides. Agriculture thus accounts for about 92 per cent of the phosphate rock used; about 5 or 6 per cent is used in the manufacture of detergents. These percentages have been calculated on a world basis; corresponding percentages are much higher in western Europe and the USA where there is significantly greater consumption of phosphate rock for non-fertiliser purposes.

The percentage of phosphate rock production used in phosphoric acid manufacture has increased relatively rapidly since the early 1960s, mainly because of the trend towards high-analysis fertilisers.

Production of phosphate rock in the EEC is extremely limited and is used only for direct application, as in France, or as a supplementary source of phosphate for basic slag manufacture, as in the Federal Republic of Germany. There would appear to be some opportunity for the expansion of phosphatic chalk production, particularly in France (and possibly elsewhere in the EEC) principally because of a general decline in the availability of basic slag.

Countries of western Europe represent by far the largest phosphate rock importing area, which in 1976 received 72 per cent of its supplies from North and West Africa. Consumption is concentrated in the EEC countries, notably in France, which is the largest world importer of phosphate rock and has West Africa as its major source, in spite of large-scale imports from North Africa, particularly Morocco. The North and West African producers also provide the bulk of United Kingdom requirements. In contrast, the Federal Republic of Germany is the largest single market in Europe for Florida phosphate and is an important outlet also for Kola apatite from the Soviet Union.

It has been estimated that western European phosphate rock demand, and hence imports, might reach 25.5 million tonnes by 1980, representing an average annual growth of 2 to 3 per cent during the 1970-1980 period.

2.5. INTERNATIONAL AGREEMENTS

Most phosphate rock is produced for export, except in the USA and the Soviet Union, where there is a large domestic consumption for phosphatic fertiliser manufacture. The bulk of the world exports has come for many years from North Africa, notably Morocco, and to co-ordinate the selling arrangements of all the producers an agency known as the Comptoir des Phosphates de l'Afrique du Nord was formed in 1933, at a time when the reduced world demand for phosphate rock threatened the sales of lower grades, particularly of Tunisian phosphate rock. This agency, which had been organised by the Comptoir des Phosphates d'Algérie et de Tunisie and the Moroccan State phosphate producer Office Chérifien des Phosphates (OCP) operated until the withdrawal of Morocco in 1960, when a new marketing agency was formed in Paris, the Union Phosphatière Africaine (UPHA), to represent Algeria, Tunisia, Senegal and Togo. Since 1960 sales of Moroccan phosphate rock have been handled exclusively by OCP which maintains a European sales office in Paris. UPHA ceased to operate in 1974, with the nationalisation of the Togolese phosphate industry. As from 1st January, 1974, sales of Togo phosphate rock have been handled by the Office Togolais des Phosphates.

The well-known phosphate research organisation, Centre d'Etudes et de Recherches des Phosphates Minéraux (CERPHOS) which had for many years provided a technical service to the Comptoir and, latterly, UPHA, through its research establishment at Aubervilliers, near Paris, was disbanded in France in 1976 and transferred to Rabat.

In the USA, the second largest world exporter, the export activities of phosphate rock producers are pooled, a feature of the industry said to account for the differences in price of similar grades of rock when sold on the export and domestic markets. In 1971 a sales group, the Phosphate Rock Export Association (PHOSROCK),was formed to establish prices and to sell rock to customers on world markets on behalf of its members. Phosrock consists of 5 major Florida phosphate rock producers which account for over 70 per cent of the production capacity in Florida, as well as one producer in Idaho. A European sales office in Paris is maintained by the association.

Among the other major sources of supply, the combined output and sales of phosphate rock produced on Nauru, Ocean Island and Christmas Island (in the Indian Ocean), was for many years controlled by the British Phosphate Commissioners (BPC) acting on behalf of the Australian, New Zealand and United Kingdom governments. BPC continue to manage the operations on Ocean Island and on Christmas Island on behalf of the Christmas Island Phosphate Commission, Australia and New Zealand receiving rock at prices tied to world market rates. Sales of Kola (USSR) apatite are handled by the Industrial Export Corporation, SOYUSPROMEXPORT, of Moscow. A sales agency, Ferchimex, operates from Antwerp.

The interests of the large international phosphate industry is at present represented by ISMA Limited, a company registered in the United Kingdom with its secretariat in Paris, whose basic aim is to promote the use of phosphate rock and phosphate fertilisers and to collect relevant production, consumption and trade statistics. Membership of ISMA, the successor to the International Superphosphate Manufacturers' Association Limited set up in London in 1927, includes over 300 organisations in 54 countries, nearly 200 of these producing phosphate rock and/or phosphate fertilisers.

The World Phosphate Rock Institute (Institut Mondial du Phosphate) was formed in 1973 essentially to promote research into the more effective use of phosphate rock both in its agricultural and industrial applications. The Head Office of the Institute is in Rabat, Morocco, but a Permanent Secretariat operates from Paris.

Attempts have been made at various times to establish separate multi-national trading agencies, but apparently with only limited success.For example, the adoption of a co-operative sales policy for Morocco, Tunisia and Jordan to be controlled by the Office des Producteurs des Phosphates, Beirut, was announced in 1964. Similarly, it was proposed in Dakar in 1976, that an agency should be set up on behalf of Senegal, Algeria, Jordan, Morocco, Togo and Tunisia, whose function would be to co-ordinate sales and to stem the erosion of prices. Exports of phosphate rock to western Europe showed a particularly pronounced decline in 1976.

Agreements among exporters of phosphate rock also have their counterparts among importers. For example, the Phosphate Rock Agency Limited, which was set up in the United Kingdom in 1952, centralised the purchasing of all rock required for fertiliser manufacture until July 1955, when the principal consumers, Fisons Limited, Imperial Chemical Industries Limited and Scottish Agricultural Industries Limited (a subsidiary of ICI Ltd), withdrew from the purchasing arrangements but remained as associated charterers. It appears that most, if not all, of the other users of phosphate rock for fertiliser manufacture still obtain their requirements through the agency. In the Federal Republic of Germany a central buying agency, Rohphosphat Gesellschaft mbH, was established before the Second World War. Neither the Phosphate Rock Agency nor Rohphosphat Gesellschaft account for a significant part of each country's phosphate rock imports, as far as is known.

2.6. SUBSTITUTION OF PHOSPHATE ROCK IMPORTS

One of several interesting developments in recent years is the increasing quantities of phosphate rock that are being utilised captively in certain producing countries in order to produce a higher value end product for export. This is largely in the form of phosphoric acid and phosphate fertilisers, notably acid-based products such as triple superphosphate (TSP) and ammonium phosphates.

The principal resource based exporters (with either captive rock or sulphur or both) of TSP are the USA, Mexico, Morocco and Tunisia. The USA is by far the biggest single exporter of ammonium phosphate. The P_2O_5 content of the TSP and ammonium phosphates exports from the resource based producers far exceeds the P_2O_5 contained in their phosphoric acid export shipments. Exports of elemental phosphorus have also been made. Basic slag and phosphatic limestone have for many years proved useful as a source of phosphate for direct application to the soil as fertiliser (Table 11).

PHOSPHORIC ACID

Total export sales of phosphoric acid exceeded 1 million tonnes P_2O_5 in 1976, accounting for about 3.4 million tonnes of phosphate rock or about 10 per cent of the present world phosphate rock export market.

Tunisia was one of the first to decide to produce phosphoric acid essentially for export. Deliveries began in 1972, notably to the Netherlands, France and Italy. In 1976, Europe accounted for some 90 per cent of Tunisian exports of 222,000 tonnes P_2O_5, but shipments were also made to Brazil, India and Iran.

The first bulk shipment in 1969 of phosphoric acid (produced from Florida phosphate rock) from Mexico to Rotterdam attracted considerable interest since it demonstrated that long distance transportation of this material had become feasible. In Mexico the Coatzacoalcos plant has an operating capacity of 345,000 tonnes P_2O_5 per annum. Shipments out of Coatzacoalcos amounted to 100,900 tonnes in 1976, but the total exports in phosphoric acid handled by the operating company amounted to 291,500 tonnes P_2O_5, sales being made to India, Brazil, the USA, the Federal Republic of Germany, and the United Kingdom.

Phosphoric acid has also been produced for export for a number of years in Iran and Israel, Iran being well placed to supply the large Asian market. Spanish phosphoric acid entered the export market at the end of 1974, and the first export sales of Moroccan acid took place in September 1976, with shipments to a wide variety of West European customers and to Brazil and India. Early in 1977, the first delivery of South African phosphoric acid was made to Brazil.

Phosphoric acid terminals have been set up in the EEC at Antwerp (Belgium), Le Havre, Rouen, Donges, La Pallice and Port La Nouvelle (France), New Ross and Cork (Ireland), Ravenna and Trieste (Italy), Rotterdam (Netherlands) and Seal Sands and Immingham (United Kingdom).

ELEMENTAL PHOSPHORUS

There is very little shipment of elemental phosphorus at present. Bulk shipments have been pioneered by the United Kingdom industrial phosphates producer, Albright and Wilson Limited. Two purpose-built ships have been brought into use, capable of carrying up to 5,000 tonnes of elemental phosphorus. The first shipment by sea to any external customer made under long-term contract took place in 1972 from Newfoundland to Japan. Bulk shipment from the Newfoundland plant at Long Harbour to the United Kingdom began in 1969.

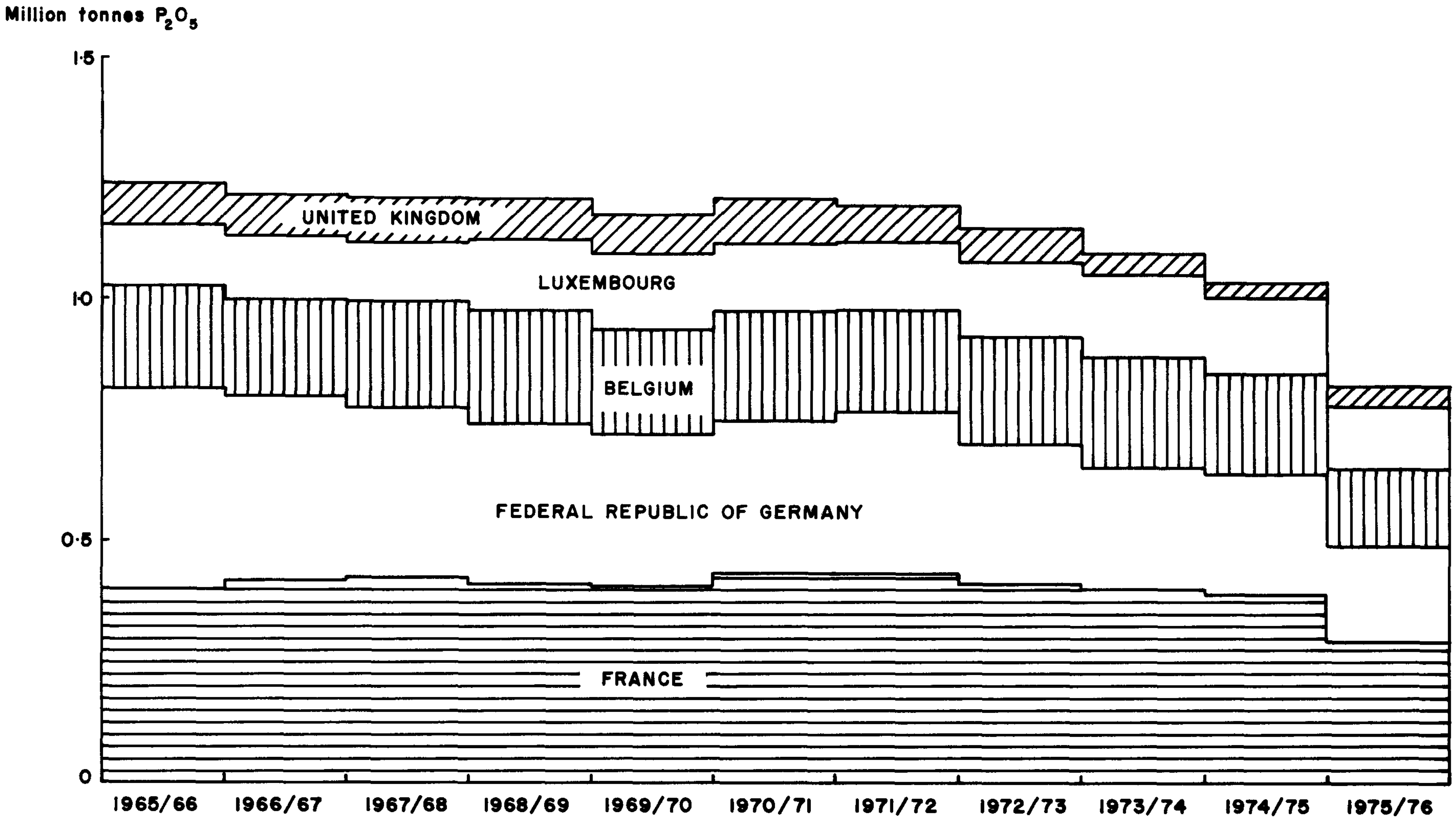


Fig 8. Basic slag production within the EEC, 1965/66 - 1975/76.

BASIC SLAG

Phosphorus occurs as an impurity in iron ores and needs to be removed prior to the production of the finished steel. Where it occurs as granular apatite, it can be removed by normal beneficiation techniques, as in the case of certain Swedish iron ores, but it may prove impossible or exceedingly difficult to eliminate very fine-grained apatite or collophane intimately associated with the iron-bearing minerals, by such methods. In consequence phosphorus remains in the pig iron produced in the blast furnace and must be slagged off during steelmaking. In the steel converter, it combines with added lime and is removed with other impurities in the form of basic slag. Ground basic slag, which is known also in western Europe as 'Thomasphosphat' or 'Scories Thomas' contains between 10 and 20 per cent P_2O_5; it has for many years ranked second in importance to superphosphate as a phosphate fertiliser, its production in part compensating for the additional difficulties of using highly phosphatic iron ores in steelmaking.

Basic slag must be ground to be fully effective. In the United Kingdom it is mainly used on grassland. It is effective also on a wide range of crops grown on both acid or neutral soils and outside the United Kingdom is used primarily for arable crops. The phosphate in basic slag is water insoluble but has a high citric acid solubility (over 75 per cent in 2 per cent citric acid). The high lime and magnesia content of the slag gives it beneficial liming properties.

Increasing quantities of basic slag are being sold as potassic slag (K - slag), a blend of basic slag and potash, with basic slag making up between 50 and 85 per cent of the total.

TABLE 7. PRODUCTION AND CONSUMPTION OF BASIC SLAG WITHIN THE EEC, 1973-1976

Thousand tonnes P_2O_5

Country	1973/74[1]		1974/75[1]		1975/76[1]	
	Production	Consumption	Production	Consumption	Production	Consumption
Belgium	218.0	87.9	198.5	80.6	136.1	67.1
Denmark	-	0.3	-	0.3	-	0.3
Federal Republic of Germany	254.6	326.2	244.5	351.4	174.9	270.9
France	399.1	477.3	392.7	451.0	318.4	354.0
Irish Republic	-	26.2	-	18.9	-	13.3
Italy	-	21.3	-	18.3	-	11.3
Luxembourg	175.9	5.7	166.9	5.8	121.8	7.0
Netherlands	-	15.4	-	14.2	-	11.8
United Kingdom	37.6	50.5	27.8	32.0	42.4	44.0

[1] July/June

Source: ISMA Ltd., Paris.
Belgium; Société Anonyme Cockerill-Ougrée-Providence et Espérance-Longdoz, Liège.
Luxembourg: Groupement des Industries Sidérurgiques Luxembourgeoises.
France: Société nationale pour la vente des Scories Thomas, Paris.
Federal Republic of Germany. Thomasphosphatfabriken GmbH, Düsseldorf.

Note: Consumption includes basic slag in compound fertilisers.

Production in the EEC

Significant quantities (Fig 8) of basic slag, containing between 10 and 20 per cent total P_2O_5, are produced in France, the Federal Republic of Germany, Belgium, Luxembourg and the United Kingdom. Despite a decline in output in recent years basic slag remains by far the most important indigenously produced source of P_2O_5, total production amounting to 0.79 million tonnes contained P_2O_5 in 1975/76, representing some 21 per cent of the total P_2O_5 in fertiliser consumed within the EEC during that period (Table 7). The main source of the phosphorus contained in basic slag is the large reserves of phosphatic iron ore existing within the EEC, although a contribution is also made by imports of phosphatic iron ore from Sweden.

Basic slag was first produced in England, at Middlesborough, in 1879 and, in the ground form, was first marketed in 1886 in Germany. The Federal Republic of Germany, France, Belgium, Luxembourg and the United Kingdom account for the bulk of the world production and consumption of basic slag, and there is considerable trade in basic slag within the Community, Luxembourg and Belgium being significant exporters.

Process description

The development by Thomas and Gilchrist in 1878 of a basic lining for the Bessemer furnace made possible the use of phosphatic iron ores in steelmaking and resulted in the large scale exploitation of the large resources of low grade, marine sedimentary (minette type), phosphatic iron ores of Europe.

In the steel converter, impurities including phosphorus, are preferentially oxidised by air or oxygen and combine with the lime flux to produce a basic slag. In order that the slag should have a high citric acid solubility it is important that the P_2O_5 be present

TABLE 8. TYPICAL CHEMICAL ANALYSES OF SOME BASIC SLAGS

	1	2	3	4	5	6
			Per cent			
P_2O_5	16-20	17	14-18	10-12	15	12-22
SiO_2	6-11	8.5	7.6	9-14	7-12	6-10
CaO	45-50	47.5	45	45-52	49-51	40-55
MgO	1-5	2.5	2.2	0.77	0.5	2-6
MnO	3-6	4.3	3.4	6.48	7.1	4-6
Fe_2O_3	14-20	16.5	16.86	14-21	11-26	11.8-17.1
Al_2O_3	1-3	1.8	0.9	n.a.	n.a.	1-5
Cr	0.15-0.5	0.3	0.2	0.005	n.a.	0.1-0.25
V	0.2-0.5	0.4	0.6	n.a.	n.a.	0.1-0.55
Ti	0.06-0.36	0.3	0.23	n.a.	n.a.	0.06-0.36
S	0.08-0.17	0.1	n.a.	n.a.	1.5	0-1.5
F	0.002-0.016	0.008	n.a.	n.a.	n.a.	n.a.
Cu	0.0009-0.0056	0.0033	0.0025	0.0026	0.002	0.013-0.021
Co	0.0002-0.0005	0.0003	0.0003	0.23	0.005	0.001-0.01
Mo	0.0001-0.0010	0.0007	0.0012	0.11	0.1	0.003-0.016
Ni	0.0001-0.0010	0.0007	n.a.	n.a.	n.a.	n.a.
B	0.0022-0.0069	0.0033	0.004	0.014	0.012	n.a.

n.a. = not available.

Sources:

1 Belgium basic slag. Range.
2 Belgium basic slag. Average.
} Société Anonyme Cockerill-Ougrée-Providence et Espérance-Longdoz, Liège.

3 German basic slag. Die Th-Dünger. Landwirtschaftliche Abteilung der Thomas phosphatfabriken GmbH. Düsseldorf. 1970.

4 United Kingdom basic slag. Fisons Ltd.

5 'Super slag'. Ground basic slag and phosphate rock. Fisons Ltd.

6 French basic slag. Société nationale pour la vente des Scories Thomas, Paris.

in calcium silicophosphate phases. The chemical composition of basic slags is variable depending on the phosphorus content of the pig iron and the type of steel converter used. The chemical composition of some typical basic slags is shown in Table 8, those produced in Belgium and Luxembourg being similar in composition.

Traditionally the Basic Bessemer process was the main process used in refining high phosphorus pig iron in Europe, although the Basic Open Hearth process was also used in the United Kingdom. The more efficient LD (Linz-Donawitz) or BOS (Basic Oxygen Steel-making) process is now being increasingly used by the European steel industry, but cannot treat phosphoric iron. The recent decline in basic slag production has, therefore, been brought about by the introduction of the LD process and a decline in demand for indigenous low grade, phosphatic iron ores in favour of imported, high grade, low phosphorus (<0.1%) ores. Variants of the LD process, for example, the L.D.A.C. process, in which powdered lime in addition to oxygen is injected into or across the metal surface, can treat phosphoric iron and produce a basic slag suitable for agricultural purposes. However, a high phosphorus content in iron ore (and thus in the pig iron) is a disadvantage since more time is required for its elimination its presence increasing slag volume, lowering steel output and increasing costs. Research into removal of phosphorus from iron ores (to produce a low-phosphorus iron ore) is being carried out but it seems unlikely that a sale-able phosphate concentrate could be economically produced from indigenous phosphatic iron ores. The economics of steelmaking are sufficiently well known to enable an estimate to be made of the extent to which the price of phosphate would have to increase to make steelmaking from phosphoric iron, with the attendant sale of the basic slag, a more attractive proposition.

Alternatives have been introduced, particularly in the United Kingdom, to extend the limited supplies of basic slag available. These include mixtures of basic slag with ground phosphate rock, and also LD slag with ground phosphate rock, although the latter mixture is no longer produced. Conventional LD slags have phosphate contents between 1 and 4 per cent P_2O_5, too low to be used as phosphatic fertilisers. Research into the extraction of phosphate from LD slags, as a by-product of the removal of other useful materials, such as iron, is being considered.

The major source of phosphatic iron ore within the EEC is the Lorraine Basin deposits of France, production amounting to some 42 million tonnes of iron ore containing an estimated 550,000 tonnes P_2O_5, most of which is recovered in basic slag. Significant quantities of Lorraine ore are delivered to the steel industries of Luxembourg, Belgium and the Federal Republic of Germany, as shown below:

Deliveries of French phosphatic iron ores, 1975-76

	Thousand tonnes	
	1975	1976
France	27,283	27,090
Luxembourg	9,989	9,347
Belgium	2,861	3,097
Federal Germany (Saar)	2,638	2,766
TOTAL	42,771	42,300

The phosphorus and iron contents of phosphatic iron ores produced within the EEC during 1976 are shown in Table 9.

TABLE 9. TYPICAL PHOSPHORUS CONTENTS OF EUROPEAN PHOSPHATIC IRON ORES

	Geological Age	Wt per cent		Iron ore Production 1976 million tonnes
		P	F	
France				
Lorraine Basin	Lower Jurassic	0.08-1.13	31-37	42.3
Belgium				
Extension of the Lorraine Basin	Lower Jurassic	0.5-0.6	35-39	0.06
Luxembourg				
Extension of the Lorraine Basin	Lower Jurassic	0.5-1.0	30	2.2
Federal Germany				
Auerbach-Leonie	Upper Cretaceous	1.28-2.09	39-47	0.13
Peize-Ilsede	Upper Cretaceous	0.9-1.6	24-33	1.5
Salzgitter	Lower Cretaceous	0.5	36	1.0
United Kingdom				
Frodingham Ironstone	Lower Jurassic	0.34	25	2.3
Northampton Sand Ironstone	Middle Jurassic	0.7	35	2.1

Reserves of iron ore in the Lorraine Basin deposits of France have been estimated at 2,350 million tonnes with a phosphate content of over 30 million tonnes P_2O_5. In addition substantial quantities of phosphate are contained in the large resources of phosphatic iron ores in the Federal Republic of Germany and the United Kingdom and to a lesser extent, in Luxembourg. These resources of phosphate are, however, recoverable only in basic slag as a by-product of steelmaking. The Swedish magnetite deposits of the Kiruna type contain appreciable amounts of apatite so that exports of Swedish phosphatic iron ore to Belgium and Federal Germany contribute to basic slag production. The phosphorus contents of some Swedish iron ores are as follows: Kiruna, 1.58 per cent, Grängesberg, 0.74 per cent, ald Malmberget, 0.36 per cent.

Apatite-bearing magnetitic iron ores of the Kiruna type do not occur in substantial quantities within the EEC.

PHOSPHATIC LIMESTONE

Within the EEC, France, the Federal Republic of Germany and the United Kingdom are important consumers of ground phosphate rock for direct application to the soil and demand in these countries is expected to rise, in part because of its use as a replacement for basic slag, supplies of which are declining. Phosphatic chalk or phosphatic limestone has been considered as a possible replacement for basic slag.

Although basic slag is an important indigenous source of phosphate for direct application, neither basic slag nor phosphatic limestone can be considered substitutes for phosphate rock in the manufacture of phosphate fertilisers and phosphorus chemicals.

IMPLICATIONS

Any future trend towards the increasing use of imported phosphoric acid, elemental phosphorus and phosphate fertilisers at the expense of imported phosphate rock would have very serious repercussions for the Community's own phosphate fertiliser industry. Following the dramatic phosphate rock price increases announced in 1973 and 1974, phosphoric acid and certain phosphate fertilisers were available on the open market at prices significantly below those for phosphate rock, thus seriously affecting the economics of phosphate fertiliser manufacturing industry within the EEC.

2.7. PHOSPHATE ROCK RESOURCES

Phosphate rock is widely distributed throughout the world, both geographically and geologically, and there are very large resources which are sufficient to meet anticipated demand for many years. Estimates of world resources vary considerably but generally indicate a total of between 100,000 million and 150,000 million tonnes of phosphate rock of widely varying grades. A large proportion, possibly more than two-thirds, of this total is in the form of either carbonate-rich phosphate rock or has a mineralogy too complex to be commercially attractive at present. Reserves are probably of the order of about 20,000 million tonnes. The bulk of the known resources are located in northern Africa, the USA and the Soviet Union (Table 10).

Many estimates, unfortunately, take little or no account of the distinction between reserves and resources and are published with inadequate detail about the technical and economic feasibility of producing marketable grades of phosphate rock. In addition, the last comprehensive and systematic survey of world phosphate rock reserves and resources, on a country basis, was prepared for the 14th International Geological Congress held in Madrid in 1926; a detailed re-assessment now seems highly desirable, therefore, in view of the changes in technology and economics of mining and processing which have taken place since that time.

EEC RESOURCES

By comparison with the phosphate resources of the major producing countries, the known phosphate resources of the EEC are insignificant. Although phosphate rock is found in all the member countries most of the known occurrences are in beds either too thin or of too limited extent to be considered of potential economic interest for large-scale mining. However, a number of deposits might be worked on a small scale for local use.

TABLE 10. IDENTIFIED RESOURCES OF PHOSPHATE ROCK, BY MAJOR SUPPLIERS TO THE EEC

	Quantity Thousand tonnes	Grade Per cent P_2O_5
MOROCCO	58,000,000 (a)	up to 32
USA		
Eastern	7,600,000 (b)	at least 30
USSR	1,600,000 (c)	18
TUNISIA	1,203,000 (d)	25-29
SENEGAL		
Taïba	100,000 (e)	38
Thiès	90,000 (f)	28
TOGO	100,000 (e)	28-32
JORDAN	2,000,000 (g)	28-32

(a) Of which about 18,000 million tonnes are estimated as recoverable at 1975 prices. Source: US Bureau of Mines.

(b) Reserves are estimated at 1,600 million tonnes. Source: US Geological Survey.

(c) Khibiny Complex.

(d) Chiefly the Gafsa Basin. About 460 million tonnes are classified as mineable.

(e) Marketable phosphate rock.

(f) Calcium-aluminium phosphate.

(g) Proved reserves are estimated at 300 million tonnes.

In 1926 resources of phosphate rock in France were estimated at 138.5 million tonnes of rock containing between 9 and 32 per cent P_2O_5. The bulk of the resources were contained in Carboniferous rocks of the Pyrenean mountain range. Resources of lower grade phosphatic chalk were not evaluated.

Up-to-date resource and reserve estimates for the EEC countries are available for only a limited number of specific areas. In northern France a number of Upper Cretaceous phosphatic chalk deposits are known which range in size from 100,000 tonnes up to 1 to 5 million tonnes. In the Ciply and Boudour areas of the Mons Basin in Belgium some 300 million to 500 million tonnes of phosphatic chalk, averaging 6 m to 10 m in thickness are believed to exist. This represents the largest single resource of phosphate rock within the EEC.

In southeastern Italy, resources of low-grade Miocene phosphatic limestone in the Salentino Peninsula were estimated as long ago as 1931 to be about 60 million tonnes averaging 7 to 8 per cent P_2O_5. In the same area, exploratory work during the 1968-1970 period indicated that some 10 million tonnes of nodular, supposedly Pliocene, phosphate rock are present. Nodular beds of Miocene age are widely distributed in southeastern Sicily; deposits at Donnalucata were reported in 1921 to be around 7 million tonnes averaging 15 per cent P_2O_5.

A drilling programme carried out by the Geological Survey of Ireland in 1976-1977 in County Clare has indicated a resource of about 3 million tonnes of Upper Carboniferous phosphate rock containing between 20 and 25 per cent P_2O_5.

Thus, in those areas for which specific quantitative estimates have been made, identified resources within the EEC would appear to be of the order of 500 million to 700 million tonnes of rock containing between 7 and 32 per cent P_2O_5. Most of this is in the form of phosphatic chalk in the Mons Basin of Belgium containing only 8 to 10 per cent P_2O_5.

3. INTERMEDIATE PRODUCTS AND PHOSPHATE FERTILISERS

The phosphorus content of phosphate rock as mined or beneficiated is not readily available either to plants as a nutrient or for use in industrial chemical products. The rock has usually to be treated in order to convert the phosphorus into a more conveniently available form. This is accomplished by either acidulation or thermal processes. Of the two routes, acidulation is the more important in the phosphate fertiliser industry from both the economic and agronomic standpoint. Any strong mineral acid may be used to acidulate phosphate rock but in commercial practice sulphuric acid and phosphoric acid have shown a clear superiority over other acids under most conditions.

Phosphoric acid is itself made either by the so-called 'wet-process', which involves the reaction of sulphuric acid with phosphate rock and the separation of insoluble residue, or by a thermal route, whereby elemental phosphorus produced in an electric furnace is first oxidised to phosphorus pentoxide, and then hydrated to phosphoric acid. For economic reasons, most of the phosphoric acid used for fertiliser purposes is produced by the wet process. Elemental phosphorus by the thermal process is an essential raw material for the commercially important chloride, sulphide and organic compounds of phosphorus.

3.1. PROCESSES AND PRODUCTS

ELEMENTAL PHOSPHORUS

Elemental phosphorus initially became of commercial importance through its use in the match industry, but now more than 75 per cent is used in the manufacture of phosphoric acid. For this purpose the raw materials required are phosphate rock, silica pebble, coke or coal, and electric energy, the reaction being represented in its simplest form by the following equation:

$$2Ca_3(PO_4)_2 + 6\ SiO_2 + 10C \longrightarrow 6\ CaSiO_3 + P_4 + 10CO - 3.06\ MJ$$

During the reaction, which takes place in an electric furnace at temperatures ranging from 1250°C to 1500°C, a mixture of phosphorus vapour and carbon monoxide gas is withdrawn continuously from the furnace and the phosphorus is condensed to a liquid, which is stored under water until required for further processing. The liquid products consist of calcium silicate slag and a small amount of ferrophosphorus, which contains from 15 to 28 per cent P.

In general, about 8 tonnes of phosphate rock are required to produce one tonne of phosphorus. Although a relatively wide variation in chemical composition of phosphate rock can be tolerated, perhaps with as little as 22 per cent P_2O_5, the furnace burden must be in lump form, chiefly because fine material tends to block the passage of the evoloved phosphorus and associated gases. Florida pebble phosphate is particularly suited to the process, but in most cases the rock has to be agglomerated.

WET-PROCESS PHOSPHORIC ACID

The wet process method involves the reaction of finely ground phosphate rock with sulphuric acid to form dilute phosphoric acid and calcium sulphate, followed by the separation of the calcium sulphate (often as phosphogypsum) usually by filtration and washing, and concentration of the phosphoric acid to the desired strength. The sulphuric acid used can have concentrations of between 55 and 96 per cent. The principal chemical reaction that takes place can probably be best represented by the following equation:

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 20\ H_2O \longrightarrow 10\ CaSO_4 \cdot 2H_2O + 6\ H_3PO_4 + 2\ HF$$

The dilute acid, containing an equivalent of about 30 to 32 per cent

TABLE 11. EEC : CONSUMPTION OF PHOSPHATE FERTILISERS, BY TYPE, 1975/76

tonnes P_2O_5

	BELGIUM-LUXEMBURG	DENMARK	FRANCE	GERMANY	IRELAND	ITALY	NETHERLANDS	UNITED KINGDOM
STRAIGHT (For direct application)								
Basic slag(1)	28,000	286	222,800	176,752	13,303	8,750	11,800	44,000
Single superphosphate	1,000	9,094	49,800	33,564	5,547	163,850(c)	3,723	3,000
Double superphosphate	-	-	37,500	-	2,101	-	-	-
Triple superphosphate	1,000	-	62,700	-	25	-	14,154	5,500
Ground rock	-	-	46,000	-	2,839	-	-	n.a.
Others	2,000	-	2,300	39,708	1,246	400	n.a.	17,500(e)
TOTAL	32,000	9,380	421,100	250,024	25,061	173,000	29,677	70,000
COMPOUND								
DAP and MAP	-	-	122,100	-	-	n.a.	163	n.a.
Other NP compounds	3,000	-		54,048(b)	-	n.a.	n.a.	n.a.
PK compounds	37,000(a)	54,986	504,700	201,804	37,963	n.a.	1,973	n.a.
NPK compounds	48,000	64,316	616,400	273,808	71,577	n.a.	41,853(d)	n.a.
TOTAL	88,000	119,302	1,243,200	529,660	109,540	297,000	43,989	321,000
TOTAL P_2O_5	120,000	128,682	1,664,300	779,684	134,601	470,000	73,666	391,000

(a) Includes 29,000 tonnes potassic slag

(b) Includes DAP and MAP

(c) Includes triple superphosphate

(d) Includes NP complex fertilisers

(e) Includes ground rock

(1) See Table 7 for revised estimates.

Source: Fertiliser Consumption Statistics 1975/76. ISMA Ltd., June 1977.

P_2O_5, is drawn off and usually concentrated to 54 per cent P_2O_5 phosphoric acid, for the production of which between 3.1 and 3.5 tonnes of phosphate rock per tonne of P_2O_5 are usually required. In addition to processes producing gypsum and 30 per cent P_2O_5 acid (Dihydrate Process) there are others which produce calcium sulphate hemihydrate and 40 to 50 per cent P_2O_5 acids (Hemihydrate or Hemihydrate-Dihydrate processes).

Phosphoric acid can also be made by using hydrochloric acid and nitric acid instead of sulphuric acid but, because of the high solubility of the calcium salts of these acids, their separation presents a problem. A comparatively new product is superphosphoric acid which may have a concentration of 70 or 71 per cent P_2O_5 or about 76 per cent P_2O_5, depending on whether it has been produced by dehydrating wet process phosphoric acid or by the thermal acid process.

SINGLE SUPERPHOSPHATE (SSP)

This fertiliser, also known as normal or ordinary superphosphate and until the end of the Second World War the most important source of phosphorus in fertilisers, has declined in popularity in the face of increasing competition from more concentrated phosphate fertilisers such as triple superphosphate and ammonium phosphate (Table 11). It represents a low-grade fertiliser, with only 20 to 22 per cent P_2O_5 but contains about 45 per cent $CaSO_4$ which supplies the nutrient element sulphur.

Single superphosphate is produced by a relatively simple process which involves mixing finely ground phosphate rock with sulphuric acid. The chemical reactions are complex, but the main reaction may be represented by the following equation:

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 \longrightarrow 3\ Ca(H_2PO_4)_2 + 7\ CaSO_4 + 2\ HF$$

The phosphate originally present as apatite in the rock is converted to water-soluble monocalcium phosphate..For the continuous production of 1 tonne of single superphosphate about 0.6 tonne of phosphate rock is required.

Higher grade, enriched superphosphate, products are obtained by acidulating phosphate rock with a mixture of sulphuric acid and phosphoric acid. These usually contain 25 to 30 per cent P_2O_5.

TRIPLE SUPERPHOSPHATE (TSP)

Triple superphosphate, normally containing from 43 to 48 per cent available P_2O_5, is an important phosphate fertiliser for direct application to the soil. It has grown rapidly in popularity chiefly because of its high plant-nutrient content and its capacity for absorption of ammonia in the manufacture of multinutrient fertilisers. TSP is formed according to the following approximate chemical equation:

$$Ca_{10}(PO_4)_6F_2 \; + \; 14H_3PO_4 \longrightarrow 10Ca(H_2PO_4)_2 \; + \; 2HF$$

Requirements per tonne of product are about 0.4 tonne of phosphate rock (34 per cent P_2O_5) and about 0.6 tonne of wet-process phosphoric acid.

AMMONIATED SUPERPHOSPHATE

All superphosphates are somewhat acidic and consequently lend themselves to ammoniation, whereby they are chemically combined with ammonia to the extent of 5.5 to 8.5 per cent by weight. Ammoniated superphosphate is produced primarily as an ingredient resulting from the ammoniation of mixed fertilisers containing superphosphate.

AMMONIUM PHOSPHATES

Ammonium phosphate fertilisers are highly concentrated sources of water-soluble plant food which, in general, are produced by the reaction of wet-process phosphoric acid and anhydrous ammonia; potash salts are added if desired and the product granulated, cooled, screened and stored. The two compounds of particular commercial interest are monoammonium phosphate (MAP) and diammonium phosphate (DAP) which contain about 52 per cent and 46 per cent P_2O_5 respectively, corresponding N contents being of 12 and 21 per cent. Commercially a number of different products may be prepared depending on manufacturing techniques. DAP is probably one of the most important fertilisers to have appeared since the 1950s, when the Tennessee Valley Authority proved its commercial value as a fertiliser in the United States and developed a process for its manufacture. Higher grades of diammonium phosphate are made by using electric furnace phosphoric acid, but commercially there has been a trend towards 48 per cent P_2O_5, 16 per cent N and, particularly 46 per cent P_2O_5, 18 per cent N grades which can be produced from cheaper wet-process phosphoric acid.

NITROPHOSPHATES

Nitrophosphates are complex fertilisers made essentially by treating phosphate rock with nitric acid and are produced in significant quantities in Europe and to a lesser extent in the USA, although much development work in this field has been undertaken by the Tennessee Valley Authority. Interest in nitrophosphates has been stimulated largely in countries which do not possess a domestic source of sulphur or sulphuric acid but, in general, the processes and the products involved are not considered to be as universally adaptable as are those based on sulphuric acid or phosphoric acid.

The chemical reaction involved may be expressed as shown below:

$$Ca_{10}(PO_4)_6F_2 + 14HNO_3 \longrightarrow 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 2HF$$

A relatively high analysis product is possible with the various processes available, many grades reaching a total plant nutrient content of 40 to 42 per cent. However, calcium nitrate is markedly hygroscopic.

In the United States a process for producing nitrophosphates from Florida leached-zone aluminium phosphate was proposed shortly after the Second World War which is based on the extraction of calcined rock by mixed nitric and sulphuric acids. The process was not adopted commercially.

METAPHOSPHATE

Metaphosphates have attracted attention because of their exceptionally high P_2O_5 content, which often exceeds 65 per cent, and the fact that the plant nutrient content is readily available to the soil even though the products are not water soluble.

Calcium metaphosphate is a relatively new fertiliser containing between 58 and 65 per cent P_2O_5, of which approximately 98 per cent is ammonium citrate soluble. A commercial process developed by the Tennessee Valley Authority involves the simultaneous oxidation of electric furnace elemental phosphorus and the reaction of the resulting P_2O_5 with finely ground phosphate rock, the main chemical reaction which takes place in a combustion chamber maintained at about 1,100°C being represented by the following equation:

$$Ca_{10}(PO_4)_6F_2 + 7P_2O_5 + 7H_2O \longrightarrow 10Ca(PO_3)_3 + 2HF$$

Potassium metaphosphate is remarkable in that it contains when pure 100 per cent plant nutrients. It is not produced commercially, attempts in the late 1960s in Europe meeting with little success in obtaining a uniform product.

CALCINED PHOSPHATIC FERTILISERS

Numerous attempts have been made to develop commercial methods of making phosphatic fertilisers without the use of acids. Most processes tend to be based mainly on either the removal of fluorine by calcination as a means of increasing the P_2O_5 availability or the fusion of phosphate rock with silica or silicate minerals (olivine and serpentine) and alkali salts. All are manufactured under conditions which require temperatures of about 1,000°C, or above and, in general, are characterised by low solubility in neutral and alkaline solutions, whereas in acid solutions the solubility is usually much higher. Typical analyses of the products obtained are shown in Table 12.

TABLE 12 TYPICAL ANALYSES OF THERMAL PHOSPHATES

	Total	Citric soluble	Water soluble	CaO	SiO_2	F
			Per cent			
Defluorinated rock	21(a)	18	-	29	47	0.06
Fused tricalcium phosphate	28	22	-	40	20	0.3
Calcium magnesium phosphate (b)	20	10	-	30	20	2.0
Calcium metaphosphates	63	62	0.8	27	5	0.2
Rhenania phosphate (c)	28	27	-	42	10	1.5

(a) Products with up to 40 per cent P_2O_5 are made by adding phosphoric acid and decreasing the amount of silica added

(b) Contains also 14 per cent MgO

(c) Contains also about 16 per cent Na_2O

The best known and most important is a product known as Rhenania phosphate, which was developed in Germany during the First World War and has since 1917 been produced on a relatively large scale at Brunsbüttelkoog at the North Sea end of the Kiel Canal. Rhenania phosphate was originally made from Lahn phosphate, but for many years production has been based on higher grades of phosphate rock from North Africa and on Kola apatite from the USSR. West African (Togo, Senegal, Western Sahara) as well as Florida rock has also been used, but the process can tolerate a wide variety of phosphate rock concentrates depending, however, on the P_2O_5 content of the final desired products. Since 1949, mixtures of Rhenania phosphate and muriate of potash (KCl) have been marketed as 'Rhe-Ka-Phos'. These products have proved equally effective on acid, neutral and alkaline soil types.

A mixture of finely ground phosphate and dry sand is proportioned with soda ash (sodium carbonate), dampened with water, and sintered in a rotary kiln. A carefully controlled temperature of about 1,250°C is maintained in the kiln, the resulting clinker being quenched with water, dried and finely ground before shipment in jute or paper bags. The product is largely a mixture of dicalcium sodium phosphate ($2CaO. Na_2O. P_2O_5$) and dicalcium silicate ($2CaO. SiO_2$). The addition of sodium carbonate apparently neutralises the adverse effect of fluorine, since most of the fluorine remains in the product. To provide the highest soluble P_2O_5 product, phosphate rock, soda ash and sand are mixed in the ratio of 10:3:1. The reaction which takes place can be expressed as follows:

$$Ca_{10}(PO_4)_6F_2 + 4Na_2CO_3 + 2SiO_2 \longrightarrow 6CaNaPO_4 + 2Ca_2SiO_4 + 4CO_2 + 2NaF$$

There are 4 kilns in operation at Brunsbüttelkoog which together produce at the rate of about 320,000 tonnes of Rhenania phosphate a year. Quartz sand containing 95 to 96 per cent SiO_2 is obtained from Quaternary deposits situated about 30 km from the plant, the soda ash being obtained from the company's plant at Heilbron in central Germany.

In the United Kingdom an extensive series of trials was conducted during the period 1940-1946 by the Building Research Station and the Rothamsted Experimental Station on the production of silicophosphate fertilisers. A so-called low-soda silicophosphate process was developed which is similar to the Rhenania process but involves the use of a lower proportion of soda ash as well as a higher temperature. The process was not taken up commercially.

DEFLUORINATED PHOSPHATE ROCK

Defluorinated phosphate rock is valuable both as a fertiliser and as a mineral supplement to animal feeds. For the latter purpose fluorine, being toxic, must be almost completely eliminated and it is reported that in general the F:P ratio should not exceed 1:40. Defluorinated phosphate is produced mainly in the United States where it has been prepared on a large scale for animal feed supplement since 1946. A large excess of silica is added to the charge to raise its fusion point above the defluorination temperature, which in the burning zone is within the range of 1,480 and 1,590°C., the removal of fluorine from the phosphate rock by means of silica and water vapour being shown generally by the following chemical equation:

$$Ca_{10}(PO_4)_6F_2 + SiO_2 + H_2O \longrightarrow 3Ca_3(PO_4)_2 + CaSiO_2 + 2HF$$

A similar product, known as <u>fused tricalcium phosphate</u>, is made by a process developed by the Tennessee Valley Authority. Fused <u>calcium-magnesium phosphate</u> has been produced in the USA, Japan and Taiwan where olivine or serpentine is found at a number of localities in sufficient quantity to provide a relatively cheap source of raw material for use in conjunction with phosphate rock. About 0.5 tonnes of olivine (or serpentine) and 0.7 tonnes of phosphate rock are required to produce 1 tonne of fused phosphate.

DICALCIUM PHOSPHATE

Dicalcium phosphate is important as an animal feed supplement, as a source of calcium and phosphorus in human foods and restoratives, and as a constituent of certain fertilisers. Substantial tonnages are manufactured annually in the United States and in western Europe. Where high standards of purity are required, dicalcium phosphate is usually made from electric furnace phosphoric acid and limestone or lime. Less pure grades may be made from hydrochloric acid and phosphate rock. When pure, dicalcium phosphate contains 41.3 per cent P_2O_5; the anhydrous product, which is also marketed, has a higher P_2O_5 content. Dicalcium phosphate is also made from defluorinated wet-process phosphoric acid. This is practised on a commercial scale in the Netherlands.

3.2. PRODUCTION IN THE EEC

The EEC is a major producer and consumer of phosphate fertilisers and intermediate products, in the manufacture of which it is almost totally dependent on external sources of phosphate rock. As a region, it ranks third in importance after North America and Eastern Europe. EEC production of phosphate fertilisers amounted to about 3.7 million tonnes P_2O_5 in 1975-1976, representing about 14 per cent of total world fertiliser production in that year. In 1974-1975 nearly 4.9 million tonnes P_2O_5 were produced. France is by far the largest producer of phosphate fertilisers, with an output in 1975-1976 of about 1.3 million tonnes P_2O_5 (Table 13). Most of the existing plants are located at or near seaports, with the notable exception of those in the Federal Republic of Germany, where some of the fertiliser complexes are also situated on the River Rhine.

More than one-half of the phosphate rock imported into the EEC is used in the manufacture of phosphoric acid. There were about 44 phosphoric acid plants operating in the EEC countries in 1976, with a combined production capacity of over 3 million tonnes P_2O_5 per annum. Production in 1976 amounted to 1.9 million tonnes P_2O_5.

In contrast with the USA, where most plants have a capacity of over 150,000 tonnes per annum, with a few exceeding 300,000 tonnes, phosphoric acid plants in the EEC (and Western Europe generally) are much smaller in size. In the EEC, only some 7 plants exceed 100,000 tonnes P_2O_5 per annum. The largest are situated at Rieme and Engis in Belgium, Grand-Couronne, Le Havre and Grand Quevilly in France, Gela in Italy, Pernis and Vlaardingen in the Netherlands and Whitehaven and Immingham in the United Kingdom.

The largest plants in Europe for manufacturing elemental phosphorus are located at Knapsack, near Cologne, in the Federal Republic of

Germany and at Vlissingen, on the River Scheldt, in the Netherlands, with annual capacities of about 80,000 and 90,000 tonnes phosphorus respectively. These plants have electric furnaces comparable in size to the largest ones operated in North America. Elemental phosphorus is also manufactured in southern France at Epierre in Savoie Department and at Pierrefitte - Nestalas in Hautes Pyrenees about 16 km south of Lourdes. Operation of the phosphorus plant at Crotone, Italy, is believed to have been discontinued. There has been no large scale elemental phosphorus manufacture in the United Kingdom since 1969.

TRADE

In terms of international trade in phosphate fertilisers, Europe is the principal source of supply, with Belgium-Luxembourg, the Federal Republic of Germany and the Netherlands being the most important exporting countries. Total EEC exports amounted to 1,015,000 tonnes P_2O_5, about 28 per cent of total world exports. A large proportion is sold within Europe. For example, Belgium-Luxembourg, the largest EEC exporter in 1975-1976, shipped a total of 493,000 tonnes P_2O_5, of which 90 per cent went to neighbouring EEC countries, chiefly to the Federal Republic of Germany and France.

There is a similar trade between EEC countries involving phosphoric acid; but imports in 1976 included shipments of acid from Tunisia, Israel, Spain, Mexico, Lebanon and the USA.

There is a growing international trade in elemental phosphorus, but most is utilised at present at or near the centre of manufacture. Much of the phosphorus produced and imported is converted into phosphoric acid and either sold in this form or utilised in the production of sodium, potassium and calcium phosphates. However, there are also important requirements for phosphorus as a raw material for the manufacture of phosphorus chlorides, sulphides, other intermediates and organo-phosphorus chemicals. In Europe, the principal producing countries supply the marginal needs of neighbouring countries. Since 1969 United Kingdom requirements have been met by imports from Canada, using specially constructed ships to transport phosphorus in bulk. There has also been some movement of elemental phosphorus between East and West Europe and to the Far East.

TABLE 13. PRODUCTION OF PHOSPHATE FERTILISERS IN THE EEC, 1975 - 1976 and 1976 - 1977

Thousand tonnes P_2O_5

	1975/76	1976/77
BELGIUM/LUXEMBOURG	625	589
DENMARK	78	85
FRANCE	1,259	1,490
GERMANY, FEDERAL REPUBLIC	649	733
IRISH REPUBLIC	89	79
ITALY	370	428
NETHERLANDS	179	307
UNITED KINGDOM	467	438
TOTAL EEC	3,716	4,149
Total West Europe	4,967	5,547
WORLD TOTAL	25,794	28,222

Source: ISMA Limited, Paris.

3.3. RECOVERY OF BY-PRODUCTS

There are a number of elements and chemical compounds present in phosphate rock which can be obtained as by-products in the manufacture of either phosphoric acid or elemental phosphorus. Commercially the most important of these by-products are gypsum, fluoride, and vanadium compounds. Calcium silicate slag and ferrophosphorus, produced during the manufacture of elemental phosphorus, have only a limited market. Uranium recovery is of considerable potential economic importance and several projects in the USA are at various stages of development.

GYPSUM

Calcium sulphate ($CaSO_4.2H_2O$) is produced as waste in the manufacture of phosphoric acid. Approximately 5.5 tonnes of phosphogypsum is normally made available for every tonne of P_2O_5 produced. Disposal presents a considerable problem and at most European phosphoric acid plants takes place in the sea or in tidal estuaries. Where this method of disposal is not possible, the phosphogypsum is pumped to settling ponds. Compared with natural forms of calcium sulphate (gypsum or anhydrite), phosphogypsum has the disadvantage of a higher water content (about 25 per cent), fine particle size and, frequently, inconsistent quality. It may contain between 0.4 and 1.5 per cent P_2O_5, up to about 1.5 per cent F, and traces of radioactive material may also be present. There are phosphoric acid processes, however, which give rise to purer forms of phosphogypsum.

Although an actual yield of phosphogypsum of some 17 million tonnes per annum is theoretically possible within the EEC, assuming a phosphoric acid capacity of around 3 million tpa, comparatively small quantities are at present utilised commercially. In Federal Germany, for example, phosphogypsum is used in plasterboard and block manufacture, as a bulk-head material in coal mines and as a retarder in cement manufacture. A plant capable of processing about 160 tonnes of phosphogypsum a day came into operation at Ludwigshaven in 1966. Other plants are operated at Castrop-Rauxel north-east of Düsseldorf and at Knapsack near Cologne. In France a plant is operated at Les Roches-de-Condrieu south of Lyon. Recent plants at Rouen (300,000 tpa), Douvrin near Arras (110,000 tpa) and plants at Rupel in Belgium and in the Federal Republic of Germany which are used almost entirely for building block manufacture show an increasing use of phosphogypsum. In the Irish Republic, a 100,000 tpa plant at Arklow has been producing plaster and plasterboard from phosphogypsum since 1976. Phosphogypsum is not used commercially in the United Kingdom although it was used at Billingham in the manufacture of plaster and plasterboard during the early 1930s and again at Severnside between 1966 and 1969. Processes for the production of plaster from phosphogypsum are currently being examined. In general, utilisation of phosphogypsum has not proved attractive where natural gypsum is readily available, because the P_2O_5 and other impurities adversely affect the setting properties of the gypsum.

FLUORINE

Phosphate rock as marketed may contain up to 3 or 4 per cent F and thus it represents a potentially large source of fluorine. Although fluorine compounds have been removed by the phosphate fertiliser industry for many years, for environmental control purposes, only within the last 10 years has serious consideration been given to the economics of recovering fluorine as a valuable by-product.

In the production of phosphoric acid, the fluorine originally present in the phosphate rock is distributed in the product acid, the precipitated gypsum and the exhaust gases (as silicon tetrafluoride, SiF_4, which is very volatile).

The relative quantities of fluorine in the final products depend on the type of rock used and the operating conditions. In phosphoric acid fluorine is present as fluosilicic acid (H_2SiF_6) and fluosilicate salts and can be economically recovered. Fluosilicic acid is usually the most desirable primary by-product in fertiliser phosphoric acid manufacture since it can be used as an intermediate material for other fluorides, notably sodium fluosilicate. Commercial recovery is being undertaken but the quantities produced at present are relatively small. Assuming a recovery of 40 kg H_2SiF_6 per tonne P_2O_5, the potential in the EEC at present amounts to approximately 125,000 tonnes of H_2SiF_6 per annum.

Fluosilicic acid is used in the USA in the manufacture of aluminium fluoride and synthetic cryolite and plants are reported to be in operation for this purpose also in Canada, France, and Austria. Only a small proportion of the fluosilicic acid produced in the United Kingdom is recovered and utilised commercially. Sodium fluosilicate is used chiefly in water fluoridation; about 200 tonnes have been imported annually into the UK. The conversion of fluosilicic acid into synthetic acid-grade fluorspar (CaF_2) or hydrofluoric acid has been investigated but no commercial production has been undertaken.

VANADIUM

Many of the phosphate deposits in the western USA are vanadium-bearing, in some cases containing up to 0.20 per cent V_2O_5, and in the manufacture of elemental phosphorus much of the vanadium present is ultimately concentrated in the ferrophosphorus slag obtained. Research has shown that extraction can best be carried out by a roast-leach process to form 'red cake', a commercial vanadium pentoxide for conversion to vanadium products. In some cases 85 per cent of the vanadium is recovered. At present recovery of vanadium from ferrophosphorus slag takes place only in the USA, as far as is known. Separation of vanadium from phosphoric acid is also technically feasible and a concentrate with 88 per cent V_2O_5 was produced intermittently in the USA between 1941 and 1955.

FERROPHOSPHORUS

The electric furnace process for manufacturing elemental phosphorus gives rise to appreciable quantities of ferrophosphorus containing usually between 20 and 25 per cent P. Ferrophosphorus has found a limited market as an additive in the manufacture of iron and steel, an alloy in special types of steel, an agent to increase the specific gravity of drilling muds, and for paint pigments. It has been used also in making high-density concrete.

CALCIUM SILICATE SLAG

Calcium silicate slag, a by-product of elemental phosphorus production, is used on only a very limited scale for ballast in the construction of roads and railways, as concrete aggregate, and for the manufacture of mineral wool for insulating purposes. Some of the more chemically basic varieties, when finely ground, have been used as a liming agent on acid soils.

URANIUM

The potential of by-product uranium extraction from phosphoric acid is considerable. For example, it has been estimated that there is an output potential of about 5,000 tonnes per annum from the processing of Florida phosphate rock, equivalent to approximately 40 per cent of US uranium production in 1976.

The recovery of uranium from phosphoric acid and from the aluminium phosphate of 'leached' zone at present removed in the Central Florida phosphate mining district as part of the overburden was investigated in the USA during the 1950s on behalf of the US Atomic Energy Commission. About 800 tonnes of U_3O_8 or yellow cake was produced in the course of phosphoric acid manufacture but falling uranium prices and recovery costs prohibited further commercial development. The recovery of uranium from phosphoric acid has become much more attractive in recent years as the price for uranium has risen and as process technology has improved. In addition, the investigations carried out reflect the fears expressed, in Florida, over the possible adverse environmental impact of uranium-bearing phosphate tailings. Highly sophisticated methods of uranium extraction have been introduced since the late 1960s, all of which employ a solvent extraction technique essentially similar to that developed by the Oak Ridge National Laboratory in Tennessee. Products in excess of 90 per cent U_3O_8 purity are obtained. At least one commercial unit is in operation.

Uranium recovery units in various stages of construction in Florida will together be able to produce about 0.6 million kg of U_3O_8 per annum. Similar recovery facilities are being installed in Louisiana with an annual capacity of approximately 313,000 kg of U_3O_8. Uranium has also been extracted on a pilot plant scale at Huelva in Spain. Details of the economics of uranium extraction from phosphoric acid have not been published but appear to depend on the production of phosphoric acid at very large plants using Florida phosphate rock, which has a relatively high uranium content of between 0.0125 to 0.025 per cent U_3O_8, equivalent to about 0.4 kg U_3O_8 per tonne of P_2O_5 in phosphoric acid.

Uranium may also be extracted directly from phosphate rock by acid leaching but the technique has not been adopted commercially. Many sedimentary marine phosphate deposits contain between 0.005 and 0.02 per cent U.

RARE EARTHS

The considerable increase in demand for certain rare earths in the early 1960s was responsible in part for the renewed interest in their occurrence and distribution in phosphate rock. Relatively large quantities are potentially made available annually in the manufacture of wet-process phosphoric acid, chiefly that made from igneous apatite rock, but there appears to be little prospect of utilising this possible source of rare earths at the present time. Chemical analyses indicate that rare earths are present in phosphate rock in amounts ranging from 110 to 1,550 ppm RE_2O_3. Florida pebble rock, for example, is reported to contain 460 ppm RE_2O_3, principally in the form of yttrium. Kola apatite concentrate contains 0.85 per cent RE_2O_3.

3.4. IMPACT ON THE ENVIRONMENT

The production of wet-process phosphoric acid and that of phosphate fertilisers generally involves the problem of disposing of several waste products that are potential environmental pollutants. These are mainly fluorides and dust, each of which may contribute to both atmospheric and water pollution, as well as gypsum and waste water.

Probably the most serious water pollution problem arises from fluorides and acidic wastes. In phosphoric acid manufacture, for example, about 20 to 30 per cent of the fluorides is contained in the acid produced, 20 to 40 per cent in the phosphogypsum and 30 to 60 per cent in gypsum pond water. Gypsum is often transported to special disposal ponds as a slurry in water; in the pond, the gypsum settles out and the pond water is recycled to the plant complex. This water is seldom released in untreated form, the usual method being to use lime or lime slurry as neutralising agents.

Fluorides and dust are of primary concern in atmospheric pollution. Fluorides are emitted from practically all manufacturing operations involving phosphate rock and unless removed, can have an adverse effect on plant and animal life. Efficient methods of removing fluorides from waste gases have been developed, but old fertiliser plants may contribute significantly to air pollution problems.

The dust arising from drying and grinding phosphate rock may contain 3 to 4 per cent water insoluble fluoride, but as far as fluoride pollution is concerned, appears to have little adverse effect on either plant or animal life. However, the dust itself is a troublesome nuisance and is dealt with by means of dry cyclone dust removers followed by wet scrubbers or electrostatic precipitators. In addition the transfer of dried and ground rock can create dust problems which may be minimised by using pneumatic equipment.

4. PHOSPHATE DEPOSITS IN THE EUROPEAN ECONOMIC COMMUNITY

4.1. BELGIUM

Phosphate rock occurs in Belgium [1-5] chiefly as beds of phosphatic chalk of Upper Cretaceous age situated along the Haine and Senne valleys near Mons, Hainaut Province, which have accounted for most of the past Belgian production of phosphate rock, and also in the Liège Province along the Meuse valley between Liège and Namur. In addition, phosphatic nodules occur in various parts of Belgium in sediments of Jurassic, Tertiary and Quaternary age, for example, in southern Vlaanderen Province, the adjacent area of Hainaut Province, and in the extreme southern part of Luxembourg Province. Phosphate in the form of phosphatic nodules was first reported in Belgium in 1856 from Tertiary rocks near Brussels.

None of the occurrences in Belgium has been of economic interest since the Second World War. However, waste phosphatic chalk arising from former washing operations was recovered from dumps until 1968 at Ciply near Mons for direct application to the soil. The manufacture of phosphate fertilisers for the country's intensive agricultural needs is therefore based on imports of phosphate rock obtained almost entirely from Morocco (Table 14).

GEOLOGY

The Belgian phosphate deposits and associated strata represent a characteristic littoral facies developed during Upper Cretaceous (Senonian) times in a gulf or arm, known as the Mons Basin[6], along the northeastern margin of the then Paris Basin sea. The Mons Basin thus has a geological history similar to that of northern France. It is made up of Cretaceous and Eocene rocks, the Mons Basin proper being incompletely separated from a southerly extension (Bavay - Grand Reng) by Devonian-Carboniferous rocks of the Blaugies Massif

(Fig 9). Such a palaeogeographical environment of basins separated by depositional 'highs' is one which is favourable to phosphate deposition. Thicknesses of strata within the basin vary considerably but total about 1,200 m.

The Upper Cretaceous and Palaeocene formations represented in the Mons Basin are listed in the accompanying table. The chalk formations[7,8] are characterised by the presence of basal conglomerates **('poudingues') which generally contain abundant phosphate nodules, and by phosphatised 'hardgrounds' representing lithified sea floor surfaces. In Liège Province the conglomerates pass laterally into a chalky breccia devoid of phosphate nodules. A disconformity separates the Poudingué de Malogne and the underlying Maastrichtian beds.**

TABLE 14. BELGIUM-LUXEMBOURG : IMPORTS OF PHOSPHATE ROCK, 1972-1976
TONNES

Country	1972	1973	1974	1975	1976
Morocco	1,377,704	1,403,420	1,478,152	1,231,439	1,087,904
Soviet Union	244,065	239,627	179,217	117,898	105,000
Togo		110,085	205,146	93,638	92,600(e)
Tunisia		46,534	49,000(e)	15,900(e)	
U.S.A.	300,000(e)	295,221	363,000(e)	223,300(e)	81,100(e)
Other countries	272,450	191,807	132,084	89,266	215,534
Total	2,194,219	2,286,694	2,406,599	1,771,441	1,582,138
(1000 Francs) C.i.f. Value	1,476,456	1,671,995	4,943,781	4,596,671	3,135,232

(e) Estimate.

Source: Bulletin Mensuel du Commerce Extérieur
de L'Union Économique Belgo-Luxembourgeoise.

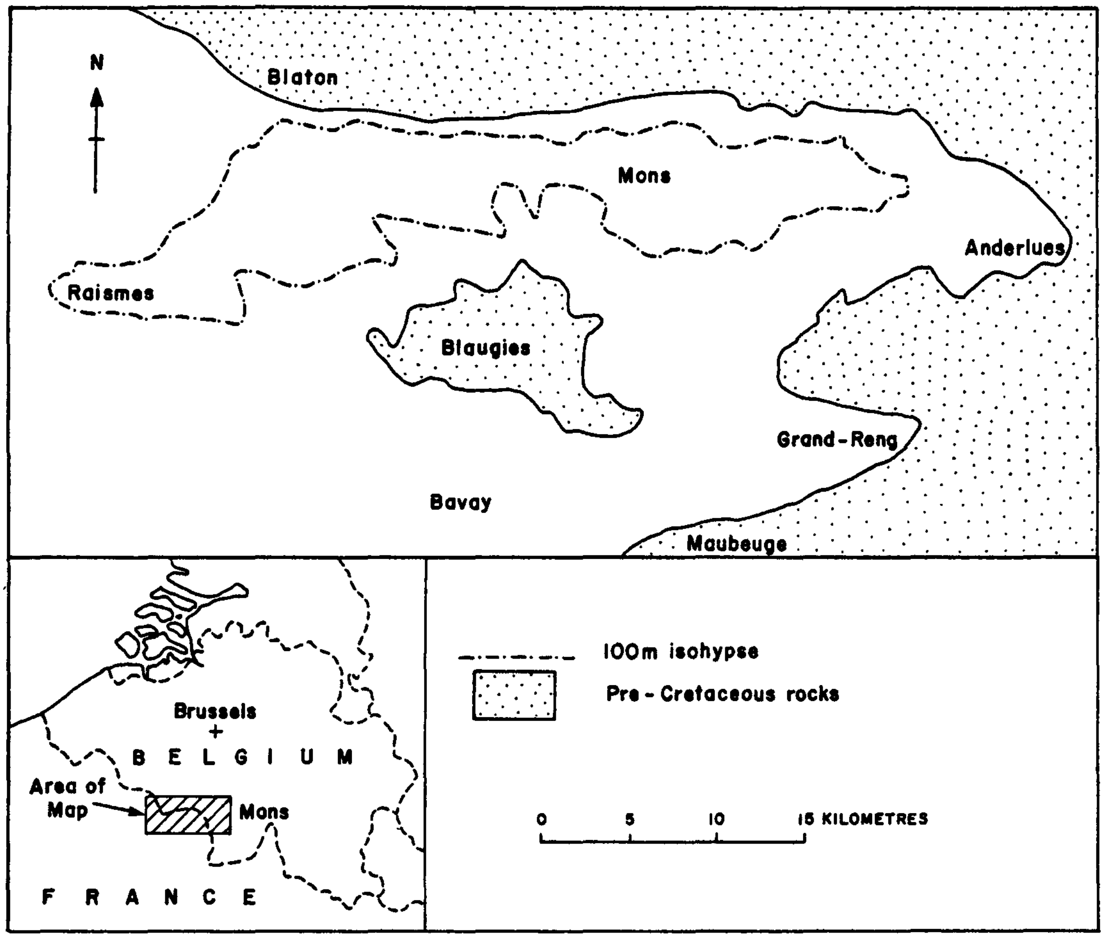


Fig 9 Location of the Mons Basin in southern Belgium. (Based on Marlière, 1970.)

	Maximum thickness[9] metres
PALAEOCENE	
Montian-Danian	
Calcaire de Mons	42
Tuffeau de Ciply	40
Poudingue de Malogne	
UPPER CRETACEOUS	
Maastrichtian	
Tuffeau de St - Symphorien	65
Craie phosphatée de Ciply	57
Craie de Spiennes	40-45
Campanian	
Craie de Nouvelles	30-36
Craie d'Obourg	49
Craie de Trivières	90

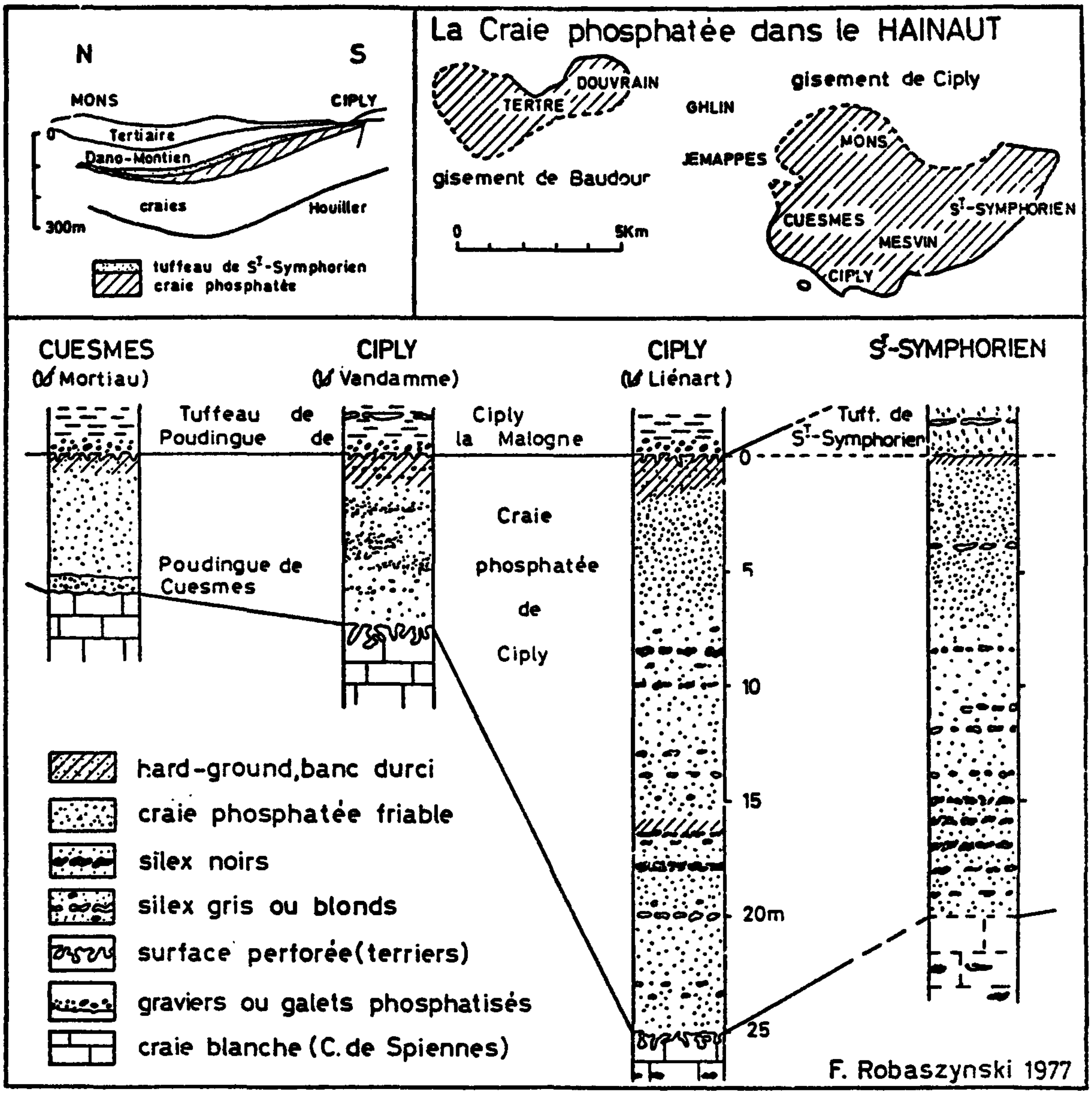


Fig. 10. Distribution of Upper Cretaceous phosphatic chalk in the Mons and Baudour areas of Hainaut Province. (Reproduced by permission of F. Robaszynski, in press.)

By far the most important commercial source of phosphate in the Mons Basin has been the Craie de Ciply[10,11], a transgressive member of the Maastrichtian sequence, which occurs at or close to the surface around Mons and Baudour (Fig 10). Also worked briefly has been the thin phosphatic conglomerate (the Poudingue de Malogne) at the base of the Tuffeau de Ciply.

The Craie de Ciply has a synclinal, lens-shaped structure, dipping gently at 8 to 10° to the north and north-east. Thicknesses vary considerably; where formerly worked the chalk is from 10 to 25 m thick, but borehole data show a range in thickness from a few metres to 58 m at Ciply and indicate also a rapid thinning of the bed northwards, reaching a thickness of only 1 m just north-west of Mons. The base of the phosphatic chalk between Mons and Ciply lies at depths of between 150 m and 200 m from the surface. In the Baudour area, where the bed is up to 20 m thick, it occurs at depths of up to 100 m.

In the western part of Hainaut Province near Flobecq,[12] some 13 km north of Ath, and in the neighbouring parts of Vlaanderen Province near Ronse (Renaix), about 10 km WNW of Flobecq, phosphatic nodules are abundant in Upper Ypresian (Eocene) clays or sands. Chemical analyses of nodules collected from the Flobecq and Ronse areas showed, respectively, 19.4 and 25.8 per cent P_2O_5, 29.6 and 39.2 per cent CaO, 7.3 and 4.9 per cent Al_2O_3 and Fe_2O_3, and 31.4 and 15.6 per cent insoluble matter, represented chiefly by sand and clay.

Sedimentary phosphate rock occurs in Liège Province within a narrow area extending from near Aachen in Germany westwards through the Hesbaye region[13,14] to Ottignies near Wavre, in Brabant Province, and a number of deposits were worked at several localities within a zone extending for some 20 km WNW of Liège and notably near Rocourt, about 5 km north of Liège. In this area a thin bed of Maastrichtian age, a few cm to about 0.6 m thick and containing small concretions and nodules of phosphate in a clayey or sandy matrix, was worked. The bed rests on Senonian chalk (Craie de Nouvelles), and is overlain by up to 48 m of silicified chalk, sand and loam. The phosphate, as mined, averaged about 21 per cent P_2O_5. The deposits are now virtually exhausted.

Phosphatic nodules, which are in many respects similar to those found in the Meuse Valley and near Mons, occur in Liassic rocks near Lamorteau, Harnoncourt, Athus and Aubange in the extreme southern portion of Luxembourg Province.[15,16] The nodules in the Grandcourt Marls are generally hard and rust coloured and contain up to 28.1 per cent P_2O_5; those in the ferruginous limestone known as 'Macigno d'Aubange' are often porous and composed of calcium phosphate ooliths, analyses showing up to 23.7 per cent P_2O_5.

Petrography and chemical composition.

The Craie de Ciply is a light brown, coarse grained, usually soft and friable and highly bioturbated chalk. It is also highly fossiliferous and sometimes contains abundant layers of flint nodules. The chalk contains up to about 16 per cent P_2O_5, averaging between 8 and 10 per cent P_2O_5, but higher grade material formed by the leaching action of surface (meteoric) waters occur in irregular pockets developed in the upper part of the chalk to depths, for example, of nearly 4 m at Ciply. These pockets consist primarily of residual, gravelly phosphate containing up to about 30 per cent P_2O_5. One of the largest was discovered at Mesvin, northeast of Ciply, in 1879.

A random sample of phosphatic chalk from old workings at Ciply analysed by the Institute of Geological Sciences, London, using a rapid colorimetric method, showed 12 per cent P_2O_5. A range of 31.8 to 52.5 ppm U has also been reported[17] from a 5 m bed of the Craie de Ciply from north of Cuesmes; and a sample of leached phosphatic chalk from the Ciply area showed 137.9 ppm U. The phosphatic chalk recovered at Ciply during the late 1960s had the following chemical composition:

	Per cent
P_2O_5	7.49
CaO	53.80
Insoluble in HCl	2.01
Al_2O_3	0.36
Fe_2O_3	0.31
MgO	0.36
SO_2	0.29
Volatile matter	35.36
Total	99.98

RESOURCES

No comprehensive, up-to-date assessement of phosphate rock resources within the Mons Basin of Belgium has been made, as far as is known. However, the deposits of phosphatic chalk near Mons and Baudour have been worked only to relatively shallow depths, probably not exceeding 30 to 40 m from the surface. Since boreholes put down in these areas have proved phosphatic chalk to depths of 150 m and more, substantial resources of this rock undoubtedly exist. Resources over an area of approximately 3200 ha in the Ciply and Baudour areas have been estimated[18] to be in region of 300 million to 500 million tonnes in the Craie de Ciply, assuming thicknesses averaging from 6 m to 10 m. A major proportion of the resources could probably only be exploited by underground mining. The chalk averages between 8 and 10 per cent P_2O_5.

PRODUCTION

Since the Second World War the only commercial operation has been to the south and south-east of Mons, particularly near Ciply and St Symphorien. The phosphatic chalk produced was ground and was used primarily for direct application to the soil. Shortly after the war a significant tonnage of washer rejects was used for a variety of purposes, chiefly as a soil additive and in the production of basic slag. At Ciply, some 18,000 tonnes were treated in 1945, the reject material generally containing 6 to 8 per cent P_2O_5, but in some instances up to 16 per cent P_2O_5.

Phosphate mining began in Belgium in 1866, when the Poudingue de Malogne bed was first worked at Ciply. Extraction of phosphatic chalk began in 1874, the deposits near Ciply and Mesvin being of particular importance. Quarries were also opened up at Spiennes and St Symphorien and, further to the north-east, at Havré, as well as south of Baudour, about 10 km WNW of Mons. A total of about 13.5 million tonnes has been produced in Hainaut Province. The nodule bed in the Hesbaye Province near Liège was first worked in 1899 and provided phosphate rock until the early part of the present century, including the First World War, and again during the Second World War. About 4.5 million tonnes of phosphate rock were produced.

An average annual output of more than 600,000 tonnes was reached between 1899 and 1904 when Belgium was an important world producer of phosphate rock. Subsequently, however, production decreased gradually, in part because of the depletion of the relatively rich portions of the deposits, but mainly due to the development of higher grade and more readily and cheaply mined deposits in other countries. Average annual output remained above 200,000 tonnes until the First World War. The phosphatic chalk, which contained up to 14 per cent P_2O_5, was for many years (including the 1939-1945 war period) exported chiefly to Germany for use as a metallurgical flux. Higher grade material with up to 32 per cent P_2O_5 was used for superphosphate manufacture. During the Second

World War production of phosphate rock was increased from about 20,000 tonnes in 1940 to some 428,000 tonnes in 1943.

REFERENCES ON BELGIUM

1 Phosphates du Hainaut. R. Marlière. *Centen.Ass.Ing.Liège Congr.,* 1947, pp. 330-341. (In French)

2 Phosphates de la Hesbaye. L. Calembert. *Centen.Ass.Ing.Liège Congr.,* 1947, pp. 341-344. (In French)

3 Mitteilungen über den Phosphatbergbau Belgiens. O. Tietze. *Z. Berg-Hütt.- u.Salinenw.*, 1908, Vol.56, pp. 485-502, (In German)

4 Phosphates sénoniens de Belgique. L. Cayeux. *Etud. Gîtes minér.Fr.,* 1939, Vol.1, pp. 259-277. (In French)

5 Le passé,le présent et l'avenir de l'industrie extractive des phosphates dans le Hainaut. R. Marlière. Extract from *Bull.Soc. Nat.Mons Borinage,* 1947, Vol.29-30,pp. 42-50. (In French)

6 Géologie du bassin de Mons et du Hainaut: un siècle d'histoire. R. Marlière. *Annls Soc. géol. Nord,* 1970, Vol.90, Pt.4,pp.171-189. (In French. English Summary,p. 171)

7 Sur le Crétacé supérieur du Hainaut et du Brabant. M. Leriche. *Annls Soc.géol.Belg.*, 1934, Vol.58,*Bull.Nos.* 3-4,pp.118-141. (In French)

8 De nombreux bancs phosphatés dans la craie à *Actinocamax quadratus* du Bassin du Mons. R. Marlière. *Annls Soc.géol.Belg.,* 1933, Vol.56, *Bull.No.* 10,pp.290-301. (In French)

9 Carte Géologique de la Belgique à l'Echelle 1:25,000. No. 151. Texte Explicatif de Feuille Mons-Givry. R. Marlière. 71 pp. (Brussels: Imprimerie Hayez, 1967.) (In French)

10 Sur les faciès de Craie phosphatée de Ciply. J. Cornet. *Annls Soc.géol.Belg.,* 1905, Vol.32, *Mém.,* pp.137-146. (In French)

11 Etude géologique sur les gisements de phosphate de chaux de Baudour. J. Cornet. Annls Soc.géol.Belg., 1900, Vol.27, Pt.1, Mém., pp. 3-22. (In French)

12 Découverte de gisements de phosphate de chaux appartenant à l'étage ypresien, dans le sous-sol de la ville de Renaix et dans celui de la région de Flobecq. E. Delvaux. Annls Soc.géol.Belg., 1884, Vol.11, Mém. 19, pp.279-294. (In French)

13 Le phosphate de chaux de la Hesbaye. Son allure, sa composition et ses fossiles. G. Schmitz. Annls Soc.géol.Belg., 1890, Vol. 17, Mém., pp. 185-208. (In French)

14 Le conglomérat à silex et les gisements de phosphate de chaux de la Hesbaye. M. Lohest. Annls Soc.géol.Belg., 1885, Vol. 12, Mém., pp. 41-81. (In French)

15 Note sur la présence de phosphates dans le lias de la Belgique. M. Jannel. Annls Soc.géol.Belg., 1881, Vol. 7, Bull.No.9, pp. cxxvi-cxxix. (In French)

16 Analyse des phosphates du lias du Luxembourg. A. Petermann. Annls Soc.géol.Belg., 1881, Vol.7, Bull.No 9, pp. cxxx-cxxxvii. (In French)

17 Perspectives de la prospection de l'uranium à l'échelle nationale. J-M. Charlet, C. Dupuis and Y. Quinif. Annls mines Belg., 1977, No.5, pp.521-531. (In French. English Summary, p.522) L'anomalie des craies phosphatées du Bassin de Mons, pp.526-527.

18 Les gisements de phosphates. F. Robaszynski. In Métallogénie de la Belgique des Pays-Bas et du Luxembourg - Commentaire de la Carte Métallogénique de l'Europe. (Paris:UNESCO.) (In French) (In the press)

4.2. DENMARK

Phosphate rock has not been recorded from the mainland of Denmark, but phosphate-bearing sedimentary rocks of Cambrian, Ordovician and Cretaceous age, chiefly as nodule beds marking breaks in sedimentation, occur in the southern part of the island of Bornholm in the Baltic Sea. All the occurrences are of relatively low grade and too thin, however, te be of economic importance. The phosphate rock requirements of the long-established Danish fertiliser industry are therefore met entirely by imports, chiefly from Morocco and the Soviet Union (Table 15).

Phosphate nodules have been reported from Jurassic rocks in East Greenland, and apatite is locally an important constituent of at least two carbonatite plugs which are situated in West and South Greenland in alkaline igneous complexes of Precambrian age.

GEOLOGY

The island of Bornholm[1] lies in the faulted zone between the Fennoscandian Shield and the Danish-Polish sedimentary basin. It consists mainly of Precambrian gneisses and granites which, in the southern part of the island are overlain by sedimentary rocks chiefly of Lower Palaeozoic(Cambrian to Silurian) age. These sediments are broken by a series of normal faults believed to be of Tertiary age, the most significant trending WNW-ESE. Dips are generally to the SE or SSE at not more than 3° to 4° except close to the faults where steeper dips may occur. In the smaller down-faulted areas of south-west Bornholm, Cretaceous strata (Wealden-Lower Senonian) resting on Precambrian-Palaeozoic basement have also been preserved (Fig 11).

The best known phosphate occurrence on Bornholm is near Arnager, some 8 km south-east of Rønne, where phosphatic nodules form a conglomerate [2,3] at the base of the Middle Cenomanian Arnager Greensand. In this area, the transgressive greensand dips west-

TABLE 15. DENMARK : IMPORTS OF PHOSPHATE ROCK, 1972-1976

TONNES

Country	1972	1973	1974	1975	1976
Germany, Federal Republic			31	84	
Israel				72	
Morocco	208,069	228,096	238,601	180,323	187,368
Netherlands		12	8		
Soviet Union	87,521	98,177	102,675	77,078	72,963
Sweden			288	130	317
Tunisia	28,760	18,615	9,200		
United Kingdom		57	18		
Other countries	5	2	58	1	30
Total	324,355	324,959	350,879	257,688	260,718
(1000 Kr) C.i.f. Value	37,915	43,596	140.128	121,123	90,390

Source: Danmarks vareindførsel og - udførsel.

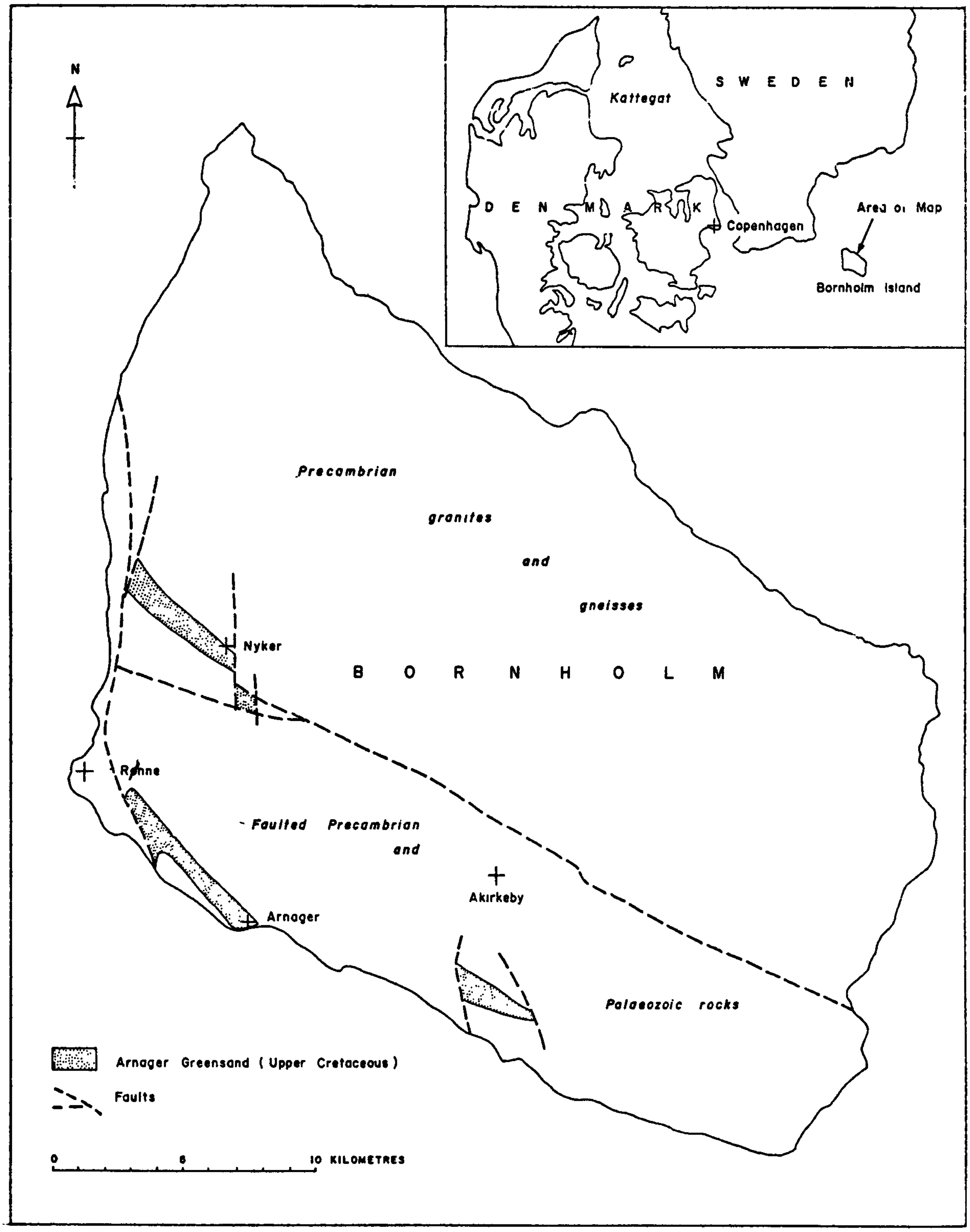


Fig 11. Generalised distribution of the Upper Cretaceous Arnager Greensand on Bornholm Island. (Based on Gry, 1960)

wards at 12 to 13° and lies directly on Lower Cretaceous (Neocomian) strata. The conglomerate is from 0.3 to 0.6 m thick, individual nodules containing about 16.5 per cent P_2O_5. It contains an abundant fossil assemblage, examination of which indicates that the nodules comprise both primary as well as secondary material reworked from older and notably Cambro-Ordovician and Lower Cretaceous (Albian) rocks. The nodules are markedly variable in shape and are up to 40 cm in diameter.

The uppermost 40 cm of the Rispebjerg sandstone contains on average about 15 per cent P_2O_5. The sandstone, which is about 3 m thick, lies at the top of the Lower Cambrian succession above 60 m of green (glauconitic) shales.[4] The shales themselves contain phosphatic nodules. In addition, phosphatic nodule beds occur in the Middle Cambrian black shales and at various levels in Ordovician rocks. The best developed is 0.3 m thick and rests on the Middle Ordovician Orthoceras limestone.

Apatite is reported to occur in significant amounts on the west coast of Greenland in the Qaqarssuk carbonatite complex[5], situated in the Sukkertoppen district east of Søndre Isortoq fjord. Within the complex carbonatite occurs as dykes and veinlets ranging from a few centimetres to more than 10 m in width. Drilling carried out by A/S Kryolitselskabet Øresund has indicated that the various rocks of this structurally very complex carbonatite contain from 1.2 to 2.5 per cent P_2O_5, although a number of bands average approximately 20 per cent P_2O_5[6]. Variable quantities of apatite are present also in the Grønnedal-Ika alkaline complex in South Greenland about 7 km north-east of Ivigtut. An average of only 1.5 to 2 per cent P_2O_5 is indicated, although locally the carbonatite is stated to contain significant amounts of apatite.[7]

In East Greenland, phosphatic nodules occur in the 'black shale' facies of the Lower and Middle Jurassic rocks mapped by the Geological Survey of Greenland in Jameson Land and Scoresby Land. Notable examples are the occurrences in the Fossilbjerget Member at the top of the Vardekløft Formation and in the Ostreaelv Member of the underlying Neill Klinter Formation. Stratigraphical sections indicate that individual nodule-bearing beds are seldom more than about 0.5 m in thickness, the nodules showing on average only 2 to 5 per cent P_2O_5.[6]

RESOURCES

Resources of phosphate rock on Bornholm have not been estimated, but these are probably extremely limited. A drilling programme carried out on behalf of the Geological Survey of Denmark in 1918 indicated that an area of 6 ha around Arnager contained about 36,000 tonnes of phosphate rock, in a bed averaging 37.5 cm in thickness.[7]

On the Danish mainland, Upper Cretaceous sedimentary rocks are widely distributed. Although they include sequences comparable in age with those known to be phosphate-bearing in Belgium and northern France, for example, they lie at considerable depths[10] and are unlikely, therefore, to attract commercial interest.

The Jurassic phosphate nodules in East Greenland are too low in grade and occur in beds too thin to be considered a resource of phosphate rock. The Qaqarssuk carbonatite has attracted attention chiefly as a possible source of niobium but its phosphate potential has not been thoroughly evaluated.

PRODUCTION

There is no production of phosphate rock in Denmark, but about 2,000 tonnes were produced on Bornholm from Madsegrav, just east of Arnager, during the 1918-1920 period because of difficulties in obtaining supplies of phosphate rock from overseas sources.

REFERENCES ON DENMARK

1 Geology of Bornholm. H. Gry. Guide Exc. Nos. A.45 and C.40, 21st int.geol.Congr., Norden, 1960. 16 pp.

2 Det cenomane Basalkonglomerat paa Bornholm. J.P.J. Ravn. Danm.geol.Unders., Ser 2, 1925, No.42. 64 pp. (In Danish. French summary, pp. 57-61)

3 Danmarks Natur. Vol.1 : Landskabernes Opståen. Edited by A. Nørrevang and T.J. Meyer. (Copenhagen: Politikens Forlag, 1967.) 448 pp. Phosphate, pp.95-97. (In Danish)

4 The Palaeozoic of Bornholm. Chr. Poulsen. Guide Exc. Nos. A.46 and C.41. 21st int.geol.Congr., Norden, 1960. 15 pp. Phosphates, pp. 5-7.

5 Geology of Greenland. Edited by A. Escher and W.S. Watt. 603 pp. (Copenhagen: The Geological Survey of Greenland, 1976.) Qaqarssuk, pp. 480-481.

6 Personal communication. J. Bondam, Director, Geological Survey of Greenland, 5.10.77.

7 The Grønnedal-Ika alkaline complex, South Greenland. The structure and geological history of the complex. C.H. Emeleus. Bull. No. 45, Grønd.geol.Unders., 1964. 75 pp. Apatite, pp.18,41.

8 Stratigraphy of the Jurassic-Lower Cretaceous sediments of Jameson Land and Scoresby Land,East Greenland. F. Surlyk, J.H. Callomon, R.G. Bromley and T. Birkelund. Bull.No.105,Grønl.geol.Unders., 1973. 76 pp.

9 Undersøgelser of Fosforitlag paa Bornholm. V. Milthers. Danm. geol. Unders., Ser.3, 1919, No.20, p.11. (In Danish)

10 Personal communication, H. Sørensen, Professor, Geological Survey of Denmark, 1.6.77.

4.3. FEDERAL REPUBLIC OF GERMANY

Phosphate rock occurs in the Federal Republic of Germany[1,2] as irregular residual deposits which were at one time worked on a small scale in Hessen and Bavaria. Phosphate nodule beds have also been worked briefly in parts of Lower Saxony and in the southern Ruhr area. There was little production after 1937, although during the Second World War deposits in Hessen again yielded a small tonnage of phosphate rock.

None of the known occurrences of phosphate rock in the Federal Republic of Germany is of commercial importance at the present time, with the notable exception of the reworked iron ore deposits in Lower Saxony, in the Lengede-Broistedt area near Braunschweig. The iron ore contains derived phosphate nodules which are recovered and have given rise to a limited production of phosphate rock since 1957. Requirements of phosphate rock for the important domestic fertiliser industry are therefore met entirely by imports, chiefly from the USA, the Soviet Union and, to a lesser extent, Morocco (Table 16).

GEOLOGY

Phosphate was first discovered in the 1850s in Hessen[3-6] during a search for iron and manganese ore near Staffel, north-west of Limburg. Subsequent investigations led to the discovery and exploitation of numerous residual deposits in the Lahn and Dill valleys, roughly within an area bounded by Diez, west of Limburg, Dillenburg and Giessen. The most important deposits are in the Lahn Valley between Diez and Weilburg; others have been found to the south of Diez and north-east of Wetzlar but these are of only limited extent.

TABLE 16. GERMANY, FEDERAL REPUBLIC : IMPORTS OF PHOSPHATE ROCK, 1972-1976

TONNES

Country	1972	1973	1974	1975	1976
Algeria					3,620
Belgium-Luxembourg	701		1,511	12,192	2,319
Curaçao	10,119	8,184	4,575	8,642	8,067
France				105	
Israel	33,169	973	9,112	15,816	5,519
Morocco	329,642	387,723	614,855	362,609	587,792
Netherlands	993	3,364	2,933	272	
Senegal	39,112	25,204	25,797	43,196	15,361
South Africa			9,316	1,268	14,617
Soviet Union	861,031	927,642	900,557	631,234	495,191
Spain	5,803	5,307	36,912	22,073	22,596
Spanish Sahara		20,542	36,399	40,760	14,772
Togo	78,295	85,104	66,210	24,054	37,754
Tunisia	66,130	80,173	74,742	40,126	23,076
USA	1,440,089	1,304,707	1,305,027	1,088,843	1,135,061
Other countries		167	1,200	391	4,128
Total	2,865,083	2,849,090	3,089,146	2,291,581	2,369,873
(1000 DM) C.i.f. Value	139,192	143,367	410,884	409,842	305,758

Source: Aussenhandel Spezialhandel nach Waren und Ländern.

The Lahn deposits occur as irregular discontinuous beds or lenses near or at the base of a deeply weathered basic tuff, several tens of metres thick, the so-called "Schalstein", covering steeply dipping Middle Devonian limestone. In places the phosphate has accumulated in solution cavities in the limestone or dolomite and quite often is associated with manganiferous limonitic iron ore. The thickness of the deposits varies considerably, generally increasing with depth, and in karstic depressions may reach several metres in thickness. The phosphorus is believed to have originated from the apatite of volcanic material in the "Schalstein", this mineral becoming dissolved by vadose carbonate waters which migrated downwards during Mesozoic and Cenozoic times and reacted chemically with the underlying carbonate bedrock.

In the Oberpfälz district of <u>Bavaria</u>[7,8] where phosphate was first reported in 1816, deposits of comparable origin were opened up in 1918 on a ridge called Erzberg, near Amberg. There pre-Cenomanian to Cenomanian reworked iron ore and phosphate blankets an irregular surface of Upper Jurassic limestone or, locally, Middle Jurassic sandstone. These rocks dip steeply to the south-west and are complexly faulted. Individual phosphatic beds consist of soft, friable material, white to yellowish-brown in colour, with clayey, calcareous and ferruginous impurities. In general, they are less than 1 m thick and contain on average 20 per cent P_2O_5. The combined alumina and iron oxide content averages 9 per cent.

Beds of phosphatic nodules and so-called 'bone-beds' have been found in various parts of <u>Lower Saxony</u> in rocks ranging from Upper Triassic to Middle Oligocene in age. Of these occurrences, the Lengede-Broistedt iron ore deposits,[9-11] situated about 16 km south-west of Braunschweig, are at present the only commercial source of phosphate rock in the Federal Republic of Germany. These are reworked clay ironstone deposits of Santonian (Upper Cretaceous) age believed to have been derived from argillaceous

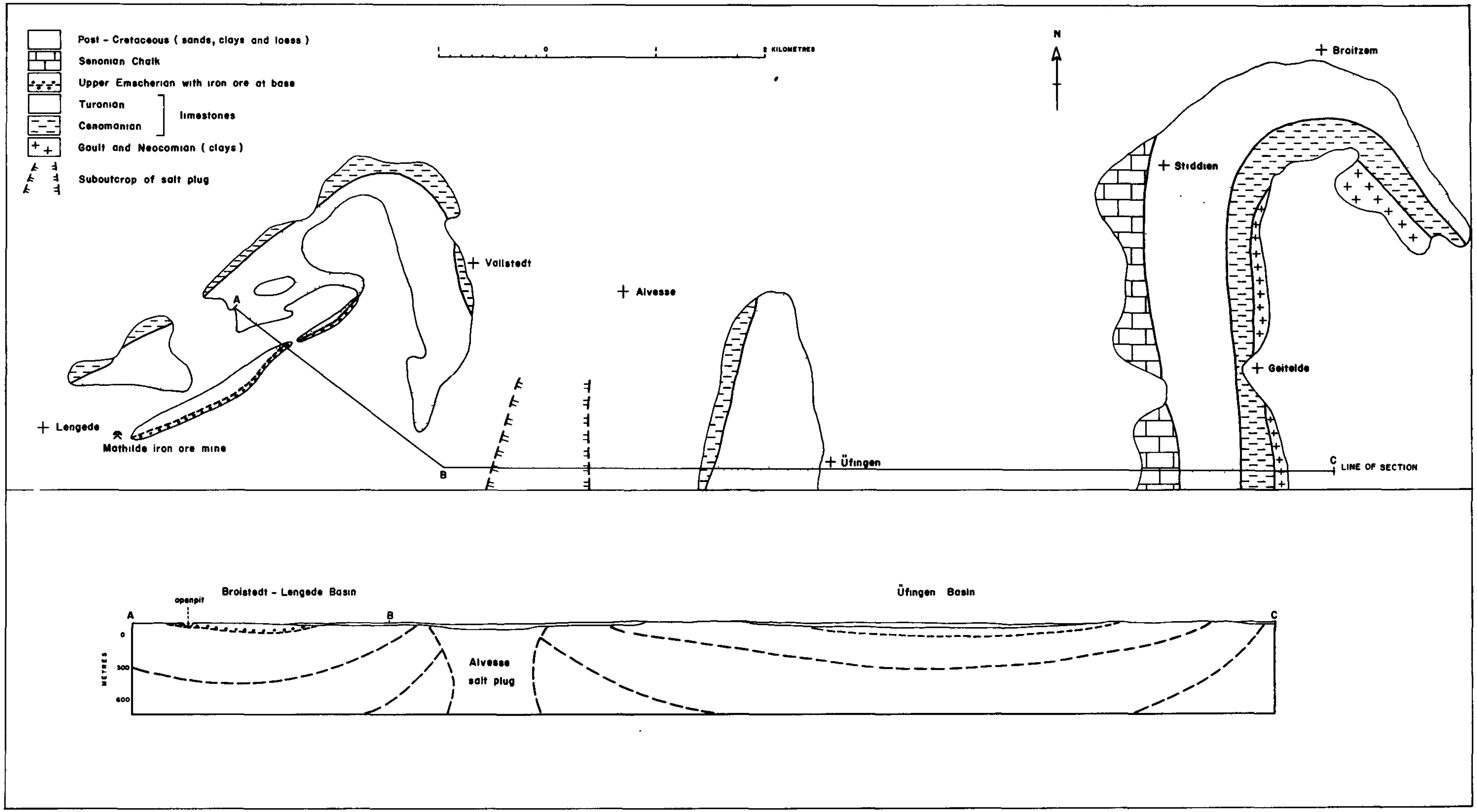


Fig 12. Generalised geology of the Broistedt - Lengede and Üfingen basins. (Based on Sheet Nos 2024 and 2025, Preussische Geologische Landesanstalt 1:25 000, 1932.)

Albian sediments. They form a basal transgressional conglomerate in which nodules of limonitic iron ore and ferruginous phosphate are embedded in a coarse carbonate - clay matrix. Phosphate nodules comprise some 6 to 10 per cent of the mined limonitic ore, which on average contains 38 to 39 per cent Fe_2O_3 and 1.8 per cent P (about 4 per cent P_2O_5). The thickness of the conglomerate is variable, reaching a maximum of 15 m, with a mined section at Broistedt (Mathilde mine) some 3 to 7 m thick.

The Broistedt-Lengede iron ore deposits occupy a SW-NE trending synclinal basin on the northern flank of the Alvesse saltplug (Fig 12), the basal conglomerate lying at a maximum depth of 100 m in the central part of the basin, where it becomes reduced in thickness to some 3 to 4 m. A characteristic feature is that the conglomerate is transgressive from NW to SE and, together with the associated sediments, generally becomes progressively thicker and coarser in grain size in a northwesterly direction. Towards the south-east the conglomerate becomes replaced by clay.

To the south of Braunschweig, near Bad Harzburg and Oker, south-east of Goslar, two Lower Senonian conglomeratic phosphate beds were formerly worked.[12,13] These beds, which are up to 1.5 m thick and contain ferruginous and calcareous concretions, are of limited lateral extent. To the east of Braunschweig, at Helmstedt and Budenstedt near the East German border, Lower Oligocene reworked phosphate pebbles occur in a glauconitic clayey and sandy matrix. They are derived from phosphate nodules of subjacent formations, especially those of early Lower Oligocene age. The P_2O_5 content of the pebbles reaches 25 per cent in beds which are less than 1 m thick.[13]

Near Uelsen, 10 km NW of Nordhorn in the westernmost part of Lower Saxony, clayey and sandy glauconitic beds, Middle Oligocene in age, contain phosphate pebbles and nodules.[14-16] The latter are thought to have been formed in situ, but the pebbles are derived from older marine Oligocene sediments. The P_2O_5 content reaches 15 per cent, with 50 per cent SiO_2 and 12 per cent CaO. The average thickness of individual beds is less than 0.6 m. In addition the beds have been disturbed by glacial action.

In the Hattingen district of the southern Ruhr area[17] the Upper Carboniferous (Namurian C, Dreckbank seam) contains syngenetic ferruginous phosphate nodules with up to 30 per cent P_2O_5. These occurrences, up to only 10 cm thick, were mined on a very small scale near Hagen and Dortmund before 1906.

There are other occurrences of phosphate rock in the Federal Republic of Germany but none of these is of potential economic interest. Probably the most interesting and best known are the apatite-bearing carbonatites which cover an area of about 1 km^2 in the central part of the Kaiserstuhl, a volcanic complex of Miocene age, situated within the Upper Rhine Graben, 15 km north-west of Freiburg in Baden-Württemberg.[18,19] Most of the Kaiserstuhl complex is covered by loess to a maximum depth of 30 m. Apatite is a common accessory mineral in the carbonatites, the largest intrusion of which is a dyke about 10 m wide near Schelingen. Thinner carbonatite dykes are also numerous elsewhere. The rocks may contain up to 10 per cent apatite by volume, equivalent to about 4 per cent P_2O_5. The apatite occurrence is of academic interest only.

In the Oberpfälzer and Bayerischen Wald of northeastern Bavaria primary and secondary phosphate minerals occur in feldspar pegmatites in a Carboniferous granite intrusion.[20,21] The Lower and Middle Jurassic sediments of Swabia in south-western Germany[22] contain phosphatic nodules scattered in argillaceous beds.

Their P_2O_5 content reaches 32 per cent. Similar material collected from Mesozoic and Tertiary sediments north of the Harz mountains contain up to 25.6 per cent P_2O_5.[23]

Petrography and chemical composition

The best known phosphate occurrences in the Federal Republic of Germany are the Lahn deposits which consist of an earthy, clayey or sandy ferruginous matrix with concretionary phosphorite nodules. The nodule to matrix ratio is about 1:4. These deposits have a cellular or porous structure, in general, but the richest types have a botryoidal structure and are mainly white or pale yellow in colour. The P_2O_5 content of the nodules averages 30 per cent, ranging from 23 to 32 per cent, while the matrix is usually much less phosphatic fluctuating considerably from a few per cent to 23 per cent P_2O_5. The deposits are characterised by the presence, as at Staffel, of a white to light green, semi-transparent crystalline incrustation, which comprises a carbonate variety of fluorapatite known as staffelite.

Recent chemical analyses of Lahn phosphate are not available but the material shipped to the United Kningdom generally contained more than 65 per cent BPL (29.9 per cent P_2O_5). However, much of the phosphate rock produced was also of lower grade, ranging down to about 52 per cent BPL (23.9 per cent P_2O_5) and up to 18 per cent combined iron oxide and alumina. Selected partial chemical analyses of these cargoes are as follows:

	Per cent			
P_2O_5	35.73	33.49	31.08	26.67
CaO	44.22	45.52	42.53	38.27
SiO_2	3.48	5.21	8.20	21.61
Al_2O_3	5.34 (a)	9.49 (b)	15.77 (c)	8.65 (b)
Fe_2O_3	7.38	3.97	-	3.41
H_2O	1.78	2.32	2.42	1.39
Total	97.93 (d)	100.00	100.00	100.00

(a) includes F

(b) includes F and CO_2

(c) includes Fe_2O_3 and CO_2

(d) total inclues 0.42 per cent MgO

Source: Jnl Roy. Agric. Soc., 1875, Ser.2, Vol. II, pp. 415-416.

The conglomeratic deposits mined at Broistedt near Braunschweig comprise nodules of limonitic iron ore ranging from 0.2 mm to about 4 cm in diameter, together with phosphate nodules of comparable size, set in a carbonate-clay matrix. Between 30 and 50 per cent of the matrix is detrital carbonate material, notably fragments of foraminifera and echinoderms in the 0.2 mm to 1.0 mm size range. The remainder consists of clay, generally composed of montmorillonite. Other minerals present in variable amounts include opal, quartz, kaolinite, glauconite and pyrite. The iron ore, as mined, has the following range in composition:

	Per cent
Fe	26-29
P	1.4-1.5
Mn	0.35-0.5
CaO	16-18
SiO_2	14-17
Al_2O_3	4-5

Source: Stahlwerke Peine - Salzgitter A.G., 1970.

RESOURCES

No up-to-date assessment of the phosphate rock resources of the Federal Republic of Germany is available. Estimates published for the Lahn[1] and Amberg[8] deposits are given below:

	Quantity Tonnes	Grade Per cent P_2O_5	Resource Category
Lahn (Hessen)	750,000	20+	Probable
Amberg (Bavaria)	30,000+	20 (average)	Probable

There are, in addition, substantial quantities of phosphate contained in the large resources of phosphatic iron ores, but these are only recoverable in the form of basic slag. A notable exception are the Broistedt-Lengede limonitic iron ore deposits from which phosphate nodules are obtained during the iron-ore beneficiation process. These deposits are part of the Upper Cretaceous Peine-Ilsede ore field, which is notable for having relatively high concentrations of phosphate.

PRODUCTION

There is no production of phosphate rock in the Federal Republic of Germany, with the exception of some output obtained as a by-product of iron ore mining. Production in 1976 was about 85,000 tonnes of rock averaging 18 per cent P_2O_5. It is stated that production will cease by the end of 1977 because of the exhaustion of the iron ores reserves.

Significant tonnages of Lahn phosphate of various grades were produced from 1867 for use domestically and for shipment to the United Kingdom until the advent of other sources of supply, chiefly Florida, and also the introduction of basic slag, led to a decline in production in 1893. Output reached a maximum of 53,807 tonnes in 1884, and for the period 1885 and 1891 annual production of between 30,000 and 41,000 tonnes was maintained. The deposits were reached by a series of small shafts. Water from the Lahn River was used to wash the clay from the phosphate which was then conveyed to Oberlahnstein at the confluence of the Lahn and the Rhine to await further shipments. Mining after 1893 was sporadic and on a much reduced scale, chiefly during and shortly after, the First World War to provide raw material for Rhenania phosphate manufacture. The deposits were worked at numerous localities, but mainly at Staffel, Dehrn and Steeden near Limburg. The annual production from 1917 to 1921 varied between 14,000 tonnes and 22,500 tonnes containing about 30 per cent P_2O_5 or less. In 1937 production again reached 3,314 tonnes and during the Second World War deposits yielded some 50 to 100 tonnes a month. Mining ceased in 1945.

In Bavaria, the Amberg deposits were worked for several years on a very small scale for use in fertiliser manufacture at Furth, Augsburg, Moosbach north-east of Amberg, and Heufeld. Output in 1920 reached 600 tonnes a month. In the 1930s the phosphate was used as an additive in iron smelting for the production of basic slag and from 1948-68 the iron ore deposit yielded 3,300 tonnes of phosphate. Mining ceased in 1968.[24]

Middle Oligocene beds near Uelsen in the westernmost part of Lower Saxony were worked from 1918 to 1920, production amounting to 2,000 tonnes per year. Very thin beds were worked on a very small scale before 1906 in the southern Ruhr area between Hagen and Dortmund, in the Hattingen district.

In Lower Saxony, east of Braunschweig, phosphate beds at Helmstedt and Budenstedt were worked underground in the 1880s and during the First World War, but the operations were soon abandoned because of high production costs. Beds were also worked near Bad Harzburg and Oker to the south-east of Goslar.

REFERENCES ON THE FEDERAL REPUBLIC OF GERMANY

1 Les Réserves Mondiales en Phosphates, Vol.1, 497 pp. (Madrid: Graficas Reunidas, S.A., 1928.) Die Phosphatlagerstätten Deutschlands. W. Kegel, pp.86-92. (In German)

2 Phosphat-Nitrat. O. Stutzer and W.Wetzel. 390 pp. (Berlin: Verlag von Gebrüder Borntraeger, 1932.) (In German) The phosphate deposits of Germany, pp. 87-102.

3 On the deposits of phosphate of lime recently discovered in Nassau, north Germany. D.C. Davies. Geol. Mag., 1868, Vol.5, No.48, pp. 262-266.

4 Die Phosphorit Lagerstätten in Nassau. W. Kegel. Jb. preuss. geol. Landesanst. Berg Akad., 1922, Vol.4-3 pp.197-240. (In German)

5 Der Bergbau und Hüttenbetrieb im Lahn-und Dillgebiet und in Oberhessen. G. Einecke and J. Ferfer. 778 pp. (Wetzlar: Berg- und Hütten-mannischer Verein, 1932.) (In German)

6 Beschreibüngen rheinland-pfälzischer Bergamts-bezirke. Vol.2. 282 pp., (Bad Ems: Bergamtsbezirk Dietz. - Obergamt Rheinland-Pfalz, 1968. (In German)

7 Geologische Notiz über das Vorkommen von Phosphat und Pechkole bei Amberg (Oberpfälz). W. Klüpfel. Z. prakt.Geol., 1921, Vol.29, Pt.4, pp. 49-53. (In German)

8 Untersuchungen über die Amberger Phosphatlagerstätten. K.D. Jensen.Sber. phys.-med. Soz. Erlangen, 1939, Vol.71, pp.285-337. (In German)

9 Mineralogische, petrographische, fazielle und chemische Untersuchung der Brauneisen - Trümmererzlagerstätten von Lengede-Broistedt. P. Ferling. Geol. Jb., 1958, Vol. 75, pp. 555-590. (In German)

10 Die Eisenerzgrube Lengede - Broistedt. 78 pp. (Peine: Stahlwerke Peine - Salzgitter AG, 1970.) (In German)

11 The Iron Ore Deposits of Europe and Adjacent Areas. Vol.1. Edited by A. Zitzmann. 418 pp. (Hannover: Bundesanstalt für Geowissenschaften und Rohstoffe, 1977.) The iron ore deposits of the Federal Republic of Germany. Chr. Neumann-Redlin, M.W. Walther and A. Zitzmann, pp. 165-186.

12 Die Phosphoritknollen des Leipziger Mitteloligozäns und die norddeutschen Phosphoritzonen. H. Credner. Abh. sächs. Akad. Wiss. 1895, Vol.22, Pt.1. 47 pp. (In German)

13 Genesis und Verwerkbarkeit der kretazischen und tertiären Phosphorit-Vorkommen im nördlichen Harzvorland. K. Fricke. 65 pp. (Göttingen: University of Göttingen, 1941.)(Unpublished dissertation.) (In German)

14 Tertiär und Diluvium im westfälisch-holländischen Grenzgebiet. A. Bentz. Z. dt. geol. Ges., 1930, Vol.82, p. 291-317. (In German)

15 Das Oligozän in der Uelsener Stauchzone (Emsland). C. Dietz and H. Hiltermann. Z.dt.geol.Ges., 1960, Vol.102, pp. 76-82. (In German)

16 Zur Geologie des Emslandes. H. Boigk, C. Dietz, H.-O. Grahle, K. Hoffmann, W. Hollstein, F. Kühne, W. Richter, H. Schneckloth, R. Wager, H. Hiltermann and W. von zur Mühlen. Beih.geol.Jb. 1960, Pt. 37. 418 pp. (In German).Phosphorit, pp. 367-369.

17 Uber das Vorkommen von Phosphaten in den Steinkohleflözen des Ruhrkarbons. G. Schöne-Warnfeld. Cr. 5e Congr.int. Strat.Geol. Carbon Paris 1963, 1964, Vol. 2, pp.771-774. (In German)

18 Beiträge zur Petrographie des Kaiserstuhls. Teil VI: Die Karbonatite. Teil VII: Zur Petrogenese des Kaiserstuhls. W. Wimmenauer. Neues Jb.Miner.Abh. 1963, Vol.99, Pt.3, pp. 231-276. (In German)

19 The eruptive rocks and carbonatites of the Kaiserstuhl, Germany, W. Wimmenauer. Pp. 183-204, in Carbonatites. Edited by O. F. Tuttle and J. Gittins. 591 pp. (London: John Wiley & Sons Ltd., 1966.)

20 Phosphatführende Pegmatite des Oberpfälzer und Bayrischen Waldes. H. Laubmann, and H. Steinmetz. *Z. Kristallogr.* 1920, Vol.55, Pt. 5 and 6, pp. 523-586. (In German)

21 Der Quarzpegmatit von Pleystein und seine Phosphatparagenese. H. Wilk. In "Zur Mineralogie und Geologie der Oberpfalz". *Aufschluss*, 1967, Vol. 16, Sonderh., pp. 199-212. (In German)

22 Konkretionäre Phosphatanreicherungen in Südwestdeutschland. W. Kass. 75 pp. (Stuttgart: Geologisch-mineralogischesinstitut der Technische Hochschule, 1954.) (In German)

23 Uber die Anreicherung von Uran und Thorium in Phosphoriten und Bonebeds des nördlichen Harzvorlands. L. Benda. *Geol. Jb.*, 1963, Vol.80, pp.313-347, (In German. English abstract, p. 313)

24 Die Kreide-Eisenerzlagerstätten in Nordost-Bayern. H. Gudden. *Geol. Jb.* Ser. D, 1975, No.10, pp. 201-238. In German

TABLE 17. FRANCE : IMPORTS OF PHOSPHATE ROCK, 1972-1976

TONNES

Country	1972	1973	1974	1975	1976
CALCIUM PHOSPHATE					
Algeria	73,935	74,573	115,756	67,265	150,967
Belgium-Luxembourg	3,093	-	7,144	6,548	4,173
Germany, Federal Republic	-	9,121	-	10,821	1,175
Israel	62,500	78,583	128,748	54,744	100,815
Jordan				43,650	80,850
Mexico		5,080			
Morocco	1,515,117	1,640,525	2,326,990	1,295,228	1,227,738
Netherlands				11,831	11,997
Niger		23,220			
Senegal	390,660	523,701	596,541	368,794	422,895
Soviet Union			11,168		
Spanish Sahara	24,917	19,467			
Togo	1,013,592	1,158,198	1,480,152	715,342	867,166
Tunisia	438,702	488,560	577,534	243,354	472,554
Turkey			1,250		
USA	522,861	668,229	327,955	485,326	604,763
Other countries	3,194	3,646	337	957	11,253
Total	4,048,571	4,692,903	5,573,575	3,303,860	3,956,346
(1000 Francs) C.i.f. Value	315,635	397,666	1,521,832	1,003,405	906,488

Source: Statistiques du Commerce Extérieur de la France - Importations : Exportations.

4.4. FRANCE

Phosphate rock is widely distributed in France, occurring in sediments of Cambrian, Ordovician, Silurian, Devonian, Carboniferous, Jurassic and Cretaceous age in widely varying terrain.[1-5] Most of the post-Devonian occurrences were exploited during the 19th and early part of the 20th centuries, the most important being those of Lower Carboniferous (Dinantian) age in the Pyrénées and the Montagne Noire and, particularly, the Upper Cretaceous (Senonian) chalk in the northern part of the Paris Basin. It is estimated that around 16 million tonnes of phosphatic chalk have been extracted since 1886. The Dinantian phosphate beds were again worked on a limited scale during the Second World War.

Deposits continue to be worked in the Paris Basin in Somme Department near Nurlu and in Aisne Department near Hallencourt, producing annually between 20,000 and 30,000 tonnes of low grade phosphatic chalk which after crushing and drying is sold for direct application to the soil as fertiliser. The marketable product contains 10 per cent P_2O_5, this grade being maintained by blending with imported higher grade phosphate rock.

Phosphate rock requirements for the large French fertiliser industry are met almost entirely by imports which have been obtained for many years chiefly from North Africa, notably Morocco (Table 17). Small quantities of aluminium phosphate are also imported (Table 18).

SOUTHERN FRANCE

Phosphate rock of Lower Carboniferous (Dinantian) age occurs in the north Pyrenean fault zone and in the Mouthoumet massif and Montagne Noire areas of Southern France. Phosphate nodules are

TABLE 18. FRANCE : IMPORTS OF PHOSPHATE ROCK, 1972-1976

TONNES

Country	1972	1973	1974	1975	1976
ALUMINIUM PHOSPHATE					
Algeria				2,960	
Germany, Federal Republic	2,322				
Israel				11,975	
Morocco		67,360	85,543	2,600	800
Senegal	106,765	130,122	194,086	115,664	107,014
Togo		11,418			
Tunisia		17,158	7,370		3,450
USA				10,335	
Other Countries		246	29	515	2,346
Total	109,087	226,304	287,028	144,049	113,610
(1000 Francs) C.i.f. Value	8,005	20,052	67,638	28,430	12,728

Source: Statistiques du Commerce Exterieur de la France - Importations : Exportations.

widely distributed in Albian to Aptian (Lower Cretaceous) sediments in the extreme southeastern part of the country and minor occurrences of aluminium phosphate have been reported from caves developed in Tertiary limestone in Hérault Department southwest of Montpellier.

Cambrian phosphate in the Monts de Lacaune

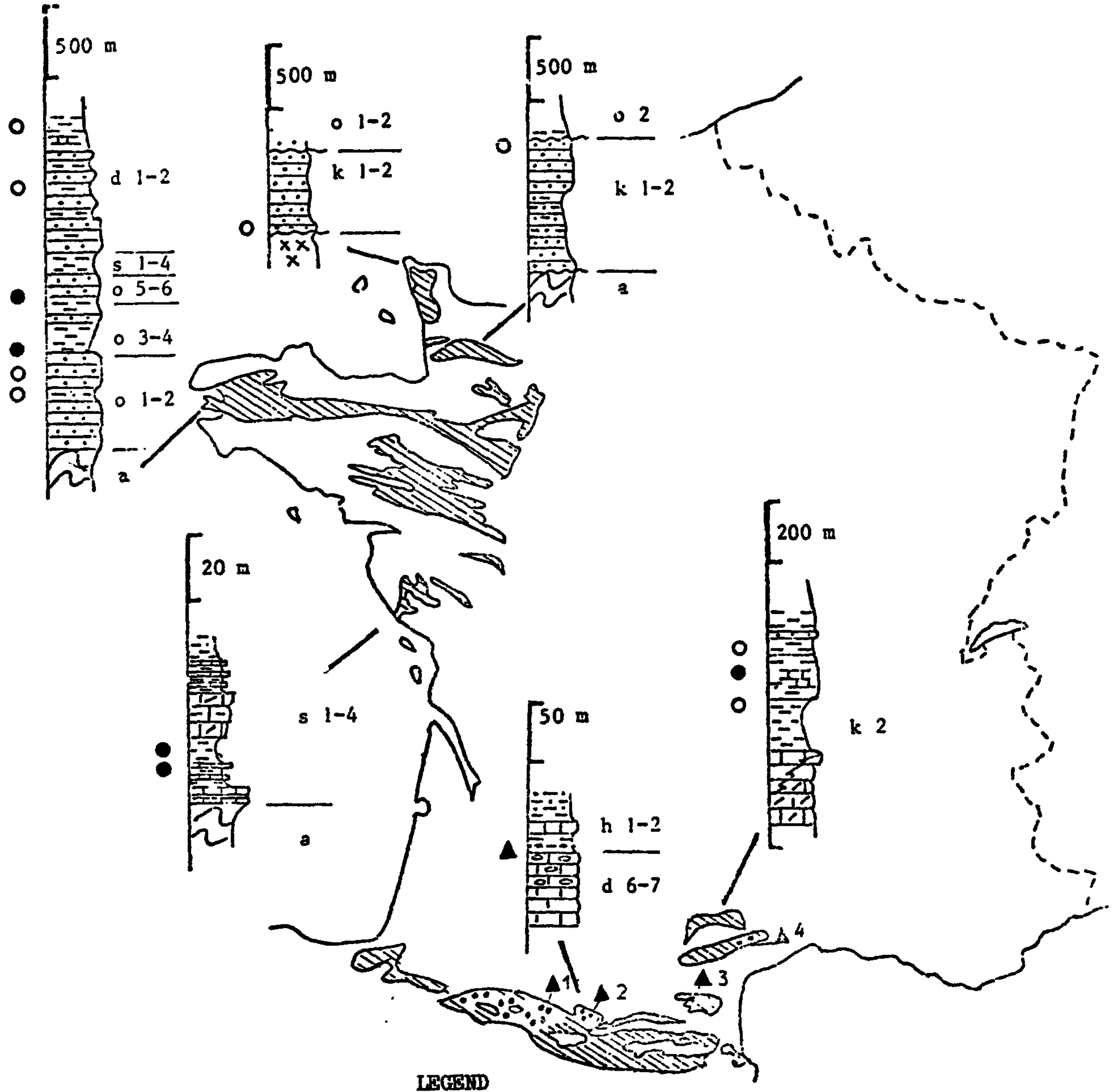
The Monts de Lacaune are situated between the Montagne Noire and the Permian sedimentary basin of Sainte Affrique, to the south of the Massif Central. There phosphate is widely distributed in the structurally complex Lower Cambrian succession in the form of fossil debris and scattered nodules and, locally, as 2 beds totalling 6 to 10 m in thickness and containing 5 to 20 per cent P_2O_5. The better bed is represented by a sandy, feldspathic and micaceous phosphatic limestone, which is about 70 cm thick and contains more than 12 per cent P_2O_5. The complicated geological structure has prevented the precise lateral extent of the occurrence from being established.

Dinantian phosphate in the Pyrénées and Montagne Noire

A prominent chert bed containing phosphate nodules which was formerly worked, particularly during the 1920s, occurs at the base of Dinantian (Lower Carboniferous) sediments in the Pyrenean mountain chain,[6-8] and can be traced almost continuously from Tarascon sur Ariège, Ariège Department, westwards through Cierp and Argelès to Accous (Basses Pyrénées) in the Gave d'Aspe south of Oloron, a total distance of about 190 km (Fig 13).

For many years considered to be discordant on Devonian limestones and dolomites, the Dinantian in the Pyrénées and Montagne Noire region is now known to have succeeded the older rocks without a break in sedimentation. It consists of a basal sequence of

PALAEOZOIC



LEGEND

Phosphate horizons

○: Minor occurrence
●: Important occurrence
▲: Accumulation
• : Deposits

Deposits cited in the text

▲1: Cierp
▲2: Las Cabesses, Labastide de Sérou, Castelnau-Durban
▲3: Alet
▲4: St Nazaire de Ladarez, Cabrières

Stratigraphy

h 1.2 : Dinantian
d 6.7 : U. Devonian
d 1.2 : L. Devonian
s 1.4 : Silurian
o 5.6 : U. Ordovician
o 3.4 : M. Ordovician
o 1.2 : L. Ordovician
k 1.2 : Cambrian
a : Brioverian

Dominant facies

▨ Nodular limestone
▨ Dolomitic limestone
▨ Limestone
▨ Shales with phosphate nodules
▨ Shales
▨ Sandstone

Fig. 13 : Distribution of Palaeozoic phosphate occurrences in France.
(Source : B.R.G.M.)

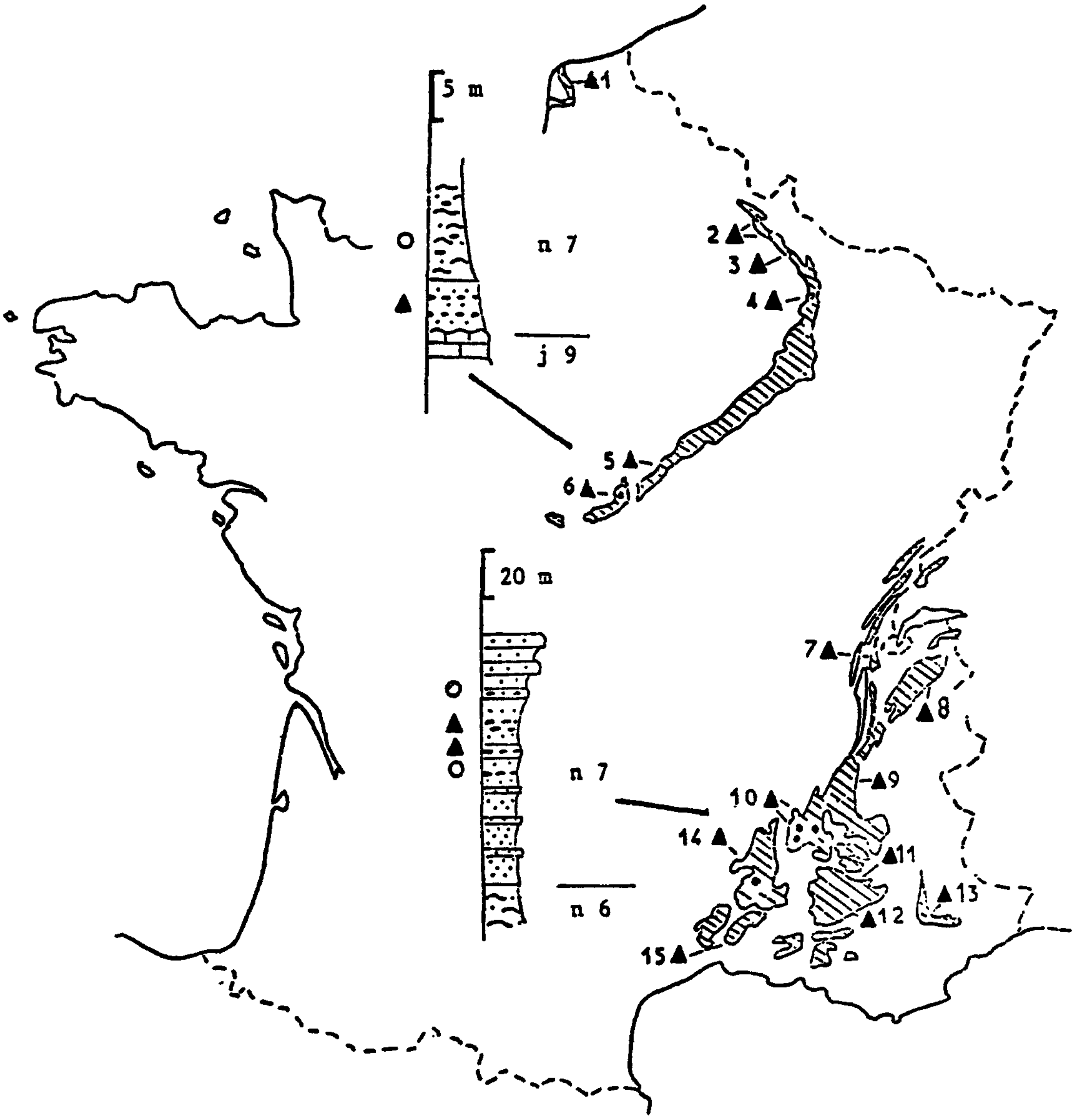
dolomitic limestone followed by black shales and radiolarian cherts (lydites) containing phosphate nodules. These cherts are rich in organic matter which gives them their characteristic black colour. They are generally well bedded, individual layers being some centimetres or decimetres thick. The grey to black nodules, which both they and the associated shales contain, are flattened parallel to the bedding, with their long axes several centimetres but sometimes exceeding 10 cm in length.

The thickness of the phosphate-bearing formation is variable. This was previously reported to range from a few metres to more than 10 m, with a maximum of 20 m, but a recent re-examination of the occurrences has shown that the most phosphatic part of the succession, situated at the base of the chert-black shale sequence is generally only several decimetres to 2 m thick, the greater apparent thickness locally (as for example, at St Nazàire de Ladare[2] east of Roquebrun in the Orb Valley) being attributed to the complicated geological structure of the area. Recent assays have indicated an average grade of 6 to 10 per cent for the entire rock and around 25 per cent for the phosphate nodules. Although these assays are only partial and locally higher phosphate contents have been observed in both the rock and the phosphate nodules, the results nevertheless contrast sharply with the maxima of 20 to 25 per cent and 30 to 35 per cent P_2O_5 respectively, reported in older literature.

Albian-Aptian occurrences of southeastern France

Beds of phosphate nodules are relatively widespread in the Albian-Aptian sediments of southeastern France,[9,10] notably to the east of the Rhône Valley between Marseille and Lake Geneva (Fig 14).

LOWER CRETACEOUS



LEGEND

Phosphate horizons

O: Minor occurrence
▲: Accumulation
•: Deposits

Groups of deposits cited in the text

▲1: Boulonnais
▲2: Ardennes
▲3: Meuse
▲4: Marne
▲5: Yonne
▲6: Cher
▲7: Ain
▲8: Hte Saône
▲9: Vercors
▲10: Diois
▲11: Drôme
▲12: Vaucluse
▲13: Alpes de Hte Prov.
▲14: Ardèche
▲15: Gard

Stratigraphy

n 7 : Albian
n 6 : Aptian
j 9 : U.Jurassic

Dominant facies

Limestone
Marl
Sand and Sandstone
Phosphate Nodules

Fig 14 Distribution of Lower Cretaceous phosphate occurrences in France (Source: B.R.G.M.)

Ain and Haute Savoie Departments: glauconitic sandstones contain 3 fossiliferous beds, with phosphate nodules containing 15 to 27 per cent P_2O_5, reaching a total thickness of 1.8 m. A thin phosphate bed occurs also in **Isère Department**, in the Vercors area to the east of Valence.

Drôme Department: phosphate nodule beds are associated with coarse green glauconitic sands of Lower Albian to Upper Aptian age. The beds are arranged en echelon with a very variable thickness, together totalling 6 to 12 m. The nodules are reported to contain 17 to 25 per cent P_2O_5, recent investigations at individual localities have given the following results:

Clansayes - St Paul-Trois-Châteaux (south of Montélimar) : 1 m of sand with 3 per cent P_2O_5, containing nodules with 30 per cent P_2O_5. A 0.3 m bed of coarse sandstone contains 10.5 per cent P_2O_5.

Allant: A 0.5 m bed of coarse sandstone contains 6 per cent P_2O_5. The phosphate nodules show 19 per cent P_2O_5. Coarse sandstone 0.4 to 0.8 m thick contains 11 per cent P_2O_5; the nodules 18 per cent P_2O_5.

Roche St Secret: A clayey, glauconitic sandstone with 7 per cent P_2O_5, of which a thickness of 0.8 m contains 10 per cent P_2O_5, with nodules containing around 25 per cent P_2O_5. This formation is lenticular, however, becoming reduced in thickness laterally.

Vaucluse and Alpes de Haute Provence Departments:
Phosphate nodule beds of Albian age have been exploited in these departments, where there is also a bed of oolitic phosphate rock in Aptian sediments.

Quercy Deposits (Departments of Lot, Aveyron, Tarn et Garonne and Tarn)

Numerous phosphate deposits associated with the Jurassic Haut Quercy limestones, which provide striking plateau landscapes ('causses') along the south-western margin of the Central Massif were worked from about 1870 until the end of the century. The deposits are situated roughly between the towns of Cahors, Figeac, Gaillac and Montauban.

At least 250 deposits of concretionary phosphate and phosphatic clay are known, partly filling karstic cavities which developed in Jurassic limestones during Eocene times. The cavities have a variable form, some exceeding 100 m in width, while others occur as vein-like masses. Concretionary phosphate in the clay contains 26 to 38 per cent P_2O_5, while the clay itself contains on average generally less than a few per cent P_2O_5. The best known are the Quercy deposits found on Causse de Limogne, west of Villefranche, where they were discovered in 1865. Most of the phosphate is dense, hard and yellow to brown in colour, with higher grade material, which contains 32.7 per cent P_2O_5 or more, frequently grey, opal-like in appearance and exhibiting a greasy lustre and conchoidal fracture.

Aluminium phosphate in Hérault Department

Aluminium phosphate occurs in caves developed in Tertiary limestones at Grotte de Minerve near Fauzan in Cesse Valley, where resources are estimated at possibly 120,000 tonnes or more. At a depth of 3 m to 4 m, compact concretionary, yellowish clay ranging from 3 to 9 m in thickness is reported to contain up to 28 per cent P_2O_5.

CENTRAL AND NORTHEASTERN FRANCE

The most important sources of phosphate in this region (fig. 15) have been beds of reworked phosphatic nodules found dispersed in the Sinemurian-Pliensbachian (Liassic) limestones which outcrop extensively between the southern Ardennes and the Morvan Mountains. Similar beds, but of Albian age, were also formerly worked in this region.

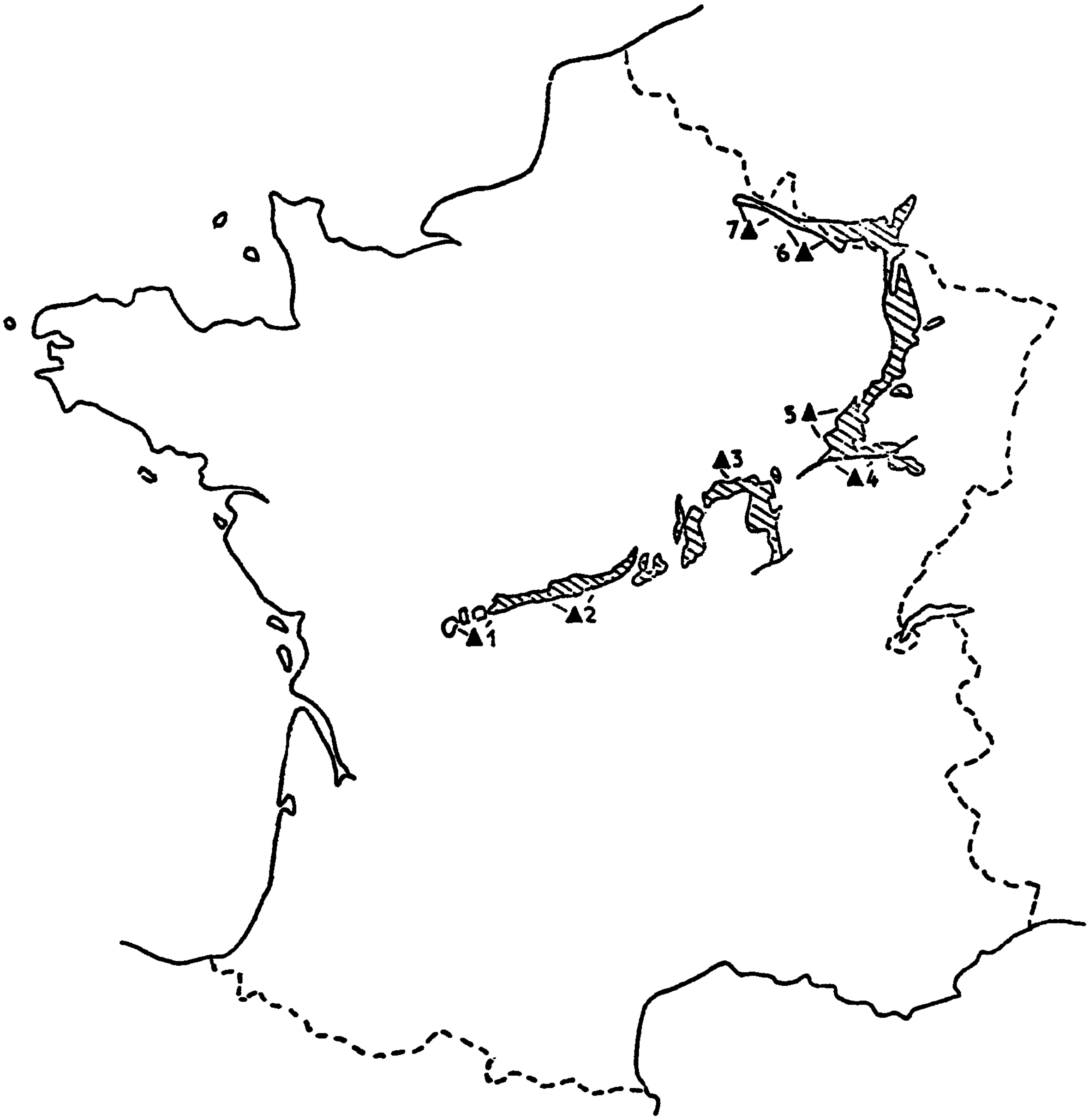
Lias

Numerous deposits were actively exploited in a number of Departments towards the end of the 19th century, the beds with the highest concentrations of nodules ranging from only 5 to 40 cm in thickness. One bed is said to have comprised 30 to 60 per cent nodules containing generally between 27 and 30 per cent P_2O_5, except in the Ardennes and Meuse areas where the nodules have been reported to contain between 10 and 21 per cent P_2O_5.

Albian

In the Ardennes, Meuse and Marne Departments, 3 principal nodule beds occur in the greensands of Lower and Middle Albian age and at the base of an Upper Albian 'gaize' facies, which is represented by a porous, partly decalcified calcareous sandstone. The nodules, which are unevenly distributed, contain between 4 and 23 per cent P_2O_5 where they occur in greensand and between 18 and 30 per cent P_2O_5 at the base of the 'gaize' formation. Individual beds range from 5 to 25 cm in thickness. In Yonne Department, a fossiliferous nodule bed 15 to 30 cm thick lies in Upper Albian sediments.

LIAS



LEGEND

Groups of deposits cited in the text

- ▲1 : Indre
- ▲2 : Cher
- ▲3 : Auxois
- ▲4 : Haute-Saône
- ▲5 : Vosges
- ▲6 : Meuse
- ▲7 : Ardennes

Fig 15 Distribution of Liassic phosphate occurrences in France (Source: B.R.G.M.)

NORTHERN FRANCE

Phosphate deposits are found at many localities in Cretaceous sedimentary rocks which underly large areas of the northern and eastern parts of the Paris Basin (Figs 14 & 16). These deposits particularly those of Senonian age, have provided the bulk of the phosphate rock produced in France since exploitation began in 1886.

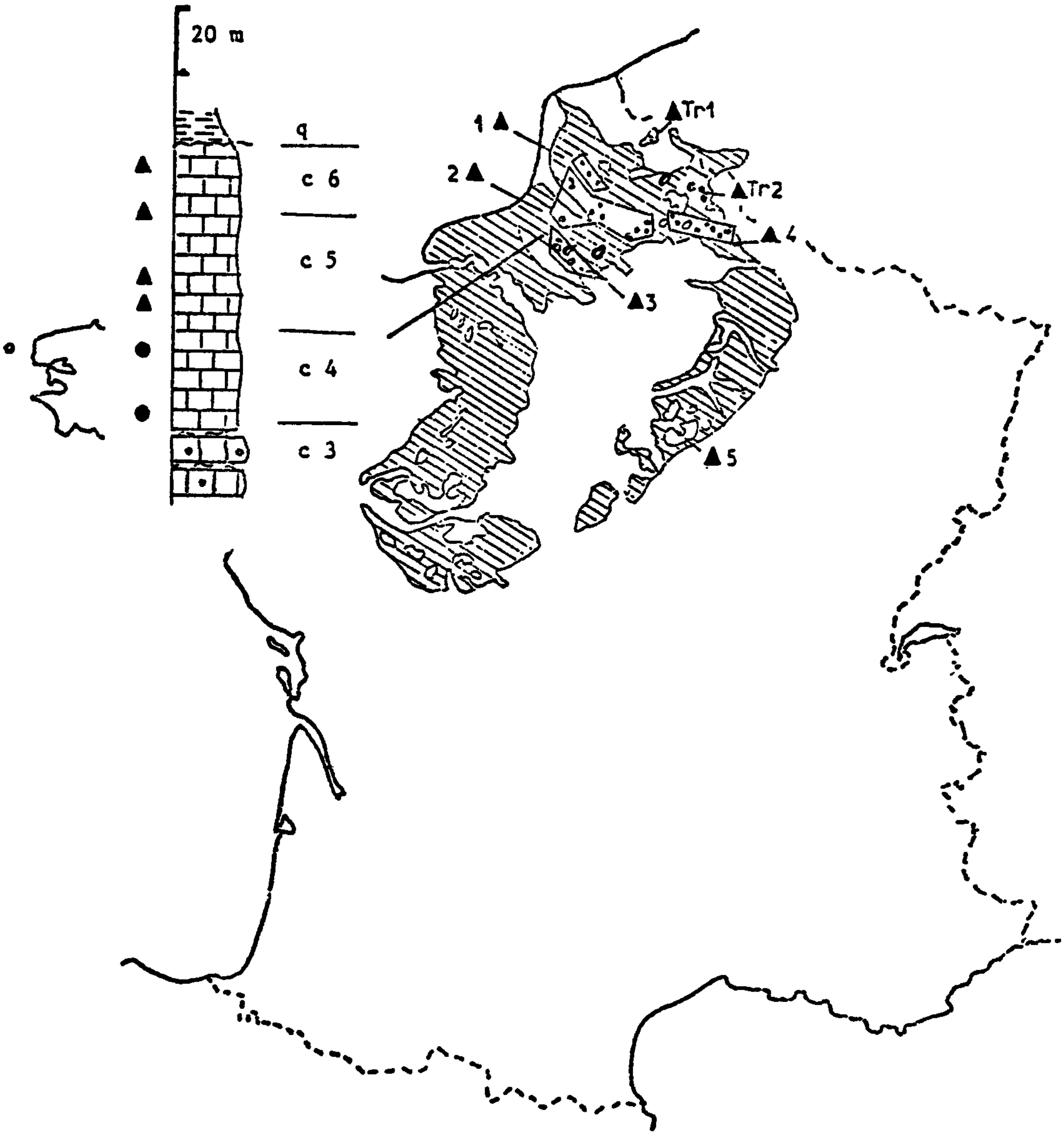
Albian

Small phosphatic nodules, occurring chiefly in glauconitic sandstones were worked extensively during the latter half of the 19th century. In the Boulonnais area (Pas-de-Calais Department) the Albian includes 6 phosphate horizons, of which the most important and the only one to have been worked systematically, lies in the Lower Albian. It has a maximum thickness of 15 cm and consists of a clayey, sandy, glauconitic rock which comprises 30 to 40 per cent nodules averaging 20 per cent P_2O_5.

In the Departments of Ardennes, Meuse and Marne, there may be 3 principal nodule-bearing beds in the Lower and Middle Albian greensands and at the base of the Upper Albian gaize formation. The nodules in the greensand contain 4 to 23 per cent P_2O_5, those at the base of the gaize showing 18 to 30 per cent P_2O_5. They are irregularly distributed in beds ranging from 5 to 25 cm in thickness, containing 500 to 1,400 tonnes of nodules per hectare.

A fossiliferous phosphate nodule bed of Upper Albian age and 15 to 30 cm thick was worked in Yonne Department. A similar bed occurs in Cher Department.

UPPER CRETACEOUS



LEGEND

Phosphate horizons

●: Important occurrence
▲: Accumulation
•: Deposits

Groups of deposits cited in the text

Turonian
▲Tr 1 : Lille Region
▲Tr 2 : Cambrésis

Senonian
▲1 : Pas de Calais
▲2 : Somme
▲3 : Oise
▲4 : Aisne
▲5 : Yonne

Stratigraphy

q : Quaternary
c 4.6 : Senonian
c 6 : Campanian
c 5 : Santonian
c 4 : Coniacian
c 3 : Turonian

Dominant facies

▤ Loam
▦ White chalk
▦ Grey chalk
▤ Marl

Fig 16 Distribution of Upper Cretaceous phosphate occurrences in France
(Source: B.R.G.M.)

Cenomanian

The base of the Cenomanian in Artois, Pas-de-Calais Department, presents a highly glauconitic, sandy or marly facies. There are local concentrations of phosphate nodules, the most important forming a bed 40 cm thick formerly worked at Pernes. The nodules in this bed contain 20 to 23 per cent P_2O_5; the gangue shows 12 per cent P_2O_5.

Turonian

The phosphate nodules in the Turonian succession near Lille,[17] known as 'tun', are of particular historical interest since they were the first occurrences of phosphate rock to have been discovered in France in 1853. Highly calcareous in composition, the nodules contain between 8 and 15 per cent P_2O_5. Nodules of this type have been found also in Sarthe and Drôme Departments.

The Turonian of the Paris Basin also marks the first appearance in the Cretaceous succession of phosphate in the form of phosphatic chalk instead of phosphate nodules. The chalk, which is also glauconitic, generally contains less than 5 per cent P_2O_5, but the bed was nevertheless worked in the Cambrésis[18] area where secondary decalcification has resulted in the formation of pockets of a phosphatic glauconitic sand with 10 to 25 per cent P_2O_5.

Senonian phosphatic chalk

The Senonian chalk formation of the Paris Basin [13-16] includes 6 phosphate-bearing horizons extending from the base of the Coniacian to the Campanian, but of those which have been worked commercially, two horizons of Santonian age and one of Lower Campanian age are the most important, in contrast to the phosphatic chalk formation formerly worked in Belgium in the Mons Basin which is of Maastrichtian age.

Three types of Senonian phosphate rock can be recognised in the Paris Basin:

1 Residual pockets of phosphatic sand which have resulted from the secondary decalcification of the phosphatic chalk. These karstic pockets are funnel shaped and are generally developed at the intersection of joint systems. Their volume is therefore limited, ranging from 1,000 to 10,000 m^3, but such deposits are nevertheless of high grade, containing 24 to 29 per cent P_2O_5. Being easily recognisable at the surface, the pockets have been actively studied geologically and worked commercially. Further discoveries of phosphate rock of this type seem unlikely.

2 Large lens shaped beds of phosphatic chalk occupying from several hectares to 1 km^2. The beds are of low grade, containing 5 to 20 per cent P_2O_5, and their thickness, which can reach many metres, is irregular.

3 Soft phosphate rock filling pre-existing submarine erosional channels. Deposits of this type have variable form being up to 5 to 20 m wide and many kilometres in length and with a thickness of 5 to 15 m. Their phosphate content generally exceeds that of the phosphatic chalk ranging from 12 to 20 per cent decreasing in amount from the base of the bed upwards and also varying laterally.

NORTHWESTERN FRANCE

Palaeozoic phosphate

The presence of phosphate horizons in the Palaeozoic sediments of the Armorican Massif has been established only comparatively recently. The occurrences have not been fully investigated but 2 horizons have been found in the Lower Cambrian, 8 in Lower Ordovician, one or more in Silurian and 3 in Devonian sediments. The Carboniferous rocks also seem to be weakly phosphatic.

Where these have been investigated, individual beds are of negligible thickness and of low grade. The most significant are in the Vendée region where a Silurian sequence about 12 m thick contains beds which are 15 cm thick and contain from 10 to 15 per cent P_2O_5. Also present are beds 30 cm thick with 6 to 12 per cent P_2O_5. However, the geological structure of the area is very complex.

RESOURCES

Although phosphate rock is known to be widely distributed in France, up-to-date estimates of resources are not available. For this reason a more systematic inventory of national phosphate resources was begun by the Bureau de Recherches Géologiques et Minières in 1975 and is continuing.

Previous estimates give an approximate indication of the resources likely to exist in specific areas. In most cases, these occur as phosphate nodule beds which are too thin to be of potential interest as a source of phosphate on a commercial scale. In 1926, probable resources were estimated[2] at about 139.5 million tonnes of rock containing from 9 to 32 per cent P_2O_5, of which 115 million tonnes with 6-7 per cent P_2O_5 were located in Lower Carboniferous sediments in the Ariège and Hautes Pyrénées departments of southern France. Resources of Cretaceous phosphatic chalk with 9 to 18 per cent P_2O_5 were placed at nearly 6.9 million tonnes in Somme, Oise, Aisne and Yonne but those occurrences with 5 to 9 per cent P_2O_5 were not evaluated.

More than 24 million tonnes of phosphate nodules in Albian sediments, almost all in Meuse Department, were estimated in 1896 to be exploitable; similarly, the quantity of nodules in Cenomanian rocks in the Artois region of Pas-de-Calais was believed to exceed 500,000 tonnes. In that year also, reserves in the Quercy deposits were placed at more than 1 million tonnes.

The full extent of the phosphate-bearing Cretaceous formations of the Paris Basin has not yet been fully determined, but total resources are probably considerable in view of the large areas underlain by rocks of this age. Exploratory work has been undertaken recently by BRGM on behalf of a number of private companies, the results of which are not yet available although it is understood that none of the known deposits has been found to be of sufficient size to support large-scale mining operations.

At least 80 deposits of Senonian (Upper Cretaceous) phosphatic chalk have been worked in the past in the Paris Basin. In terms of size, they may be grouped into 3 categories, namely, small deposits containing up to 100,000 tonnes of phosphate rock, medium-sized deposits with 100,000 to 1 million tonnes and large deposits ranging from 1 to 5 million tonnes. Many of the deposits are still incompletely known, while their variable dimensions and irregular distribution in the sedimentary sequence have also complicated the assessment of resources.

Bearing in mind the data currently available on the stratigraphy and structure of Upper Cretaceous rocks of the Paris Basin, it would appear that new discoveries of phosphatic chalk still remain to be made.

PRODUCTION

Since the Second World War a number of deposits of phosphatic chalk have been in production in the Somme, Oise and Aisne Departments, in the northern part of the Paris Basin. These include deposits worked at present near Nurlu, 14 km east of Peronne, in Somme Department, and near Hallencourt in Aisne Department, as well as those worked until 1963 near Beauval by the Compagnie Française de Phosphates. The Nurlu and Hallencourt deposits, which are worked on behalf of Compagnie Française de l'Azote (COFAZ), together produce around 20,000 to 30,000 tonnes annually, the rock being ground, dried, screened and blended with imported phosphate rock to provide a marketable product averaging 10 per cent P_2O_5.

A substantial quantity of phosphate rock of various kinds and geological ages has been produced in the past, the principal years of production being during the latter part of the 19th and early part of the 20th centuries. Subsequent output dwindled rapidly with the depletion in reserves of higher grades of phosphate rock and the development of the North African deposits. These economic factors have also been largely responsible for preventing the complete exploitation of deposits worked in parts of eastern and southern France, including the Quercy deposits north-east of Montauban which yielded significant tonnages for export to the United Kingdom. By far the most important sources of supply have been the Senonian phosphatic chalk of the Paris Basin and the Dinantian phosphate beds of the Pyrénées and the Montagne Noire.

Senonian phosphatic chalk of the Paris Basin

It is estimated that the Senonian chalk formations of the Paris Basin have yielded around 16 million tonnes of phosphatic chalk since these were first worked in 1886. Mining was initially based on the higher grade pockets of residual phosphatic sand, and during 1895-1900 on the 'channel' or 'trough' type of deposits, before the bedded lower grade phosphatic chalk formations began to be worked some 15 years later. The higher grade deposits provided an estimated 8 to 9 million tonnes, the phosphatic chalk some 7 to 8 million tonnes. Most of the deposits were worked by openpit methods, galleries being developed from the base of the quarries when the thickness of the overburden made openpit mining prohibitive, as at Hallencourt.

Deposits of Senonian phosphatic chalk were actively exploited from 1886 until the First World War, production from the Somme Department exceeding 300,000 tonnes in 1899, while Pas-de-Calais and Aisne each produced more than 100,000 tonnes. After the war, mining was on a greatly reduced scale and annual production did not exceed 20,000 tonnes. Total output in individual Departments since mining began is as follows:

Somme : 9 million tonnes
Pas-de-Calais : 3 million tonnes
Aisne : 2.5 million tonnes
Oise : 1 million tonnes
Yonne : 0.6 million tonnes

Dinantian of the Pyrénées and Montagne Noire

Numerous deposits were worked in southern France at the beginning of the present century, particularly in the Departements of Ariège (Las Cabesses, La Bastide de Serou, Castelnau Durban), Haute Garonne (Cierp), Aude (Alet) and Hérault (Cabrières, St Nazaire de Ladarez) and an extensive network of underground galleries is still visible. The Cierp deposits were the most important, providing about 140,000 tonnes from 1900 to 1930, with a maximum annual output of 45,000 tonnes in 1928. There were attempts to revive commercial interest during the Second World War but, as far as is known, no further mining took place. The hard nodules were calcined to facilitate fine grinding to provide a phosphate for direct application to the soil, but the product, which contained about 32 per cent P_2O_5 did not find a ready market as fertiliser because of its black colour and somewhat graphitic texture.

Intermittent production by openpit methods took place from the St Nazaire de Ladarez deposits and continued until 1930, with a total annual output generally around 1,000 tonnes and,exceptionally, 4,200 tonnes.

Lias

Beds of phosphate nodules were extensively worked at the end of the 19th century, notably in the Auxois district, where there were more then 40 sites of production, in the Departments of Cher, Indre (10 sites), Haute Saône (15 sites) Ardennes and Meuse (7 sites) and in the Lorraine district of Vosges Department (15 sites). A total of less than 100,000 tonnes of phosphate rock was produced.

Albian to Aptian

Albian to Aptian nodule beds were actively exploited in the Paris Basin and in southeastern France during the 19th and, occasionally, in the present century in the following areas:

In the Boulonnais (Pas-de-Calais), production began in 1860, becoming more important after 1873, to achieve a regular annual output of around 20,000 tonnes. It is estimated that 300,000 tonnes had already been extracted by 1889 from more than 20 sites. Beds of the same age were worked in Ardennes, Meuse and Marne Departments. Deposits in Ardennes and Meuse yielded 21,000 tonnes and 42,000 tonnes respectively, in 1896, but produced only 7000 to 9000 and 12,000 tonnes in 1900. Production from each of these two Departments amounted to 2000 tonnes in 1913, 3000 tonnes in 1920, 1,250 tonnes in 1931 and 250 tonnes in 1932. It is estimated that the total quantity of phosphate nodules extracted in this region during the 1886-1913 period exceeded 800,000 tonnes and probably approached 1,000,000 tonnes. The Meuse Department was the principal producing area, yielding a maximum of 68,000 tonnes in 1886 from 332 quarries.

In Yonne Department, a bed discovered in 1875 was worked intermittently until 1909, annual production varying between 50 and 1,000 tonnes. By means of hand sorting and screening a product containing 14 to 18 per cent P_2O_5 was obtained. A similar bed was worked in Cher Department, particularly between 1871 and 1906 in trenches 2 to 3 m deep. Annual production apparently never reached 3,000 tonnes of rock which averaged 17 per cent P_2O_5 and was used for direct application to the soil.

In southeastern France production in Ain and Haute Savoie Departments began in 1871 and continued intermittenly until 1900, the Bellegarde (Ain) and Seyssel (Haute Savoie) areas producing annually 2,000 to 4,500 and 5,000 to 7,000 tonnes respectively. The output was used in superphosphate manufacture. The principal centres of production in Drôme Department were situated at Allan, Roche St. Secret, Clansayes, St Paul-Trois-Châteaux which, between 1886 and 1895 yielded annually an average of 7,000 to 8,000 tonnes of nodules for superphosphate manufacture. A still smaller output was obtained from the Vaucluse and Alpes de Haute Provence Departments, reaching at best only some 1,200 tonnes a year. Small quantities of Albian phosphate rock were produced also in Ardèche Department (Saut de l'Egue, La Roussette) and in Gard Department (Salazac, La Capelle Masmolène, St. Julien de Peyrolas).

Cenomanian

In the Artois area of Pas-de-Calais Department, the nodule bed at the base of the Cenomanian was worked at numerous sites, the most important being that at Pernes, where a bed 0.4 m thick was quarried to a depth of 7 m, then worked in adits to 20 m and finally mined through shafts. Production began in 1877 and apparently continued until 1913. Annual output reached 20,000 tonnes towards 1890. Samples of several cargoes shipped to the United Kingdom as Boulogne phosphate showed on analysis a range of 18.6 to 22.6 per cent P_2O_5, 30.5 to 33.9 per cent CaO, 16.9 to 20.0 per cent combined iron dioxide and alumina, 23.4 to 27.5 per cent siliceous matter and 2.9 to 4.0 per cent water.

Turonian

Deposits developed in the Turonian chalk were worked from 1889 until 1931 in the Cambrésis area of the Paris Basin, where there were 9 main extraction sites, situated near Cateau and Cambrai.

Quercy

The well-known Quercy deposits situated in southern France in the Lot, Aveyron, Tarn et Garonne and Tarn Departments, were discovered in 1865. They were worked between 1870 and 1900 and particularly between 1875 and 1880, when production reached nearly 50,000 tonnes per annum. Part of the output, averaging 32 to 35 per cent P_2O_5 was exported to the United Kingdom where it was known as French or Bordeaux phosphate. Similar deposits have been worked in Gard Department.

REFERENCES ON FRANCE

The contribution on France is based essentially on internal notes and reports prepared by the Bureau de Recherches Géologiques et Minières, Orléans. Where appropriate, however, reference is made in the text to the following published literature:

1 Les phosphates de chaux sédimentaires de France. L. Cayeux. Etud. Gîtes minér. Fr., 1939, Vol.1, 312 pp. (In French)

2 Les Réserves Mondiales en Phosphates, Vol.1. 497 pp. (Madrid: Graficas Reunidas, S.A., 1928.) Phosphates de France. E. Raguin, pp. 197-215. (In French)

3 Die Phosphatlagerstätten Frankreichs. O. Tietze. Z. prakt. Geol., 1907, Vol. 15, pp. 117-124. (In German)

4 Les phosphates de chaux métropolitains. V. Charrin. Chim. Ind., 1942, Vol.48, No.4, pp. 243-244. (In French)

5 La concessibilité des gisements de phosphate de chaux et son influence possible sur leur exploitation. V. Charrin. Génie civ., 1961, Vol. 138, No.22, pp.481-484. (In French)

6 Mémoire sur les phosphates noirs des Pyrénées. D. Levat. Annls Mines, Paris, N.S., 1899, Mém., Vol.15, pp. 5-100, (In French)

7 Observations sur quelques gisements du Carbonifère des Pyrénées. G. Dolépine, G. Dubar and J.W. Laverdière. C.r. somm.Séanc.Soc. géol.Fr., 1929, No. 16, pp.236-238. (In French)

8 Sur le problème de l'existence d'une lacune sous les lydiennes à nodules phosphatés du Dinantien des Pyrénées et de la Montagne Noire (France, Espagne). F. Boyer, S. Krylatov and D. Stoppel. Geol. Jb., Ser. B, 1974, Pt.9. 60 pp. (In French. English abstract, pp. 6-7)

9 Les nodules phosphatés de l'Albo-Aptien de la Bâtie (Basses-Alpes). Leur signification paléo-océanographique. P. Cotillon. C.r. somm. Séanc. Soc. géol. Fr., 1962, Pt.3, pp.82-83. (In French)

10 Sur les phosphorites du Bas-Languedoc. B. Gèze. Bull.Soc. géol.Fr., Sér. 5, 1940, Vol.10, pp. 87-94. (In French)

11 Contribution à la connaissance des phosphorites de Quercy. B.Gèze. Bull.Soc.géol.Fr., Sér. 5, 1938, Vol.8, pp.123-146. (In French)

12 Présence d'uranium dans les nodules phosphatés du Lias moyen des Vosges. G. Jurain. C.r. hebd. Séanc. Acad.Sci.Paris, 1956, Vol.242, No.13, pp. 1748-1750. (In French)

13 Les craies phosphatées en France. Beauval (1886-1963). G. Negre. Indust.chim.Phosph., 1963, Vol.50, No.555, pp.383-386. (In French)

14 Les craies phosphatées en France. 2.Saint-Martin-du-Tertre, près de Sens (1912-1934). G. Negre. Indust.chim.Phosph., 1964,Vol.51, No. 564, pp. 248-249, (In French)

15 La craie phosphatée en Picardie-Perspectives d'avenir de la prospection. P. Broquet. Annls Sci. Univ. Besançon, Sér.3, 1973, Pt.20, pp.143-152. (In French)

16 Discontinuités et condensations stratigraphiques dans la craie phosphatée de Picardie (Nord du Bassin de Paris). C. Monciardini and P. Broquet. Bull.Bur.Rech.géol.min., Sér.2, 1974, Sect.2, No.1, p. 35. (In French. Abstract only)

17 Les craies de Sainghin-en-Melantois (Nord): faunes du passage turono - coniacien, tectonique cisaillante, physico-chimie. J.P. Colbeaux, P. Debrabant, L. Leplat and F. Robaszynski. Ann.Soc.géol.Nord, 1975, Vol.95, No.1, pp. 17-35. (In French)

18 Géologie du Cambrésis et des régions environnantes. P. Celet. Ann.Soc.géol.Nord, 1969, Vol.89, No.1, pp.91-102. Phosphatic chalk, pp.95-96. (In French)

4.5. IRISH REPUBLIC

Sedimentary phosphate rock of Upper Carboniferous (Namurian) age occurs in Western Ireland north of Ennistimon, in north-west County Clare[1,2]. Known deposits are small and of comparatively low grade, containing 20 to 25 per cent P_2O_5, but were worked on a limited scale between 1927 and 1939 and more particularly during the Second World War when overseas suppliers were restricted. Total production amounted to about 105,000 tonnes. There has been no production of phosphate rock in the Irish Republic since 1947 and requirements are met entirely by imports, notably from Morocco (Table 19). In recent years there has been renewed interest in the County Clare deposits as a possible commercial source of phosphate rock and a drilling programme carried out by the Geological Survey of Ireland in 1976-1977 has indicated a resource of about 3 million tonnes.

TABLE 19. IRISH REPUBLIC: IMPORTS OF PHOSPHATE ROCK, 1972-1976.

			Tonnes		
Country	1972	1973	1974	1975	1976
Morocco	297,148	430,113	433,407	143,454	142,335
Other countries	23	4,076	7,808	2,799	45,957
Total	297,171	434,189	441,215	146,253	188,292
c.i.f. value(1000£)	1,976	3,392	10,158	3,892	5,503

Source: Trade Statistics of Ireland

GEOLOGY

Phosphate rock occurs in a condensed sequence of basal Namurian strata, the Clare Shales Formation, in north-west County Clare near the northern margin of a Namurian sedimentary basin[3]. The axis of the basin approximates to the present line of the Shannon estuary. South of the Shannon estuary the Namurian sedimentary basin extends into County Limerick, its southern margin lying near the town of Ballagh, approximately 27 km south of the Shannon (Fig 17). The Clare Shale rests disconformably on Carboniferous Limestone of predominantly Viséan age and geological studies[4] have indicated that this disconformity is a major non-sequence, with a general progressive stratigraphical overlap of older by younger formations northwards from the Shannon. North of the Shannon, the formations have a very low regional dip to the south or south-west modified by broad folds plunging gently to the WSW. Major faulting is not evident. The striking difference in lithology between the black Clare Shale and the Carboniferous Limestone has greatly facilitated mapping of the boundary but over large tracts the solid geology is obscured by peat bogs or glacial deposits.

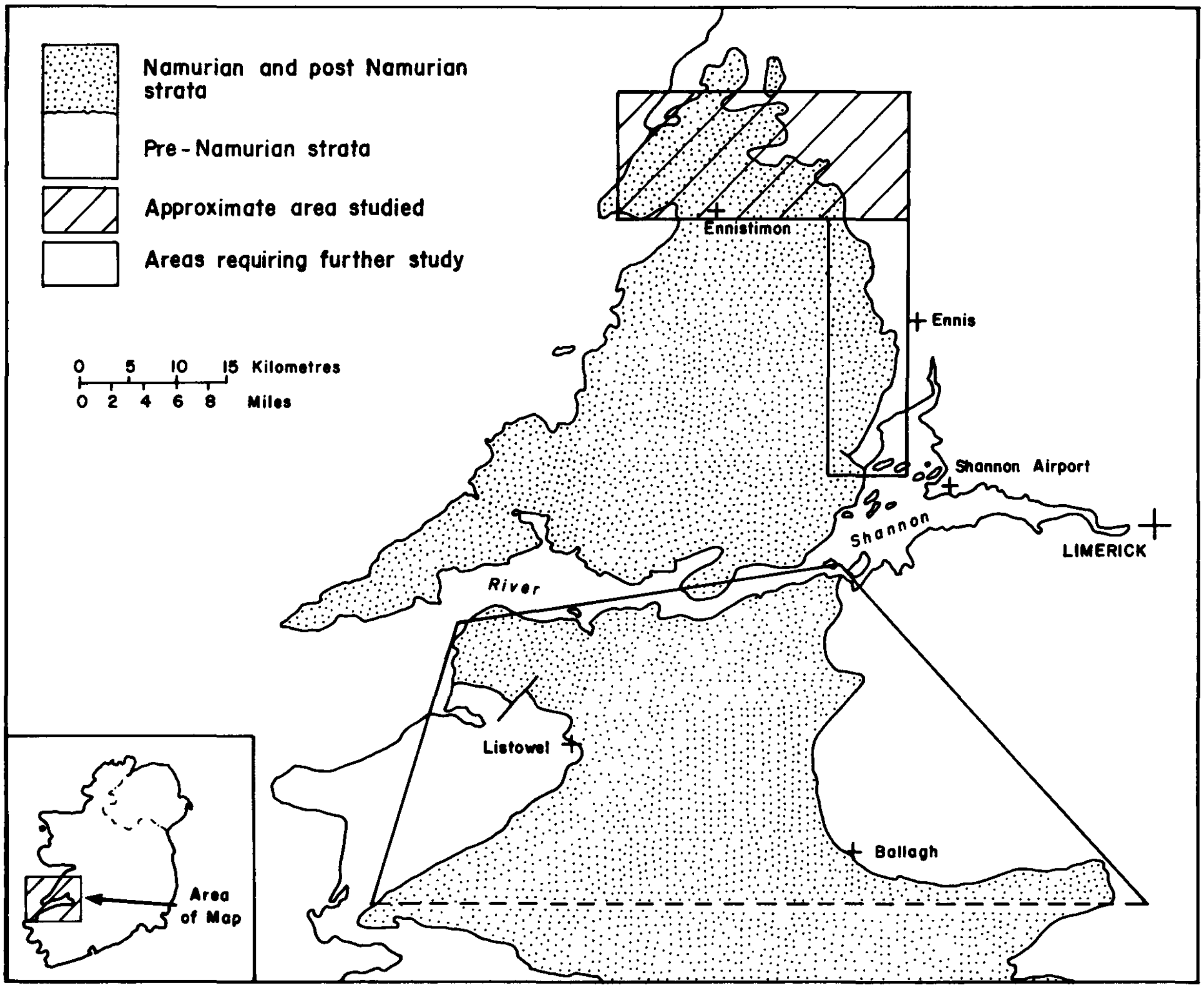


Fig 17 Distribution of Namurian strata in County Clare and County Limerick (Based on the Geological Map of Ireland. 1 : 750 000, 1962.)

South of the Shannon a similar condensed sequence of basal Namurian sediments occurs, although the structure is more complex. The phosphate potential of the Clare Shales in this region has not been investigated, although initial field surveys by the Geological Survey of Ireland have shown the sediments, as well as those outcropping along the edges of Upper Carboniferous outliers in the east Midlands, are sufficiently radioactive to merit more detailed study. The thickness of the black Clare Shale facies in County Clare and County Limerick varies considerably, from about 18 m to nearly 490 m.

In north-west County Clare the main phosphate occurrences lie in the area to the south-west and south-east of Lisdoonvarna from Fisherstreet in the west to Noughaval in the east. Recent investigations by the Geological Survey of Ireland have led to a provisional three-fold subdivision of the phosphate-bearing Clare Shale Formation in north-west County Clare[5]. The generalised stratigraphical succession is shown in Fig 18, although attenuation and overstep of the basal units in a northwesterly direction complicates this general succession.

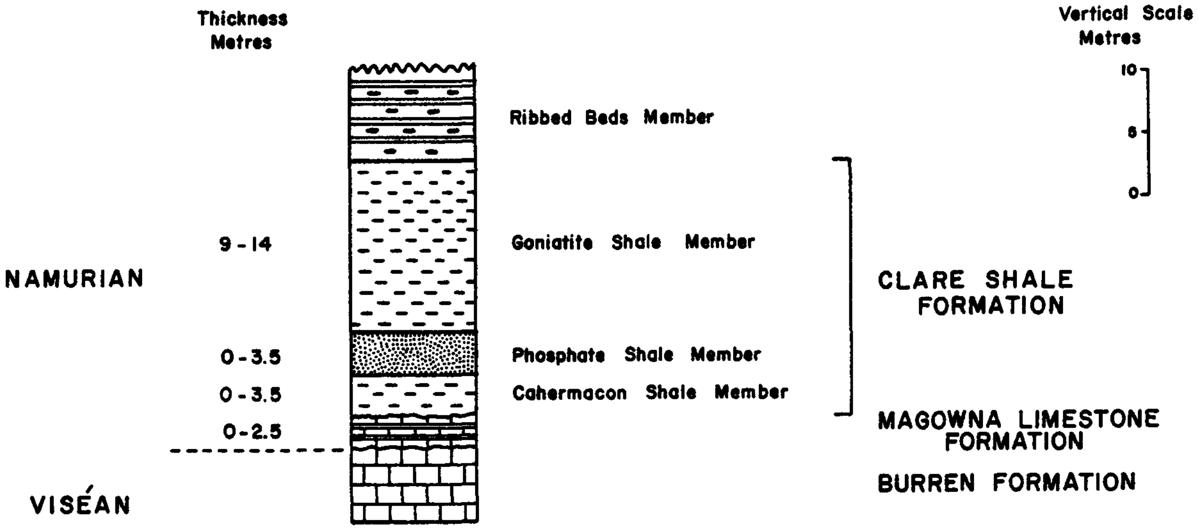


Fig 18 Generalised stratigraphical succession in north-west County Clare

Phosphate rock has been encountered in all the boreholes drilled on behalf of the Survey[6] within an area of approximately 160 km^2 (Fig 19) in the lowermost 6 m of the Clare Shale, occurring as beds and nodules up to 1 m thick at the junction of the Phosphate Shale and the Cahermacon Shale, and as nodules in the Cahermacon Shale. Thin beds of chert and limestone are also occasionally present. Individual phosphate beds are generally unfossiliferous, but the interbedded black shales, which are usually also slightly phosphatic, sometimes contain coaly plant fragments and marine fossils, notably goniatites. Conodont assemblages have also been identified.

Three north-south trending elliptical lenses have been delineated within the Phosphate Shale Member in areas where phosphate rock forms a bed more than 0.3 m in thickness. These are the Doolin and Noughaval deposits, which were worked during the Second World War, and the 'Ballykeel-Cohy' lenses north of Kilfenora identified during the 1976-1977 drilling programme. The 'Ballykeel-Cohy' lenses are together some 2.5 km in length and up to 1.3 km wide. Overburden thicknesses range from 30 m to 36 m. At Doolin the phosphate bed reaches a maximum thickness of 1.4 m. Thicknesses of up to 1 m and 0.7 m have been recorded from the Noughaval and Ballykeel deposits respectively. Close to the lenses the phosphate bed is rapidly reduced to some 5 cm to 10 cm in thickness. North of the Lisdoonvarna area the Phosphate Shale and the basal 2 m of the Goniatite Shale condense into a basal conglomeratic, pyritic phosphatic bed 5 cm to 15 cm thick which lies directly on successively lower beds of Carboniferous Limestone.

Other members of the Clare Shale Formation are only weakly phosphatic. For example, seams of phosphatic nodules and beds of pyritic, siliceous phosphate rock rarely more than a few centimetres thick, occur in the Cahermacon Shale. The uppermost Carboniferous Limestone, the Magowna Limestone, is also partially phosphatic, with burrows in the upper surface of the limestone filled with phosphatic limestone. Available analyses show up to 2.5 per cent P_2O_5. North of Lisdoonvarna the Magowna Limestone, which is 2.5 m thick and of Namurian age, is progressively overstepped so that Clare Shales rest directly on the Viséan limestones of the Burren Formation.

MINERALOGY AND CHEMISTRY

Clare phosphate rock is dark grey to black, very hard and compact and generally exhibits a granular texture, the phosphate occurring as euhedral and irregular grains of fluorapatite and collophane with an average grain size of between 100 and 200 microns. Conodonts may make up to 20 per cent of the rock. Brown collophane contains numerous inclusions of pyrite and silica and occasional apatite grains, while the apatite itself is essentially free of inclusions but may be also associated with carbonaceous matter. Both are set in a carbonate, mainly calcite, matrix, although dolomite and ankerite are sometimes also present. Chemical analysis of a bulk sample of rock obtained from the Doolin deposits during the 1974-1977 exploration programme indicates the following mineralogical composition:[7]

		Percentage
Apatite		60.5
Calcite		20.7
Silica		13.1
Pyrite		2.4
Carbon		1.5
	Total	98.2

Silica appears to occur principally as cryptocrystalline secondary quartz associated with collophane, although some detrital quartz

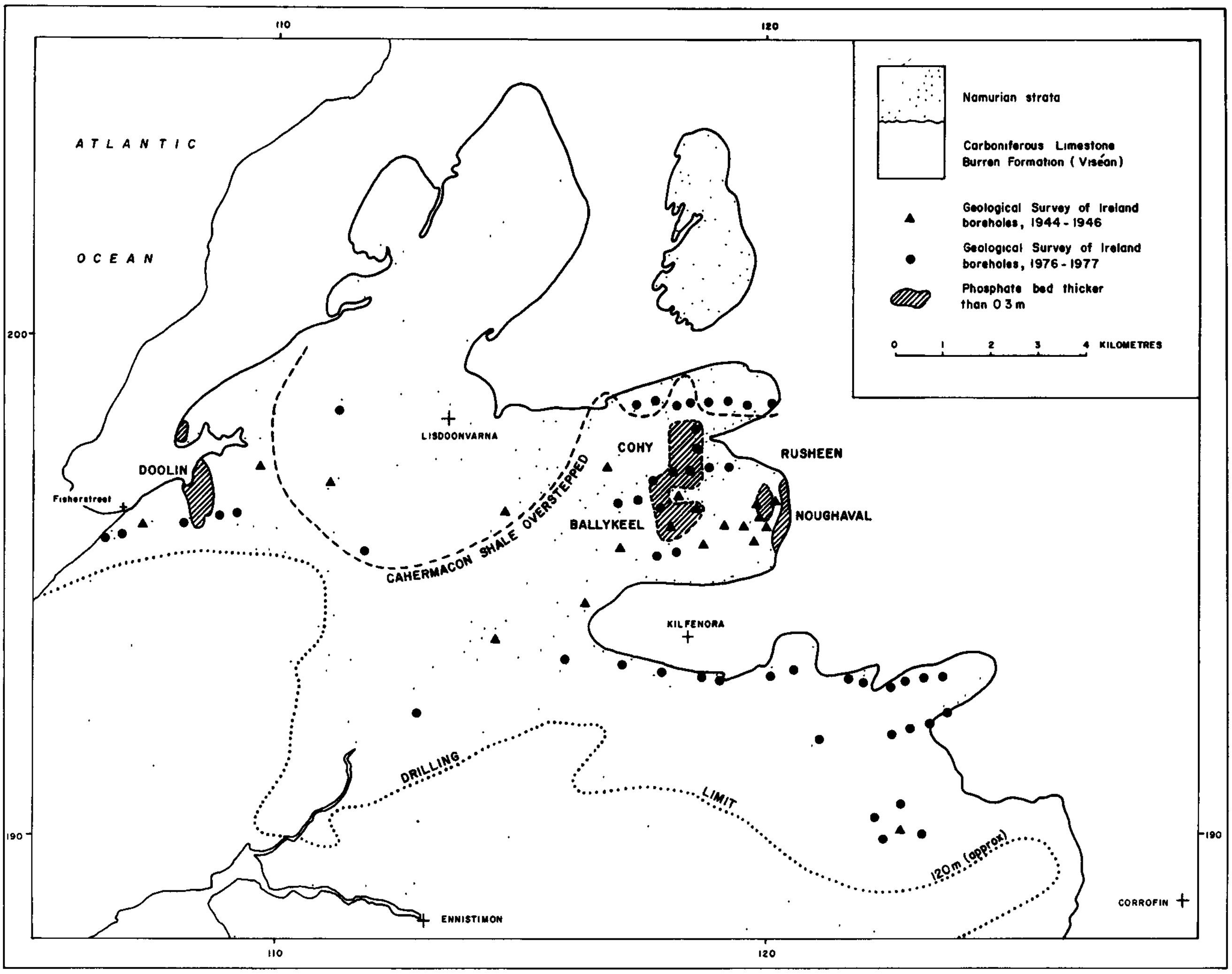


Fig 19 Location of exploration boreholes and phosphate deposits in north-west County Clare. (Reproduced by permission of the Geological Survey of Ireland.)

grains have also been recorded. Occasionally, almost complete rings of silica encapsulate the collophane.

Chemical analyses of samples of Clare phosphate rock are shown in Table 20. These show a P_2O_5 content ranging from about 18.1 to nearly 27.9 per cent, the samples being characterised also by high contents of SiO_2 and objectionable amounts of combined iron and aluminium oxides. An analysis of the rock by X-ray fluorescence gave a uranium content of 0.0135 per cent, a comparatively high figure for a sedimentary marine apatite. The Institute of Industrial Research and Standards, Dublin, have carried out preliminary investigations on the mineralogy and chemistry of phosphate rock obtained during the 1974-1975 exploratory work by the Geological Survey of Ireland.

TABLE 20. PARTIAL CHEMICAL ANALYSES OF COUNTY CLARE PHOSPHATE ROCK

	Doolin			Per cent		Noughaval		
	1	2	3	4(a)	5	6	7	8
P_2O_5	27.88	21.50	23.53	25.1	24.75	18.11	22.71	21.64
CaO	44.02	42.72	45.00	41.2	38.86	32.26	34.72	44.72
SiO_2	17.74	7.00	10.75	13.1	18.66	29.66	27.24	11.36
CO_2	4.44	17.00	11.75	8.3	1.32	0.92	3.92	18.14
Fe_2O_3	2.8	3.05	2.16$^{(b)}$	2.9	5.87	9.40	5.27	3.23$^{(c)}$
Al_2O_3		1.00	1.05	n.d.				0.36
F	1.80	0.80	2.00	3.5	2.24	4.33	1.83	2.36
MgO	1.01	n.d.	n.d.	0.8	0.94	0.58	1.59	0.29

(a) Bulk sample

n.d. = not determined

(b) FeS_2 recalculated as Fe_2O_3

(c) FeO recalculated as Fe_2O_3

Sources:

Miner. Resour. Mem. geol. Surv. Ire., 1951, pp.44-45. (Samples 1,2,5,6 and 7)

Scient. Proc. R. Dubl. Soc., 1942. Vol.22, No.48, p.468.[8] (Sample 3)

Wartime Pamphl. geol. Surv. Eng Wales, 1942, No.8, Pt.4, p.20. Analysis by Building Research Station, Garston, Hertfordshire. (Sample 8)

Unpublished report of the Institute of Industrial Research and Standards, (1977), p.4. Analysis by Nitrigin Eireann Teoranta, Dublin. (Sample 4)

PRODUCTION

The County Clare phosphate deposits were worked in a small way between 1927 and 1939 and on a larger scale during the Second World War when overseas supplies were cut off. The output, which was insufficient to meet demand, was carried in trucks to the railway at Ennistimon, a distance of about 11 km, for distribution to various fertiliser works, including those situated at Dublin, Cork and Galway, for use in superphosphate manufacture.The phosphate mining operations became uneconomic because of increased overburden thicknesses and difficulties of extraction and production ceased in 1947.

Initial production was by the Clare Phosphate Company but in 1942 the state sponsored Mineral Development Company (Mianrai Teoranta) also commenced operations both at Doolin and at Noughaval and continued mining phosphate rock until 1947. During the period 1933-1947 total production was some 105,000 tonnes of which the Doolin and Noughaval lenses produced some 76,000 and 29,000 tonnes, respectively. Almost all production took place between 1940 and 1947. The Noughaval lens was worked entirely by opencast methods but at Doolin both opencast and adit mining was practised, total production from the mine, which operated a longwall system of working, was 40,800 tonnes in the period 1942 to 1947. Maximum annual output from both deposits reached about 22,000 tonnes in 1945.

RESOURCES

A resource of 1.25 million tonnes of phosphate rock containing 20 to 25 per cent P_2O_5 and in beds over 0.3 m in thickness were outlined in northwest County Clare as a result of exploration carried out by the Geological Survey of Ireland between 1944 and 1946, when 22 boreholes were drilled in the region. However, more extensive investigations by the Geological Survey in 1974-1977 involving the drilling of an additional 55 boreholes, has indicated a resource of the order of about 3 million tonnes of phosphate rock of comparable grade and thickness.[6] The area investigated covers approximately 160 km^2. There are, in addition, resources of associated phosphatic shale in the Clare Shale Formation and of phosphatic limestone in the Carboniferous Limestone, which have not been estimated but are probably of very low grade.

Drilling towards the south, particularly in the western part of the area investigated,was limited by increasing overburden thickness, but prospects still exist in this direction where the Clare Shale thickens as the Namurian basin is entered. In addition, further areas worthy of investigation occur along the poorly exposed Clare Shale outcrops on the eastern margin of the basin, and also on its southern margin, south of the Shannon estuary (Fig 17). Basal Namurian sediments in the east Midlands are also worth investigating and high gamma readings have been noted in water boreholes in this area.

The limited resources of phosphate rock established to date in County Clare are unlikely to attract commercial interest except for small-scale production of ground rock for local direct application to the soil.

UTILIZATION

Considerable difficulties have been experienced in the possible use of Clare phosphate rock as a fertiliser raw material in view of the poor P_2O_5 availability of the products obtained.[9] For example an experimental batch of single superphosphate produced in 1933 from Doolin rock assayed approximately 14 per cent P_2O_5, of which only 80 per cent was water soluble. Low yields (70-75 per cent water soluble P_2O_5) also characterised the single superphosphate produced during the Second World War. A protective coating of silica on the phosphate particles in the rock was believed to be primarily responsible in preventing or hindering complete interaction with sulphuric acid. However, more or less complete digestion of the rock was obtained with both nitric and hydrochloric acids, and, in addition, the fine grinding that was thought necessary to liberate the phosphate from the silica proved to have only a marginal beneficial effect on the solubility of Clare phosphate rock.

Work carried out by the Institute of Industrial Research and Standards, Dublin, on phosphate rock obtained during the 1976-1977 drilling programme in County Clare, has shown that the observed frequency of silica sheathing is low and that, instead, the presence of carbonaceous material in the rock and the formation of calcium sulphate during the initial reaction with sulphuric acid could be possible causes of low or poor reactivity.[7] Problems were also encountered in the use of Clare phosphate rock in the preparation of phosphoric acid by the Nissan process. The product acid was of low grade, containing only about 20 per cent P_2O_5, and unless vigorous agitation was employed a proportion of the rock remained unreactive or only slowly reactive. In addition, a well crystallised calcium sulphate filtrate was not produced. However, with some optimisation of conditions, more recent work has indicated that high grade phosphoric acid can be produced from County Clare rock by the Nissan process.

Forestry tests using ground Clare phosphate rock for direct application are being pursued after initially favourable results.

REFERENCES ON THE IRISH REPUBLIC

1 The phosphorites of County Clare. J.A.G. McCluskey. Miner. Resour. Mem. geol. Surv.Ire., 1951, 106 pp. Unpublished typescript.

2 Phosphatic horizons in the Upper Carboniferous of Ireland. M.V. O'Brien. C. r. 19th int.geol.Congr., Algiers, 1952, 1953, Sect. 11, Pt. 11, pp. 135-143.

3 A mid-Carboniferous (Namurian) basin in parts of the counties of Limerick and Clare, Ireland. F. Hodson and G.C. Lewarne. Q. Jnl.geol. Soc. Lond., 1961, Vol. 117, Pt. 3, No. 467, pp. 307-333.

4 The beds above the Carboniferous Limestone in North-West County Clare, Eire. F. Hodson. Q. Jnl.geol. Soc. Lond., 1954, Vol. 109, Pt. 3, No. 435, pp. 259-279. Discussion, pp. 279-283.

5 Personal communication. C. MacDermot, Geological Survey of Ireland, March 1977.

6 Namurian Phosphate Occurrences in Ireland. Progress and Prospects. C. MacDermot and A. Flegg. 7 pp. (Dublin : Geological Survey of Ireland, 1977.) Unpublished typescript.

7 Clare Phosphate Project. Preliminary Investigations in the Processing of Clare Phosphate Rock. D. McKernan, D. Galvin, C. Burton and A.P. Carroll. 31 pp. (Dublin : Institute for Industrial Research and Standards, 1977.) Unpublished typescript.

8 Note on the analysis of an Irish phosphate ore. C.L. Simpson and J. Reilly. Scient. Proc. R. Dubl. Soc., N.S., 1942, No. 48, pp. 459-469.

9 The activation of Clare phosphate as a fertiliser. P.H. Gallagher and T. Walsh. Econ. Proc. R. Dubl. Soc., 1943, Vol.3, No.14, pp.172-189.

4.6. ITALY

Sedimentary phosphate rock in the form of phosphatic nodules and concretions and phosphatic limestone is found along the Adriatic coast of Lecce Province in the 'heel' of southern Italy, and nodule beds occur also in the southern parts of Sicily and Sardinia. None of the occurrences has been worked commercially, although the deposits in Lecce Province were of particular interest during the Second World War when shipments of phosphate rock from North Africa were curtailed and were again investigated briefly between 1968 and 1970. Substantial resources of low grade phosphate rock in the Lecce Province have been established. Italian requirements of phosphate rock are met entirely by imports, chiefly from Morocco and, to a much lesser extent the USA (Table 21).

GEOLOGY

Phosphate rock occurs in Italy in marine sediments primarily of Miocene and Pliocene age, notably in the Salentino Peninsula, although in Sicily phosphate mineralisation has been recorded also from Triassic rocks and in Sardinia from Siluro-Devonian strata.

The most extensive phosphate occurrences are to be found in the Salentino Peninsula[1], in Lecce Province, which is composed of sediments ranging from Upper Cretaceous to Pleistocene age (Fig 20). The Cretaceous is widely exposed in the peninsula, consisting predominantly of dolomitic limestones and dolomites, with a total outcrop thickness of a few hundred metres. Drilling for oil has indicated, however, that the total thickness of the Cretaceous amounts to some 4,400 m. Tertiary formations have a fairly extensive outcrop commencing with white detrital Eocene limestones which are transgressive over the Cretaceous in the S. Maria di Leuca - Otranto area. Oligocene limestones also occur but the most extensive Tertiary formation is the Lecce Stone (Pietra Leccese), a yellowish, highly fossiliferous and sometimes finely detrital marly

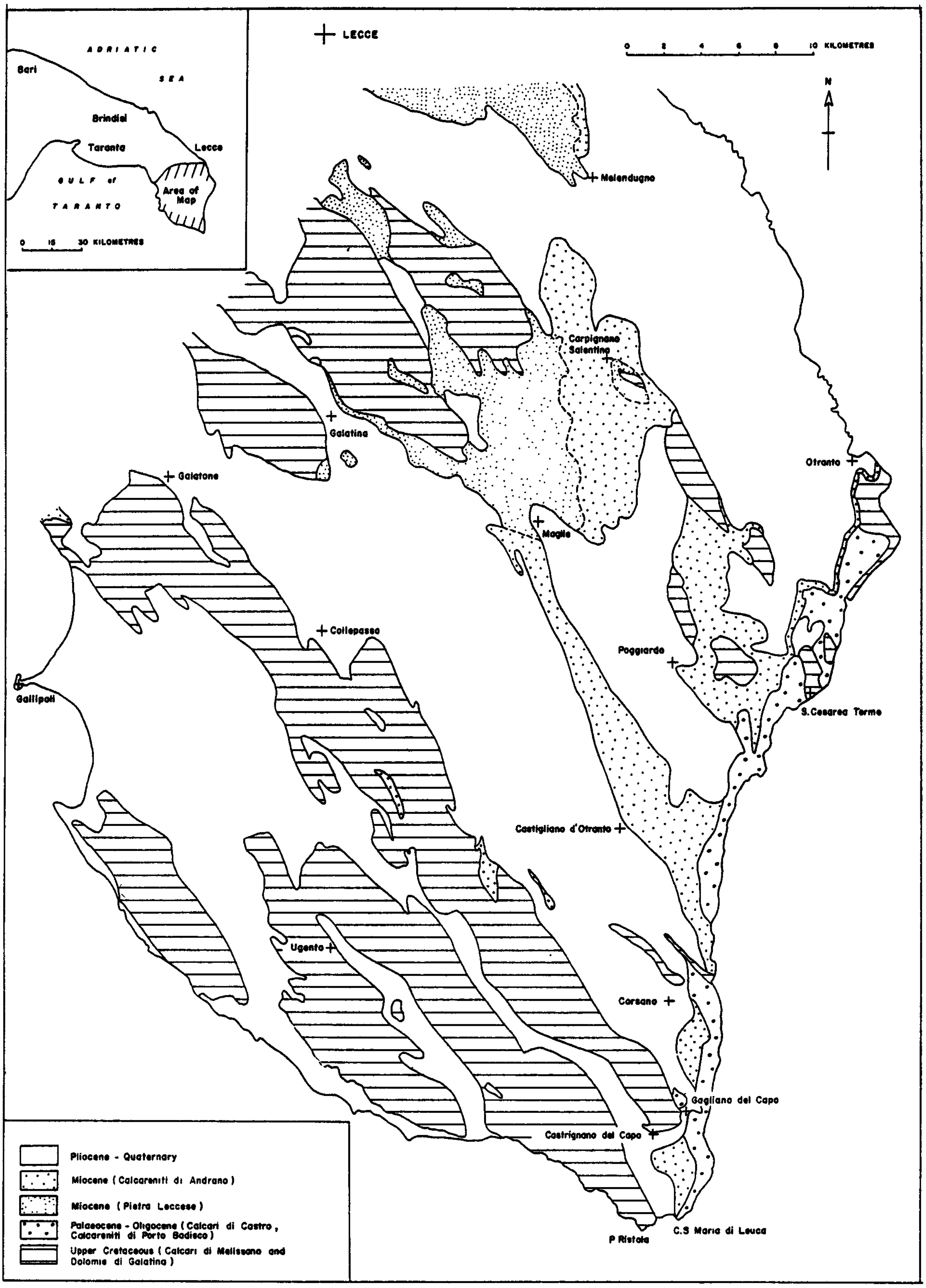


Fig 20. Generalised geology of the southern Salentino Peninsula. (Based on Martinis, 1962 and Sheet Nos 204, 214 and 215 Carta Geologica d'Italia. 1: 100 000, 1968.)

TABLE 2:1 ITALY : IMPORTS OF PHOSPHATE ROCK, 1972-1976

TONNES

Country	1972	1973	1974	1975	1976
Algeria	1,300				
Canada	2,100	23,140	17,140		
Germany, Federal Republic	32,920	6,719	500		
Iceland	3,194				
Iraq	2,952				
Israel	126,400	103.032	61,530	65,000(e)	
Jordan				9,800	
Mexico	15,000				
Morocco	1,176,584	1,109,585	1,389.128	1,208,454	1,113,837
Senegal	32,285	38,231	50,761	31,695	27,000(e)
Somalia	4,150				
Spanish Sahara	3,328		2,920		
Syria		1,564	19,192		
Tunisia	28,397	37,261	74,041	5,000(e)	41,100(e)
U.S.A.	766,029	528,224	523,193	206,902	71,824
Uruguay	2,004				
Other countries	1,921	3,621	20	112,279	216,328
Total	2,198,564	1,851,377	2,138,425	1,639,130	1,532,795
(1000 Lire) C.i.f. Value	15,887,876	16,690,100	68,154,623	74,684,877	60,405,890

(e) Estimate

Sources: Statistica Annale de Commercio con l'Estero.
Statistica Mensile de Commercio con l'Estero.

limestone which is predominantly of Middle Miocene (Helvetian/ Langhian) age. The Lecce Stone is succeeded by sandy, fossiliferous limestones and yellowish sands, with subordinate shales, of Pliocene and, to a greater extent, Quaternary age. Fold structures are well developed in the Salentino Peninsula and trend NNW-SSE or NW-SE; anticlines are markedly asymmetric with a steep and frequently faulted NE flank. Dips average 5 to 15°. The cores of the anticlines are composed of Cenomanian (Upper Cretaceous) to Miocene sediments. Faulting is of the normal type and occurred chiefly in Pleistocene times.

Nodular phosphate beds, all presumed to be of Upper Pliocene age, occur at various localities in the southern part of the Salentino Peninsula[2-5], those near Diso, Carpignano and Castrignano del Capo (Fig 21) being sufficiently well developed to have been investigated by the Servizio Minerario, Rome, during the 1930s and, together with the S. Maria di Leuca occurrences, by the French Société d'Etudes et de Recherches (SODEREC) during the 1968-1970 period. Although further exploratory work by SODEREC, including drilling, was contemplated, this was not undertaken because of the unfavourable commercial prospects of the occurrences in the face of cheaper phosphate rock imports.

Phosphate rock was recorded from the Salentino Peninsula in 1869, from the Capo Santo Maria di Leuca area at the southernmost tip of the peninsula. There a phosphatic conglomerate from 50 cm to 1 m thick occurs near the top of the transgressive Pliocene Calcareniti del Salento formation. The conglomerate, which contains 11 to 18 per cent P_2O_5[6], comprises hard, pebble-shaped, yellowish-brown phosphate nodules up to several centimetres in diameter as well as partially rounded nodules of reddish-brown glauconitic, phosphatic limestone, embedded in a matrix of both light grey to reddish-brown glauconitic limestone and of hard white pink, fine grained limestone. The carbonate cement contains 4.5 per cent P_2O_5.

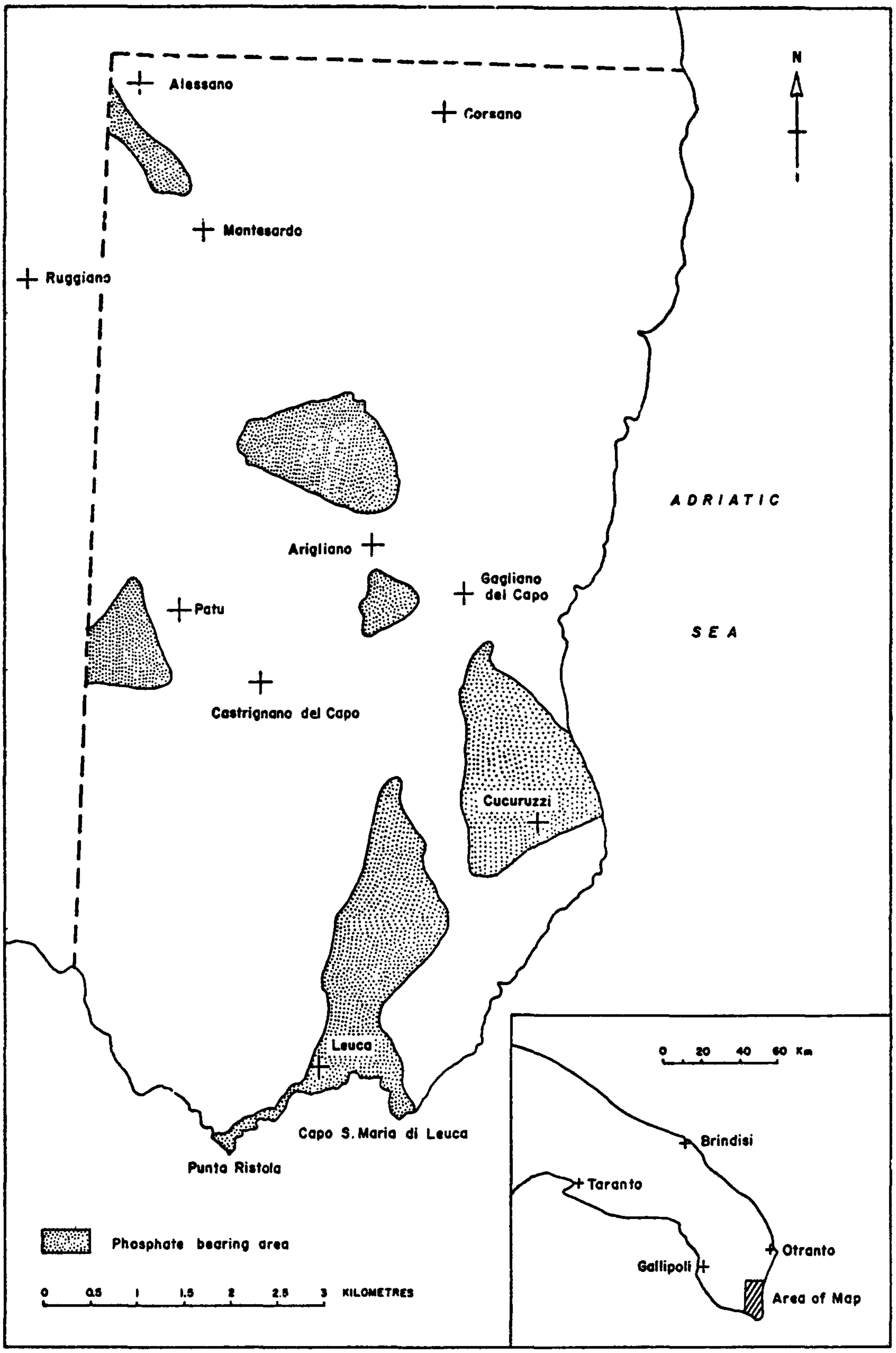


Fig. 21. Distribution of nodular phosphate beds in the southernmost Salentino Peninsula. (Based on SODEREC, 1969.)

TABLE 22. CHEMICAL COMPOSITION OF NODULAR PHOSPHATE ROCK, SALENTINO PENINSULA[3]

	1	2	3	4	5
			Per cent		
P_2O_5	10.074	10.79	17.68	20.47	7.16
CaO	50.276	52.56	28.20	n.d.	n.d.
SiO_2	0.700	n.d.	2.00	2.36	3.54
Al_2O_3	n.d.	n.d.	0.66	n.d.	n.d.
Fe_2O_3	2.476	n.d.	1.40	1.72	2.15
MgO	0.993	0.52	0.80	1.30	0.78
H_2O	0.540	n.d.	n.d.	n.d.	n.d.
CO_2	31.265	n.d.	22.87	n.d.	n.d.
SO_3	0.432	n.d.	n.d.	n.d.	n.d.
Organic matter	0.196	n.d.	n.d.	n.d.	n.d.
Loss on ignition	n.d.	32.01	23.00	18.99	33.33

n.d. = not determined

1 Capo di Leuca. Analysis published in 1907.

2 Lower phosphate bed, Maglie - S. Maria di Leuca road. Analysis by Société Française de Minérais et Métaux, Paris.

3 Upper phosphate bed, Maglie - S. Maria di Leuca road. Analysis by Studi di Trattamento dei Minerali del Commissariato all ' Energia Atomica.

4 Cucuruzzi area. Analysis by Laboratorio Minerali e Metalli, Milan.

5 Punta Ristola, west of S. Maria di Leuca. Analysis by Laboratorio Minerali e Metalli, Milan.

The rock is also highly fossiliferous with abundant remains of phosphatised bryozoa, corals, gastropods, molluscs and shark's teeth. A similar bed, but with nodules up to 10 or 15 cm in diameter, was found in 1890 along the road from Vigna Castri to Castro, about 0.5 km from the sea. The nodules contain between 2.7 and 17.5 per cent P_2O_5.

Geological investigations by SODEREC in the Castrignano del Capo, Gagliano del Capo and Capo di S. Maria di Leuca areas have revealed that in places the nodule bed is underlain by phosphatic limestone. Sections situated about 2 km NNW of Capo di S. Maria di Leuca, where SODEREC extracted a 20-tonne sample for test purposes, show a full phosphatic sequence in which the nodular bed is approximately 0.5 to 0.6 m thick. It appears to have been reworked from the underlying light reddish-brown phosphatic limestone which is some 4 m thick. The overlying limestone is essentially non-phosphatic. The base of the phosphatic limestone is marked by a layer 5 to 10 mm thick of phosphate on white, compact, fine-grained, cross-bedded sandy limestone.

Samples of phosphate rock collected by SODEREC showed between 7.16 and 20.5 per cent P_2O_5, a selection of partial chemical analyses of samples being given in the accompanying table (Table 22). Assays of samples, 2,3 and 4 by the Centre d'Etudes et de Recherches des Phosphates (CERPHOS), Paris, gave confirmative results for P_2O_5. In addition a sample from Madonna del Rasche analysed by CERPHOS gave 14.82 per cent P_2O_5 and 23.41 per cent loss on ignition.

Phosphate in variable concentrations has been recorded in almost all the Miocene rocks of the Salentino Peninsula[6,7]. These sediments occur at shallow depths over a total area of about 150 km^2. Phosphate mineralisation is best developed, however, in the 'piromafo' and underlying Lecce Stone ('Pietra Leccese'), both of which form part of the Middle Miocene Pietra Leccese formation. The 'piromafo' is a greenish-brown limestone characterised also by

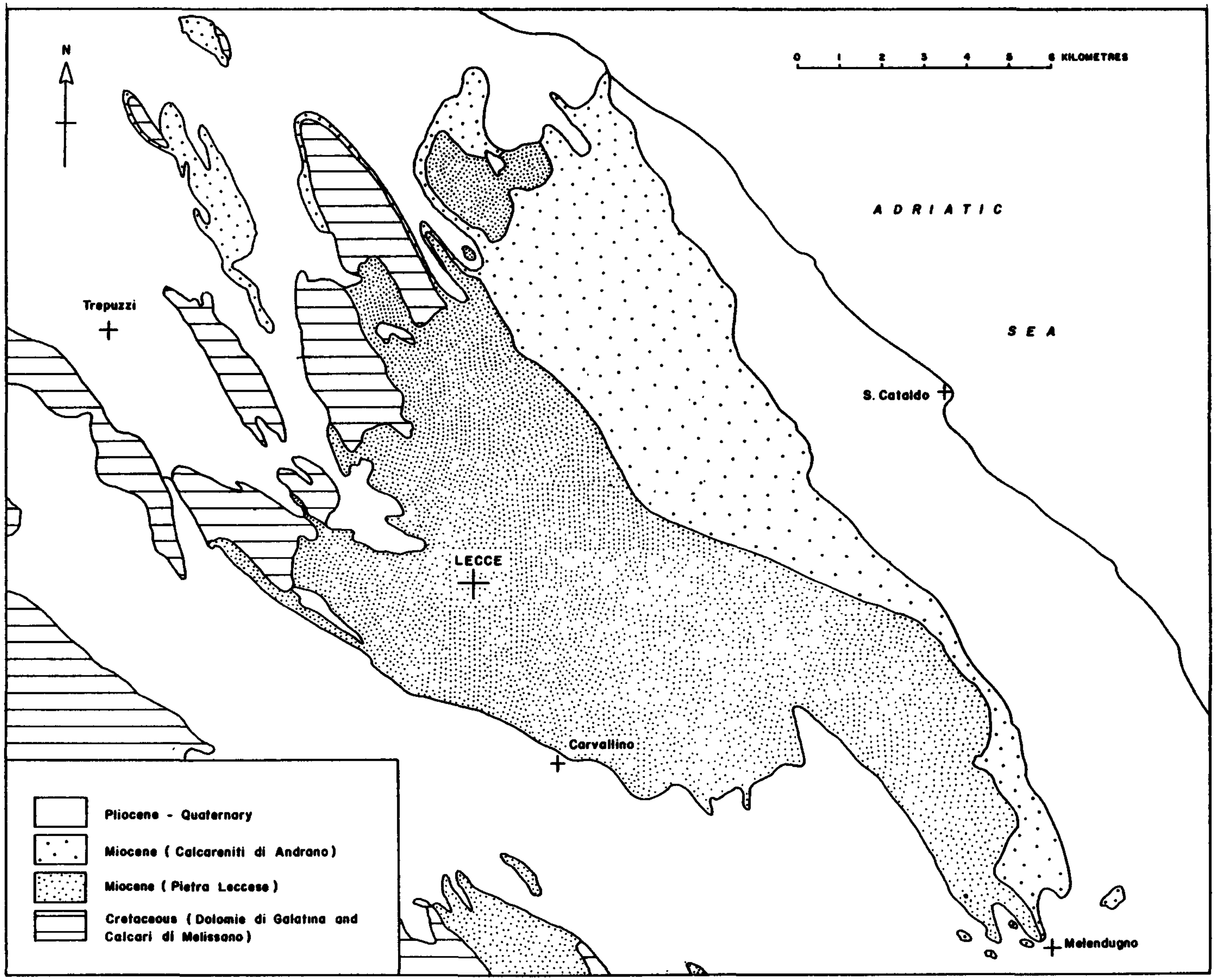


Fig 22. Distribution of the Miocene Pietra Leccese Formation, Lecce area. (Based on Sheet Nos 204 and 214, Carta Geologica d'Italia. 1: 100 000, 1968.)

the presence of very fine glauconitic grains and granules and by phosphate nodules which may be 3-4 cm in diameter, in contrast with the Lecce Stone, which is less fossiliferous and is represented by a soft, homogeneous,yellowish or greyish-white bioturbated limestone which has been quarried for many years in the Salentino Peninsula as a building material. In the Lecce area (Fig 22), the Lecce stone is at least 30 m thick. The 'piromafo' bed contains abundant fish teeth and cetacean remains, particularly of Carcharodon megalodon.

The 'piromafo' and Lecce Stone formations are both easily recognisable in the numerous quarries operating or abandoned in the Lecce area, including those situated close to the Lecce-Maglie road (Fig 23).

There are variations in thickness and phosphate content, but in general grey to yellowish limestones generally containing less than 4 per cent P_2O_5 grade into the underlying 'piromafo', which ranges from 0.80 to almost 2 m, and averages 1.2 m in thickness. This in turn grades downwards into the more compact Lecce Stone. Excluding the Lecce Stone, it is probable that an average aggregate thickness of some 3 m of Middle Miocene strata can be regarded as phosphate-bearing, the 'piromafo' averaging 8.7 per cent P_2O_5. A chemical analysis of 'piromafo' rock is given below (Table 23). Available analyses indicate that the Lecce Stone contains only between 3 and 4 per cent P_2O_5.

Between Malpignano and Cursi, south of Lecce, the junction between 'piromafo' and Lecce Stone is marked by an erosion surface, burrows in the upper surface of the Lecce Stone being filled with glauconitic limestone from the overlying 'piromafo', and by accumulations of shell debris. In addition, solution pipes occur in the Lecce Stone which in quarry faces penetrate to depths of up to 4 m. These are filled with a red clayey sand presumably derived from the decalcification of limestone and contain quartz, clay and glauconite and abundant mammalian remains. A random sample of this material gave 12 per cent P_2O_5.

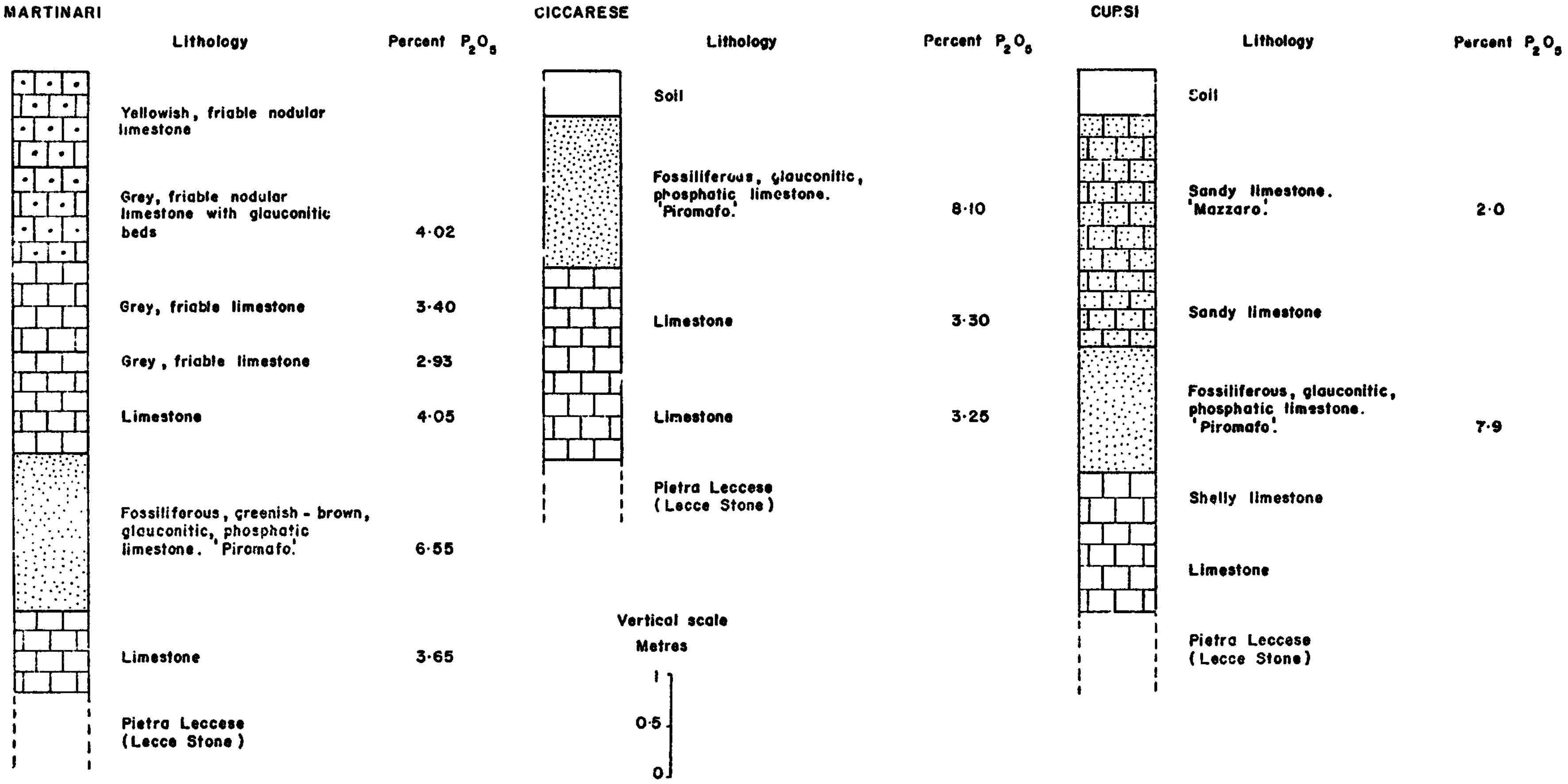


Fig 23. Generalised stratigraphy and phosphate content of Miocene sediments, north of Maglie, Salentino Peninsula. (Based on Martelli, 1931 and Carta Geologica d'Italia.)

TABLE 23. CHEMICAL COMPOSITION OF 'PIROMAFO' PHOSPHATE ROCK

	Per cent
P_2O_5(a)	8.97
CaO	41.09
SiO_2	9.82
Al_2O_3	5.08
Fe_2O_3	4.14
MgO	1.10
Na_2O	0.67
K_2O	0.62
CO_2(a)	24.60
H_2O	2.93
Total	99.02

(a) average of 2 samples

Source: Boll.Soc.geol.Ital., 1931, Vol.50, Pt.2, p.185.
Analysis by Instituto Superiore Agrario Forestale di Firenze.

Random samples of phosphatic rocks from various localities in the Salentino Peninsula analysed in 1977 by the Institute of Geological Sciences, London, using a rapid colorimetric technique, gave the following results:

	Percentage P_2O_5
Lecce Stone, abandoned quarries north of Lecce	3
Lecce Stone, between Malpignano and Cursi	1
Lecce Stone, dust from stone dressing operations	3
'Piromafo', between Malpignano and Cursi	11
Highly fossiliferous, phosphatic nodular bed near Gagliano del Capo	18
Phosphate nodule, 2km north of Capo. S.Maria di Leuca	18
Phosphatic limestone underlying nodular bed, 2km north of Capo S. Maria di Leuca	4
Phosphatic limestone, road section at Castro	2

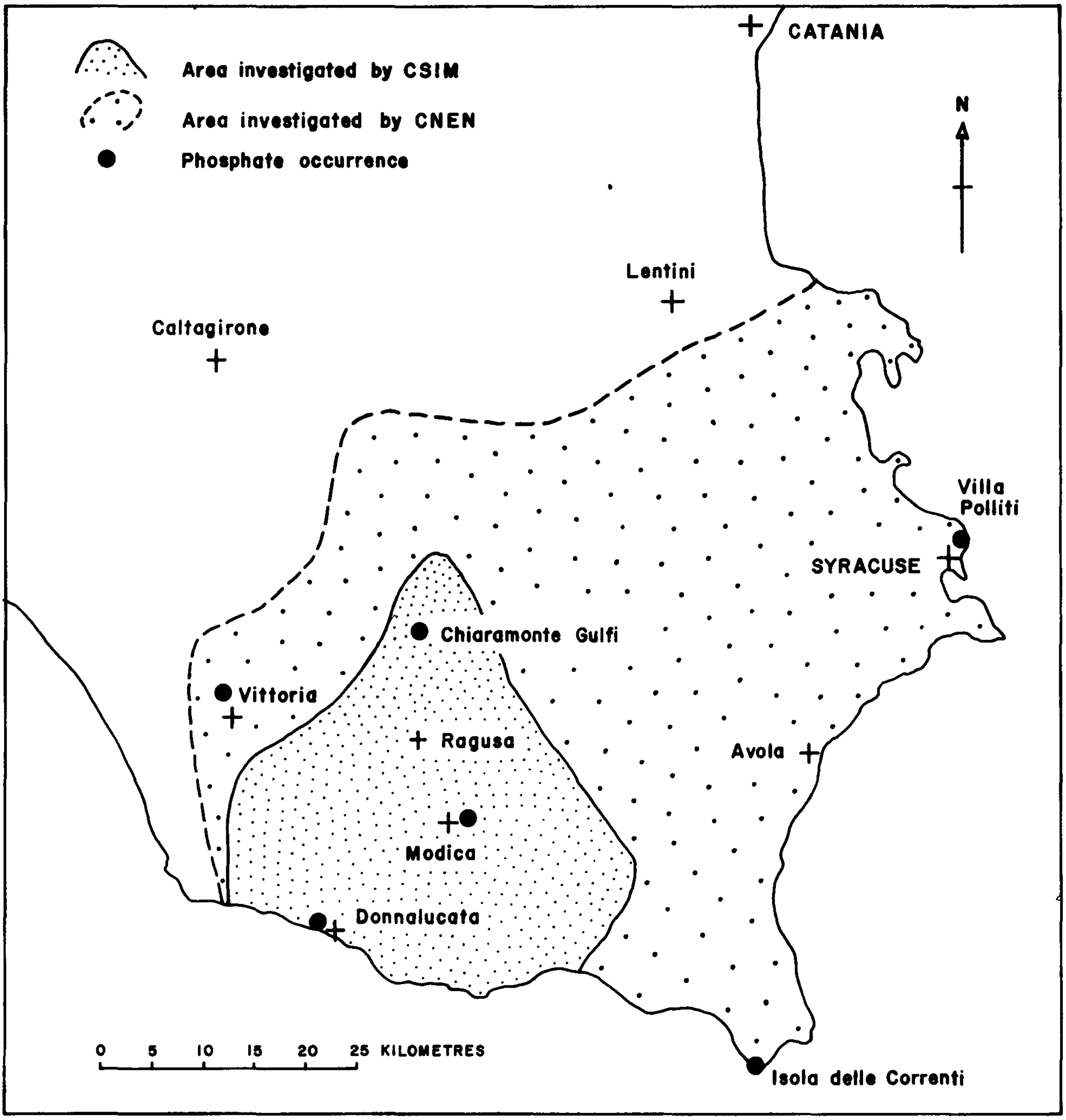


Fig 24. Distribution of phosphate occurrences in southeastern Sicily. (Based on Tedesco , 1966 .)

In southeastern Sicily[8,9] the presence of phosphate near Modica, south of Ragusa, has been known since about 1902 but it was not until 1962 that investigations by the Centro Sperimentale per l'Industria Mineraria (which was reorganised in 1963 to form part of Ente Minerario Siciliano) revealed numerous other occurrences in Ragusa Province. Outcrops of phosphate rock of Miocene and other ages have since been found within an area of about 3,300 km^2 covering most of Ragusa and Siracusa (Syracuse) provinces explored by the Comitato Nazionale per l'Energia Nucleare in 1965 (Fig 24).

Southeastern Sicily is made up of the Ragusa-Monti Iblei Plateau, which is regarded as a palaeogeographical unit, comparable with the Apulian and Monte Gargano areas of the Italian Peninsula, that has been relatively unaffected by Alpine mountain-building movements. For example, the Mesozoic rocks are predominantly limestones exhibiting an epicontinental facies and include formations which are absent from the rest of Sicily. Similarly, the Miocene, in which most of the phosphate occurrences have been reported, is again composed chiefly of limestones which show similarities with the Miocene carbonate rocks found in Malta. The Ragusa-Monti Iblei Plateau is broken up by a network of normal faults that strike NNE-SSW and NNW-SSE.

There is generally one widely distributed bed of phosphatic nodules up to 0.8 m thick in limestone which forms the Lower Miocene Irminio member of the Ragusa formation, but at Donnalucata on the south-west coast of Sicily two nodule beds each about 10 cm thick are separated by about 1 m of limestone. The lower bed, which contains nodules with 14 per cent P_2O_5 is underlain by a bed of phosphatic sandstone 5 to 10 cm thick. Float material found between Sicili and Sampiere contains 18.54 per cent P_2O_5; in the same area sandstone float 2-3 m thick contains up to 8 per cent P_2O_5. A 0.5 m bed of phosphatic nodules which are up to 5 cm in diameter occurs in Lower Miocene rocks near Chiaramonte Gulfi, about 11 km NNW of

Ragusa, and at Modica a similar bed 0.3 m thick lies in Lower-Middle Miocene Globorotalia limestones. At Chiaramonte Gulfi, a sample of limestone 4 m thick above the nodule bed contains 4.41 per cent P_2O_5. Brown, compact and slightly cavernous Lower Miocene phosphatic limestone is 15 cm to 20 cm thick at Isola delle Correnti south of Pachino.

In Siracusa Province phosphatic beds have also been found which appear to represent material reworked from Lower Miocene phosphate-bearing strata chiefly during post-Pliocene times. For example, beds containing dark phosphatic nodules up to 10 cm in diameter occur just north-east of Syracuse at Villa Polliti and there are similar reworked deposits in Ragusa Province near Vittoria.

Samples of nodules chiefly from parts of Ragusa Province showed on analysis a range of 7.68 to 25.08 per cent P_2O_5, 0.47 to 1.56 per cent F, as well as 60.7 to 205 ppm U_3O_8 and 62 to 127 ppm V[9]. Samples made up of nodules and matrix showed from 1.92 to 18.54 per cent P_2O_5, one from Modici with 4.95 per cent P_2O_5 containing also 217 ppm U_3O_8. Phosphate beds of limited extent and very low grade have been reported also from sediments of Upper Triassic, Upper Cretaceous and Lower Tertiary age[10]. Details are not available but nodules in Lower Tertiary marls contain 4.5 to 5 per cent P_2O_5.

Phosphatic nodules occur in southern Sardinia[11] near Villaputzu, north-east of Cagliari, and are reported to have been found near Nuraminis, some 26 km NNW of Cagliari. Details are not available, however, Near Villaputzu also, phosphate rock forms an irregular lens in steeply dipping limestones and schists of Siluro-Devonian age. The rock is black, earthy or cavernous, with inclusions of small quartz grains, and is probably an isolated occurrence of secondary phosphate. A sample contained 16.22 per cent P_2O_5, 49.79 per cent insoluble matter, 4.86 per cent CaO, 11.08 per cent Fe_2O_3 and 3.83 per cent Al_2O_3.

RESOURCES

The largest known phosphate resource in the Salentino Peninsula of southeastern Italy occurs in the Lecce Stone by virtue of its geographical extent and thickness. The Lecce Stone is, however, of very low grade, available chemical analyses showing a P_2O_5 content of only 3 to 4 per cent, and no quantitative estimates of resources have been made. There are, in addition, about 60 million tonnes of phosphatic limestone ('piromafo') averaging 7 to 8 per cent P_2O_5, which have been estimated for the Lecce area[7]. Both the Lecce Stone and the 'piromafo' form part of the Middle Miocene Pietra Leccese formation.

Resources of nodular, supposedly Upper Pliocene, phosphate rock in the southern part of the Salentino Peninsula have been estimated at 10 million tonnes of variable grade ranging from 10.5 to 20.5 per cent P_2O_5. One of the deposits, the 'Torre Mazzo' deposit near Castrignano del Capo, has been estimated previously to contain 40,000 tonnes of phosphate rock, assuming a mineable thickness of about 1 m[12].

Preliminary surveys in southeastern Sicily have indicated that nodular phosphate beds of Miocene age are widely distributed but, again, total resources have not been estimated, as far as is known. The occurrences are most probably a continuation of those of the same age found extensively in Malta. The results of the survey carried out by the Comitato Nazionale per l'Energia Nucleare in 1965 suggested that workable deposits might be found but no subsequent assessment work has been carried out. Resources of phosphate rock in the Donnalucata area alone were reported in 1921 at about 7 million tonnes averaging 15 per cent P_2O_5[13].

PRODUCTION

There has been no production of phosphate rock in Italy to date. However, about 1,500 tonnes was obtained in 1942 from deposits in Lecce Province for beneficiation tests. No further development work took place, apparently because of the difficulty in achieving a sufficiently high grade phosphate concentrate.

BENEFICIATION

Experiments carried out on phosphatic limestone from the Pietra Leccese formation showed that calcination at 900°C and subsequent slaking of lime did not provide a phosphate concentrate sufficiently high in grade for it to be suitable for fertiliser manufacture[7]. In addition, the removal of lime was accompanied by high phosphate losses. However, acidulation of phosphatic limestone ('piromafo') containing between 7 and 10 per cent P_2O_5 from Cursi in Lecce Province, has apparently proved successful on a laboratory scale. It was claimed that a concentrate with 35 per cent P_2O_5 could be obtained.

SODEREC has tested a beneficiation process which consists of grinding and roasting the carbonate rich phosphate rock, which was then reacted with a solution of ammonium chloride or, preferably, of ammonium nitrate, since the latter is more soluble when cold and less corrosive. The phosphate concentrate is filtered and recovered, while the calcium chloride (or nitrate) solution is treated with a mixture of CO_2 gas and ammonia (present in the solution) to produce a pure calcium carbonate which is recovered by filtering. The ammonium chloride (or nitrate) is recycled. By this process it is claimed that a phosphate concentrate which is suitable for the manufacture of both superphosphate and phosphoric acid can be produced.

REFERENCES ON ITALY

1 Lineamenti strutturali della parte meridionale della Peninsula Salentina. B. Martinis. Geol. Rom., 1962, Vol.1, pp.11-23. (In Italian. English abstract, pp.20-22.)

2 Giacimenti di Fosfati in Italia. L. Toni. 6 pp. (Roma: Direzione Generale della Miniere, Ministerio dell'Industria e del Commercio, 1973.)(Unpublished typescript)

3 Relazione di Lavori. Permesso di recerca, mineraria per fosfato. 'Montelungo' e Porcinaria, Communi di Gagliano del Capo e di Castrignano del Capo in Provincia di Lecce. 23 pp. (Roma: Soderec, Filiale per l'Italia, 1969.) (Unpublished typescript)

4 Note illustrative della Carta Geologica d'Italia alla Scala 1: 100,000. Foglio 223. Capo S. Maria di Leuca. B. Martinis. 69 pp. (Roma: Servizio Geologico d'Italia, 1970.)(In Italian.) Phosphate, pp. 47-48.

5 Sulla fosforite di Leuca. A. Galdieri. Atti R. 1st. Incoragg. Napoli, Ser. 6, 1918, Vol.10. 10 pp. (In Italian)

6 Minerali fosfatici nella provincia di Lecce. G. Tarulli and A. Marcucci. Annali Chim. appl., 1928, Vol.18, pp.40-46. (In Italian)

7 Sui fosfati del Leccese. A. Martelli. Boll. Soc. geol. ital., 1931, Vol. 50, Pt. 2, pp.171-188. (In Italian)

8 Les Réserves Mondiales en Phosphates, Vol. 1. 497 pp. (Madrid: Graficas Reunidas, S.A.,1928.)Giacimenti italiani di fosfati. L. Testa, pp.217-224. (In Italian)

9 Ricerche sulle mineralizzazioni fosfatiche della Sicilia orientale ed esame comparativo dei metodi di prospezione. C. Tedesco. Riv. Mineraria sicil., 1966, Vol. 17, No. 97-99, pp. 3-17. (In Italian. English abstract, pp. 4-5)

10 Prime notizie su alcuni miori orizzonti fosfatiferi siciliani. T. de Stefani. Riv. miner. sicil., 1955, Vol. 5-6, No. 33, pp. 129-130. (In Italian)

11 Su un affioramento fosfatico nel Sarrabus (Sardegna) (Nota preliminare). A. Marchesini and V. de Michele. Atti Soc. ital. Sci. nat. 1967, Vol. 106, Pt. 2, pp. 167-170. (In Italian. English summary. p. 170)

12 Notizie sull'industria mineraria nel mezzogiorno d'Italia. F. Squarzina. Industria min. Roma, Ser. 2, 1963, Vol. 14, No. 2, pp. 89-104. (In Italian.) Phosphorite, pp. 96-98.

13 I fosfati a noduli terziari in Italia. E. Cortese. Miniera ital., 1921, Vol. 5, pp. 49-50. (In Italian)

4.7. LUXEMBOURG

There are no significant recorded occurrences of phosphate rock in Luxembourg. The only source of phosphate are the marine sedimentary phosphatic iron ores of Late Toarcian to Early Aalenian (Lower Jurassic) age, which form an extension of the Lorraine deposits of France. The phosphatic iron ores contain 0.5 to 1 per cent P and contribute to basic slag production in Luxembourg.

4.8. NETHERLANDS

Phosphate rock in the form of phosphate nodules occurs in Tertiary sediments in the eastern part of the Netherlands and in the Rhine Delta area south-west of Rotterdam. Phosphate nodules have been found also in Upper Cretaceous (Senonian) rocks in southern Limburg.

None of these occurrences is of economic importance, so that the phosphate rock requirements of the large domestic fertiliser industry are met entirely by imports, chiefly from the USA, Morocco and, to a lesser extent, Togo (Table 24).

GEOLOGY

Sedimentary phosphate rock of Tertiary age was discovered during the First World War in the Drenthe and Overijssel provinces. In Overijssel Province a discontinuous bed 18 cm to 1 m thick and containing 6.9 to 9.2 per cent P_2O_5 was found at the junction of Eocene and Oligocene sediments at Oostmarsum north-east of Hengelo.[1] The bed occurs at the surface and has also been encountered at depths of up to 8 m. Other occurrences are reported to contain up to 14 and 15 per cent P_2O_5. Phosphate nodules are abundant in the eastern part of the Netherlands at the base of the Middle Oligocene (Rupelian) succession, occurring in glauconitic sand.[2]

TABLE 24. **NETHERLANDS : IMPORTS OF PHOSPHATE ROCK, 1972-1976**

TONNES

Country	1972	1973	1974	1975	1976
Belgium-Luxembourg	24,111	11,911	7,048		1,791
Curaçao			6,045	9,982	
France	830				
Germany, Federal Republic	153		2,049		253
Israel					91
Morocco	522,497	502,028	620,243	521,901	579,401
Niger		5,700			
Senegal	237,134	243,393	267,790	158,724	44,400
Soviet Union	56,246	74,622	49,614	29,375	48,931
Spain			32,671		
Spanish Sahara			10,360		
Togo	520,817	584,196	618,611	354,758	497,260
U.S.A.	644,850	670,763	750,950	516,213	590,508
Other countries		59		181	85
	2,026,638	2,092,672	2,365,380	1,591,134	1,762,720
(1000 Gld) C.i.f. Value	90,099	97,241	282,269	263,041	199,864

Source: **Maandstatistiek van de buitenlandse handel.**

In the Rhine Delta area, phosphate nodules occur between approximately 123 and 137.5 m below the surface near Haamstede on the island of Schouwen,[3] in boreholes drilled by the Delta Dienst Rijkswaterstaat. They lie at (a) the unconformable boundary of the Lower Pliocene Kattendijk Sands and the Upper Miocene Deurne Sands (b) the junction of the Deurne Sands and the Middle Miocene Antwerp Sands, and (c) within the Antwerp Sands. Phosphate nodules have been found also at comparable stratigraphical levels in boreholes on the islands of Walcheren, Tholen, Zuid Beveland,Zeeuws Vlaanderen and in the Westerschelde estuary. Individual nodules consist of light green glauconite and quartz which, together with subordinate feldspar, are embedded in a brown cryptocrystalline matrix of apatite. Apatite makes up about 30 to 40 per cent of the nodules and chlorite, zircon, garnet, epidote, sphene and hornblende are present as accessory minerals. Analyses of samples from 13 boreholes showed a range of 11.17 to 31.23 per cent P_2O_5. Very low concentrations of uranium have also been recorded. A leaching technique based on a system of pumping dilute sulphuric acid into the phosphate beds to extract the phosphate has been suggested by the Geological Institute of the State University of Utrecht as an alternative to conventional mining methods which would not be advisable in the Delta area. However, no further work has been carried out on this method, as far as is known.

The stratigraphically important Upper Cretaceous boundary between the Campanian and Maastrichtian is represented in southern Limburg by a well developed 'hardground'[4] which is marked by a glauconitic horizon containing numerous phosphatic nodules. Details of its thickness and extent, and of the nature and phosphate content of the associated nodules are not available.

RESOURCES

No estimates of the phosphate rock resources of the Netherlands have been made. It is reported[5] that reserves in the Overijssel and Drenthe provinces were estimated in 1940 at only 500 to 700 tonnes, the rock containing 14 to 15 per cent P_2O_5.

It is generally accepted that the Upper Cretaceous sediments in the Netherlands were laid down under shallow water marine environments with little supply of clastic material. A predominantly chalky facies has thus been developed. Conditions of deposition are therefore comparable with those of the Upper Cretaceous sediments in, for example, Belgium. In this context, it is of interest to note that the Maastrichtian Kunrade Chalk in southern Limburg has been correlated with the Craie phosphatée de Ciply in the Mons Basin. However, the possible phosphate potential of the Upper Cretaceous chalky facies in the Netherlands has not been investigated, as far as is known.

PRODUCTION

The deposit at Oostmarsum near Hengelo was worked briefly during 1919-1920, producing a total of about 10,000 tonnes of phosphate rock. Because of the irregularity of the bed, however, mining proved to be difficult and expensive.

REFERENCES ON THE NETHERLANDS

1 Conditions in the European phosphate market. W.C. Phalen. Am. Fertil., 1920, Vol.52, No.5, pp. 138,140,142,144. Netherlands, p. 138.

2 Geology of the Tertiary in the Netherlands. J. Keizer and W.J. Letsch. Verh. K. ned. geol. -mijnb. Genoot., 1963, Vol.21, Pt.2, pp. 147-172.

3 The discovery of uranium at Haamstede (Netherlands). H.M. Harsveldt. Verh. K. ned. geol.-mijnb.Genoot., 1973, Vol.29, pp. 63-72.

4 Present knowledge of the stratigraphy of the Upper Cretaceous (Campanian-Maastrichtian) and Lower Tertiary (Danian-Montian) calcareous sediments in southern Limburg. B.J. Romein. Verh. K. ned. geol.-mijnb. Genoot., 1963, Vol.21, Pt.1, pp. 97-104.

5 Personal communication. B.P. Hageman, Director Rijks Geologische Dienst, 19.10.77.

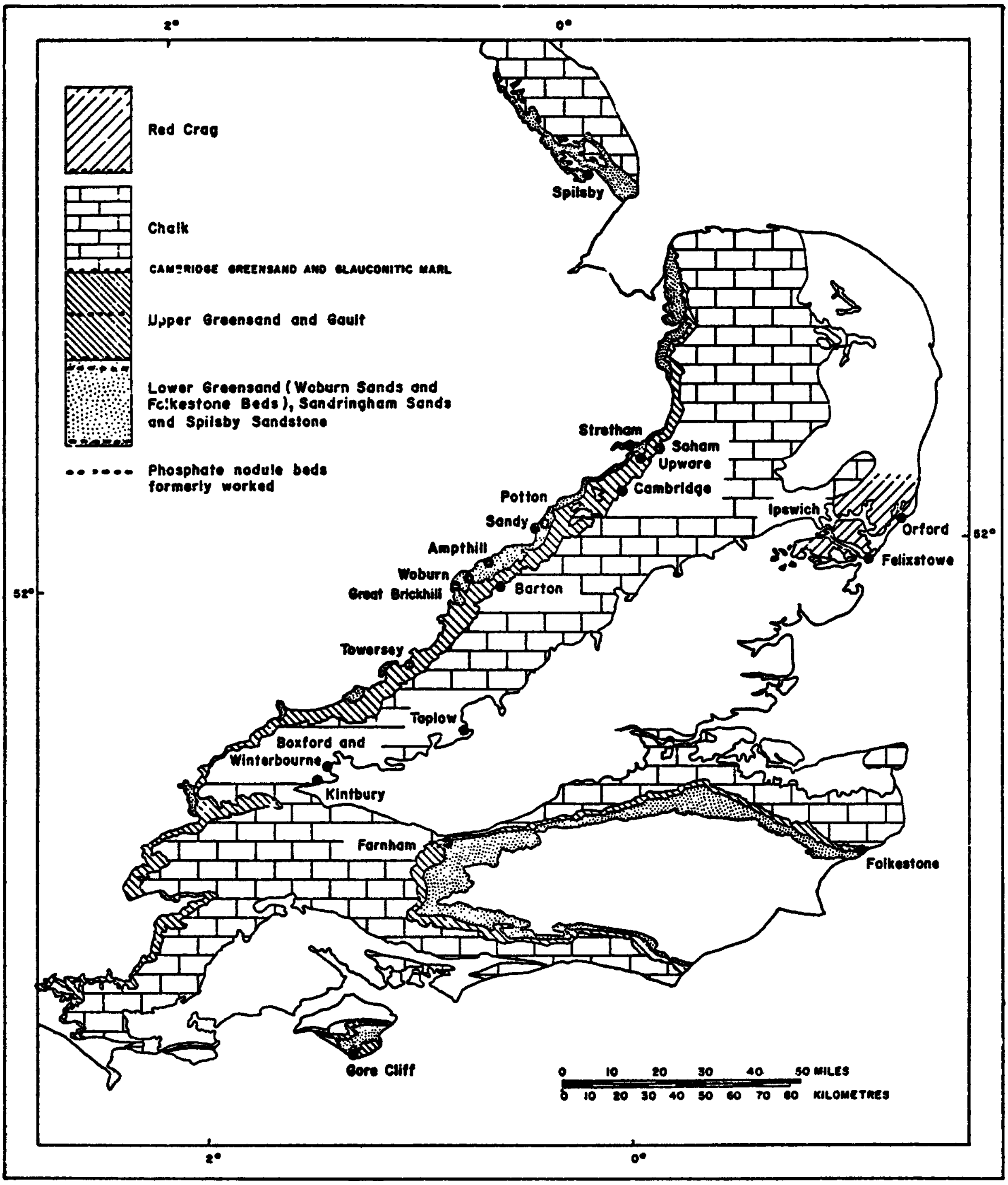


Fig 25. Distribution of major phosphate occurrences in south-east England. (Based on the Geological Map of Great Britain. Sheet 2. 1 : 625 000, 1957.)

4.9. UNITED KINGDOM

Phosphate rock is widely but sporadically distributed in the United Kingdom principally in the form of phosphatic nodule beds and the phosphatised casts of fossils. These occur at numerous stratigraphical horizons, of which those of Cretaceous and Pleistocene age in southeastern England were commercially the most important and were extensively worked during the latter half of the 19th century (Fig 25).[1] Except for a small output during the First World War there has been no production of phosphate rock since 1909, so that the United Kingdom is dependent upon imports for her requirements of this essential raw material. Morocco is the principal supplier of phosphate rock to the United Kingdom (Table 25). Apatite occurs as a common accessory mineral in many igneous rocks in the United Kingdom but significant concentrations of apatite have been recorded to date only from the Loch Borralan Complex in north-west Scotland.

GEOLOGY

The presence of phosphate rock in the United Kingdom appears to have been first reported in 1829 from the Lower Cretaceous Gault formation in southeastern England. Since then phosphate has been found at numerous localities, chiefly as phosphate nodule beds in shallow-water marine sediments of Jurassic and Cretaceous age; particularly noteworthy are those deposits associated with the widespread marine transgression which took place at the beginning of Upper Cretaceous times. Individual nodule beds are thin, exceeding 1 m in thickness only exceptionally, and some workings had to contend with considerable overburden thicknesses. There are few significant occurrences of massive, granular phosphate rock, known occurrences being confined to relatively low grade phosphatic chalk, limestone and shale. The stratigraphical distribution of the more prominent phosphate occurrences in the United Kingdom are shown in Table 26.

TABLE 25. UNITED KINGDOM : IMPORTS OF PHOSPHATE ROCK, 1972-1976

TONNES

Country	1972	1973	1974	1975	1976
Belgium-Luxembourg	40	945			
Denmark		1,165			
France	486				
Germany, Federal Republic	3,424	6,962			
Irish Republic		570			
Israel	6,586	12,643			
Morocco	1,237,816	1,455,352	1,522,035	1,145,657	1,261,988
Netherlands	15,617	15,062	4,033	1,767	4,454
Senegal	246,413	225,622	265,068	234,656	241,793
Tunisia	102,379	125,187	131,029	44,689	60,140
U.S.A.	49,039	118,759	72,551	140,950	165,413
Other countries		500	46,839	20,461	30,280
Total	1,661,800	1,962,767	2,041,555	1,588,180	1,764,068
(£ 1000) C.i.f. Value	11,205	15,979	51,106	49,903	51,237

Source: H.M. Customs & Excise.

TABLE 26. STRATIGRAPHICAL DISTRIBUTION OF THE MORE PROMINENT PHOSPHATE ROCK OCCURRENCES IN THE UNITED KINGDOM.

Geological Age	Formation	Locality	% P_2O_5 content
PLEISTOCENE	Red Crag (nodules)	Suffolk	24.2 (average)
UPPER CRETACEOUS			
Campanian	Phosphatic chalk	Buckinghamshire	up to 14
	White Limestone (nodules)		
	Hibernian Greensand (nodules)	Antrim, N. Ireland	-
	Morvern Greensand (nodules)	Highland Region	25.6
Cenomanian	Glauconitic Marl (nodules)	Isle of Wight	8.24
	Cambridge Greensand (nodules)	Cambridgeshire	up to 27
LOWER CRETACEOUS			
Albian	Gault (nodules)	S.E. England	25
	Carstone (nodules)	Lincolnshire, Norfolk	23.6
Aptian	Woburn Sands (nodules)	Bedfordshire, Buckinghamshire, Cambridgeshire	15-27
	Folkestone Beds (nodules)	Surrey	25
	Sutterby Marl (nodules)	Lincolnshire	-
Valanginian-Hauterivian	Claxby Ironstone (nodules)	Lincolnshire	11.6
Ryazanian	Speeton Clay (nodules)	N. Yorks	26-28
UPPER JURASSIC			
Portlandian	Spilsby Sandstone (nodules)	Lincolnshire	10.8-24.6
Kimmeridgian	Kimmeridge Clay (nodules)	Central England	-
Callovian-Oxfordian	Ampthill Clay (nodules)	Central England	-
	Brora Arenaceous & Argillaceous Series (nodules)	N.E. Scotland	19.3
MIDDLE JURASSIC			
	Dogger (nodules)	N. Yorks	26
Bajocian	Inferior Oolite (nodules)	Skye	23
	Northampton Sand Ironstone (nodules)	Lincolnshire	24.5
LOWER JURASSIC			
Pliensbachian	Marlstone Rock Bed (nodules)	Oxfordshire, Leicestershire	10.43
TRIASSIC			
Rhaetian	Bone Beds	Central England	-

TABLE 26b

Geological Age	Formation	Locality	% P_2O_5 content
CARBONIFEROUS			
Westphalian	Marine bands, e.g., Alton Marine Band (nodules)	Derbyshire	23.9
Namurian	Nodules marine shales, e.g., base of Edale Shales	Derbyshire	-
DEVONIAN			
Downtonian	Fish beds	Welsh Borders	-
Middle Old Red Sandstone	Uraniferous phosphate beds	N.E. Scotland	18
		Orkney	-
ORDOVICIAN			
Caradocian	Nod Glas (nodules and phosphatic limestone)	Powys	31.5
	Apatite rock in volcanic rock	S. Scotland	30.3
Arenig	Bolopora nodules	N. Wales	20
CAMBRIAN			
Tremadoc	Tremadoc Beds (nodules)	Gwynedd	18.6
PRECAMBRIAN			
Torridonian	Aultbea Formation (nodules)	N. Scotland	-

TABLE 27. AVERAGE PHOSPHATE CONTENT OF JURASSIC IRONSTONES[1]

	Age	Approx. thickness metres	P_2O_5 content Per cent
North ampton Sand Ironstone	Bajocian	up to 6	1.6
Marlstone Rock Bed (Oxfordshire)	Pliensbachian	up to 8	0.6
Marlstone Rock Bed (Lincolnshire and Leicestershire)	Pliensbachian	up to 4.5	0.7
Cleveland Ironstone (Main Seam)	Pliensbachian	3.5	1.2
Frodingham Ironstone	Sinemurian	11	0.8

[1] Dry weight basis

ENGLAND

Phosphatic horizons are most widespread in Jurassic and Cretaceous sediments; no significant Palaeozoic occurrences are known, although nodule beds occur at numerous horizons and partially phosphatised Carboniferous (Visean) limestone has been recorded in Derbyshire and Yorkshire[6].

Jurassic

The low-grade, marine sedimentary, phosphatic ironstones of central England have in the form of basic slag, provided the bulk of the phosphate produced in the United Kingdom and continued to supply some 42,000 tonnes of equivalent P_2O_5 in 1975/76, despite a considerable decline in output in recent years. The geological age, thickness and phosphate content of Jurassic ironstones is shown in Table 27.

The United Kingdom ironstone mining industry has declined markedly in recent years and only the Frodingham Ironstone and Northampton Sand Ironstone are now worked, a basic slag being derived from iron and steel production only from the latter. Reserves of Northampton Sand Ironstone are considerable. Thin phosphatic nodule beds occur associated with some of the Jurassic ironstones but none has been worked commercially.

A bed of Upper Jurassic phosphate rock at the base of the Spilsby Sandstone (Portlandian) in Lincolnshire was investigated as a potential source of phosphate on behalf of the Ministry of Supply during the early part of the Second World War.[3,4] The bed appears to be extensive but, where investigated by trenching at Partney, near Spilsby, was only 0.2 m thick and consisted of a partially phosphatic, glauconitic sandstone containing abundant phosphate nodules. The phosphate is confined mainly to the lower 0.1 m of the bed which at Partney contained only 11.19 per cent P_2O_5. Individual phosphatic nodules were reported to contain up to 24.6 per cent P_2O_5.

No further work was carried out but, assuming a workable thickness of 0.2 m, estimated yields of low-grade phosphate rock would amount to only about 5,000 tonnes per hectare. The deposits are not thought to have any future economic potential.

Lower Cretaceous

Phosphatic nodules, pebbles and fossil casts are common in the Lower Cretaceous of south-eastern England, principally within the Lower Greensand and the Gault. The nodules usually occur as discrete beds at several horizons. Some of the more prominent beds were worked during the latter part of the 19th century.

The most important deposits occur within the Woburn Sands of Buckinghamshire, Bedfordshire and Cambridgeshire[7-11] where the main concentration of workings was established. Perhaps the best known horizon was the Potton Nodule Bed, in the upper part of the formation, which was worked near Potton and Sandy in Bedfordshire. The bed,which is lenticular, ranged between 2 m and 0.15 m in thickness, with an average of about 0.6 m, and consists of pebbles derived from older formations and phosphatised fossils and lumps of clay. Two partial analyses of bulk samples of phosphate nodules from the Potton area gave 15.12 per cent and 22.93 per cent P_2O_5 respectively. Other nodule horizons occur within the Woburn Sands; one near the base of the formation was worked near Great Brickhill in Buckinghamshire and at Woburn and Ampthill in Bedfordshire. Phosphatic nodules were also extracted from the Lower Greensand at Haddenham, Stretham, Upware and Wicken in Cambridgeshire.

Phosphate nodule beds occur at several horizons within the Gault, notably in the middle of the formation where a persistent band of nodules marks the junction of the Lower and Upper Gault. This bed was formerly worked at Towersey near Thame in Buckinghamshire, and elsewhere in southern England phosphatic nodules at the junction of the Lower Greensand and Gault have been worked at Folkestone in Kent and Farnham in Surrey.

Phosphatic nodules were formerly mined from the base of the Speeton Clay (Ryazanian) by adits driven into the foot of the cliffs in Filey Bay, North Yorkshire[12]. Some 500 tonnes annually were produced until 1869 but the bed was only 0.12 m thick. The same bed of similar thickness is also exposed inland. In Lincolnshire impersistent masses and nodules of ferruginous phosphatic limestone containing 11.20 per cent P_2O_5 and 24.2 per cent Fe_2O_3 occur with the Claxby Ironstone (Valanginian-Hauterivian). The phosphate was not recovered and working of the ironstone was abandoned in 1969. Elsewhere in Lincolnshire thin phosphatic nodule beds occur at the base of the Sutterby Marl (Aptian) and at the top and base of the Carstone (Albian).

There is a reference[13] to the presence of 13.5 per cent P_2O_5 in an ironstone from the Roach in the Fulletby Beds (Barremian) of Lincolnshire. However, in the Institute of Geological Sciences' Skegness borehole the bed was found to contain an average of only 1.1 per cent P_2O_5 and 52.4 per cent Fe_2O_3 over a thickness of 5 m.

Upper Cretaceous

Phosphatised faecal pellets occur as a minor constituent throughout the chalk but only very rarely are they concentrated at condensed and winnowed horizons to become an essential constituent of the rock. In the United Kingdom such restricted occurrences of phosphatic chalk have been known for many years but, unlike similar deposits in Belgium and France, have never been exploited. In contrast certain phosphatic nodular horizons at the base of the Lower Chalk (Cenomanian) notably within the Cambridge Greensand, have been extensively worked and provided most of the phosphate rock produced in the United Kingdom during the latter half of the 19th century.

Glauconitic Marl

Phosphatic nodules, chiefly phosphatised fossils and fossil moulds and occasionally phosphatic pebbles derived from the underlying Gault clay and Upper Greensand,are abundant in the Glauconitic Marl (Cenomanian) which represents the basement beds facies of the Lower Chalk of south-eastern England.[14] Phosphatic nodules are concentrated where the Glauconitic Marl is condensed, and over most of south-east England rarely exceeds 2 m in thickness, typically consisting of bioturbated glauconitic chalk crowded with phosphatic intraclasts. Although formerly worked as a source of phosphate the deposits are not likely to be of any future economic interest.

Between Harlington (Bedfordshire) and the Cambridge fens the Glauconitic Marl, which is here known as the Cambridge Greensand, rests with a major non-sequence on Gault clay (Upper Albian).[15] The Cambridge Greensand consists of a thin bed of glauconitic sandy marl, with at its base a concentration of phosphate pebbles referred to as the 'Coprolite Bed'. The phosphate pebbles which are pale buff and dark-brown to black in colour, but light-brown or buff internally, are mainly the casts and moulds of fossils derived from the underlying Gault clay. These deposits formed the basis of an important industry in the late-19th century and were extensively worked, particularly between 1850 and 1880, along the outcrop of the Cambridge Greensand both to the north-east and south-west of Cambridge in a line extending from Barton to Soham (Fig 25).[16] The productive horizon was generally less than 0.3 m thick and average yields amounted to only 750 tonnes per hectare. The average chemical composition of samples are shown in Table 28.[17]

TABLE 28. CHEMICAL COMPOSITION OF CAMBRIDGESHIRE PHOSPHATIC NODULES

	Per cent		
P_2O_5	25.29	26.75	27.01
CaO	43.21	45.39	46.60
Insoluble siliceous matter	8.64	6.22	6.04
Al_2O_3	1.36	2.57	1.41
Fe_2O_3	2.46	1.87	2.08
MgO	1.12	0.48	1.06
Na_2O	0.50	0.73	n.d.
K_2O	0.32	0.84	n.d.
Moisture and organic matter	4.63	4.01	3.52
CO_2	6.66	5.13	5.49
SO_3	0.76	1.06	n.d.
F and loss	4.96	4.95	6.79

n.d. = not determined

Source: Jnl Roy. Agric. Soc., 1860, Ser.1, Vol.21, p. 358.[17]

The Cambridge Greensand deposits were again worked during the First World War near Burwell, north-west of Newmarket and in the Clayhythe and Horningsea area north-east of Cambridge. Overburden thicknesses of up to 6 to 7m were removed and most of the more easily accessible deposits have been exhausted.

Phosphatic chalk

The characteristic soft, white chalk facies contains only minor amounts of phosphate (probably less than 0.15 per cent P_2O_5), but the most widespread occurrence of phosphate within the Chalk is associated with the so-called 'hardgrounds'.[18] These hardened chalk beds, which are rarely more than 0.5 m thick, represent lithified sea floors produced during breaks in sedimentation when contemporaneous hardening and submarine erosion took place. Phosphate is commonly found associated with hardgrounds, principally as replacement zones on their surfaces or lining borings. Discrete grains of phosphatic material, such as fossil debris and faecal pellets, may also be present, commonly infilling burrows. There are numerous hardgrounds within the Chalk and they occur at several different levels, perhaps the best known being the extensive Chalk Rock (Turonian) on average about 2 m thick which represents a series of superimposed closely spaced phosphatised and glauconitised hardgrounds. Phosphatisation of hardground is normally confined to a thin layer and although little chemical data are available it is unlikely that the P_2O_5 content of bulk samples of hardgrounds exceeds 5 per cent.

Phosphatic chalks with higher concentrations of faecal pellets are present only rarely. The best known and only occurrence to have been considered of economic potential in the United Kingdom is at Taplow in Buckinghamshire.[19-22] Here two beds of pelletal phosphatic chalk occur in a condensed and non-sequential Santonian-Campanian sequence extending from the upper part of the Micraster coranguinum Zone to low in the Offaster pilula Zone. The beds, which are 2.6 m and 1.2 m thick, respectively, immediately overlie hardgrounds and are separated by 3.6 m of white chalk with extensive burrow infillings of phosphate chalk. A generalised stratigraphical succession is shown in Table 29.

Analyses for the upper bed range between 7 and 13 per cent P_2O_5 and those for the lower bed 11.5 to 14.8 per cent P_2O_5. The intervening partially phosphatised chalk had P_2O_5 contents between 1.83 and 6.18 per cent.[21] More complete analyses of the Taplow phosphatic chalk are shown in Table 30.

TABLE 29. GENERALISED SUCCESSION OF THE PHOSPHATIC CHALK AT TAPLOW, BUCKINGHAMSHIRE

		Thickness metres
Chalk, with phosphatic grains, richer below	Pilula Zone	1.07
PHOSPHATIC CHALK		2.6
Phosphatic hardground	Marsupites Zone	0.08
White chalk, with abundant phosphatic borings		3.58
PHOSPHATIC CHALK	Uintacrinus Zone	1.22
Phosphatic hardground		0.08
White chalk with phosphatic borings, poorer below	Coranguinum Zone	1.45

TABLE 30. CHEMICAL COMPOSITION OF TAPLOW PHOSPHATIC CHALK

		Per cent	
P_2O_5	11.11	11.6	14.47
CaO	53.79	53.7	53.18
SiO_2	0.21	0.5	0.42
Al_2O_3	0.56	0.8	1.21
Fe_2O_3	0.29	0.1	0.36
MgO	0.32	-	0.25
Na_2O	-	0.2	-
K_2O	-	0.1	-
CO_2	25.14	28.7	26.52
SO_3	0.17	0.7	0.16
Cl	-	trace	-
F	1.62	0.7	1.82
Organic matter	-	2.3	-
Ignition loss	32.50	-	29.70

Sources: Analyses 1&3. Building Research Station, Garston. Monogr. No. 11-108, Minist Supply, 1951, p. 21.

Analysis 2. Q. Jnl geol. Soc., Lond., 1881, Vol.47, No. 187, p. 364.[19]

Phosphatic chalk beds comparable to those at Taplow have been known for many years in the Campanian (Offaster pilula Zone) around Winterbourne and Boxford near Newbury in Berkshire[23] and phosphatic chalk at a similar horizon has been discovered more recently at Kintbury also near Newbury. The quality and extent of the deposits are not known, although these are believed to be of low grade. A very low grade and thin bed of phosphatic chalk also occurs in a non-condensed Turonian Chalk sequence near Lewes in East Sussex.[24] Numerous other phosphatic chalk occurrences have been found in recent years in southern England, but details of their extent and quality are not yet available.

Pleistocene

The phosphatic nodule bed of the Red Crag in Suffolk was the first to be worked commercially in the United Kingdom.[25] The deposits were worked within a triangular area bounded by Ipswich, Orford and Walton-on-the Naze and notably in a tributary valley west of the River Deben. The Red Crag is composed chiefly of ferruginous, cross-bedded shelly sands, but an impersistent phosphatic, conglomeratic bed at the base occupies depressions in the sub-Red Crag surface, the London Clay. It is usually between 0.08 m to 0.6 m thick, although locally it may be much thicker. The bed, which was referred to as the Nodule Bed, Suffolk Bone Bed or Coprolite Bed contains a variety of derived fossils and rocks as well as hard, smooth, yellowish-brown phosphatic nodules and phosphatised bones and teeth, mainly derived from the London Clay. Chemical analyses of Suffolk phosphate are given below, the material containing 24.24 per cent P_2O_5 being regarded as representative of an average sample.

TABLE 31. CHEMICAL COMPOSITION OF SUFFOLK PHOSPHATE

	Per cent	
P_2O_5	28.32	24.24
CaO	40.70	38.20
Insoluble siliceous matter	10.01	12.27
Al_2O_3	4.87	4.81
Fe_2O_3		3.72
MgO	0.34	1.34
Na_2O	0.25	1.18
K_2O	0.78	0.56
H_2O (a)	5.76	2.53
CO_2	5.08	5.37
Cl	trace	0.07
F and loss	3.02	4.31

(a) Including a trace of organic matter.

Source: Jnl Roy. Agric. Soc. 1860, Ser.1, Vol.21, p. 17.

SCOTLAND

Phosphate has been recorded from a number of localities in Scotland and from several geological environments. For example, nodular phosphate beds occur in Jurassic and Cretaceous sediments and fine-grained apatite is associated with uranium mineralisation in Devonian sediments in north-east Scotland. Apatite is widely distributed in Scotland as an accessory and locally abundant mineral in many igneous complexes and, to a lesser extent, in metamorphic rocks, and in some pegmatites. None of the known occurrences in Scotland is of economic interest at present, although apatite associated with the rocks of the Loch Borralan Igneous Complex is worthy of further investigation.

Precambrian

Brown to black small phosphatic nodules and lenticles occur in shales in the Aultbea Formation of the late Precambrian Torridon Group near Loch Broom[26]. They are the first occurrence of phosphate to have been recorded in Precambrian sediments, as far as is known. Local concentrations of apatite have been found also in the Moine Schists.

Post-Cambrian intrusions

The association of apatite with many alkaline igneous rocks is widely recognised and in Scotland these are represented by the Loch Borralan, Loch Ailsh and Loch Loyal complexes in the north-west Highlands. Significant concentrations of apatite have been shown to occur in pyroxenites in the Loch Borralan Complex. The intrusion, which is laccolithic in form, comprises a later suite of syenites, intruding an earlier suite with pyroxenites. The latter have only a limited outcrop on the western margin of the complex but are considered to form the basal layers of the intrusion. A P_2O_5 content of 2.31 per cent was recorded[27] for a melanite-pyroxenite. More recently, significant magnetic anomalies over the poorly exposed western margin of the complex have been drilled to reveal predominantly pyroxenite, but with gradations through hornblende pyroxenites to pure hornblendites. Apatite is always present within these rocks in varying amounts, averaging about 10 per cent in the mode.[28] Titano-magnetite is also abundant and olivine and phlogopite-rich rocks have been encountered, being more predominant near the margin of the intrusion. One borehole revealed predominantly pyroxenite over 152 m (the depth of the hole) and samples from varying depths contained between 6 and 17 per cent apatite[29] (2.4 and 6.8 per cent P_2O_5) with crystals varying in size from less than 0.1 mm to over 10 mm. Fine scale layering in the ultramafic rocks is interpreted as direct evidence for a cumulate origin.

The results of a magnetic survey indicate that the ultramafic rocks form a near vertical lenticular body, possibly extending at least 2 km south-east of Ledmore, which may be due to either faulting or upward squeezing from a more continuous layer. The main magnetic anomaly dies out towards the south-east but lesser anomalies occurring nearer to Ledmore and Loch Borralan may reflect the presence of further parallel bodies of ultramafic rock.

Ordovician

A vertical lenticular mass of apatite-rich rock (30.3 per cent P_2O_5), only a few centimetres wide and traceable over a distance of a few metres, has been reported as an inclusion in a volcanic vent of Ordovician (Caradocian) age at Bail Hill, 3.5 km north-east of Sanquahar in the Southern Uplands of Scotland.[30] The fine-grained rock consists principally of tiny apatite prisms in a matrix of granular calcite. Barytes, mica (probably phlogopite), magnetite and quartz are also present. The apatite rock, which appears to have formed in situ, is believed to be of volcanic-pneumatolytic origin. This unusual occurrence is of interest but has not been evaluated.

Devonian

Some recent discoveries of phosphate in north-east Scotland and on Orkney have been made during exploration for uranium carried out by the Institute of Geological Sciences.[31,32] Uranium mineralisation occurs in a number of geological environments in Scotland, being associated with phosphate notably in sediments of Devonian (Middle Old Red Sandstone) age. These occur in the large Orcadian Basin which extends from the Moray Firth northwards to the Caithness area of north-east Scotland, and into Orkney and Shetland.

Uranium enrichment has been recognised in phosphatic lacustrine sediments ranging from dark siltstones to grey-green sandstones which occur in cyclic units within the Stromness and Rousay Flags. The main occurrences are in northern Caithness and the Stromness district of Orkney, in the lower part of the succession adjacent to the overstep of the Old Red Sandstone onto the metamorphic basement. The phosphatic horizons have thicknesses of only 0.1 m to 0.35 m and show rapid variation in radioactivity along the strike. A linear relationship between uranium and phosphate content has been recognised with an approximate increase of 100 ppm U per 1 per cent increase in P_2O_5 content. The phosphate horizons may exceptionally contain up to 0.2 per cent U and 18 per cent P_2O_5 but the phosphate occurs as very fine-grained collophane which would be difficult to liberate. These uranium deposits are not presently of economic significance.

Jurassic

A 3 m bed of glauconitic sandstone containing phosphatic nodules, occurs some 30 m above the Brora Main Coal in the Upper Jurassic coalfield at Brora on the north-east coast of Scotland. Examination of borehole samples by the Institute of Geological Sciences in 1967 showed that although the nodules contain on average 19.3 per cent P_2O_5, the bed contain less than 1 per cent P_2O_5.[33] A similar Middle Jurassic phosphatic nodular bed a few centimetres thick occurs on Skye, south of Portree.

Cretaceous

Phosphate rock is present in thin sequences of Cretaceous sediment which outcrop beneath Tertiary basalts in the Morven area and on Mull on the west coast of Scotland.[33] At Poll Luachrain, north-west of Barr (some 13 km north-west of Loch Aline) a metre bed of glauconitic sandstone of Cenomanian age consists essentially of approximately equal amounts of dark-green glauconite and quartz in a pale brown matrix composed chiefly of collophane and, locally, some calcite. Chemical analysis of a bulk sample by the Macaulay Institute for Soil Research, Aberdeen, showed 25.6 per cent P_2O_5. The deposit has only a very limited extent, however. Slightly phosphatic, glauconitic sandstones occur throughout the area between Loch Sunart and Loch Aline and are also present on Mull.

WALES

Phosphate rock occurs at numerous localities in Wales, in sediments ranging from Cambrian to Jurassic in age.[2] None of these occurrences has been of economic interest, however, with the notable exception of a thin bed of nodular phosphate which occurs over a relatively wide area between Welshpool and the Berwyn Mountains in north-eastern Powys.[3,34] The bed, which is of Upper Ordovician (Caradocian) age and between 0.3 m and 0.5 m in thickness, was worked between 1865 and 1884 at Cwmgwnen and at several other localities near Llangynog on both the eastern and western limbs of the Berwyn Anticline (Fig 26).

Geology

Two phosphatic nodule beds are known within the Upper Ordovician sediments of the Berwyn Mountains area. The better developed, and the bed formerly worked, occurs within the Nod Glas Formation of Caradocian age; scattered, small, black phosphatic nodules also

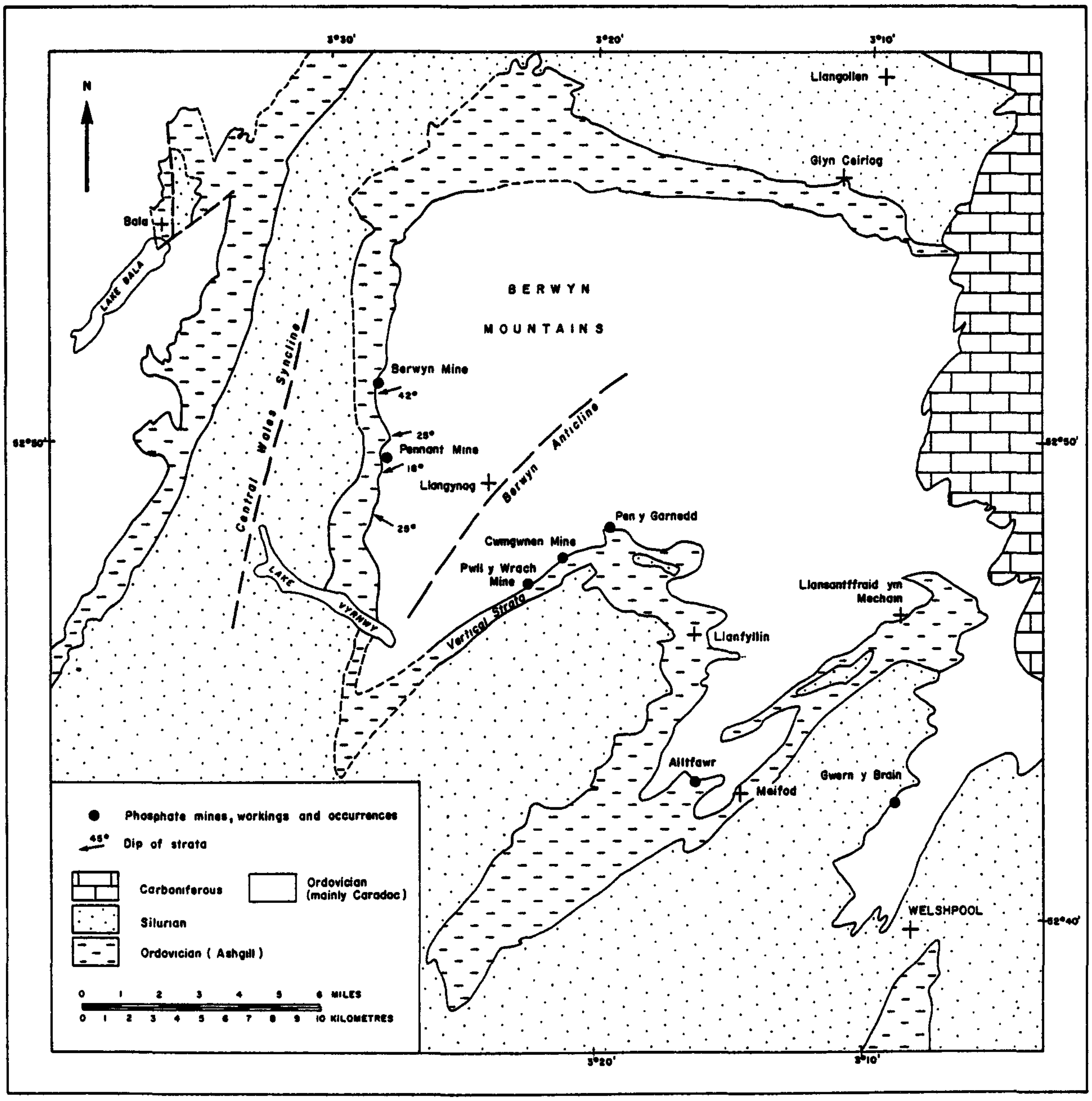


Fig 26. Distribution of phosphate occurrences and former workings in Powys, Wales.(Compiled by R.Cave, Institute of Geological Sciences.)

occur in basal Ashgillian mudstones. The two beds are stratally very close and, as the Ashgillian is transgressive onto the underlying Caradocian sediments, in places the two beds must be in juxtaposition, although this contact is nowhere exposed. The Nod Glas Formation is poorly exposed over much of the area and the phosphate bed is rarely seen. Former underground workings are now inaccessible.

North-west of Welshpool the Nod Glas consists of some 10 m of black shale, phosphate rock and limestone. The formation is divided into an upper Pen y Garnedd Shale member and a lower Pen y Garnedd Phosphorite member, the latter comprising a basal phosphatic limestone with the main nodular phosphate bed at the top (Fig 27)[35].

Most of the former phosphate workings, including those at Cwmgwnen, Pen-y-garnedd and Pwll-y-Wrach, lie to the south-east of Llangynog on the eastern limb of the Berwyn Anticline and the strata here are steeply dipping or overturned so that the phosphate bed had to be mined by methods like those used for a vein deposit. On the western limb of the anticline the dip varies between 15° and 45° and two mines, Berwyn and Pennant, were developed. In addition there were small workings near Llanfyllin.

At Cwmgwnen, thicknesses of 1 m of phosphatic shale and 3 m of phosphatic limestone have been recorded, the phosphatic limestone having a reported P_2O_5 content of over 16 per cent. These sequences are no longer visible at outcrop, but at Gwern-y-Brain near Welshpool a sample of phosphatic limestone 0.15 m beneath the main nodular bed contains 6.4 per cent P_2O_5, and black shales 0.5 m above the nodular bed contain 5.5 per cent P_2O_5. Phosphatic limestone is absent beneath the nodular bed at Alltfawr near Meifod.

The Caradocian Nod Glas Formation also occurs to the west and north-west of the Berwyn Mountains but apparently is not phosphatic. Within the formation the Pen-y-Garnedd Phosphorite is restricted to the summit and edges of a rising shelf which occupied the Bala - north Powys area during Caradocian times.

Petrography and chemical composition

The main phosphate bed consists of closely packed, ellipsoidal, hard, black shiny nodules generally about 6 cm but occasionally 15 cm in diameter, embedded in a matrix of calcareous mudstone. In thin section the nodules show a pale-brown almost isotropic groundmass of granular phosphate. Varying amounts of quartz and pyrite are present,the latter giving the rock a rusty-red appearance on weathering at the surface. There is also a rich assemblage of microfossils, chiefly the remains of sponge spicules, ostracods and bryozoa.

Chemical analyses indicate that the phosphatic nodules contain between 27.5 and 32.5 per cent P_2O_5 and an average of about 21 per cent P_2O_5 for the entire bed has been reported. An analysis of an 8-tonne bulk sample of nodular rock from the Berwyn Mine showed 23.79 per cent P_2O_5; 32.62 per cent CaO; 28.75 per cent SiO_2 and 4.60 per cent Fe_2O_3 and Al_2O_3.[36] Compared with these results the grade of the nodular bed collected during a brief reconnaissance of the deposits by the Institute of Geological Sciences in 1976 showed lower P_2O_5 values than had been anticipated, although samples were not collected from the former workings. Some phosphatic nodules have been found to contain 0.003 per cent U_3O_8.[5] Elsewhere in Wales phosphate nodules have been reported from a number of localities notably in the Upper Cambrian Dolgelly Beds and Tremadoc Beds and at the base of the Arenig (Ordovician).

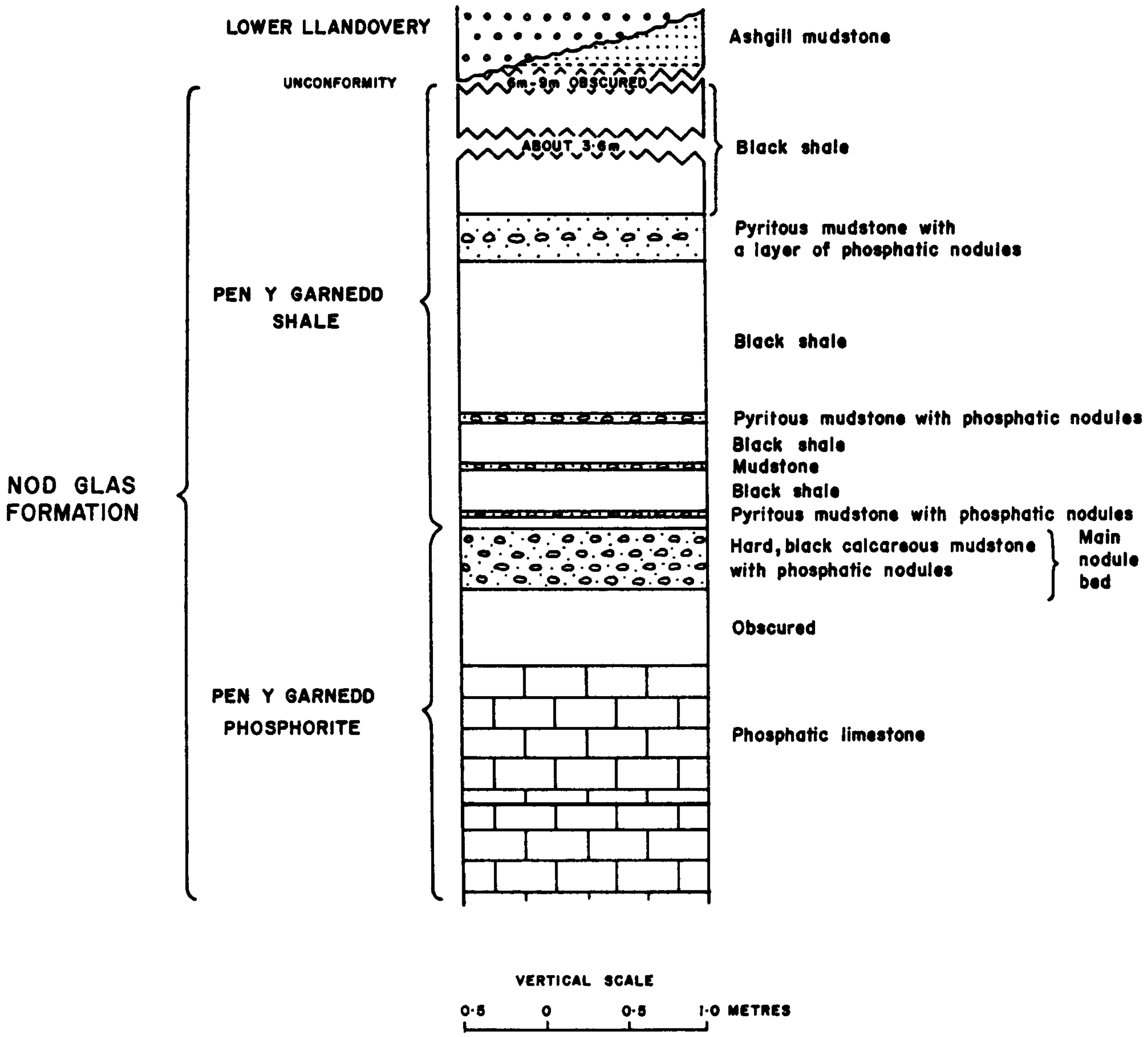


Fig 27. Stratigraphical section through the Nod Glas Formation, Gwern y Brain, near Welshpool. (Based on Cave, 1965.)

NORTHERN IRELAND

Phosphate nodules and phosphatised fossils have been found at various localities in the coastal area of County Antrim in rocks of Upper Cretaceous and Carboniferous age, chiefly in the Turonian Glauconitic Sands and Sandstones within the Hibernian Greensand. A phosphatic nodule bed within glauconitic chalk occurs also at the base of the White Limestone. The occurrences are too limited in extent and thickness to be of economic interest.

PRODUCTION

There is currently no production of phosphate rock in the United Kingdom but during the latter half of the 19th century the country was an important producer. Production was based almost entirely on phosphatic nodule beds (erroneously referred to as 'coprolites') within the Glauconitic Marl (Cenomanian) at the base of the Chalk, particularly the Cambridge Greensand; the Red Crag (Pleistocene); the Lower Greensand (Aptian) and Gault (Albian); at the base of the Speeton Clay (Ryazanian - Aptian) and in the Nod Glas Formation (Ordovician) in Wales. There has been no recorded output of phosphate rock in Scotland or Northern Ireland.

Recorded production of phosphate rock began in 1874 but it is thought that mining began as early as 1842. Last recorded production was 4 tonnes in 1909, except for a small output from Cambridgeshire under the emergency conditions during the 1914-1918 period. Total recorded production during the period 1874 to 1909 was 1,205,000 tonnes. Including an estimated total output of 737,000 tonnes in Suffolk and Cambridgeshire prior to 1874, it is probable that nearly 2 million tonnes of phosphate rock were produced during the life of the phosphate mining industry in the United Kingdom. Annual output reached a maximum of some 262,000 tonnes in 1876, but subsequently declined sharply in the face of competition from imported higher grade rock.

An estimated 325,000 tonnes of phosphate rock were produced from the Red Crag deposits in Suffolk. The bulk of the remaining output was obtained from the Cambridge Greensand deposits and smaller quantities from the Lower Greensand of Buckinghamshire, Bedfordshire and Cambridgeshire and deposits elsewhere. No records exist of the quantity produced from the Nod Glas Formation in Wales prior to 1874, but from that year until 1884 a total of only 1,154 tonnes was produced from deposits in the Berwyn Mountains. A maximum recorded annual output of 512 tonnes was achieved in 1874. Phosphate rock produced in the United Kingdom did not contain more than about 27 per cent P_2O_5 and frequently had a relatively high iron oxide content.

RESOURCES

Individual occurrences of phosphate rock in the United Kingdom are of relatively low grade, apparently of limited extent, and as beds too thin to be of current economic interest. Since the beginning of the present century only a small number have been of interest as a potential source of phosphate, notably during the two World Wars. During the emergency conditions imposed by the Second World War a comprehensive record of phosphate rock occurrences was made.[2-4,21] A limited amount of exploration and evaluation work was carried out but no phosphate rock was ever produced. No attempt was made to calculate total phosphate resources and no further phosphate resource assessment work has been carried out since, although some commercial interest was again apparent after the dramatic phosphate rock price increases announced in 1974.

The geology of the Jurassic rocks of the United Kingdom is relatively well known and it is therefore not likely that any significant occurrence of phosphate rock has been overlooked. Nevertheless, certain condensed Jurassic sequences may be worth examining, although any occurrences, if found, are likely to be of low grade.

Resources of phosphate within the Lower Greensand are likely to be small, due to the limited thickness of the nodule beds, and the known deposits are not considered to have any future economic potential. Minor tonnages of phosphatic nodules might be recovered during the course of working the Lower Greensand for construction sand.

Drilling of the Cambridge Greensand deposits carried out in 1918 by the Department for the Development of Mineral Resources in the United Kingdom indicated that in places about 880 tonnes per hectare of nodules grading 25.8 to 26.7 per cent P_2O_5 could be recovered. Reserves over 285 hectares were estimated at 246,000 tonnes to an average depth of overburden of 5.3 m. Such deposits are unlikely to have any further economic potential.

The deposit of phosphatic chalk at Taplow in Buckinghamshire was investigated as a potential commercial source of phosphate during the First World War and re-surveyed on behalf of the Ministry of Supply in 1940, when sampling, pitting and augering was carried out.[21] Resources adjacent to the Lodge Pit on the southwestern side of Taplow were estimated at 500,000 tonnes. However, the full extent of the deposit has never been delineated by drilling. Part of the deposit lies beneath Taplow itself but if an extension of the deposit was proved beneath the thin Tertiary cover to the east resources would be considerably increased. Similarly the deposit may extend down dip to the south but at increasing depth.

Beneficiation tests carried out by the Building Research Establishment, Garston,[37] showed that a concentrate (Table 32) containing about 28 per cent P_2O_5 could be obtained from Taplow phosphatic chalk by calcining at 1100 to 1200°C, hydrating, and separating the dried slaked lime by air elutriation, the phosphate concentrate remaining in the coarser fraction.

TABLE 32 TAPLOW PHOSPHATIC CHALK CONCENTRATE

	Per cent
P_2O_5	27.80
CaO	60.55
SiO_2	1.88
Al_2O_3	0.10
Fe_2O_3	0.41
MgO	0.14
CO_2	1.19
F	3.60
Ignition loss	6.51

Source: Building Research Station, Garston. Monogr. No. 11-108, Minist. Supply, 1951, p. 21.[3]

The area of maximum stratigraphical condensation of the Chalk at or near the base of the Campanian over the western part of the London Platform would appear to be the most promising area for further investigation. The known phosphatic chalks at Taplow, Winterbourne, Boxford and Kintbury all occur in this area and at this horizon. They appear to occupy submarine erosion channels. The same horizon to the south in West Sussex and Hampshire may also be worth investigating. The Chalk in Yorkshire and Lincolnshire, in contrast, exhibits a very stable sedimentary succession with no phosphatisation or glauconitisation.

Phosphate rock in various forms is widely distributed in Scotland, although none of the known occurrences have as yet been of economic interest. The thin phosphatic, glauconitic sandstones of Upper Cretaceous age in the Morven district on the west coast of Scotland were examined recently by Robertson Research International Ltd as part of a mineral survey of the area carried out on behalf of the Highlands and Islands Development Board. No significant occurrences were found and while it is possible that richer beds may be present in pockets beneath Tertiary basalts such beds would be difficult and expensive to locate. During the Second World War an investigation[38] conducted on behalf of the Ministry of Supply showed that the relatively rich phosphatic sandstone at Poll Luachrain did not extend for more than 12 m westwards along the strike of the beds, which within a short distance to the east are also cut by igneous dykes and become attenuated. Any mining would have to be undertaken underground in view of the thick overburden of basaltic lava.

The most interesting to have been identified in the United Kingdom to date is the occurrence of significant amounts of apatite associated with the pyroxenites of the Loch Borralan Complex. Limited drilling (for titanium minerals, not phosphate) has revealed an abundant, although variable apatite content in the pyroxenites over considerable thicknesses. Up to 17 per cent apatite (7 per cent P_2O_5) has been recorded[29] and the mineral may be present in even greater amounts. Further exploration to determine the extent and shape of the ultramafic body and the variation in apatite content is justified. Beneficiation tests on core material should also be carried out. The pyroxenites on the south-eastern margin of the nearby Loch Ailsh alkaline intrusion are also worth investigating although the apatite content here appears to be extremely variable.

No detailed geological survey and economic assessment of phosphate occurrences in the Berwyn Mountains of Wales has been carried out. In 1941 preliminary field investigations were carried out under the auspices of the Ministry of Supply to test the value of the phosphate when finely ground for application to acid soils. The results obtained were not favourable and no further work was carried out.

The Pen-y-Garnedd nodular phosphate bed in the Nod Glas Formation appears to extend over a wide area, although exposures are poor.

The thickness of the bed (<0.5 m) and its structural complexity are such that it is unlikely to be of future economic interest. However, associated with the nodular bed are phosphatic shales and phosphatic limestone, which appear to have received little attention as potential sources of phosphate rock. Taking these phosphatic beds into account, there are geological grounds for believing that the phosphate-bearing sequence, if perhaps of low grade, is thicker than was previously thought. A borehole programme would be required to determine the thickness and grade of this sequence.

The extent to which the Nod Glas sediments might be phosphate bearing elsewhere in North Wales is unknown. With the exception of the Nod Glas, significant occurrences of phosphate have not been recorded from Lower Palaeozoic sediments. However, certain Lower Palaeozoic condensed mudstone sequences in Wales, the Southern Uplands of Scotland, the Lake District and the Isle of Man may warrant examination. For example, in the Southern Uplands of Scotland Caradocian and Ashgillian black graptolitic shales with interbedded cherts (the Glenkiln Shales and the Hartfell Shales) are highly condensed in the Moffat area and elsewhere. The mudstones represent either slow accumulation in the deeper part of a depositional basin or may have accumulated at more moderate depths on submarine highs remote from other sources of sediment. The latter conditions may be favourable to phosphate deposition. Other incompletely known Lower Palaeozoic sequences might also be worth investigating.

REFERENCES ON THE UNITED KINGDOM

1 Phosphate of lime. A. Strahan. Mem.geol.Surv.Spec.Rep.Miner. Resour.Gt Br.,1917,Vol.5,pp.15-24.

2 Occurrences of phosphate in Pre-Cretaceous rocks. K.P. Oakley. Wartime Pamph.geol.Surv.Engl.Wales,1942,No.8,Pt.4.29 pp.

3 Phosphorites of Lower Cretaceous age in Lincolnshire and of Ordovician age in Montgomeryshire. K.P. Oakley and H.G. Dines. Wartime Pamph.geol.Surv.Engl.Wales, 1941, No.8, Pt.3. 29 pp.

4 Lower Cretaceous phosphorites, Isle of Wight to Yorkshire, with supplementary notes on Lincolnshire. K.P. Oakley. Wartime Pamph. geol.Surv.Engl.Wales, 1941, No.8, Pt.3. 29 pp.

5 Radioactivity studies of some British sedimentary rocks. D.R.A. Ponsford. Bull.geol.Surv.Gt Br., 1955, No.10, pp.24-44.

6 Uraniferous collophane in the Carboniferous Limestone of Derbyshire and Yorkshire. J.D. Peacock and K. Taylor. Bull.No.25, geol.Surv.Gt Br. 1966, pp.19-32.

7 On the occurrence of Neocomian sands with phosphatic nodules at Brickhill, Bedfordshire. W. Keeping. Geol.Mag., New Ser., Decade 2, 1875,Vol.2,No.8, pp.372-375.

8 Geology of the country around Huntingdon and Biggleswade. E.A. Edmonds and C.H. Dinham. Mem.geol.Surv.Engl.Wales, 1965. 90 pp.

9 Geology of the country around Cambridge. B.C. Worssam and J.H. Taylor. Mem.geol.Surv.Engl.Wales, 1969. 159 pp.

10 On a deposit of phosphatic nodules in the Lower Greensand, at Sandy, Bedfordshire. P.B. Brodie. Geol.Mag.,1866,Vol.3,No.22, pp.153-155.

11 The Potton and Wicken Phosphatic Deposits being the Sedgwick Prize Essay for 1873. J.J.H. Teall. 44 pp. (Cambridge: Deighton, Bell, and Co., 1875.)

12 On the subdivisions of the Speeton Clay. G.W. Lamplugh. Q.Jnl geol.Soc.Lond.,1889,Vol.45,No.180,pp.575-618. The coprolite-bed, pp.583-585.

13 The geology of East Lincolnshire. A.J. Jukes-Browne. Mem.geol. Surv.Engl.Wales.,1887. 181 pp.

14 Morphology and genesis of nodular phosphates in the Cenomanian Glauconitic Marl of south-east England. W.J. Kennedy and R.E. Garrison. Lethaia, 1975, Vol.8, No. 4, pp. 339-360.

15 Foraminiferal evidence for the age of the Cambridge Greensand. M.B. Hart. Proc.Geol.Ass., 1973, Vol.84, Pt.1, pp. 65-82.

16 The Cambridgeshire Coprolite Mining Rush. R. Grove. 51 pp. (Cambridge: The Oleander Press, 1976.)

17 On the chemical composition and commercial value of Norwegian apatite, Spanish phosphorite, coprolites and other phosphatic materials used in England for agricultural purposes. A.Voelcker. Jnl Roy.agric.Soc.,1860, Ser.1, Vol.21, pp.350-381. Cambridgeshire coprolites, pp.357-359. Suffolk coprolites, pp.359-360.

18 Morphology and genesis of nodular chalks and hardgrounds in the Upper Cretaceous of southern England. W.J. Kennedy and R.E. Garrison. Sedimentology, 1975, Vol.22,No.3, pp.311-386.

19 On a phosphatic chalk with Belemnitella quadrata at Taplow. A. Strahan. Q.Jnl geol.Soc.Lond.,1891,Vol.47,No.187,pp.356-366. Discussion, pp.366-367.

20 On the age and relations of the phosphatic chalk of Taplow. H.J.O. White and L.Treacher. Q.Jnl geol.Soc.Lond.,1905,Vol.61, No.243, pp.461-493. Discussion, pp.493-494.

21 Phosphatic chalk of Taplow. H.L. Hawkins. Wartime Pamph.geol. Surv.Engl.Wales, 1940, No.8, Pt.1. 6 pp.

22 The origin of beds of phosphatic chalk with special reference to those at Taplow, England. N.R. Willcox. C.r. 19th Int.geol. Congr.,1952,Sect.11,Pt.11,pp.119-133. (Algiers: 1955.)

23 The phosphatic chalks of Winterbourne and Boxford (Berkshire). H.J.O. White and L. Treacher. Q.Jnl geol.Soc.Lond., 1906, Vol.62,No.247,pp.499-521.Discussion, pp.521-522.

24 On a phosphatic chalk with Holaster planus at Lewes. A. Strahan. Q.Jnl geol.Soc.Lond., 1896,Vol.52, No.207, pp.463-472.

25 The Pliocene deposits of Britain. C. Reid. Mem.geol.Surv.U.K., 1890. 326 pp. The Nodule Beds, or basement beds of the Crag, Ch.2, pp. 6-18.

26 The geological structure of the North-West Highlands of Scotland. B.N. Peach, J. Horne, W. Gunn, C.T. Clough, L.W. Hinxman and J.J.H. Teall. Mem.geol.Surv.Gt Br., 1907. 668 pp. Phosphatic nodules, pp. 287-288.

27 Loch Borrolan laccolith, north-west Scotland. S.J. Shand. J.Geol., 1939, Vol.47, pp. 408-420.

28 Layered ultramafic rocks within the Borralan Complex, Scotland. D.W Matthews and A.R. Woolley, Scott.Jl.Geol.1977,Vol.3, No.3, pp. 223-236.

29 A.R. Woolley. Personal communication, October 1977.

30 An apatite rock from Dumfriesshire. W.Q. Kennedy and C.O. Harvey. Mem.geol.Surv.Summ.Prog., 1935, Pt.2, pp. 53-59.

31 New evidence of uranium and other mineralization in Scotland. M.J. Gallagher, U. McL. Michie, R.T. Smith and L. Haynes. Trans Inst. Min.Metall., Sect.B, 1971, Vol.80, pp. B150-B173.

32 Distribution and origin of uranium concentrations in the Pre-Carboniferous rocks of Scotland. M.J. Gallagher and U.McL. Michie. Proc.1st scient.Conf.Iraq.atom.Energ.Commn,Baghdad,1975, pp.479-488.

33 A summary of the mineral resources of the 'Crofter Counties' of Scotland, comprising Argyllshire, Caithness, Invernessshire, Orkney and Shetland, Ross and Cromarty and Sutherland. N.G. Berridge. Rep.No.69/6, Inst. geol.Sci., 1969, p. 10.

34 The phosphorite deposits of North Wales. D.C. Davies. Q.Jnl geol.Soc.Lond., 1875, Vol.31, No.123, pp.357-365. Discussion, pp. 366-367.

35 The Nod Glas sediments of Caradoc age in North Wales. R. Cave. Geol.Jnl, 1965, Vol.4, Pt.2, pp. 279-298.

36 A Treatise on Earthy and Other Minerals and Mining. 3rd Ed. D.C. Davies and E.H. Davies. Pp. 129-142. (London: Crosby Lockwood & Son, 1892.)

37 The production and agricultural value of silicophosphate fertilisers. Monogr. No. 11-108, Minist.Supply,1951. 283 pp.

38 Report on the Poll Luachrain Phosphatic Deposit, Morven District, West Argyllshire. W.R. Jones. 10 pp. (London: Royal School of Mines, 1941.) (Typescript.)

5. RECOMMENDATIONS

1 Although it is recognised that none of the known occurrences is at present of commercial interest as a source of phosphate rock for phosphoric acid or phosphate fertiliser manufacture, several interesting new discoveries have been made in recent years. It is likely that other, similar discoveries remain to be made as systematic exploration proceeds, and the possibility of relatively large deposits being located at depths greater than those known to occur at present within the EEC cannot be entirely excluded.

2 Only a limited amount of systematic work relating to the phosphate rock resources of the EEC has been carried out within the Member States. In addition, the character of phosphate rock is such that it has not always been recognised even where it has been uncovered in the course of other investigations. It is recommended, therefore, that a working party with available phosphate expertise be set up, which would stimulate, guide and co-ordinate investigations likely to be undertaken. It is anticipated that much, if not all, of the work outlined below would be conducted by the national agencies, with certain, perhaps somewhat more academic,aspects being allocated to appropriate private institutions.

RESOURCE EVALUATION

3 Quantitative estimates are available for certain phosphate deposits within the EEC, the economic potential of which merits further assessment.

The deposits in this category include:

(a) the Upper Cretaceous phosphatic chalk formations of Belgium (Mons Basin) and northern France (Paris Basin), and

(b) the Tertiary phosphatic limestones of the Salentino Peninsula of southern Italy.

The largest known resources in the EEC are in the Mons Basin,where between 300 million and 500 million tonnes of phosphatic chalk, which averages 8 to 10 per cent P_2O_5, are estimated to be present.

REGIONAL AND NATIONAL RESEARCH

4 Exploratory work should be undertaken in each of the EEC countries as part of a long-term research project to establish a more comprehensive national inventory of phosphate rock resources and to erect a monitoring system whereby it might be possible to ensure that potential resources of phosphate rock are not overlooked due to inadequate surveillance as geological data continue to become available. Investigation of the phosphate potential of major sedimentary basins is recommended, placing individual phosphate occurrences, where known, in their precise palaeogeographical context, i.e. their stratigraphy and the sedimentological and structural parameters controlling their deposition. Such a systematic analysis could lead to the delineation of areas more favourable to phosphate deposition than those identified to date.

5 On a regional basis, it is recommended that the full extent of the phosphate-bearing carbonate sedimentary facies of Upper Cretaceous age be investigated. The facies occurs in the United Kingdom and is well developed in France and Belgium (Paris and Mons Basins). Geological data suggest that phosphatic beds of comparable age might exist within a much larger sedimentary phosphate province which embraces parts of the Netherlands, the Federal Republic of Germany and Denmark, although in the latter two countries the phosphatic beds may lie at depths which would prohibit economic mining.

6 It is recommended that the general initiatives outlined above should include or be supplemented by research on:

(a) the Lower Carboniferous phosphate-bearing sequence in the Pyrenean and Montagne Noire areas of southern France.

It is of interest that the sequence, which probably contains the largest potential resource of phosphate rock in France at present, is known to extend from Cantabria and Asturia in northwestern Spain, through the Pyrenees and the Montagne Noire, and into the Federal Republic of Germany.

(b) the phosphate beds of Upper Carboniferous (Namurian) age in the western part of the Irish Republic (County Clare and County Limerick), where appreciable areas remain unexplored; in addition, the possibility of discovering extensions of the phosphate-bearing horizons into the basal Namurian of the East Midlands should not be ignored.

(c) the apatite-bearing pyroxenites of the Loch Borralan alkaline igneous complex in northern Scotland (United Kingdom). This is the most encouraging of the phosphate occurrences found in the UK to date and the most unconventional occurrence within the EEC;

(d) the Ordovician Nod Glas Formation in the Berwyn Mountains of Wales (United Kingdom), where there are geological grounds for believing the entire phosphate-bearing sequence to be thicker than was previously thought. In general, the Lower Palaeozoic sequences in the United Kingdom are incompletely known, and may be worth investigating.

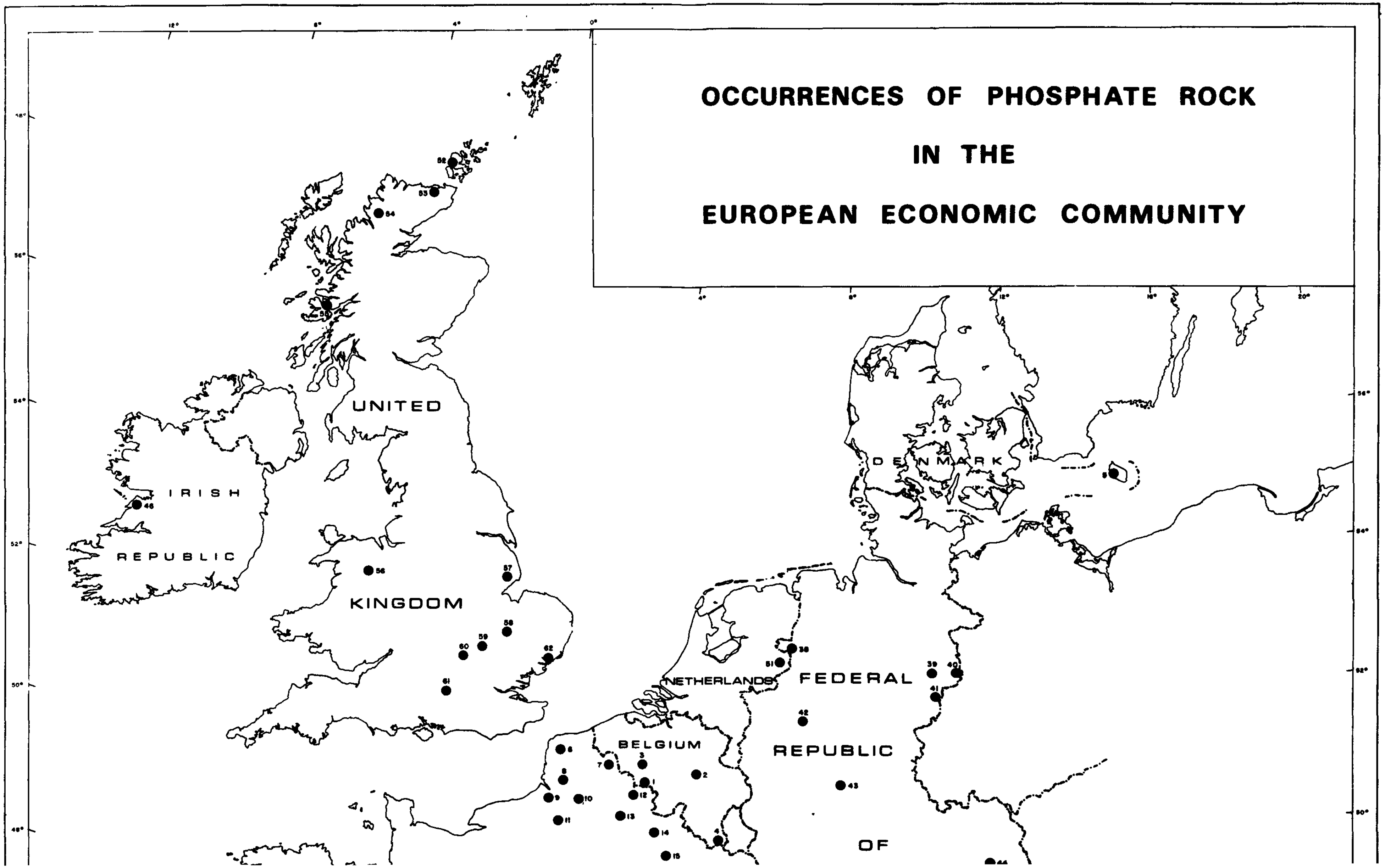
BENEFICIATION AND PHOSPHATE ROCK CHARACTERISATION STUDIES

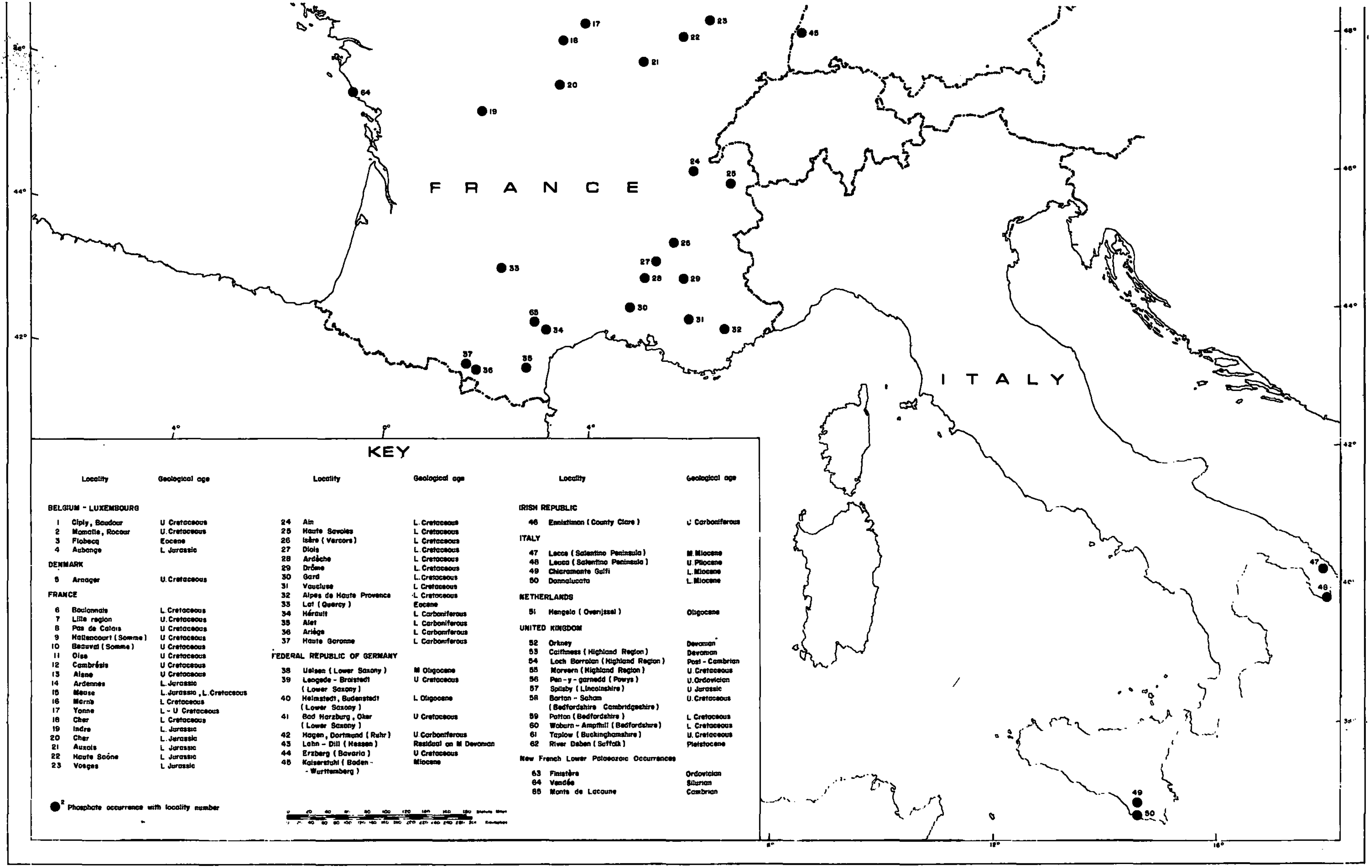
7 If development work on individual phosphate deposits appears justified, beneficiation studies should be carried out at some stage to determine the feasibility of producing phosphate concentrates suitable for phosphoric acid and phosphate fertiliser manufacture. It should be noted that the bulk of the phosphate rock resources of the EEC is in the form of carbonate-rich rock (phosphatic chalk or limestone) the economic beneficiation of which has been largely unsuccessful.

8 Phosphate rock characterisation studies form an essential, integral but unfortunately hitherto largely neglected, part of any beneficiation work carried out. Mineralogical and chemical analyses are essential in selecting suitable methods of processing phosphate rock from individual deposits.

9 It is recommended that the economic benefit which might result from the commercial extraction of uranium during phosphoric acid manufacture should be assessed fully. In this context, both the County Clare (Irish Republic) and Ciply (Belgium) phosphate deposits are reported to be highly radioactive.

OCCURRENCES OF PHOSPHATE ROCK
IN THE
EUROPEAN ECONOMIC COMMUNITY





KEY

	Locality	Geological age
BELGIUM - LUXEMBOURG		
1	Ciply, Baudour	U Cretaceous
2	Momalle, Rocour	U. Cretaceous
3	Flobecq	Eocene
4	Aubange	L. Jurassic
DENMARK		
5	Arnager	U. Cretaceous
FRANCE		
6	Boulonnais	L. Cretaceous
7	Lille region	U. Cretaceous
8	Pas de Calais	U Cretaceous
9	Hallencourt (Somme)	U Cretaceous
10	Beauval (Somme)	U Cretaceous
11	Oise	U Cretaceous
12	Cambrésis	U Cretaceous
13	Aisne	U Cretaceous
14	Ardennes	L. Jurassic
15	Meuse	L. Jurassic, L. Cretaceous
16	Marne	L Cretaceous
17	Yonne	L - U Cretaceous
18	Cher	L Cretaceous
19	Indre	L. Jurassic
20	Cher	L. Jurassic
21	Auxois	L Jurassic
22	Haute Saône	L Jurassic
23	Vosges	L Jurassic
24	Ain	L. Cretaceous
25	Haute Savoies	L Cretaceous
26	Isère (Vercors)	L Cretaceous
27	Diois	L. Cretaceous
28	Ardèche	L Cretaceous
29	Drôme	L. Cretaceous
30	Gard	L. Cretaceous
31	Vaucluse	L Cretaceous
32	Alpes de Haute Provence	L Cretaceous
33	Lot (Quercy)	Eocene
34	Hérault	L Carboniferous
35	Alet	L Carboniferous
36	Ariège	L Carboniferous
37	Haute Garonne	L Carboniferous
FEDERAL REPUBLIC OF GERMANY		
38	Uelsen (Lower Saxony)	M Oligocene
39	Lengede - Broistedt (Lower Saxony)	U Cretaceous
40	Helmstedt, Budenstedt (Lower Saxony)	L Oligocene
41	Bad Harzburg, Oker (Lower Saxony)	U Cretaceous
42	Hagen, Dortmund (Ruhr)	U Carboniferous
43	Lahn - Dill (Hessen)	Residual on M Devonian
44	Erzberg (Bavaria)	U Cretaceous
45	Kaiserstuhl (Baden - - Wurttemberg)	Miocene
IRISH REPUBLIC		
46	Ennistimon (County Clare)	U Carboniferous
ITALY		
47	Lecce (Salentino Peninsula)	M. Miocene
48	Lecce (Salentino Peninsula)	U. Pliocene
49	Chiaramonte Gulfi	L. Miocene
50	Donnalucata	L. Miocene
NETHERLANDS		
51	Hengelo (Overijssel)	Oligocene
UNITED KINGDOM		
52	Orkney	Devonian
53	Caithness (Highland Region)	Devonian
54	Loch Borralan (Highland Region)	Post - Cambrian
55	Morvern (Highland Region)	U. Cretaceous
56	Pen - y - garnedd (Powys)	U. Ordovician
57	Spilsby (Lincolnshire)	U Jurassic
58	Barton - Soham (Bedfordshire Cambridgeshire)	U. Cretaceous
59	Potton (Bedfordshire)	L Cretaceous
60	Woburn - Ampthill (Bedfordshire)	L Cretaceous
61	Taplow (Buckinghamshire)	U. Cretaceous
62	River Deben (Suffolk)	Pleistocene
New French Lower Palaeozoic Occurrences		
63	Finistère	Ordovician
64	Vendée	Silurian
65	Monts de Lacaune	Cambrian

●^{2} Phosphate occurrence with locality number

6. GENERAL REFERENCES

Phosphates and Superphosphate. 2nd Ed. A.N. Gray. 416 pp. (London: E.T. Heron & Co.Ltd., 1944.)

Phosphorus and its Compounds. Vol.2. Technology, Biological Functions and Applications. Edited by J.R. Van Wazer. 2046 pp. (New York: Interscience Publishers, Inc., 1961.)

Fertilizer Manual. 218 pp. (New York: United Nations Industrial Development Organization, 1967.)

The production and properties of basic slag. G.G. Brown and K.F.J. Thatcher. Proc.Fertil.Soc., 1967, No.96. 47 pp. Discussion, pp. 48-56.

Phosphorus and Potassium. (London: The British Sulphur Corporation Limited.) (Bi-monthly.)

Phosphate fertilizers. Properties and processes. A study of technological, economic and agronomic considerations. D.W. Bixby, D.L. Ducker and S.L. Tisdale. Tech.Bull.No.8, Sulphur Inst.,1964. 64 pp.

Die Rhenania-Dünger. W. Werner. 120 pp. (Hannover: Verlag M. & H. Schaper, 1967.) (In German.)

Rock-Forming Minerals. Vol.5. Non-Silicates. W.A. Deer, R.A. Howie and J. Zussman. 333 pp. (London: Longmans, Green & Co.Ltd.,1962.) Apatite, pp. 323-338.

Cento Symposium on the Mining and Beneficiation of Fertilizer Minerals, Istanbul, 1973. 345 pp. (Ankara: Central Treaty Organization, 1974.) Mining and beneficiation of phosphates, pp. 131-242.

The phosphorite facies and the genesis of phosphorites. A.V. Kazakov. Trudy nauch.Inst.Udobr.Insektofung No.142,1937. 22 pp. (English transl.)

Phosphate rock: world production, trade and resources. A.J.G. Notholt. Proc. 1st 'Industrial Minerals' int.Congr.Lond, 8-9 July 1974, 1975, pp. 104-119.

Engrais et phosphate. P. Lafitte. Chron.Rech.min.,1977, Vol.45, No.435, pp. 3-14. (In French. English abstract, pp. 3-4.)

Disponibilité et besoins futurs en minerais phosphatés compte tenu de la lutte anti-pollution et de nouvelles applications possibles. M. Slansky. 70 pp. (Orléans: Bureau de Recherches Géologiques et Minières, 1975.) (In French.)

Répartition et possibilités de concentration de l'uranium dans les phosphates sédimentaires. M. Slansky. Pap.Adv.Com.Mtg Uranium Deposits Afr., int. atom. Energy Ag., Lusaka, 1977. 10 pp. (In French. Typescript.)

Phosphorus, phosphoric acid and inorganic phosphates. A.F. Childs. Pp. 375-402 in The Modern Inorganic Chemical Industry. (London: The Chemical Society, 1977.)