

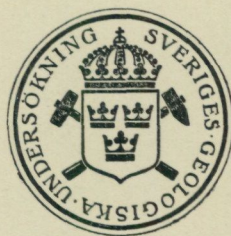
SVERIGES GEOLOGISKA UNDERSÖKNING

SERIE C NR 626 AVHANDLINGAR OCH UPPSATSER ÅRSBOK 61 NR 11

OLOF ARRHENIUS

ORE, IRON, ARTEFACTS AND
CORROSION

WITH 4 PLATES



STOCKHOLM 1967

SVERIGES GEOLOGISKA UNDERSÖKNING

SERIE C NR 626

ÅRSBOK 61 NR 11

OLOF ARRHENIUS

ORE, IRON, ARTEFACTS AND CORROSION

WITH 4 PLATES

STOCKHOLM 1967

Contents

The conditions of the investigation	3
Elements on which studies are made.	3
Methods and sources of material	4
Conditions of analysis	4
What ores were first used in the production of iron?	5
The formation, occurrence and chemical composition of limonite ores	7
Synopsis of regions in which lake iron ore has a relatively high frequency of high concentration of the elements indicated	10
Rock ores	11
Synopsis of regions in which rock ores have a relatively high frequency of high concentrations of the elements indicated	13
Artefacts	17
Synopsis of regions where artefacts show relatively high frequencies of the elements indicated	17
Phosphorus in iron	23
Coal in iron	27
Alloying elements. Rust	28
Summary	33
Appendix: The microstructure after reduction of phosphorus-rich iron ore with charcoal at different temperatures. By Torsten Hansson and Sten Modin	34
Literature	38

Abstract

The study of the properties of ancient iron may give interesting information which can be applied in modern engineering. The knowledge of the provenance of our old iron implements and of the alloying elements in these tools is of the utmost interest. The content of those elements in the ore and their transition into iron, thus may give us the clue to the origin of the metal.

Studies of the old mining and iron industry may both throw light on our old history and also give us some information where we may find alloying elements.

Redaktör J. Lundqvist

Stockholm 1967

Kungl. Boktryckeriet P. A. Norstedt & Söner

The conditions of the investigation

The knowledge of the occurrence of minor elements in both ore and artefacts is very limited but in many ways of extreme interest.

Just as it has long been known from experience that phosphorus in iron was responsible for »freedom from rust», it should be possible to determine the presence of other alloys and to discover how they affect the properties of iron. Alloy elements play such an important role in modern iron working that this alone would justify a comprehensive investigation of their occurrence, not only in iron, but also in various ores. (Alexander 1965.)

Such studies would naturally be of great value in archaeology. They might possibly solve the riddle of »barren» periods.

It may also be possible to show how much ancient iron masters knew about the material they used. Analyses of ore and artefacts may throw light on the provenance of the objects.

Today iron and concrete have superseded wood almost completely for building in soil, although wood is very durable in airtight material. In Sweden, with its rapid land elevation and extensive drainage, there is great danger of air penetration into the layers into which piles have been driven.

In the following, only the problem of the corrosion of iron will be discussed. We know far too little about the durability of this material during a century or so. And yet we often use iron in the erection of buildings that are to stand even longer than that. (Arrhenius 1956, 1964.)

Extrapolation based on the results of short-term tests is not satisfactory. It is much better to find objects that have lain in the earth for a long time and endeavour to draw conclusions from a study of the degree of corrosion. One such study, which gave interesting results, was made on board the *Wasa*. (Arrhenius 1963.)

Other objects that should give valuable information are those brought to light during the excavation of historic and prehistoric sites. A recent study attempts to give a picture of the deterioration of finds from the Viking Age and the early Middle Ages. (Arrhenius 1959.)

Numerous problems of engineering and archaeology might be elucidated in quite a new way.

Elements on which studies are made

The elements that in the first place should be studied are those wholly or largely brought over from ore into iron. Our present knowledge of these is based mainly on the products of modern iron and steel works, where high temperatures are the rule. Unlike the Chinese, who produced pig-iron in relatively tall

furnaces (Needham 1964) the ancient European iron workers mostly used small furnaces and low temperatures, which produced malleable iron by direct methods (Gilles 1936, 1958 a, b, c, 1960). Studies of the impurities remaining in the iron from the ore are required.

Elliot (Elliot et al. 1954) has drawn a scheme showing the oxide stability of the various elements at high temperatures. He shows there that Cu, Ni, Co, Sn, As, W and Mo, as well as phosphorus, are incorporated directly (provided the burden is not basic). V, Mn and Zn are taken up to some extent.¹

Modin and Hansson (1967) have shown that in iron reduced by charcoal at relatively low temperatures, the phosphorus is present in a ternary eutectic, steadite. Analyses made by the present author have shown that P most likely remained in the iron in the old processes (p. 24).

Methods and sources of material

Approximately 400 samples of lake and bog iron ore and about 100 specimens of iron ore from the bedrock were obtained from the Geological Survey of Sweden, the Museum of Technology, the Institute of Geology at the Royal Institute of Technology, and the Institute of Geology, Lund.

To a large extent, the artefacts used were the specimens on which the 1959 study (Arrhenius 1959) was based. Material also was supplied by the Lund Museum of Antiquities, the Gotland Museum and Väjö Museum, and by Dr Inga Serning and Dr A. Oldeberg, to all of whom I express my gratitude.

The samples were examined spectrochemically to ascertain the presence of As, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn, and Ag at the laboratories of Analytica, Ltd. I am very grateful to the chief there, Mr I. Nilsson. He has kindly provided me with the following description of the method used.

»The purpose of the analysis was to determine the impurities in iron in relation to the iron content. It was therefore natural to choose iron lines near the lines of analysis as reference. One advantage of this is that disturbances due to dilution of the samples containing foreign materials are reduced.

»Accuracy was estimated to half an order of magnitude. This means that if the content is estimated at C, it will probably lie between the limits $\frac{C}{3}$ and 3C.

Conditions of analysis

Electrodes: RW O, electrodes with centre shaft, electrode distance 3 mm.

Excitation: multisource direct current arc, 7 amp, electrodes positive.

Exposure: 20 sec.

Spectrograph: Hilger large.

¹ As an extension of the sphere of analysis, studies made on certain precious metals by activation analysis may be mentioned. Interesting results have been obtained in the studies of some ores.

Primary optics: middle reproduction.

Photographic registration: Ilford Process N 40 plates, development in Kodak D-19, 5 min. at 20°C, fixation 5 min.

Analysis lines: Ag 3280.7, As 2780.2, Co 3453.5, Cr 2843.3, Cu 3274.0, Cu 2824.4, Mn 2933.1, Mo 3170.4, Ni 3050.8, Pb 2833.1, Sn 2840.0 V 3185.4, Zn 3345.0.»

P, Mn and Fe were analyzed in my own laboratory, P, according to Bell and Doisy (1920), and Mn and Fe according to Shapiro and Brannock (1956).

About 100 metal-microscopic studies were made by Mining Engineers Modin and Hansson at the Institute of Metallography. I thank them for a very pleasant collaboration.

What ores were first used in the production of iron?

Swedish literature on the earliest production of iron always assumes one thing; iron-working in olden days was based on bog iron ore. I quote from one of many authors: »Die Hüttenindustrie Schwedens geht in die Zeit um Christi Geburt zurück. Das ursprüngliche Rohmaterial wurde dabei von dem Sumpferz genommen«. (Naumann 1922.)

On the other hand Olaus Magnus (1565) and Olof Rudbeck (1679) mention only iron from mines. Agricola (1928) refers to mountain iron mines only in Central Europe, as does Biringuccio (1925).

Swedenborg (1923) wrote as follows: »The oldest method of smelting iron in Sweden seems to have been using this ore [limonite]¹, for before people had learnt to open up iron mines and penetrate into the bowels of the earth, the surface provided minerals. That this was Sweden's ancient way of obtaining iron to forge axes, spearheads, shields and edged weapons of attack is clear from finds in the old heathen mounds overgrown with ancient trees. — — —.» It seems very likely that the surface of the earth was exploited first, but lake and bog iron are not found on the surface. Lake iron ore occurs mainly at depths of about six yards. Bog iron ore is covered with layers of vegetation, and good knowledge of its occurrence is required before it can be found. But lying on the surface are blocks which glaciers have ripped from the bedrock and transported some distance. The great iron ore prospecting schemes carried out in northern Sweden have shown how important tracing such blocks has been in the search for unknown ore fields. It may be objected that the action of glaciation was not understood then, and that people would therefore be unable to use erratic blocks as indicators. Let me quote what Tilas (1740), a contemporary of Swedenborg, wrote in a short essay.

»In the brief account of experience and experiments in the Mineral kingdom

¹ (authors remark).

I published in Åbo in 1738, I stressed rather more than previously the need for studies of the bedrock, so that, from the relation of the bedrock and mineral blocks to each other, it should be possible to make rather exact calculations whether minerals are to be found in one or another spot. The study of bedrock, therefore, is not only useful for those who wish to learn the geology of a place, but it is quite necessary for those prospecting for ores. Knowledge should not be restricted only to the bedrock, . . . but should also include the loose boulders scattered over the earth, for very often they will be found to consist of elements quite different from the underlying bedrock; indeed, they often have a rich content of metal, although, as experienced miners can tell, no signs of such metal and mineral are found for miles around . . .

When, therefore, minerals are found in blocks, endeavours should be made to ascertain from which direction the loose blocks came; the direction is not always the same, but, at a guess, should, here in the north, be between NW and NE.»

Thus the study of erratics was known to Tilas, as was the direction of their dispersion. It is probable that he got his information from »experienced miners».

Even in ancient times these blocks must have aroused the curiosity of hunters and woodcutters. Above all, their specific gravity must have attracted their attention. One condition of such finds is, of course, that shallow deposits of ore must exist within the region. South of the »iron country» proper, from Skåne northwards, are innumerable shallow deposits of iron ore. They, and the erratic blocks originating from them, could serve to supply the small furnaces, whose daily output could be counted in pounds rather than tons. The necessary conditions for iron-working based on rock ore were thus present in most parts of the country, which were inhabited in old times.

The proof that Swedenborg gave for the age of iron working was that the »heathen mounds» were overgrown with large trees. This proof is based on a very common over-estimation of the age of woods. An »ancient» pine can hardly be more than 400 years old. The »venerable» pines in the south parts of Haga Park (just outside Stockholm) are growing in soil that was used for cultivating tobacco during the latter half of the eighteenth century. It is improbable that oaks are to be found on the »mounds» mentioned by Swedenborg, and no other Swedish trees become »ancient». Thus with Swedenborg's evidence, we cannot go farther back than to the fourteenth century.

From this the conclusion must be drawn that the possibilities of using rock ores and limonite in iron working were equally great in olden days. If we accept Swedenborg's evidence, we must agree that the first material used was rock ore.

A scrutiny of medieval land registers reveals that rents in iron were concentrated to Bergslagen, the iron-mining regions of central Sweden. There were three exceptions, however, all in Småland. Three forges paid rent in iron to Arvid

Trolle. But no furnaces are mentioned. The term »furnace» (*hytta* = smelting house) occurs only in Bergslagen districts. (Arrhenius 1947).

Märta Eriksson (1940), in her interesting book, *Järnräntor*, mentions the same thing from the time of Gustaf Wasa, with the addition that also along the transport routes there were farmers who paid their taxes in iron.

The production of limonite iron must have been very small in Småland in those days, when even such a strict tax collector as Gustaf Wasa did not consider it worth while to tax this product.

It seems very likely that the period between the end of the seventeenth century and the middle of the nineteenth was the time when most limonite iron was made. During the nineteenth century there were 40 or so smelting-houses working in Småland.

The formation, occurrence and chemical composition of limonite ores

Lake and bog iron ores are found in all parts of Sweden except the silurian and limestone regions. A map drawn by G. Lundqvist (1942, also in Arrhenius 1959) illustrates these circumstances. These ores occur in especially large quantities in Småland and Värmland. The few finds made in Norrland are undoubtedly due to insufficient prospecting.

According to Sundelin (1918), the formation of limonite increased in volume simultaneously with the so-called deterioration of the climate about 2500 years ago. The spruce came to Sweden then, precipitation increased and leached the soil nutrients, which caused a rapid rise in the growth of peat bogs and increased waterlogging. All these factors encouraged the formation of limonite ores.

Swedenborg wrote about limonite ore that »it seems to owe its creation and physical origin in the iron juice found in marshes». This is about the line that has been followed down the years. Generally speaking, Aschan's (1908) view has been accepted by later chemists, that when ferruginous water, which has appeared by the leaching of mineral soils, comes into contact with humus-rich soil solutions, a colloidal solution is formed which carries the ferruginous water to lakes, where sedimentation occurs.

Stapf (1865), who has probably studied these problems most thoroughly, maintains that also decomposing vegetable matter can yield elements that dissolve in subsoil water.

The iron content of ground water (such as is found in springs and wells) is, in south Småland, about 0.6 mg/l, and in the northern parts somewhat higher (Arrhenius 1954).

If the claims made by former lake iron ore prospectors that ore at the bottoms of lakes is renewed after 50 years (Naumann 1922) are correct, it means that in a lake like Vidöstern, where the iron ore deposit is about 380,00 tons (with an iron content of 40 per cent, equivalent to approximately 150,000 tons), at least 3000

tons Fe must be transported into the lake every year. The lake has a catchment area of 87 square miles¹ and receives about 200 mm precipitation that has percolated through soil (one-third of the precipitation evaporates, one-third runs off the surface, and one-third percolates through the soil down to the water in the surface layers of soil). If it is this water that occurs in springs and wells, it means a contribution of ca. 270 tons of iron a year, less than onetenth of the calculated requirement.

It has been shown, however, that water percolating through spruce humus and spruce litter becomes rich in iron and manganese (Arrhenius 1957). I have therefore experimented with the percolation of soil profiles from spruce forests with a dense ground layer of bilberry, and from moss-rich spruce forests. The water had a content of 18 and 15 mg Fe/l and would thus satisfy the lake's need for iron. In addition, lake ores contain great amounts of biophile elements (Goldschmidt 1958) such as Mn, Co and phosphorus, and these are present in such great amounts in the percolating water as to explain their high concentration in lake iron ore. The calculations presented here are based on the assumption of a 50 year renewal cycle, a figure that is only an estimate. But the calculations made illustrate the tendency.

Thus a large part of the cause of the increased formation of limonite ore is to be found in the rapid immigration of the spruce and the great amount of raw humus this caused, the relative high Fe and Mn content of spruce humus and the strong acidification of the soil. (Arrhenius 1957.)

The colloidal, or chelated, iron later enters the lake and comes into contact with the vegetation there. Odén (1922) has shown that no decomposition of humus substances occurs by contact with the oxygen in the water. But if they meet oxygen in *statu nascendi*, they decompose rapidly. The oxygen emitted by the plants during assimilation has this property, and it must therefore be assumed that the precipitation of iron occurs with the help of green plants. Naumann (1922) considers that no connection can be demonstrated with amount of light (and thus the assimilation). In opposition to this view are Lundqvist's (1942) and Thunmark's (1937) studies on translucency and depth of precipitation, which show strong relationship between light and precipitation.

According to Odén (1922), a fine powder of ferric hydroxide (particle size ca. 1 μ) sinks to the bottom. Naumann (1922) has described in detail how this fine powder is attracted by bits of bark, grains of sand, vegetable matter, shells and stones, and grows (dependent on the substratum) into coin, pea, pearl or powder ore.

These ores change in the course of time.

An attempt has been made to ascertain how external conditions can affect the further development of the ore.

Solutions of which the pH was adjusted by different mixtures of citric acid

¹ 225 sq. kilometers.

and citrate of sodium were allowed to act on finely pulverized bog iron ore. It was found that iron was dissolved more rapidly than manganese in the pH range 3—5 (the range within which the water and the bottom deposits are). It may be assumed that during the lighter months of the year precipitation is rapid, and during the darker months this separation takes place.

»Skragg» ore was considered already in olden times as an ageing phase in the formation of lake iron ore. If the relative content of manganese (Mn/Fe) is placed in relation to the impurity of the ore (residual value when the Fe + Mn content is subtracted from the total substance) it will be found that the higher the ratio Mn/Fe is, the more impurities are present. This suggests that »skragg» ore is a leaching product. The ore gradually becomes rich in phosphoric acid and manganese, while the iron content declines.

Table 1 shows how the elements are distributed in pearl ore and »skragg» ore.

All elements have declined relatively except manganese, lead, silver and phosphorus.

The often numerous concretions of manganese found at the bottoms of the oceans are the results of thousands of years of development. The final product is a formation consisting mainly of manganese and iron, with concentrations of ca. 0—20 per cent Fe and 20—40 per cent Mn. Thus the content of manganese is from two to ten times as great as that of iron (Mero 1965). It is probable, however, that these concretions are due to submarine volcanic activity.

Bog iron ore occurs mainly as a powder, or as amorphous concretions in bogs. Formerly it was thought that lake iron ore was formed by bog ore being washed into the lakes.

van Bemmelen (1900) gave what is probably the best account of the origin and occurrence of bog iron ore. According to van Bemmelen, it most likely formed in shallow pools in marshy ground. The iron is precipitated there by the assimilation process of green vegetation. Eventually turf grows over the old pools and covers the iron.

When a deposit of bog iron ore is exhausted, it does not, like lake iron ore, seem able to become renewed. Bog iron ore in Sweden has never had the importance of lake iron ore, particularly since tall blast furnaces came into use. In some north Småland works, bog iron ore was used, but had always to be mixed with mountain ore in order not to have a too closed charge. The small furnaces were not packed so tightly.

Products very similar to bog iron ore are the ochres deposited at sources of iron. These have probably been of minor importance for the production of iron.

Claims have often been made in the literature (Molisch 1910, Lieske 1911) that iron bacteria play a prominent role in the formation of limonite ores. Often a mantle of iron ochre is formed on the bacteria. Lieske has shown that such precipitation occurs on pieces of gelatine in suspensions of ochre. Recently,

Table 1. The content of elements

	Number of samples	Iron %	Co % of iron	Cr	Cu	Mn
Pearl ore	28	34.2	0.119	0.002	0.0028	7.14
Skragg ore	19	19.9	0.112	0.0008	0.0016	74.8
		-14.3	-0.007	-0.0012	-0.0012	+67.7

however, Wolfe (1964) has started a series of experiments that may settle the vexed question of the oxidation of iron and manganese compounds in water.

The composition of lake and bog iron ore is as shown in Table 4. There are two main divisions of lake iron ores: ores from all parts of the country and a large group of ores from Lake Hjälmaren (Hjälmare ores). This latter group deviates greatly in composition from the other ores, and is therefore described separately.

It will be seen from the Table that high concentrations of arsenic, tin and silver are rare. Chromium, copper and molybdenum occur rather more frequently. Cobalt, nickel and vanadium have a high frequency of high concentrations. Manganese occupies an exceptional position, for the frequency of manganese contents higher than the contents of iron (>100 per cent) is rather high. The frequency of phosphorus contents exceeding 1 per cent is around 40—50 per cent in all samples, and below 0.25 per cent the frequency is between 1 and 2 per hundred.¹

Synopsis of regions in which lake iron ore has a relatively high frequency of high concentrations of the elements indicated

- Ag: Värmland, Södermanland
 Co: Kalmar, Jönköping, Östergötland, Västergötland, Södermanland, Hjälmaren
 Cr: Jönköping, Östergötland, Västergötland, Södermanland, Hjälmaren
 Cu: Östergötland, Södermanland, Hjälmaren, Gävleborg, Dalarna
 Mn: Kalmar, Jönköping, Östergötland, Västergötland, Södermanland, Hjälmaren
 Mo: Jönköping, Hjälmaren, Gävleborg
 Ni: Jönköping, Östergötland, Gävleborg
 Pb: Kronoberg, Jönköping, Östergötland, Värmland, Hjälmaren
 Sn: Jönköping, Hjälmaren
 V: Kronoberg, Jönköping, Hjälmaren, Gävleborg
 Zn: Kronoberg, Värmland, Hjälmaren, Södermanland, Gävleborg, Dalarna
 P: Skåne, Kronoberg, Kalmar, Jönköping, Östergötland, Södermanland, Hjälmaren

¹ Aarnio's (1918) material contains samples with low phosphorus content.

investigated in pearl ore and »Skragg» ore

Mo	Ni	Pb	Sn	V	Ag	Zn	P
0.009	0.016	0.030	0.0014	0.024	0.0003	0.070	1.28
0.0013	0.009	0.071	0.0010	0.019	0.0014	0.055	1.39
-0.0008	-0.007	+0.041	-0.0004	-0.005	+0.0011	-0.015	+0.11

Only in two elements can really great differences be found in the three materials. The manganese content is highest in the Hjälmare material, which is not surprising, for it is classified as »skragg» ore. As already mentioned, bog iron ore is much poorer in manganese than lake iron ore. The Hjälmare material is also richest in phosphorus. A slight difference can be observed between lake iron ores and bog iron ores.

Studies must also be made to find out whether local variations occur. The material, classified as earlier in lake iron ore (including Hjälmare ores) and bog iron ore, is shown in diagram form by provinces. (Plate 1.)

Thunmark (1937), however, points out that previously it was assumed that dark, humus-rich water was necessary for the formation of limonite ores. He measured the translucency and colour of lakes in Småland and southern Östergötland, and found that in southern Småland the water is brown, with low translucency, while in the northern parts of the province the water is translucent and green to greenish-yellow in colour. There is no definite limit but a line through Sävsjö — Vetlanda — Målilla would serve as an approximation. This means that there are entirely different types of water with different productions of limonite ores.

The Hjälmare samples have a high content of micro-elements, especially around the mouth of the brook Forsån.

The few samples from Värmland have relatively low values. Hälsingland and Gästrikland samples have low concentrations of phosphorus.

Distribution is more even in bog iron ores.

The southernmost counties have a relatively high frequency of high concentrations.

The samples from the counties of Kalmar and Kronoberg have much lower frequencies of such elements compared with the counties of Jönköping, Östergötland and Älvsborg. There is only one sample from Södermanland, but that is a very rich one. The northern counties have relatively few samples, with a somewhat lower frequency than the Jönköping county.

Rock ores

Glaciation is the ore prospector's best friend. As the ice progressed over the land, it ripped boulders from more or less shallow deposits of ore, and ground

material to dust. These boulders and the ground material were left behind as the ice melted, and striae cut in the surface of the bedrock showed in which direction the ice had travelled. Chemists, by the help of analyses, can follow the fine material for miles from the mother rock (Arrhenius 1950). Most blocks are found in the vicinity of the ore bodies; the material spreads fanwise from the mother rock, and the frequency declines with distance.

Often, these blocks are of such a size and such curious appearance that they are noticed during highway construction and the like. Then samples are frequently sent to geologists for analyses, sometimes in the belief that they are meteorites (Grip 1953, Sauramo 1924).

As the people living in contact with nature are good observers, it must be assumed that when in old days they found such blocks of iron ore, they searched for more of them and endeavoured to find out where they had come from. Often they traced them back to the mother rock. Excavating for ores was sometimes practised. Old timber-lined shafts have been found in South Germany (Frei 1965). These blocks and ore nodules found on the surface provided excellent opportunities for iron smelting.

It is usually considered that the land south of the iron country of central Sweden is free from iron ore. Modern iron and steel works would probably find the supplies wholly inadequate, but in olden days, when a melt gave only twenty or so pounds of iron, demands were not so great. There are quite a number of small mines in the southern parts of Sweden.

Carlberg (1879) and Tegengren (1924) give numerous historical data based on documents, usually medieval, but, unfortunately, from the later Middle Ages. Most of the medieval land registers refer to the late fifteenth century, too.

To solve the problem of ancient mines, it must be assumed that all mines now being worked are old, unless the contrary can be proved.¹

The focus of interest will then be on the mines in regions where Iron Age settlements have been discovered. In these regions, a search must be made for traces of iron smelting, to see if charcoal can be found there for C¹⁴-analysis, or slags for age determination by aid of radioactivity.

It is also possible with the help of comparative analyses of ore and iron in archaeological artefacts to find clues leading to certain mines.

A study of the composition of the ore in respect of the more frequent tracer elements will then be necessary.

The Swedish Iron Masters' Association (Jernkontoret 1906, 1931) has collected a large number of analyses (ca. 3500) of ores from iron fields now being exploited; they refer to the contents of iron, manganese, sulphur and phosphorus in iron ores. Below this material is tabulated by parish. The manganese and phosphorus concentrations are, as elsewhere in this article, calculated in percentages of iron.

¹ According to Carlberg (1879), Grängesberg was called Nyberget in 1644 (*Ny* = new).

It will be observed that very few of the samples reported have P concentrations higher than 0.25 per cent. If the Grängesberg and Lapland mines are excluded, the samples of ore with a high content of phosphorus represent only about 3 per cent of the material. If these mines are included, the proportion is 10 per cent.

One-fourth of all the samples had manganese concentrations exceeding 1 per cent.

The localisation of these samples is very pronounced.

Landergren (1948) has described the occurrence of the ferrides in the ores of central Sweden. He gives the results of his analyses in percentage of ore. I have revised his table on the assumption that the ores contained 50 per cent Fe (see Table 3).

Thus the ores of central Sweden have low contents of Co, Cr, Mo, Ni and V. Manganese, as shown earlier, is present in larger quantities.

On the initiative of N. H. Magnusson, then Deputy Director of the Geological Survey, an extremely interesting study of the concentrations of 25 or so elements in iron ore was begun. Unfortunately, the work has, as yet, been concerned with only about 60 series of analyses of samples from about a dozen iron fields in Bergslagen.

All that remains, therefore, is to acquire as many analyses as possible, beginning in Götaland and Svealand (ignoring, as a rule, Bergslagen), the Norrland coastal regions and Jämtland.

There are specimens of ore from all these regions in museums.

Altogether, I have received a hundred or so specimens, which have been analysed chemically and spectrochemically. A summary of the results of these analyses is given in Table 4; the results of studies of limonite ores are added for comparison.

A scrutiny of Table 4 reveals that typical of rock ores, compared with limonite ores, are higher concentrations of As, Cu, Pb, Sn, Ag and Zn. In respect of phosphorus and manganese, limonite ores are richer beyond comparison. Curiously enough, rock ores are poorer in Cr than lake and bog ores. (Plate 2.)

Of great interest is to attempt to discover whether rock ores from different regions differ in respect of content of micro-elements. For this reason I have attempted in a diagram to show, by regions, the frequencies of the micro-elements studied. (Plate 3.)

Synopsis of regions in which rock ores have a relatively high frequency of high concentrations of the elements indicated

Ag: Småland, Norrland, Norrbotten

As: Skåne, Småland, Södermanland

Co: Skåne, Småland, Dalarna, Norrland, Norrbotten

Cr: Skåne, Norrland

Table 2. Mn and P in ores according to the Swedish Iron Masters' Association analyses

Parish	Number of samples analysed	% samples with P < 0.25 %	Number of samples with Mn > 1 %
Ryssby	1	0	0
Ed	2	100	0
Ukna	3	66	0
Fröderyd	1	100	0
Månsarp	1	100	1
Ramkvilla	2	100	1
Mogata	1	100	0
Skällvik	10	100	0
Botkyrka	1	0	—
Börstil	9	100	0
Häverö	19	100	0
Järna	1	100	0
Singö	2	100	0
Söderby Karl	4	100	4
Valö	19	100	0
Gräsö	1	100	0
Österhaninge	5	80	2
Floda	11	100	6
Gåsinge	4	100	1
Sköldinge	25	100	0
Svärta	21	100	17
Tunaberg	3	100	2
Åker	2	100	1
Österåker	1	100	1
Grythytte	50	100	15
Linde	174	76	50
Nora	178	100	6
Viker	102	97	6
Ramsberg	51	100	16
Hjulsjö	44	100	0
Järnboås	54	100	0
Hällefors	35	97	10
Ljusnarsberg	222	100	117
Karlskoga	1	100	1
Hammar	3	100	2
Knista	1	100	1
Kvistbro	4	100	3
Tysslinge	1	100	0
Vintrosa	7	100	2
Film	213	100	170
Vendel	1	100	1
Alunda	18	100	17
Lena	31	100	4
Rasbokil	1	100	0
Tensta	1	100	1
Skinnskatteberg	73	100	7
Enåker	1	100	1
Sala	9	100	5
V. Våla	3	100	0
Österfärnebo	2	100	0

¹ Including Guldsmedshytte.

Parish	Number of samples analysed	% samples with P < 0.25 %	Number of samples with Mn > 1 %
Västansfors	95	100	17
Norberg	454	100	186
Nordmark	64	100	13
Färnebo	161	100	30
Kroppa	19	100	0
Gåsborn	10	100	9
Karlstad	1	100	1
Säter	90	100	0
Garpenberg	70	100	44
Husby	54	100	2
Vika	9	100	7
Folkärna	18	100	1
St. Tuna	196	75	49
Ludvika	6	100	6
Norrbärke	107	100	5
Svärdsjö	26	100	8
Söderbärke	8	100	1
Silvberg	10	100	0
Kopparberg	5	100	0
Avesta	1	100	0
By	2	100	0
Sundborn	3	100	0
Leksand	1	100	1
Säfsnäs	2	100	0
Ål	1	100	1
Grangärde	271	30	23
Torsåker	93	100	31
Hille	2	100	0
Årsunda	5	100	3
Järvsö	5	100	0
Valbo	2	100	0
Voxna	1	100	0
Alnö	3	100	3
Nätra	9	100	1
Gällivare	92	78	0
Jukkasjärvi	70	36	0
Ned. Luleå	1	100	0
Kvikkjokk	2	100	0

Cu: Småland, Dalarna, Norrland, Norrbotten

Mn: Småland, Södermanland, Närke, Dalarna, Norrland, Norrbotten

Mo: Norrbotten

Ni: Skåne, Småland, Närke, Norrland, Norrbotten

Pb: Västmanland, Dalarna, Norrland, Norrbotten

Sn: Närke

V: Skåne, Småland, Närke, Norrland, Norrbotten

Zn: Småland, Södermanland, Västmanland, Dalarna, Norrland, Norrbotten

P: Skåne, Småland

Much more material must be collected, however, preferably in such a way that reliable average values are obtained.

Table 3. Distribution of micro-elements in iron ore from central Swedish mines, calculated on basis of iron (after Landergren). 50 % iron content assumed

Cobalt %	0.02—0.06	0.012—0.02	0.006—0.012	0.002—0.006	<0.002	
<i>Magnetite</i>	1.5	1.5	3.0	11.0	83.0	
<i>Hematite</i>	7.0	3.5	10.5	79.0	0	
Chromium %		0.1—0.2	0.02—0.1	0.01—0.02	0.002—0.01	<0.002
<i>Hematite</i>		2.5	9.0	4.5	34.0	50.0
Manganese %	2.0	1.0—2.0	0.2—1.0	0.1—0.2	0.02—0.1	<0.02
<i>Magnetite</i>	4.5	11.0	37.0	23.0	23.0	1.5
<i>Hematite</i>	0	3.0	28.0	30.0	33.0	6.0
Nickel %			0.012—0.02	0.006—0.012	0.002—0.006	<0.002
<i>Magnetite</i>			0	0	2.0	98.0
<i>Hematite</i>			10.5	14.5	35.5	39.5
Molybdenum %	0.006—0.02	<0.006				
	37	63				
Vanadium %	>0.2	0.1—0.2	0.02—0.1	0.01—0.02	0.002—0.01	<0.002
<i>Magnetite</i>		0	3.0	0	1.5	95.5
<i>Hematite</i>		3.0	12.0	14.5	47.0	23.5
<i>Apatite ore</i>	45.5	27.5	18.0	9.0	0	0

Artefacts

About 280 artefacts from different parts of the country, and another 260 or so from Helgö, have been studied. The analyses of the former are shown in Table 5.

Arsenic, like chromium, seldom occurs in high concentrations in the iron studied.

Cobalt is present in rather high concentrations (ca. 10 per cent of the specimens had more than 1 per cent). Both manganese-rich and manganese-poor iron occur. About 25 per cent of the objects had a manganese concentration exceeding 1 per cent.

Molybdenum is present in very small concentrations in this iron.

In some cases the content of nickel is as high as 1 per cent.

Vanadium at concentrations of ca. 0.1 per cent is present in only few specimens.

Lead and zinc are present in astonishingly great amounts, probably due to the low temperatures used in ancient iron working.

Tin and silver are rare in high concentrations.

Rather more than half of the material has a low content of phosphorus (<0.25 per cent). But variations are great between different parts of the country.

The results are presented graphically in a diagram. (Plate 4). Fewer than five specimens were studied from the following provinces: Blekinge, Halland, Bohuslän, Dalsland, Värmland and Lapland. For these regions the results are unreliable.

Synopsis of regions where artefacts show relatively high frequencies of the elements indicated

Ag: Västmanland

As: Skåne, Gotland

Co: Skåne, Småland, Gotland, Östergötland, Västmanland, Gästrikland, Dalarna, Lapland

Cr: Småland

Cu: Skåne, Småland, Östergötland, Gästrikland, Dalarna, Medelpad

Mn: Småland, Östergötland, Närke, Västmanland, Gästrikland, Dalarna, Jämtland

Mo: Skåne, Gotland, Medelpad

Ni: Skåne, Småland, Östergötland, Västmanland, Gästrikland, Dalarna, Lapland, Härjedalen

Pb: Småland, Östergötland, Västmanland, Dalarna

Sn: Småland, Lapland

V: Småland, Östergötland, Västmanland, Gästrikland, Dalarna

Zn: Småland, Östergötland, Gästrikland, Dalarna

P: Skåne, Gotland, Småland

Table 4. Analysis of rock ores compared with limonite ores. The figures give % of total number of ores examined. Contents of elements in ores in % of Fe

% of Fe		>5	1—5	0.5—0.9	0.1—4	0.05—9	0.01—4	0.005—9	0.001—4	<0.001	Indeterminable amount
As	Rock ore				2	3	12				83
	Lake ore						5				95
	Hjälmare ore										100
	Bog ore						6				94
Co	Rock ore		2	2	8	11	27	9	3	16	22
	Lake ore			4	34	29	12	4		8	9
	Hjälmare ore			2	24	20	15	3		26	10
	Bog ore		4	5	32	24	15	3		6	11
Cr	Rock ore						2				98
	Lake ore						19	6		26	49
	Hjälmare ore					1	38			49	12
	Bog ore				1	1	21	1		40	36
Cu	Rock ore		3		2	9	20	5	28	33	
	Lake ore						8	6	46	40	
	Hjälmare ore						14	11	44	31	
	Bog ore				1	2	9	7	43	38	
Mo	Rock ore					3	2	7	4	70	14
	Lake ore						4	27	14	52	3
	Hjälmare ore						8	33	9	35	15
	Bog ore				1	2	4	16	24	43	10
Ni	Rock ore		2	2	6	6	11	15	21	14	23
	Lake ore				2	3	18	29		39	9
	Hjälmare ore				1	3	19	14		48	15
	Bog ore				1	4	20	19		44	12
Pb	Rock ore		8	6	8	10	29	13	14	12	
	Lake ore		1		6	11	29	10		33	10
	Hjälmare ore		1	2	8	8	26	8		33	14
	Bog ore				4	6	34	13		30	13

Sn	Rock ore					3	11	20	25	33	8
	Lake ore						6			46	48
	Hjälmare ore					2				57	41
	Bog ore						6			48	46
V	Rock ore				3	3	20	6	5	11	52
	Lake ore				3	3	15	16		43	20
	Hjälmare ore				3	4	21	21		39	12
	Bog ore			1	4	6	23	19		34	13
Ag	Rock ore					3	11	20	25	35	6
	Lake ore						1	1	26	60	12
	Hjälmare ore							7	8	85	
	Bog ore						1	5	32	58	4
Zn	Rock ore		7	10	31	15	20			12	5
	Lake ore			1	12	11	38			34	4
	Hjälmare ore			1	6	9	40			34	10
	Bog ore		3	1	9	13	38			30	6
		150—199	100—149	60—99	30—59	10—29	5—9	1—4.9	0—0.9		
Mn	Rock ore					6	5	14	75		
	Lake ore	1	5	12	8	19	11	36	8		
	Hjälmare ore	9	20	35	21	6	6	2	1		
	Bog ore	2	2	2	5	13	12	42	22		
		3.0—4.9	1.0—2.9	0.5—0.9	0.25—0.49	<0.25					
P	Rock ore			11		6	83				
	Lake ore		7	35	38	17	3				
	Hjälmare ore		52	41	4	3					
	Bog ore		9	31	38	21	1				

Table 5. Analyses of iron objects from different parts of Sweden.
The figures give % of total number of objects examined in each group.
Content of elements analyzed in % of Fe

	5—	1—4	0.5— 0.9	0.1— 0.4	0.05— 0.09	0.01— 0.04	0.005— 0.009	0.001— 0.004	<.001	Non- mea- surable
As						5	3	0.7	—	91
Co	0.7	10	6	20	16	9	2	2	3	31
Cr							14		42	44
Cu			0.4	9	25	32	9	20	5	
Mn	8	18	4	14	8	20	6	6	15	1
Mo				0,4	0,8	7	13	1	48	30
Ni		3	1	7	14	30	14	10	7	14
Pb			0.3	16	16	22	6	8	1	31
Sn				0.8	0.4	2	13	7	39	38
V				1	5	31	28	1	3	31
Ag						0.8	9	50	18	22
Zn			2	20	24	16			1	37
P		>1	0.5— 0.9	0.26— 0.49	<0.25					
		6	17	24	53					

The following must be borne in mind when the provenance of artefacts is being determined.

Only relatively few objects are available. Thus tests must be made to ascertain whether the ore has such high contents that they are comparable with the highest contents in the artefacts. The lowest contents must be compared in the same way.

Finally, it must be emphasized once again that knowledge of the transport from ore to iron of the elements examined is very small, in view of the low temperatures used in the old smelting furnaces.

Characteristic of iron from Skåne are relatively frequent high contents of arsenic, low contents of chromium and manganese but a high frequency of relatively high concentrations of molybdenum. The phosphorus-rich iron may scarcely have been made from local ore, but the iron poor in phosphorus can not originate from Scanian ore. This iron was imported.

Småland iron is practically completely free from arsenic, has high frequencies of high cobalt contents, and an unusual frequency of chromium, high Mn contents and low contents of molybdenum. Nickel is present in high frequencies, as are lead, vanadium and zink. Both lake iron ore and mountain ore from the province may have been the sources of the Småland iron.

The few specimens from Blekinge, Halland and Bohuslän are quite free from As and Co, have low contents of chromium, and very low contents of Mo, manganese, vanadium, tin and zink. The silver content may be relatively high. Ore from the vicinity may have been used.

Gotland iron is very similar to the Scanian specimens, except that the concentrations of copper, lead and tin are lower. Imported iron or ore from foreign countries must have been used in Gotland, too.

The iron from Västergötland and Värmland contains moderate amounts of manganese and lead. Värmland iron has also moderate contents of Ni. Otherwise, iron from these provinces, like that from Dalsland, has very low concentrations of micro-elements. The ores may very well have been taken from the nearest mines.

The Närke specimens contain no As, Co, or Cu, have relatively low concentrations of manganese, low Mo content, and medium nickel and Pb concentrations, low contents of tin, vanadium, silver and zink. The iron is probably of local origin.

The Östergötland material is composed wholly of finds from Alvastra, and is therefore medieval material. The phosphorus content is consistently high; only one-sixth of the material has low P content. The content of cobalt is also unusually high, and the contents of manganese, nickel, lead, zink are high, too. Relatively high concentrations of vanadium are also present. Limonite ores in the neighbourhood, may well have been used to make this iron. It may have been derived from the daughter cloister, in Julita, which held fishing rights in Lake Hjälmaren.

Bergslagen and the country to the north (except Gästrikland) had a strong predominance of iron poor in phosphorus, with relatively high contents of cobalt and copper, and medium manganese concentrations (except for Medelpad and Jämtland). This iron also may have been manufactured from local ores.

The diagram shows best the composition of iron in the various regions (Plate 4.)

Thus, it seems as if the chemistry of the objects is connected with the provenance of the ore. A study of the specimens of ore shows that the phosphorus-rich iron may very well originate from lakes and bogs in the vicinity. The irons low in phosphorus may originate from mines in the neighbourhood and from erratic blocks spread by ice from these ore bodies.

As far as Skåne and Gotland are concerned, it is quite likely that the iron or ore used there was imported from foreign countries.

The Helgö material has high contents of Co, Cu, Mn, Ni and Pb, and to a certain degree molybdenum, and much phosphorus.

This may be interpreted to mean that the ore was taken from lakes in Södermanland or from Lake Hjälmaren. The iron poor in phosphorus is also rich in micro-elements. It, too, may have been taken from mines in Södermanland or imported from abroad.

Strong evidence of the local origin of the iron is in finds from different parts of Småland.

Table 6. Micro-elements in Helgö-iron. The figures give % of total number of objects examined

% of Fe	5	1—4	0.5—0.9	0.1—0.4	0.05—0.09	0.01—0.04	0.005—9	0.001—4	<0.001	Indeter- minabel
As										
Phosphorus-poor iron										100
Phosphorus-rich iron										100
Co										
Phosphorus-poor iron		17	17	23	30	13				
Phosphorus-rich iron		10	11	27	23	25	3	0.5		0.5
Cr										
Phosphorus-poor iron						3	27		20	50
Phosphorus-rich iron					0.5	1	28		33	38
Cu										
Phosphorus-poor iron				17	56	27				
Phosphorus-rich iron		1	0.5	11	55	33				
Mn										
Phosphorus-poor iron	0.3	33	27	20	17	3				
Phosphorus-rich iron	9	29	21	37	3	1				
Mo										
Phosphorus-poor iron						3	40		53	4
Phosphorus-rich iron				0.5	1	3	24		70	2
Ni										
Phosphorus-poor iron		7		17	30	46				
Phosphorus-rich iron		2	2	9	28	55	4			0.5
Pb										
Phosphorus-poor iron				40	27	30	3			
Phosphorus-rich iron				23	31	43	3			0.4
Sn										
Phosphorus-poor iron						10	33		57	
Phosphorus-rich iron						6	24		69	1
V										
Phosphorus-poor iron				17	13	63	7			
Phosphorus-rich iron				4	19	71	6			
Ag										
Phosphorus-poor iron							10	37	53	
Phosphorus-rich iron						0.5	3	49	48	
Zn										
Phosphorus-poor iron				30	33	37				
Phosphorus-rich iron		0.5	2	21	39	37			0.5	

Tab. 7. Per cent of microelements in lake ore and in artefacts from N. and S. Småland

Lake ore from	As	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sn	V	P
N. Småland	0	0.13	0.002	0.003	21.5	0.003	0.006	0.023	0.002	0.01	0.97
S. Småland	0	0.08	0	0.002	18.5	0.001	0.003	0.046	0.001	0.005	0.91
Iron from											
N. Småland	0	0.370	0.003	0.140	0.8	0	0.5	0.04	0.002	0.02	0.60
S. Småland	0	0.022	0	0.040	0.06	0	0.04	0.03	0.003	0.02	1.91

It was mentioned earlier that Thunmark found differences in the colour of water in north and south Småland. In the former the water is greenish-yellow, in the latter brown. It seems likely, therefore, that different types of ore precipitation occur in the different regions. I have compared the compositions of the lake iron ores, and found the following means. Deviation is great in each group. (Tab. 7.)

Thus it will be seen that lake ore has a lower content of micro-elements Co, Cr, Cu, Mn, Ni in the southern parts of the province than in the northern parts. The same is also true of the iron made from this ore. It would seem, therefore, that the composition of the local ore is reflected in the iron.

It must be stressed, however, that if really reliable results are to be obtained, the investigation should be extended considerably. At least a couple of thousand samples, obtained in a statistically satisfactory way, should be analysed. In the same way, the background, *i.e.* the composition of mountain and lake iron ores, must be elucidated. In the last, the problem is a financial one, whether we can afford to spend another £ 10,000 or so on such work.

Phosphorus in iron

The low reduction temperature used in Europe may have influenced the transition of phosphorus from the ore to the iron and the slag. Thus the phosphorus content in the old iron can be not only a function of that of the ore but also a function of the reduction temperature. An ore low in phosphorus can only give an iron low in that element (provided that the coal does not add any phosphorus). The interesting and crucial question is what happens when reducing an ore rich in phosphorus (rock or lake ore).

To illustrate this question an investigation has been carried out in order to study the reduction process of iron ores rich in phosphorus and to follow how the phosphorus is taken up by the steel and influences the structure obtained. The ores have been reduced at low temperatures (up to 1200°C). The phosphorus content in the iron and in the slag has been analysed chemically after treating at different reducing temperatures. As such an analysis only gives an idea of the total content of the sample investigated, one may object to the results

remarking that slag intrusions in the iron may have ruptured the results. A microscopical analysis therefore is absolutely necessary in order to obtain knowledge of the different phases present in the iron. Such an investigation has kindly been carried out by S. Modin and T. Hansson¹ (1967) who have made a separate report of their work. (See appendix.)

Schürmann (1958) in his paper referring to Oelsens calculations discusses the pronounced influence that both phosphorus and carbon have on the reduction process. If the reduction takes place in a temperature range above 720°C (A_1) both ferrite and austenite may exist. Phosphorus rises the temperature where austenite is formed, while carbon lower this temperature. Both lower the melting point. Ferrite has a higher solubility for phosphorus than austenite. At 700°C the maximum solubility for phosphorus in ferrite is 0.8 % and this value rises to 2.6 % at about 1020°C, the melting point. When the iron is in the austenitic condition, the solubility for phosphorus is dependent both of the carbon content and of the temperature. The solubility for phosphorus in austenite rises with the temperature up to the melting temperature. The maximum solubility is just above 0.4 % phosphorus at 0.5 % carbon where melting will start at about 1020°C. At the ternary melting point, about 980°C, the composition of the austenite is only 0.38 % phosphorus and about 1.15 % carbon. The carburizing of the reduced iron takes place mainly in the austenitic condition as ferrite only can dissolve very minute carbon and over that range above A_1 , transforms to austenite.

Oelsens (Schürmann 1958) calculations are of course only valid for equilibrium condition and equilibrium is certainly not obtained during the reduction process. The question is now how fast the reduction to iron and later the carburizing is, compared with the reduction rate to phosphorus or, expressed in other words: how much ferrite with low carbon content but perhaps high phosphorus content is formed compared with austenite with higher carbon but perhaps lower phosphorus content at a given reduction temperature. This question has to be investigated experimentally, and below the reduction experiments made are described. From what precedes, it will also be seen, that if old iron implements with different carbon contents are compared with regard to their phosphorus content we may expect a difference. Implements with medium or high carbon content should have lower phosphorus content than such with low carbon content if they are made from ores with about the same phosphorus content. About 20 iron implements from the iron age have been analyzed on their carbon and phosphorus content in order to check this suggestion. The result of this investigation will be discussed later in the paper.

The lake ore is an amorphous mixture of iron hydroxide and other iron compounds, amongst others iron phosphate. Further silicates, organic substance

¹ Members of the Institute of Metal Research, Stockholm.

Table 8. Grängesberg and lake ore reduced at different temperatures

The figures give the P content (%) in the fractions.

	Grängesberg ore	Lake ore
Ore untreated		
Magnetic fraction	0.58	—
Non magnetic fraction	3.50	0.83
Reduced at 650° C		
Magnetic fraction	0.61	0.96
Non magnetic fraction	3.60	—
Reduced at 1050° C		
Magnetic fraction	1.30	1.05
Non magnetic fraction	2.60	—
Reduced at 1200° C		
Magnetic fraction	1.75	1.30
Non magnetic fraction	0.18	—

and other soil constituents intermixed. After grinding only coarse sand particles may be separated.

In the mountain ore from Grängesberg the phosphorus chiefly is contained in apatite crystals which, when separated magnetically, remain in the non magnetic portion. The iron occurs as the magnetic Fe_3O_4 .

The following experiment, therefore, has been carried out. Lake ore from Vidöstern (Äminne) and mountain ore from Grängesberg were well mixed with charcoal grains (3—5 mm) of beach from the Perstorp factory and put in crucibles (for the lower temperatures of pottery, for the highest of graphite). The crucibles were heated, one series to about 650°C and one to about 1050°C in a Siemens electric furnace. The atmosphere in the furnace was nitrogen gas. The heating time was 12 hours and the cooling time 6 hours¹. Another series was heated to 1200° in an induction furnace. The temperature was kept for 3 hours and the cooling time was 2 hours².

The samples were taken out and were crushed in an agate mill. The blooms from 1200° were impossible to crush. Therefore a part of the iron was cut off and analyzed. The slag was hammered off from the iron. The ground samples from 650° and 1050° were separated magnetically. It must, however, be pointed out, that a total separation was not reached. Small pieces of slag were frequently found on the iron particles.

The chemical analysis has been carried out as follows. The different separated samples were digested with nitric acid (1:1) for 24 hours. The nitric acid was then driven off with conc. sulphuric acid. The solution was diluted to 100 ml with distilled water. Out of these samples fractions were taken for phosphorus determination with the Bell-Doisy method (colorimetrically as molybdenum blue). The results we find in Tab. 8.

¹ The reduction was carried out in the laboratory of the Wasa wharf.

² The reduction was carried out at the Dept. of Ferrous Metallurgy, Royal Inst. of Technology, Stockholm.

Of these investigations is seen, that the higher the temperature the higher is the content of phosphorus in the iron both from the source of lake ore and rock ore.

If we look more in detail, we will find, that the reduction to phosphorus from the ore at 650°C seems to be a slower process than the reduction to ferrite, according to the microscopical investigation of the mountain ore (Modin and Hansson 1967), as practically all iron ore has been reduced but not all apatite. The whole phosphorus content of the iron, 0.61 %, is here in solid solution in the ferrite.

At 1050°C reduction temperature the phosphorus content of the iron obtained is higher. According to the microscopical investigation, the iron was at the reduction temperature entirely austenitic with about eutectoid carbon content. Also a small amount of a melt was formed. During the solidification of this melt a ternary eutectic was formed with austenite, cementite and iron phosphide, steadite. The total phosphorus of the iron from the rock ore is 1.3 %. At the reduction temperature the iron as mentioned was austenitic. According to Oelsens calculations this constituent can only dissolve about 0.4 % phosphorus as a maximum. The rest of the phosphorus content has thus to be in the iron phosphide in the ternary eutectic formed by the solidification of the melt. Also at this temperature not all apatite is reduced.

At 1200°C all the iron was melt as seen from the microscopical investigation. At the solidification a pig iron was produced with 1.75 % phosphorus. All apatite is now reduced.

At the lowest reduction temperature, 650°C, only ferrite but not austenite can exist. The carbon content is very low as no cementite is seen in the structure. At 1050°C the sample seems to have been entirely austenitic. This austenite has dissolved carbon up to about eutectoid composition, when cooling to room temperature pearlite was formed. If the reduction process is carried out at an intermediate temperature a mixture of austenite and ferrite will be formed. The austenite will dissolve some carbon but the ferrite will not. After cooling to room temperature there will be a pronounced difference between these two areas. Large ferritic areas with a relative coarse grain-size will be intermingled with areas with a mixture of pearlite and ferrite islands. The latter represents the transformed austenite, while the large ferritic areas represent regions, which always have been ferritic. The structure described is very common in archaeological iron. Thus the conclusion can be drawn, that the reduction temperature has been lower than 1050°C but above A_1 (about 720°C).

There is an insignificant difference between the reduction behaviour of the rock ore and the lake ore. The structures of the iron obtained are very similar.

The result of the reduction investigation may be summarized: At a temperature of 1200°C and excess of coal all the iron is melt and an iron with a great amount of steadite and therefore rich in phosphorus is formed from an ore rich

Table 9. Phosphorus in antique iron implements with different carbon content

The figures give the phosphorus content in % in ferritic resp. pearlitic implements.

Ferritic structure	Pearlitic structure
0,001	0
0,002	0
0,025	0,002
0,040	0,005
0,057	0,006
0,200	0,012
0,218	0,017
0,281	0,017
	0,022
	0,047
	0,088
	0,096
	0,200
	0,200
	0,300

in phosphorus. After reduction at 1050°C the presence of a small amount of steadite shows that a partial melting has taken place. The temperature by the reduction process assumed to be used for Viking Age implements may thus have been below 1050°C but above 650°C where the iron is entirely ferritic. Provided the experiments carried out are imitating the conditions in the old small furnaces, artefacts rich in phosphorus may be deriving from lake or bog ores or other ores rich in phosphorus.

The result of the analyses of twenty iron implements from the Iron Age is seen in Table 10. In accordance with Oelsens calculation, as mentioned, one may expect lower phosphorus content in implements with high carbon content than in such with low carbon content. Statistically one may say with regard to the few analyses made, that the frequency of high and low phosphorus content is the same in the ferritic group with low carbon content and in the pearlitic group with high carbon content, but the phosphorus content in the samples in neither of these groups is exceptionally high. For this reason a difference may not be observed.

Coal in iron

The most important micro-element, carbon, is not really suitable for chemical analysis. Carbon particles are often present in the slag included in the iron and may distort the results of the analysis completely. The most important thing, however, is to find out how the carbon entered the iron, where in the constitutional diagram we stand.

Modin and Hansson made metal-microscopic studies of about 50 objects, and

the report of their results was illustrated with a number of excellent photographic enlargements¹.

— I will attempt to summarize their study.

— It is remarkable how uneven the content of carbon is, *i.e.* a mixture of pearlite and ferrite. The low content of carbon is also striking. Almost half of the objects consist of ferrite (low in carbon), only about one-fourth being pearlite (medium carbon) and only 5 per cent of the material is martensite (high C content).

The content of slag is high in about half of the cases. This nearly always happens when malleable iron is made by a direct method. One-third of the material has intergranular rust.

In rather many cases (one-seventh of the total), nitrides are found in the iron.

One case of twin bands (Neumann lamellae) was found. Two knives that had been tempered were found (martensite).

— It seems remarkable to me that apart from these very few, no other tempered objects were found. It is curious, for example, that a lamella from a suit of armour with a pearlitic structure, from Gotland, was not tempered, which seriously impaired its protective function.

An axe from Jukkasjärvi contained very little pearlite, and the basic substance was ferrite, but had a very high content of phosphorus (2.5 per cent), which makes iron hard, but very brittle.

A knife from Småland is not tempered, but has a phosphorus content of ca 1 per cent. Two socketed axes from Gotland, also untempered, have a phosphorus content of 0.4 and 1.87 respectively.

No swords are available in the material, so it is impossible to say anything about the quality of such weapons.

All that can be said about tempering in olden days founded on this material is that it aroused little interest. On the other hand, it seems as if the properties of alloys were known.

Alloying elements. Rust

Bain (1943) has given an account of the influence of alloys on iron. However, studies of such low contents as those in the iron analysed in the present work have not yet been made (except for phosphorus and manganese).

Phosphorus, Bain (1943) says, hardens iron and protects it from rust. Rinman (1782, 1788) found the same thing, and A. Rönnquist and Nils Erik Karlsson (in manuscript) have shown that protection from corrosion remains at high temperatures.

The Helgö material studied, 90 per cent of which is rich in phosphorus, is in a remarkably good state of preservation.

This study will be published by Modin.

Tab. 10. Average percentage of micro-elements in various groups of objects

	Number of objects	P	As	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sn	V	Ag	Zn
Swords	7	0.25	0.003	0.02	0.001	0.014	0.048	0.001	0.01	0.005	0.005	0.005	0.001	0.04
Sword-hilts	3	0.30	—	0.02	—	0.021	0.004	<0.005	0.01	0.008	—	0.002	0.001	0
Axes	9	0.23	0.01	<0.005	0.014	0.040	0.040	0.007	0.011	0.01	0.001	0.003	0.004	—
Socketed axes	6	0.29	0.002	0.05	<0.005	0.02	0.02	0.004	0.003	0.001	—	0.003	0.001	—
Knives	19	0.30	0.001	0.15	<0.005	0.07	0.15	<0.005	0.002	0.002	<0.001	0.001	<0.001	<0.01
Spears	33	0.37	0.002	0.03	<0.005	0.010	0.18	0.001	0.015	<0.001	<0.001	0.003	0.001	—
Arrows	30	0.31	<0.001	0.17	<0.005	0.043	0.21	<0.005	0.060	0.030	<0.001	0.001	—	—

Objects studied and belonging to various groups of tools are compared in respect of micro-elements in Table 10. It will be seen from the table that swords and axes, which were meant to be used over and over again, have a lower average content of phosphorus, while arrows and spears, which were more in the nature of »one-shot» weapons, have a higher average content of phosphorus, which makes them harder, but more brittle.

It was mentioned above that the carbon content of the iron is consistently low, and in the objects in which tempering was possible, it was clearly not done. Did the ancient smiths use phosphorus-rich iron to make hard weapons?

Both iron and rust have been examined in a group of artefacts. The content of iron in the rust varies widely. If it is assumed that a high content of iron in the rust means greater migration of iron from the object (*i.e.* greater corrosion of the object), and a low iron content in the rust means less iron lost from the object, the objects can be divided into two groups according to the content of iron in the rust; one group with more than 20 per cent of iron in the rust and one with less than 10 per cent.

The least corroded iron then contains 3 per cent manganese and 0.18 per cent nickel, while the most corroded iron contains only 1.6 per cent Mn and 0.10 per cent Ni. This may be taken as an indication that higher contents of Mn and Ni should counteract corrosion.

I have stated in another context (Arrhenius 1956) that what is called rust on iron buried in the ground is a very complicated phenomenon. It seems mostly to be a conglomerate of gravel, sand and other mineral soils cemented by humus compounds (which make it brown in colour), lime compounds, ferrous oxide hydrates, phosphates and some iron compounds emanating from the iron around which the so-called rust is formed.

In an experiment with sheets of metal in soil, the crusts of »rust», were examined, with the following results:

	Fe%	P/Fe%
Rust of sheets of iron in sand	24,5	7,0
Rust on sheets of iron in clay	25,6	2,9
Rust on sherardized sheets in sand	18,0	9,9
Rust on sherardized sheets in clay	30,3	3,1

The sherardized sheets did not, of course, lose either iron or phosphorus. Everything must have moved in. Weighing the sheets of iron showed that only about one-tenth of a gramme had been released, and no release of phosphorus could have taken place either. In this case, too, it must be assumed that the greatest part must have moved in from the soil.

A picture, Fig. 1, shows the crust on a sheet of sherardized iron.

Samples of »rust» and iron were taken from 50 or so artefacts. These samples were analysed and the means of the results are given here.



Fig. 1. A piece of sherardized iron that has been in soil for two years. A crust hard as stone is formed on that part which has been in the soil. The crust is formed from sand cemented with calcite and other salts, amongst others, large amounts of phosphate. The colour is dark brown because of a high humus content. Half natural size.

	%Fe	Co ¹	Cu ¹	Mn ¹	Ni ¹	Pb ¹	P ¹
Rust.....	9%	0.064	0.055	2.9	0.053	0.141	3.93
Iron	80	0.084	0.050	2.8	0.235	0.062	0.54

Cr, Mo and V showed no determinable values.

¹ Relative Fe.

Under the conditions in which these artefacts have lain in the earth, copper and manganese have clearly migrated at the same rate as iron.

Alloys of cobalt and, above all, nickel remained in the iron. Lead and primarily phosphorus were concentrated in the rust by migration from the soil.

These examples of migration of elements into the »rust» show how important it is to clean the object before an analysis is made.

No conclusions can be drawn from analyses of the rust.

Slags, which have lain in the earth for a long time, have mostly suffered disintegration, sometimes followed by leaching and sometimes by concentration. Great care must therefore be taken in the evaluation of analyses of slag. As mentioned earlier, microscopic analysis revealed many cases of intergranular rust. Tests with a microprobe should be made to determine whether immigration of substances has taken place here, and if so, whether it has occurred to such an extent that the analysis is affected. An investigation has been made by the Inst. of Metallurgy. The content of P is very low. The possibility of immigration of elements from outside is, thus, very low.

A term used by archaeologists is »barren periods»; used to describe periods for which no finds have been made in the earth, and assumed to indicate cultural regression.

Study of the distribution of resistivity in Swedish soils (Arrhenius 1964) has shown that the mean value is around $20,000 \Omega \text{ cm}^1$. The rate of corrosion at this resistivity is, in Sweden (within the regions populated in ancient times), about 20 gm per square metre and year. This means that after 400 years, rust has penetrated to a depth of 1 mm in objects made of iron. This, in a thousand years, means that an object 5 mm thick would be completely corroded.

But not all soils have average qualities. About one-third of them have such resistivity that half or less than half the corrosion rate is to be expected. Thus about one-third of the number of objects should survive a thousand years in the soil.

One object which, on account of its function, does not seem to have altered much down the years is the knife.

All finds of knives reported in *Statens Historiska Museum och Kungl. Myntkabinettet. Samlingarnas tillväxt* (Growth of collections in the National Museum of Antiquities), 1946—1962, have been studied, and the results are given below.

No material from Öland and Gotland is included in this inventory, for these provinces differ greatly from other parts of the country pedologically and climatically. The number of knives found is calculated on the number of find localities.

Period	Number of knives/100 sites	Number of sites
Viking Age-Vendel Age	61	70
Late Iron Age	29	55
Early (Late Roman) Iron Age	24	37

¹ Resistivity is the inverted value of the conductivity, and is therefore a measure of the salt content of soil. Low resistivity = high salt content; high resistivity = low salt content.

In order to obtain more comparable material, Östergötland, Västergötland and Uppland were chosen. The soils in these regions cause, on average, a high rate of corrosion. On the other hand, there are soils there with high resistivity, so that great differences may be expected between year 1000 and year 0. The following results were obtained.

Period	Number of knives/100 sites	Number of sites
Vendel Age, Uppland.....	140	5
Late Roman Iron Age, Uppland	50	6
Early Iron Age, Väster- and Östergötland	15	20

Thus, when barren periods are to be determined, great attention should be paid to the effects of corrosion.

Summary

An investigation has been made on the content of Ag, As, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V and Zn in lake, bog and rock iron ore and in artefacts from olden time.

The author has, contradictory to most workers in this field, made very probable that our old iron manufacture was founded on both rock and limonite ores.

In Sweden to the south of Bergslagen (the mining district proper) there are hundreds of small iron mines and veins.

The limonite ores are formed, to a certain extent, by the action of plants and plant debris. They are, thus, rich in biophile elements as Mn, Co, Ni, Mo and P. Some of them are very rich in manganese and could possibly be used as a source of this element.

There are great differences in the content of the different elements investigated both in ore and artefacts.

The "skragg" ore seems to be the result of a leaching process dissolving iron and leaving manganese and phosphorus and other elements.

It is very probable that local ore has been used for iron production. In some cases it is possible to point out the probable origin of the ore.

The carbon content in most of the artefacts investigated is low.

The content of phosphorus causes an iron low in corrosion. Even some few percent nickel and manganese seem to be anti-corrosive.

It seems as if the old smiths had a knowledge of such effects.

What we call rust is mostly a complex of soil components which have been attracted by iron.

A low frequency of artefacts may be due to corrosion.

Appendix:
The microstructure after reduction of phosphorus rich iron ore with charcoal at different temperatures

by

TORSTEN HANSSON AND STEN MODIN

Communication from the Swedish Institute for Metal Research

The present investigation has been actualized in connection with studies of archaeological iron samples, where the question how the iron was produced often has been the centre of attention. The main interest has here been devoted to the reduction of ores rich in phosphorus in order to determine if and how the phosphorus is taken up by the iron during the reduction process.

The initiative to this investigation has been taken by Dr. O. Arrhenius. For these studies rock ore from Grängesberg, one sample with 5 mm material and one of fines, were used. Of bog iron ore a sample was acquired from lake Vidöstern (Åminne bruk) and a different one from Grangärde. The reduction temperatures chosen were 650, 1050 and 1200° C. The experimental details are described in the report by Dr. O. Arrhenius.

PREPARATION OF SAMPLES

The samples have been moulded in bakelite, ground and polished. Because of the brittleness and porosity the material showed a tendency to split and to fall out of the bakelite.

THE STRUCTURE OF THE UNTREATED ORE

With regard to structure there was no real difference between the crushed Grängesberg ore and the fines. The description given below therefore applies to both samples. The ore was lighter than the gang. To distinguish between silicate and apatite was a little more difficult as both were transparent and therefore shone in dark-field illumination. Added

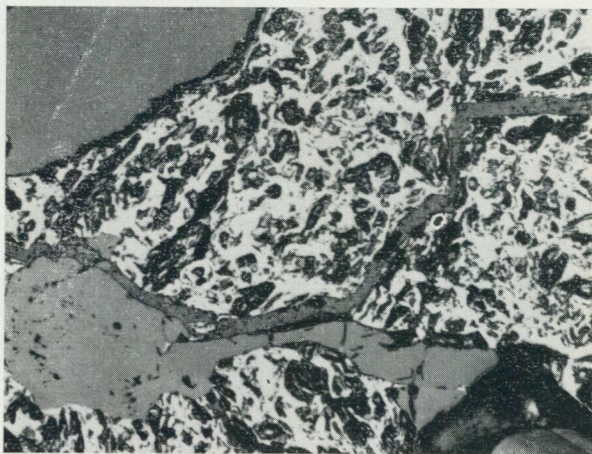


Fig. 2. Crushed ore from Grängesberg. Iron ore (mottled light grey), apatite (dark grey band), silicate (medium grey). 750 ×.

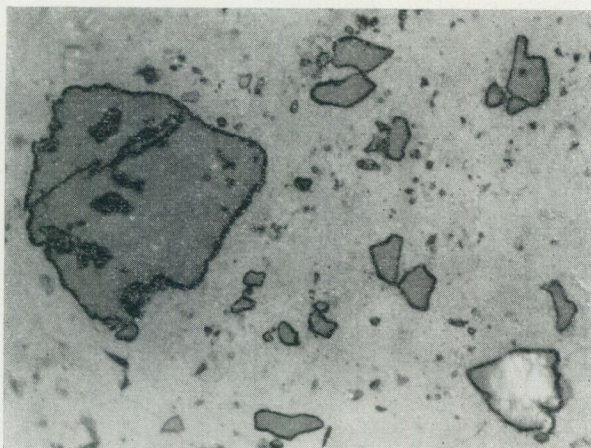


Fig. 3. Lake ore. Silicate particles (dark grey). 750 \times .

to this the gang had the same appearance as the bakelite. The silicate particles, however, were harder than those of apatite. When both were lying next to each other the silicate particles stood out in relief after a polish with aluminium oxide and were thus well identified.

The bog iron ore consisted of a hydrate, which was the transparent matrix in which silicate particles were embedded. Here also dark paths were found, which probably were the remnants of organic material. The two samples of bog iron ore showed no visible difference.

THE STRUCTURE OF ORE REDUCED AT 650°C

In the two reduced samples from Grängesberg there still was some iron oxide. Thus the samples were not entirely reduced. In the iron both silicate and apatite particles were still found. The samples have been etched with nitric acid in ethyl alcohol in order to

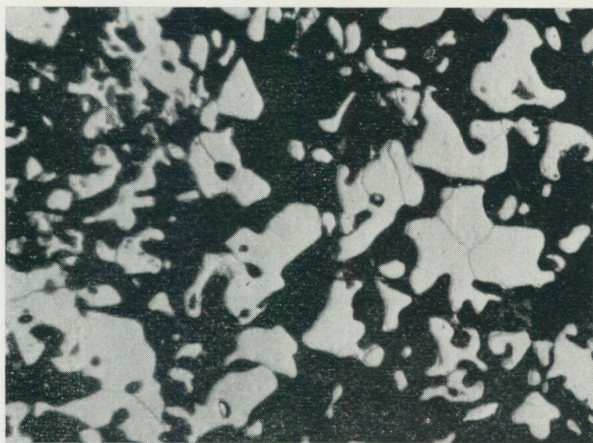


Fig. 4. Crushed ore from Grängesberg reduced at 650° C. Iron (light areas). 750 \times .

reveal the structure. The metallic matrix was entirely ferritic and carbide particles have not been noted. Etching has also been made in order to identify iron phosphide. No phosphide could be observed.

The structure of the reduced bog iron ore sample was quite similar to the reduced Grängesberg samples. Thus, here also silicate particles were found in the iron. The matrix was ferrite and neither carbide nor phosphide particles were to be seen.

It is an old observation that hardly any cementation occurs as long the iron is in the α -modification. This modification can only dissolve 0.02 % carbon as a maximum. Perhaps a very thin film of cementite may precipitate on the surface of the iron, after which this reaction stops owing to the low carbon diffusion through this film.

The chemical analysis showed a phosphorus content of about 0.6 % for the iron from Grängesberg ore and about 0.8 % for the iron from the bog iron ore.

THE STRUCTURE OF THE ORE REDUCED AT 1050°C

After the reduction of the Grängesberg samples the metallic matrix showed embedded silicate particles but all apatite seemed to be gone. The structure was now quite different. The matrix consisted mainly of pearlite, but also a small amount of the ternary eutectic, steadite, was observed.

The iron was in the austenitic condition at the reduction temperature. The austenite dissolved both carbon and phosphorus in solid solution until the concentration was high enough for a melt to form. The quantity of this melt was small. During the cooling period this melt solidified and formed the observed eutectic with about 2 % phosphorus and 6.9 % carbon. The austenite transformed later at a lower temperature to ferrite and cementite, mainly as pearlite as mentioned before.

The carbon content has been estimated to be about 0.8 %. The phosphorus content was now 1.0—1.3 %. A part of this phosphorus was as mentioned before precipitated as iron phosphide, which is a hard and brittle constituent. The reduced bog iron ore had a similar structure.



Fig. 5. Fines from Grängesberg reduced at 1050° C. Pearlitic matrix. Steadite (mottled light grey band) and a silicate inclusion (dark grey). 750 ×.



Fig. 6. Lake ore reduced at 1200° C. Pearlitic matrix with steadite. Graphite flakes (dark grey). 150 ×.

THE STRUCTURE OF ORE REDUCED AT 1200°C

As the reduction temperature was raised to 1200° C the reduced iron, austenite, dissolved carbon and phosphorus and a melt was formed. At the solidification a typical pig iron was produced. The carbon content was estimated to be more than 4 %, the main part was in the form of graphite flakes. The phosphorus content was a little more than 1 %. As a consequence a lot of iron phosphide was found in the structure. The reduced bog iron ore had also in this case a similar structure.

DISCUSSION

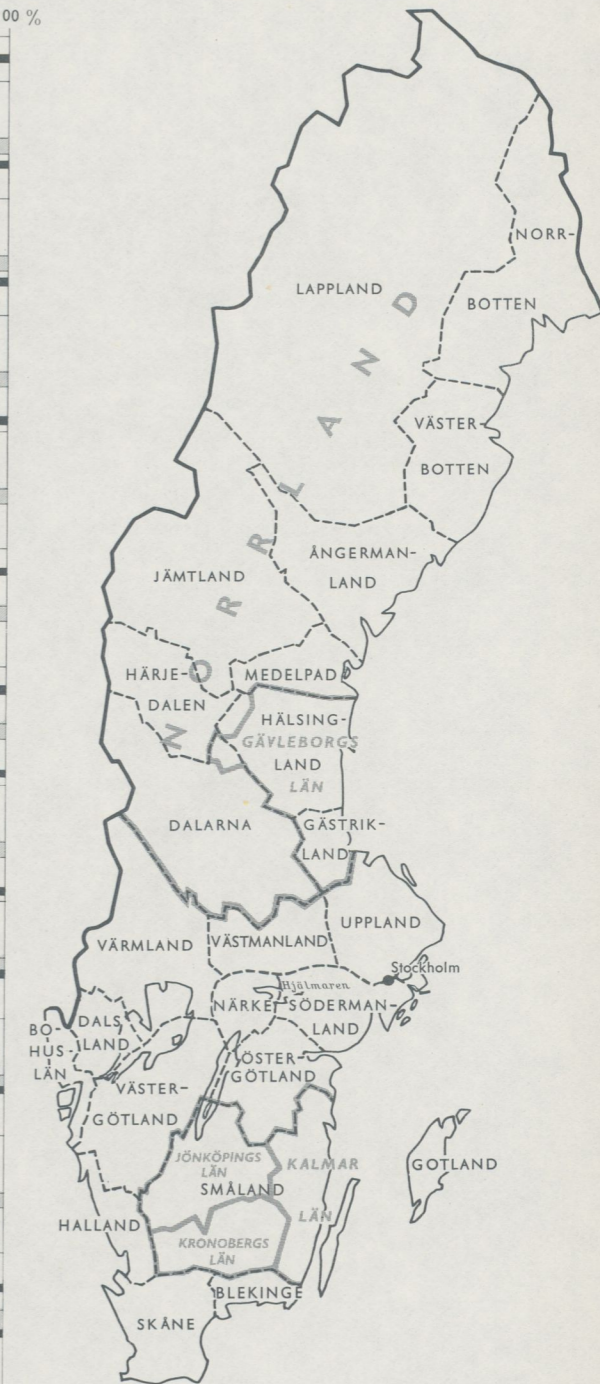
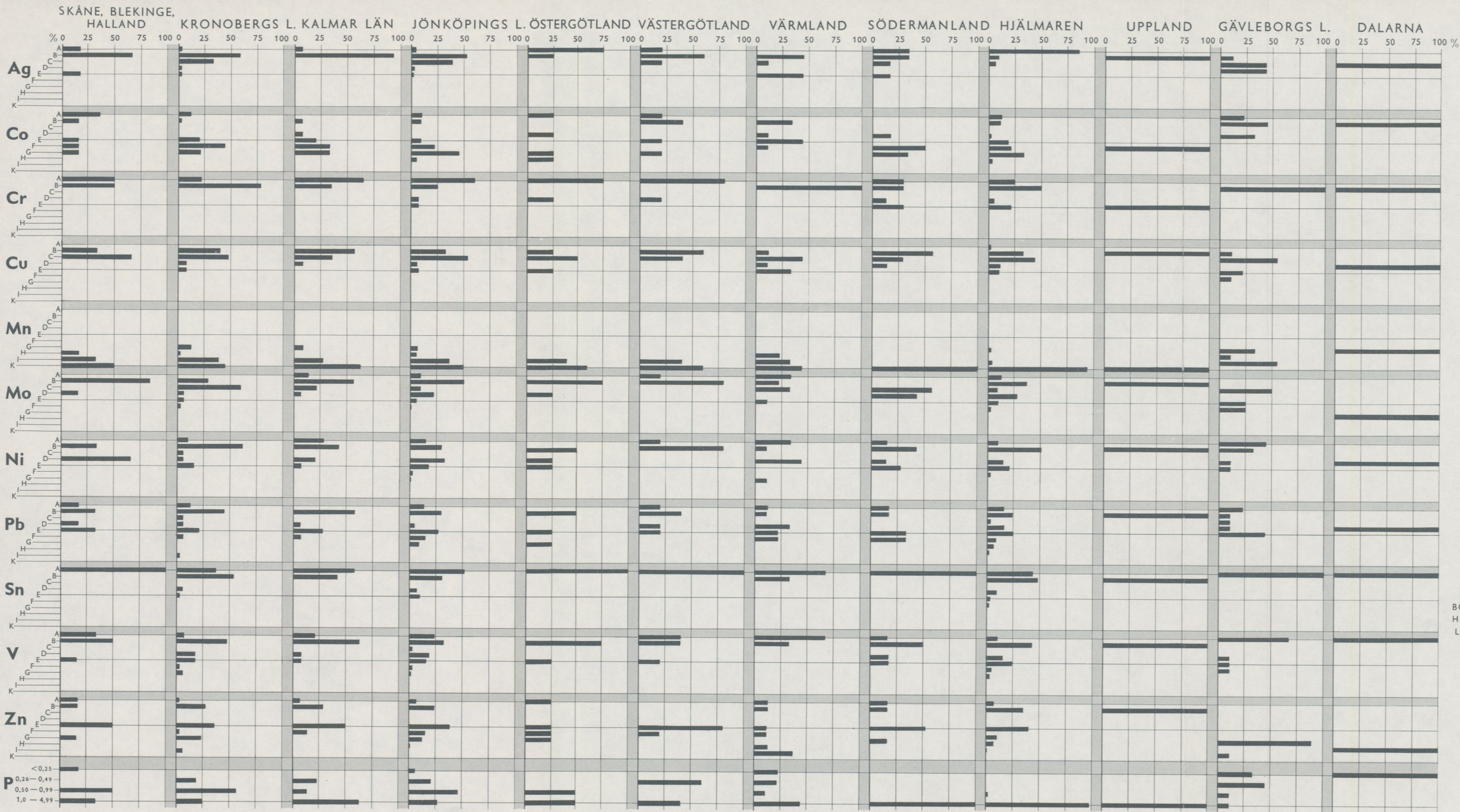
In the archaeological iron samples the carbon content is as a rule very low. This observation seems to indicate that the ore was reduced at a temperature below 1000° C. With the very simple furnaces in which the process was carried out, this temperature seems to be quite reasonable. The archaeological iron investigated was thus produced in one process, whereas the low carbon iron today is produced in two processes as a rule. In the first the ore is reduced at a high temperature, which gives a pig iron as described. In the second process this pig iron is decarburised in a fining process.

The present investigation shows that also at a low reduction temperature the iron dissolves most of the phosphorus content in the ore, whether this is rock ore or bog iron ore. A part of this phosphorus may precipitate as iron phosphide. The dissolved phosphorus makes the iron hard and in higher quantities brittle. At the phosphorus contents in the samples mentioned here the iron is both hard and brittle.

Literature

- AARNIO, B., 1918: Om sjöalmerna i några sjöar i Pusula, Pyhäjärvi, Loppis, Somerniemi och Tammela socknar. — Geol. Komm. Finland, Geotekn. Med., 16.
- AGRIGOLA, G., 1928: Zwölf Bücher vom Berg- und Hüttenwesen. Agricola Gesellschaft beim Deutschen Museum. — Berlin.
- ALEXANDER, W. O., 1965: Metallurgical achievements. — Belfast.
- ALMQVIST, J., 1938: Arvid Trolles Jordebok 1498. — Hist. Handl., 31.
- ARRHENIUS, O., 1947: Organisatoriska tendenser inom medeltida jordbruk. — K. Lantbruksakad. Tidskr.
- 1950: Vissa ämnens fördelning i marken i Kopparbergs län. — Sver. Geol. Unders., C 518.
- 1954: Chemical denudation in Sweden. — Tellus, 6.
- 1956: The corrosion of steel in soil. — Tekniska Skrifter, Stockholm.
- 1957: Plant food from decayed leaves and conifer needles. — Acta Agricult. Scand., VII.
- 1959: Die Grundlagen unserer älteren Eisenherstellung. — Antikvariskt Arkiv, 13.
- 1963: Korrosion ombord på regalskeppet Wasa. — Metallen, 19.
- 1964: Soils and Corrosion. — Scandinav Corrosion Congress. Helsinki.
- ASCHAN, O., 1908: Humusämnena i de nordiska inlandsvattnena och deras betydelse särskilt vid sjöalmernas daning. Bidr. till kännedom af Finlands land och folk. — Finska Vetensk. Soc. Helsingfors, 66.
- BAIN, E. C., 1943: Functions of the alloying elements in steel. — Cleveland.
- BELL, R. D. and DOISY, E. R., 1920: Rapid Colorimetric methods for the determination of phosphorus in urine and blood. — J. Biol. Chem., 44.
- VAN BEMMELEN, J. U., 1900: Über das Vorkommen, die Zusammensetzung und die Bildung von Eisenanhäufungen in und unter Mooren. — Z. anorg. Chemie., 22.
- BIRINGUCCIO, VANOCGIO, 1925: Pirotechnia, Übersetzt und erläutert von Dr. Otto Johansen. — Braunschweig.
- CARLBERG, J. O., 1873: Historiskt sammandrag om svenska bergverkens uppkomst. — Stockholm.
- ELLIOTT, J. F., JACOBS, C. B. and TENENBAUM, N., 1954: Significance of minor elements in iron bearing raw materials for integrated steel plants. — American Steel Inst. *Preprint*.
- ERIKSSON, MÅRTA, 1940: Järnräntor under 1500-talet. — Jernkontorets Bergshistoriska skriftserie, 11.
- FREI, HANS, 1965: Die frühgeschichtliche Eisengewinnung im nördlichen Voralpenland. — *Vortrag 28 Sitz, Geschichtsaussch. Ver. d. Eisenhüttenleute 1965. Unpublished.*
- GEIJER, PER and MAGNUSSON, N. H., 1944: De mellansvenska järnmalternas geologi. — Sver. Geol. Unders., Ca 35.
- GILLES, J. W., 1936: Die Grabungen auf vorgeschichtlichen Eisenhüttenplätzen des Siegerlandes ihre Bedeutung und die hüttentechnischen Erfahrungen im Vergleich mit anderen Funden. — Stahl und Eisen, 56.
- 1958 a: 25 Jahre Siegerländer Vorgeschichtsforschung durch Grabung auf alten Eisenhüttenplätzen. — Westfälische Forschungen, 11.
- 1958 b: Vorgeschichtliche Eisengewinnung. — Siegerland, 35.
- 1958 c: Versuchsschmelze in einem vorgeschichtlichen Rennofen. — Stahl und Eisen, 78.
- 1960: Rennversuch im Gebläseofen und Ausschmieden der Luppen. — Stahl und Eisen, 80.
- GRIP, E., 1953: Tracing of glacial boulders as an aid to ore prospecting. — Economic Geology, 48.
- GOLDSCHMIDT, V. M., 1958: Geochemistry. — Oxford.
- HARDER, E. G., 1919: Iron depositing bacteria and their geological relations. — U.S. Geol. Survey, Prof. Pap. 113.
- JERNKONTORET, 1906: Analyser av svenska järn- och manganmalmer, I. — Stockholm.
- 1931: Analyser av svenska järn- och manganmalmer, II. — Stockholm.
- LANDERGREN, S., 1948: On the geochemistry of Swedish iron ores and associated rocks. — Sver. Geol. Unders., C 496.
- LIESKE, R., 1911: Beiträge zur Kenntnis der Physiologie von Spirophyllum ferrugineum (Ellis) einen typischen Eisenbakterium. — Jahrb. wissensch. Bot., 49.
- LUNDQVIST, G., 1942: Sjösediment och deras bildningsmiljö. — Sver. Geol. Unders., C 446.
- MAGNUS, OLAUS, 1565: Historia delle genti et della natura della cose settentrionale. — Venedig.
- MERO, J. L., 1965: The mineral resources of the sea. — New York.
- MOLISCH, H., 1910: Die Eisenbakterien. — Jena.
- MODIN, S. och HANSSON, T., 1967: The microstructure after reduction of phosphorus rich iron with charcoal at different temperatures. [See appendix.]

- NAUMANN, E., 1922: Södra och mellersta Sveriges sjö- och myrmalmer. — Sver. Geol. Unders., C 297.
- NEEDHAM, J., 1964: The development of iron and steel technology in China. — Newcomen Society, W. Haffer Sons. Cambridge.
- NIHLÉN, J., 1932: Studier rörande äldre svensk järntillverkning med särskild hänsyn till Småland. — Jernkontorets Bergshist. Skrifter, 2.
- ODÉN, S., 1922: Die Huminsäuren. — Kolloidchem Beih., 11.
- OLDEBERG, A., 1966: Metallteknik. — Stockholm
- RANKAMA, K. and SAHAMA, TH. G., 1950: Geochemistry. — Chicago.
- RINMAN, S., 1788—89: Bergwerks-Lexikon I, II. — Stockholm.
- 1782: Försök till järnets historia. — Stockholm.
- RUDBECK, O., 1679: Atland. — Upsala.
- SAURAMO, M., 1924: Tracing of glacial boulders and its application in prospecting. — Bull. Comm. Geol. Finlande, 67.
- SCHÜRMAN, E., 1958: Die Reduktion des Eisens im Rennfeuer. — Stahl und Eisen, 78.
- SHAPIRO, L. and BRANNOCK, W. W., 1956: Rapid analysis of silicate rocks.—U.S. Geol. Survey Bull. 1036 C.
- STAPP, F. N., 1865: Om sjömalms uppkomst. — Jernkontorets Annaler.
- SUNDELIN, U., 1918: Om limonitbildningar m. m. i Småland. — Bil. Jernkontorets Annaler.
- SWEDENBORG, E., 1923: Om järnet. Red. av Hj. Sjögren. — Stockholm.
- TEGENGREN, F. R., 1924: Sveriges ädlare malmer och bergverk. — Sver. Geol. Unders., Ca 17.
- TILAS, D., 1740: Tankar om malmletande i anledning af lösa gråstenar. — Sv. Vetenskaps Acad. Handl., 1.
- THUNMARK, S., 1937: Über die regionale Limnologie von Südschweden. — Sver. Geol. Unders., C 410.
- VOGT, J. H. L., 1906: Über Manganwiesenerz und das Verhältnis zwischen Eisen und Mangan in den See- und Wiesenerzen. — Z. prakt. Geol., 14.
- WOLFE, R., 1964: Iron and manganese bacteria. Principles and applications in aquatic microbiology. (Ed. by Heukelekian). — New York.



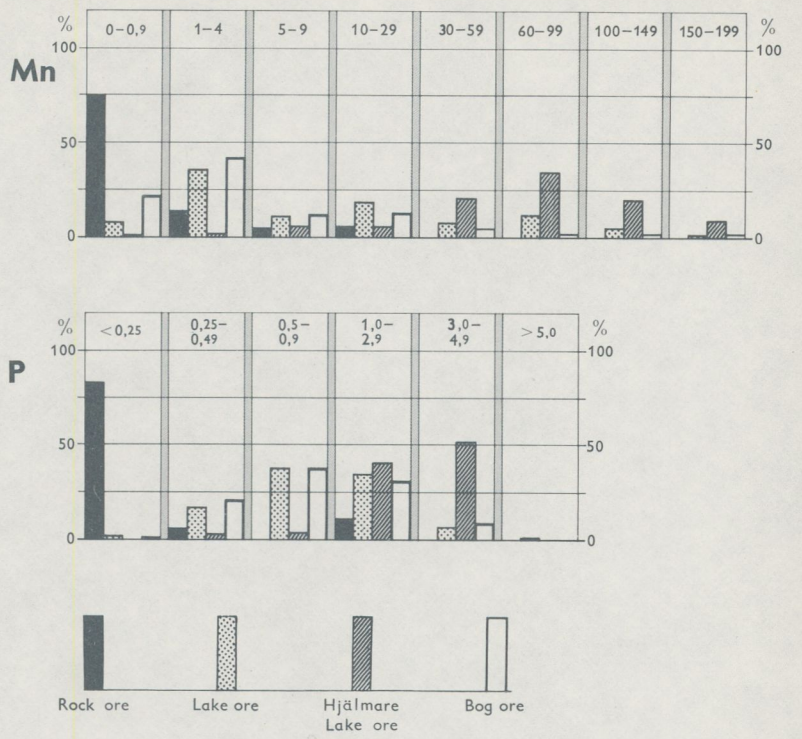
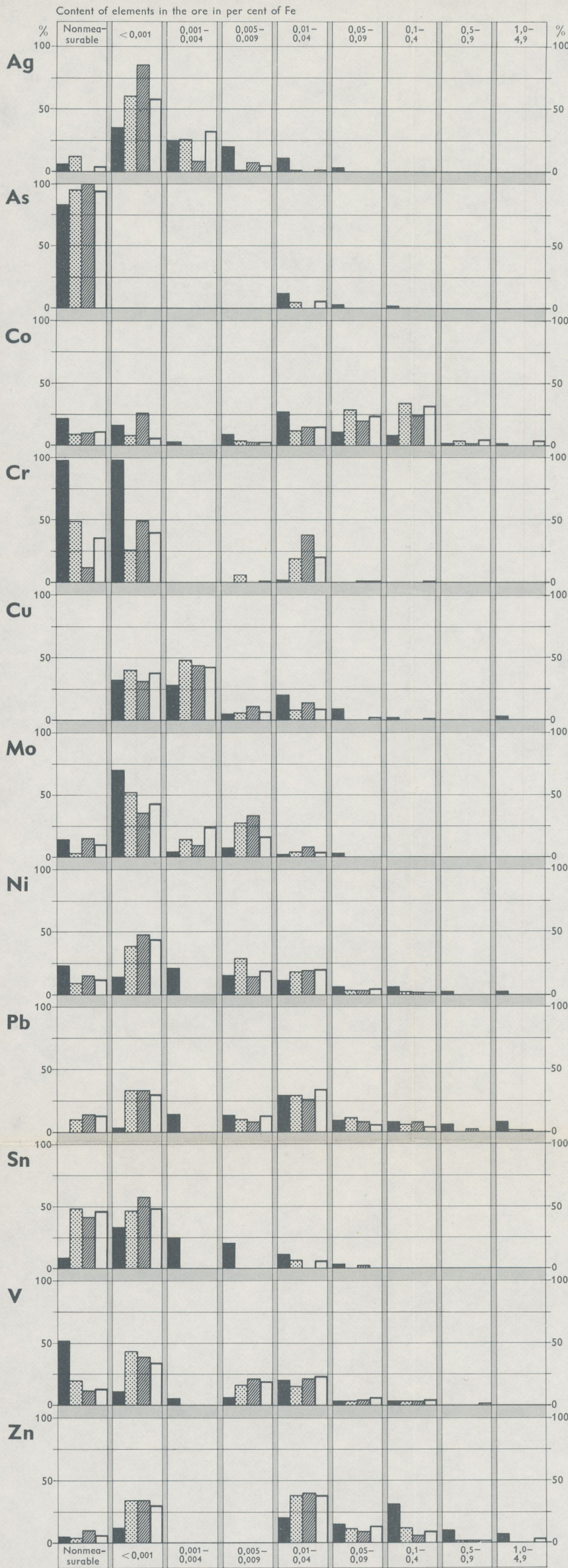
A = Nonmeasurable
 B = < 0.001 %
 C = 0.001 — 0.004 %
 D = 0.005 — 0.009 %
 E = 0.01 — 0.04 %
 F = 0.05 — 0.09 %
 G = 0.1 — 0.4 %
 H = 0.5 — 0.9 %
 I = 1.0 — 4.9 %
 K = > 5.0 %

THE CONTENT OF CERTAIN MINOR ELEMENTS IN LAKE ORE

The length of the piles gives the frequency (in % of the number of samples from the district in question) of samples with that concentration which the place of the pile indicates. The concentration is indicated by letters (to the left) which are explained and evaluated in figures (below the diagram). If we, thus, want to know the distribution of molybdenum in different classes of concentration in the district Kronoberg we can find from the diagram that

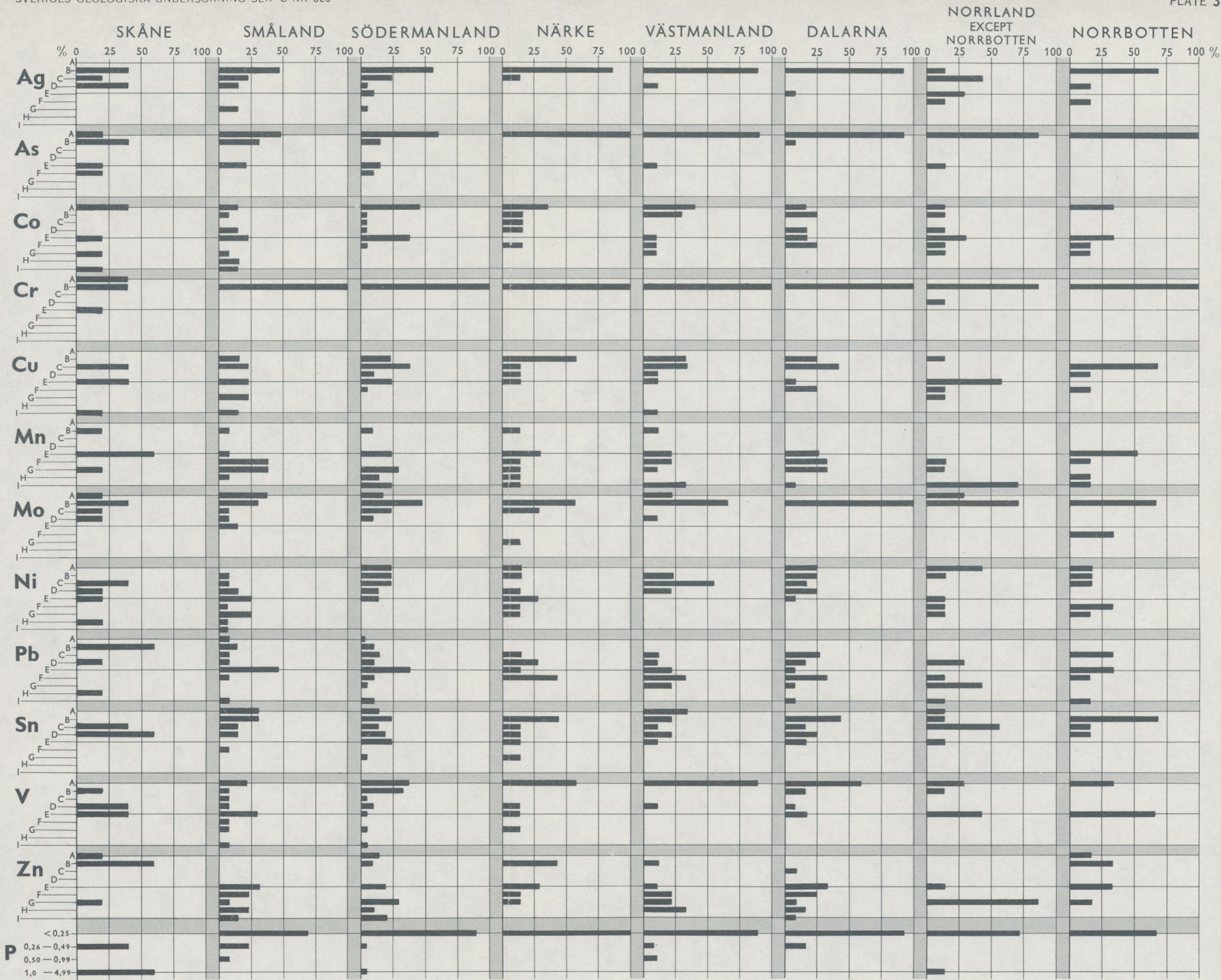
29 % of the number of samples belong to the group < 0.001 % Mo
 60 % » » » » » » » » » 0.001 — 0.004 % »
 5 % » » » » » » » » » 0.005 — 0.009 % »
 5 % » » » » » » » » » 0.01 — 0.04 % »
 1 % » » » » » » » » » 0.05 — 0.09 % »
 Arsen in lake ore shows a low concentration (not detectable) and is thus omitted.

From Skåne, Halland and Blekinge the numbers of samples is low, the analyses on the other hand are very similar. The results are thus given in one group. From Uppland and Dalarna there is only one sample of each analyzed.



THE CONTENT OF DIFFERENT ELEMENTS IN ROCK-, LAKE- AND BOG ORE

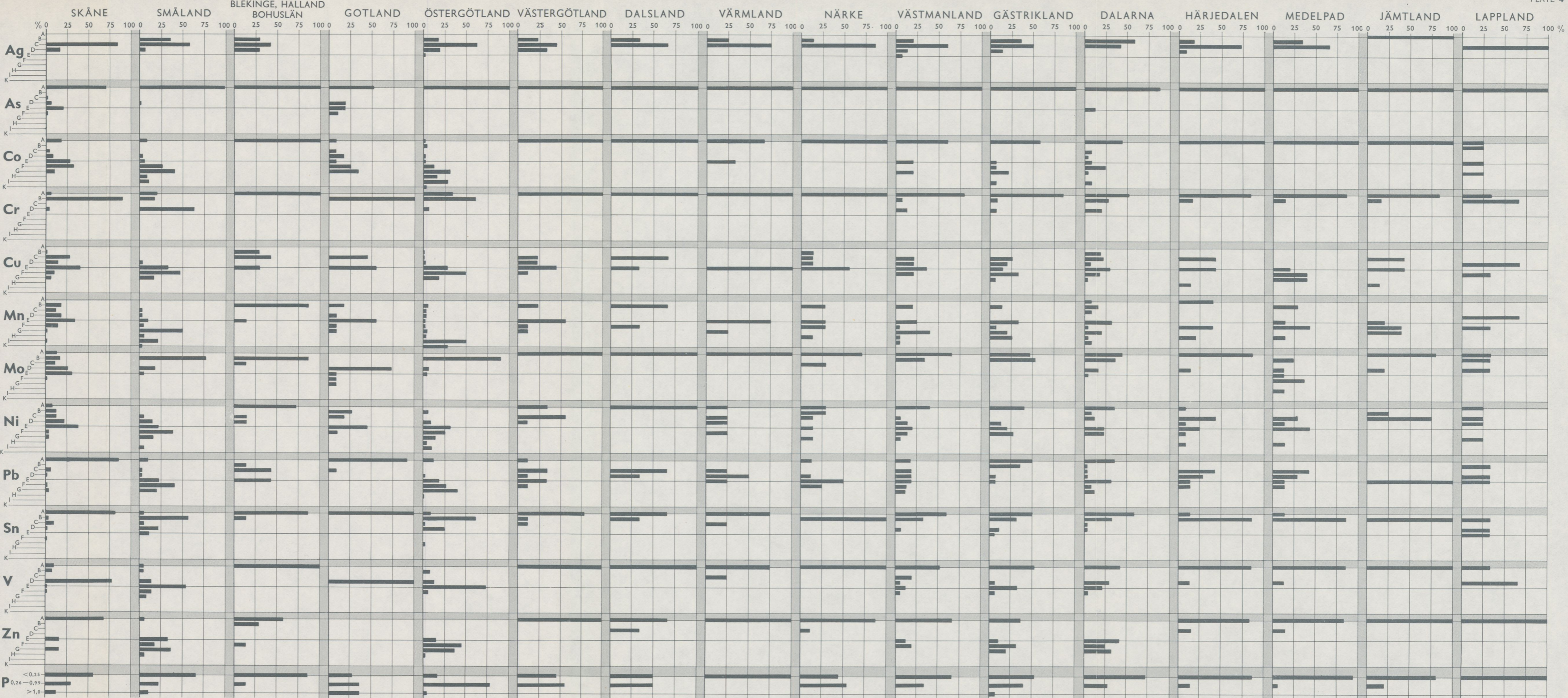
For the figures, see Table 4



A = Nonmeasurable
 B = < 0.001 %
 C = 0.001 — 0.004 %
 D = 0.005 — 0.009 %
 E = 0.01 — 0.04 %
 F = 0.05 — 0.09 %
 G = 0.1 — 0.4 %
 H = 0.5 — 0.9 %
 I = > 1.0 %

THE CONTENT OF CERTAIN MINOR ELEMENTS IN ROCK ORE

How to read the diagram, see Plate 1



A = Nonmeasurable
 B = < 0.001 %
 C = 0.001 — 0.004 %
 D = 0.005 — 0.009 %
 E = 0.01 — 0.04 %
 F = 0.05 — 0.09 %
 G = 0.1 — 0.4 %
 H = 0.5 — 0.9 %
 I = 1.0 — 4.9 %
 K = 5.0 — 9.9 %

THE CONTENT OF CERTAIN MINOR ELEMENTS IN OLD ARTEFACTS
 How to read the diagram, see Plate 1

PRIS 10 KRONOR

Distribueras genom
SVENSKA REPRODUKTIONS AB
FACK VÄLLINGBY 1

STOCKHOLM 1967. KUNGL. BOKTRYCKERIET P. A. NORSTEDT & SÖNER

PRINTED IN SWEDEN