

Bulletin de la  
**Commission  
Géologique**  
de Finlande

N:o 228

Trace-elements in the Finnish  
Precambrian phyllites as indicators of salinity  
at the time of sedimentation

by Anssi Lonka



Geologinen tutkimuslaitos • Otaniemi 1967

Bulletin de la Commission Géologique de Finlande N:o 228

TRACE-ELEMENTS IN THE FINNISH PRECAMBRIAN  
PHYLLITES AS INDICATORS OF SALINITY AT  
THE TIME OF SEDIMENTATION

BY  
ANSSI LONKA

WITH 24 FIGURES AND 12 TABLES IN TEXT

GEOLOGINEN TUTKIMUSLAITOS  
OTANIEMI 1967

## ABSTRACT

Concentrations of nineteen trace-elements in the Precambrian phyllites in Finland have been determined. A total of 174 samples have been collected from eighteen different areas. Special attention is paid to the contents of B, Ga, Rb, Li and V. The observed concentrations have been compared with the trace-element concentrations of the fresh-water and marine clay sediments of different ages in U.S.A. The principal component and factor analysis methods have been used when analysing the results. The investigation shows that in the Precambrian schists now studied, especially B and Ga can be used as indicators of the salinity of the water during the sedimentation. The results also indicate that the salinity of the oceans has very probably been lower during the Precambrian than at the present time. Among the phyllites now studied the Hyrynsalmi phyllites have been deposited in the most saline water, the phyllites of Tampere, Sotkamo and Tervola being nearest to them.

## ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Professor K. J. Neuvonen, Ph. D., for suggesting this subject, as well as for the invaluable advice he offered during the course of this investigation and for reading the manuscript.

I wish to thank also Professor Th. G. Sahama, Ph. D., for kindly reading and criticizing the manuscript.

I am very grateful to Mr. Oiva Joensuu, M. Sc., who made the trace-element determinations on all the samples in the Marine Laboratory on Miami University.

I thank Professor Vladi Marmo, Ph.D., Director of the Geological Survey of Finland, for allowing my investigation to be published as a Bulletin of the Geological Survey.

Thanks are also due to Mr. Harri Lonka, Ph.D., for the excellent instruction I received from him pertaining to mathematical problems and for the constructive criticism he made concerning the mathematical part of the manuscript. Likewise my appreciation is given to Mr. Pertti Hyyrynen, M.Sc., for his help in dealing with certain problems arising in the statistical part of the work.

The numerical work was done by the Computing Center of the University of Helsinki. My gratitude is especially due to Mr. Jorma Torppa, M. Sc., for his invaluable suggestions and help with the multivariate analysis of the results.

I wish to thank my late superior Mr. Toivo Mikkola, Ph.Lic., the Chief Geologist of the Finnish Prospecting Company, for his sympathetic attitude concerning all phases of geological investigations.

I express my appreciation to Mr. Ilmari Salli, Ph.D. and Docent Antti Savolahti, Ph.D., for their valuable help in collecting the sample material. Mr. Viljam Hyppönen, M.Sc., Mr. Viljo Hämäläinen, M.Sc. and Mr. Esko Sipilä, M.Sc. also assisted in collecting the samples.

This study was financed by the Cultural Foundation of Finland (Suomen Kulttuuri-rahasto), the Emil Aaltonen Foundation (Emil Aaltosen Säätiö) and the Outokumpu Oy Foundation (Outokumpu Oy:n Säätiö), for which I am very grateful.

I furthermore extend my thanks to Miss Karin Dahl, who ably drew the figures and diagrams, to Mr. Edvin Risser, and Mrs. Gillian Häkli, B. A., for translating and correcting the English, and to all the other persons who in one way or another helped me during the course of this study.

November 1966

Anssi Lonka



## CONTENTS

Abstract .....	2
Acknowledgements .....	3
Introduction .....	7
Previous works.....	9
Investigations based especially on the boron contents .....	9
Studies on the role of metamorphism .....	10
Later investigations mainly in North America .....	13
Material and methods .....	17
Collection of samples .....	17
Petrographic classification of samples .....	18
Analytical methods .....	26
General discussion of material and analytical results .....	34
Comparison of trace-element contents with earlier results .....	34
Variations in trace-element contents in different beds of phyllites .....	38
Effect of metamorphism on trace-element contents .....	39
Consequences of the metamorphic and bedding variations .....	40
Contents of boron and gallium .....	41
Contents of manganese .....	43
Multivariate analysis of trace-element concentrations .....	43
Theory of principal component analysis .....	43
On factor analysis .....	46
Principal component analysis of observation material .....	47
Analysis of thirteen variables .....	47
Analysis of six variables .....	49
Factor analysis of observation material .....	49
Dispersion of observation points in $F_1 F_2 F_3$ space .....	51
Discussion of results .....	54
Cr-Ni-V-Co-Cu-Zn factor .....	55
Pb-Zn factor .....	55
B-Ga-Ba-Be factor .....	56
Be-Ga factor .....	57
Li factor .....	59
Summary .....	59
References .....	62



## INTRODUCTION

In the winter of 1961—62 Professor K. J. Neuvonen called the attention of the writer to certain investigations mainly in North America dealing with the determination of the deposition conditions of clay sediments on the basis of their trace-element contents. Of these investigations, especially the works of Degens, Williams and Keith (1957 and 1958), as well as Keith and Degens (1959) are to be mentioned. The studies of these workers indicated that on the basis of the abundance ratios between boron, gallium and rubidium and furthermore between boron and gallium, as well as between boron and lithium it is possible to ascertain whether deposition occurs in marine or fresh water. The sediments studied were especially suitable for trace-element investigations, since the salinity of the water during deposition could be determined by means of the assemblage of fossils in the sediments.

The sediments studied in America, whose conditions of formation at the time of deposition were been investigated by trace-element analyses, vary in age from modern to Pennsylvanian. The Finnish Precambrian phyllites and mica-schists are considerably older. Consequently, the trace-element contents prevailing at the time of deposition may have been altered later as a result of ionic migration and granitization related to metamorphic processes. Despite these factors, which probably would make the work more difficult, the author believes it to be justified for studying the environmental conditions at the time of the formation of the phyllites in Finland, using mainly the Li, B, Ga and Rb contents in these rocks.

Naturally the reliability of the results obtained in the study is the greater the larger is the number of analysed samples. However, owing to the substantial economic costs involved in collecting and analysing a material as large and homogeneous as would be wanted, the original plan had to be restricted. In the years 1962—63 a total of 174 phyllite and mica-schist samples were collected in 18 areas in the schist regions of Finland (Fig. 1). The samples were analysed by Mr. Oiva Joensuu, M.S., at the Marine Laboratory of the University of Miami, U.S.A.



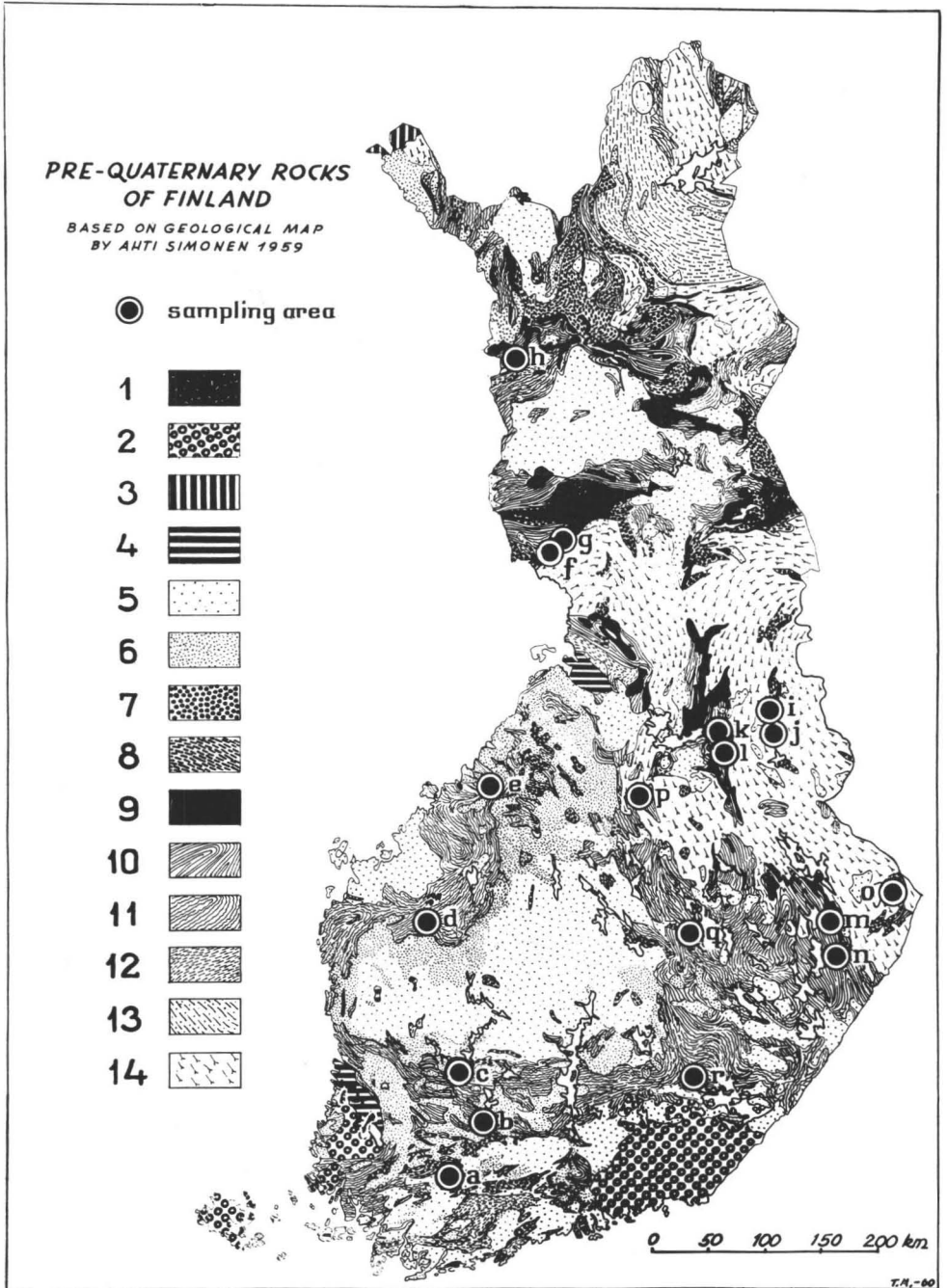


FIG. 1. Location of sampling areas in Finland.

Explanation to FIG. 1: Pre-Quaternary rocks of Finland. 1 diabase, 2 granite, mainly rapakivi (Precambrian), 3 Paleozoic schists (Caledonian), 4 siltstone and slate, arcose sandstone (Jotnian), 5 acid plutonic rocks in general and granite, 6 granodiorite and quartzdiorite, 7 gabbro, anorthosite and ultrabasic rocks, 8 metabasalt, amphibolite and hornblende gneiss, 9 quartzite, 10 phyllite and mica schist, 11 mica gneiss and migmatite, 12 quartz felspar schist, felspar and quartz porphyry, 13 granulite, 14 granite gneiss. Sampling areas: a Forssa, b Kalvola, c Tampere, d Seinäjoki, e Central Ostrobothnia f Taivalkoski (Kemi commune), g Tervola, h Kolari, i Hyrynsalmi, j Kuhmo, k Jormua, l Sotkamo, m Kontiolahti, n Pyhäselkä, o Ilomantsi, p Viiremä, q Kuopio, r Ristiina

## PREVIOUS WORKS

## Investigations based especially on the boron contents

The first noteworthy investigations on the depositional conditions of marine clay sediments were the studies of Goldsmith and Peters (1932 a, b). Their works dealt with the geochemical cycle of boron and showed that this element was particularly enriched in marine clay sediments. According to these authors, boron originally occurs in ocean water, from which, by means of adsorption, it becomes incorporated in the sediments. The extent of such incorporation depends, first on the boron content of the water and second, on the chemical and physical properties of the sediments. Moreover, the boron content of these sediments may also be influenced by metamorphism, which may cause migration of the element out of the sediments. The results of the studies of Goldsmith and Peters on Paleozoic and modern sediments indicated that the older schists apparently contained more boron than the younger ones. On the basis of this discovery, they claimed that the boron content of the sea water has steadily decreased and that this process is still continuing.

After the work of Goldsmith and Peters, the geochemistry and behaviour of boron in marine clay sediments has been studied by Landergrén (1945) in particular. He carried out extensive investigations on present-day marine waters and their sediments in Sweden. He also studied the Rhaetic and Liassic sediments of the Jurassic as well as the Cambro-Silurian slates. Furthermore, Landergrén determined the influence of metamorphism on the trace-element concentrations in Eocambrian schists as well as in the Precambrian sediments of the Grythytté and Larsbo regions. Table 1 summarizes the results of Landergrén (1945). All the samples were collected in Sweden. In the original paper some of the results are given as per cent B and some as  $B_2O_3$ . In Table 1 all the values have been converted to B and are indicated as ppm.

TABLE 1  
The boron contents of some clay-sediments in Sweden.  
After Landergrén (1945).

Age and type of sediment	B (ppm)
Modern marine bottom sediments .....	3—140
Rhaetic-Liassic clay sediments .....	15— 73
Silurian slates .....	20— 45
Ordovician slates .....	9— 90
Cambrian alum-shales and clay slates .....	34— 70
Eocambrian sediments	
— Glacial series .....	15— 54
— Clay slates of the Ström quartzite series .....	20— 50
— High metamorphic schists .....	5— 84
— Low metamorphic schists .....	34— 73
Precambrian sediments	
— High metamorphic schists .....	5—852
— Low metamorphic schists .....	15— 17

Landergren does not agree with the conception of Goldsmith and Peters concerning the variation of the content of marine boron with geologic time. As mentioned above, Goldsmith and Peters (1932 a, b) claimed that the boron content of sea water has been constantly decreasing and that this process is still continuing. On the basis of his results from Cambro-Silurian sediments, Landergren considers the possibility of a tendency towards reduced marine boron content from the Cambrian to the Silurian age. He points out, however, that the variations in boron content even in one sediment profile or on one and the same stratigraphic level may be extremely great. For this reason, he does not consider justified in making sweeping conclusions simply because some Paleozoic samples give higher boron contents than some modern clay sediments. On the basis of his studies, Landergren is of the opinion that taking into consideration local variations, which may be rather large, the boron content of sea water has remained approximately the same ever since the Cambrian at least. If a decrease in this original boron concentration did take place, it possibly occurred in Precambrian times.

Landergren also studied the relationship between the abundance of boron and the grain size of clay sediments. On the basis of his preliminary investigations (1958) it appears that the boron content of the sediments increases with the decrease in grain size. This is in agreement with the statement of Goldsmith and Peters (1932 a, b) that the boron in clay sediments has been adsorbed from sea water, since the more fine-grained sediments (the portion rich in clay minerals) have a larger capacity for the adsorption of such elements.

### Studies on the role of metamorphism

The most interesting results of Landergren's investigations are those regarding the Precambrian schists. In studying the variations in the boron content in these schists, he tried to ascertain the possible effect of metamorphism on the boron concentrations. Unfortunately, the number of Precambrian samples he investigated was only 14, which naturally limits the possibility of drawing reliable conclusions. According to Landergren, it is impossible to determine whether the variations in boron content in these metamorphic rocks are primary or whether they have been caused by the process of metamorphism. As regards the less metamorphic Precambrian schists, however, he is of the opinion that the amounts of boron are primary, adsorbed entirely from sea water.

The influence of metamorphism on the trace-element content of pelitic rocks was also investigated by Shaw (1954 a). His material was taken from the Devonian Littleton formation in New Hampshire. A total of 63 samples collected from different rocks were classified into three groups on the basis of their grade of metamorphism. The low-grade rocks included shales and slates from the Littleton formation, but some pelitic samples of different ages were also taken from other places. The second group,

TABLE 2

Average Composition of Low-, Medium- and High-grade Rocks. Values in ppm. After Shaw (1954).

Element	Low-grade	Medium-grade	High-grade	Final-average	Final S.D.	Number of rocks	Final average (rounded of)
Ga .....	20.8	15.9	19.8	18.8	6.34	63	19
Cr .....	116	113	109	112	33.1	63	110
V .....	109	125	120	119	38.5	63	120
Li .....	54.7	108	127	106	104	63	110
Ni .....	80.5	63.7	57.4	64.2	25.5	63	64
Co .....	16.8	19.4	18.0	18.2	6.59	63	18
Cu .....	23.1	23.8	12.5	18.3	18.0	63	18
Sc .....	11.3	11.9	15.6	13.5	7.35	63	14
Zr .....	191	213	203	204	72.7	63	200
Y .....	38.8	37.9	51.7	44.7	20.0	63	45
Sr .....	524	731	760	705	310	57	710
Pb .....	16.1	23.3	27.3	23.7	12.3	63	24

consisting of medium-grade metamorphic rocks, was made up of schistose rocks whose mineral paragenesis included mica, quartz and small amounts of felspar. Sometimes these schists also contained chlorite, garnet, staurolite, cyanite, andalusite or chloritoide. The third group of high-grade rocks comprised sillimanite schists and rocks which, according to field studies, were related to them even though they did not contain sillimanite. The samples were analysed for Ga, Cr, V, Li, Ni, Co, Cu, Sc, Zr, Y, Sr and Pb. Table 2 gives the results of the analyses.

On the basis of Shaw's studies, regional metamorphism did not have much effect on the trace-elements analysed. According to Shaw, the most noteworthy changes in concentration, as seen in Table 2, occurred with Li and Pb, both of which showed a marked increase with the increasing degree of metamorphism. On the other hand, a notable drop is seen in the case of Ni and Cu. Shaw believes that the increase in Li and Pb may possibly have been caused partly by the appearance of potassium metasomatism in certain areas of the region studied. The behaviour of copper, on the other hand, may have been due to sporadic chalcopyrite impregnations observed in connexion with the microscopic study.

An extremely interesting study, even though it was based on rather limited material, was Shaw's investigation on the concentrations of the above-mentioned trace-elements in the dark and light portions of banded gneiss. Analyses were made on two pairs of bands, and the results are shown in Table 3. The dark (mafic) bands contain abundant biotite and, in addition, albite, quartz and a small amount of apatite. The light (felsic) bands, on the other hand, are composed of oligoclase and quartz as well as small quantities of biotite and muscovite. In addition, the dark portion of the second pair (L 36 a) has abundant graphite. The results of this comparison are very clear. Only Sr and Pb occur more abundantly in the light bands, accompanying plagioclase and muscovite, while all the other elements (Cr, V, Li, Ni, Co, Cu, Sc and Zr) are associated with the biotite, or its accompanying minerals, of the dark bands.

TABLE 3  
Composition of Banded Gneiss. Values in ppm. After Shaw (1954).

Sample number	Ga	Cr	V	Li	Ni	Co	Cu	Sc	Zr	Y	Sr	Pb
25 (mafic) .....	19	130	210	170	100	33	30	22	400	61	940	11
26 (felsic) .....	10	12	43	38	10	7	4.4	6.2	110	55	1 580*	33
Average L 25, L 26 ....	15	71	127	104	55	20	17.2	14.1	260	58	1 260	22
L 36 a (mafic) .....	33	170	140	330	72	16	5.8	21	240	43	590	tr.†
L 36 b (felsic) .....	9	50	52	74	25	11	1.3	7.1	130	44	1 700	29
Average L 36 a, L 36 b	21	110	96	202	49	14	3.6	14.0	185	44	1 095	17

\*This figure uncertain

†Taken as 5 ppm

Shaw also calculated the average concentrations of the trace-elements in both pairs of bands. If these averages are compared with the average values in Table 2, a close similarity is seen except for strontium and in part chromium, lithium and copper. On the basis of this comparison, Shaw claims that the banding of gneiss is more likely to be attributed to metamorphic differentiation than to penetration of magma.

In the second part of his study dealing with pelitic rocks, Shaw (1954 b) discusses in greater detail the above-mentioned analytical results, as well as the so-called trace-element correlations, on the basis of analyses reported in the literature on studies carried out in different parts of the world. According to Shaw, there is a strong positive correlation between Ni and Cr. A positive correlation also exists between Ni, Cr, V and to some extent also Co.

The effect of metamorphism on the distribution of trace-elements in Precambrian rocks is also discussed by Gorlitskiy and Kalyayev (1962). They determined the contents of V, Cr, Ni, Ga, Co, Mn, Ba, Cu and Sr in the quartzites, sandstones, quartz-biotite schists, quartz-carbonate schists and dolomites of the Krivoy Rog formation. The results from these metamorphic rocks were compared with those obtained from the younger marine sediments of corresponding composition at Donbass. According to Gorlitskiy and Kalyayev, the distribution of trace-elements in the Krivoy Rog metamorphic series and in the corresponding Donbass sediments indicates that metamorphism did not cause appreciable changes in the quantitative distribution of these elements. An exception, however, concerned Ba and Sr. These elements were presumed by the authors to have been enriched initially in the limestones, but at a later stage, even during the period of diagenesis, to have moved into quartzites or often into sandstones with a lime matrix. These authors are of the opinion that an important role in the distribution of trace-elements in the Krivoy Rog sediments was played by lithologic and sedimentary factors.

### Later investigations mainly in North America

The studies of Degens, Williams and Keith (1957) pertained to the sediments of the Allegheny series of the Appalachian coal basin. These formations are especially suitable for the study of environmental conditions during the deposition of e.g., shales and slates, since on the basis of the assemblage of fossils occurring in some places, it is possible to draw a distinction between the sediments deposited in fresh and in marine water. A total of 75 samples were taken from these clay sediments and analysed for B, Ga and Rb. In addition, 33 samples were analysed for Ag, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, Sr, V and Zr. The organic matter was mechanically separated from 10 samples and analyses for the above elements were made on its ash. Furthermore, illite, kaolinite and chlorite determinations were made on 59 samples. Of the above-mentioned 33 samples, 11 were from fresh-water sediments, 11 from marine and 11 from brackishwater sediments. The aim of these studies was to find out what elements could possibly be used as indicators of the salinity of the water. The results showed that the concentrations of only five elements, namely B, Ga, Rb, Ni and Cr, were significantly different in marine and fresh-water sediments. In marine clay sediments the amounts of B, Rb and Ni were higher, while in fresh-water sediments Ga and Cr dominated. The authors considered B, Ga and Rb to be the best indicator elements.

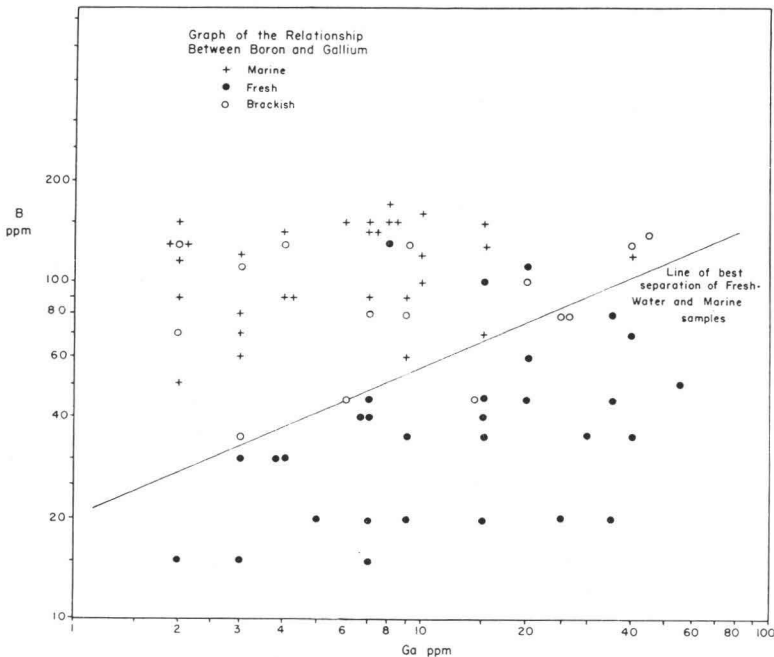


FIG. 2. Graph of relationship between boron and gallium. After Degens, Williams, Keith (1957).

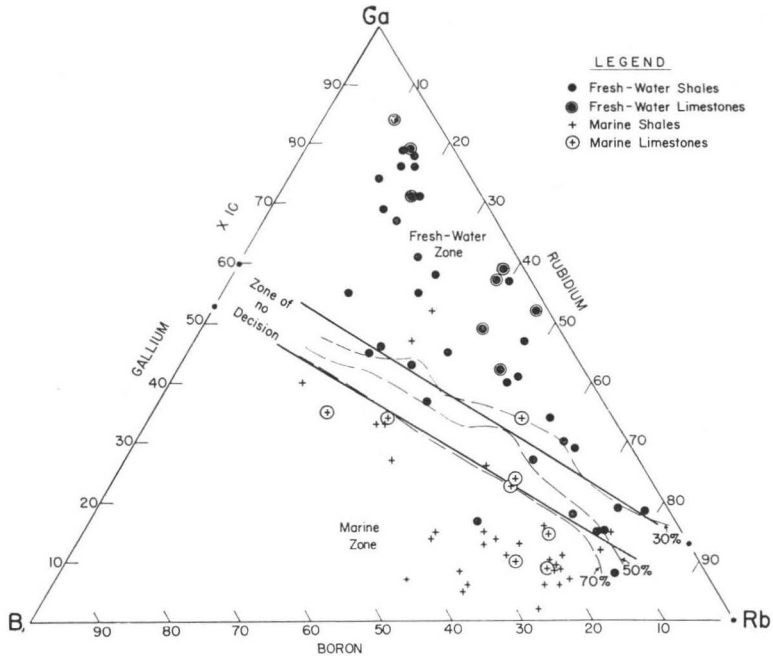


FIG. 3. Relative abundance of boron, gallium, and rubidium in marine and fresh-water shales and in clay fraction of limestones. After Degens, Williams, Keith (1958).

Degens, Williams and Keith (1957) analysed their results both graphically and statistically. The Kolmogorov-Smirnov test (*cf.*, *e.g.*, Siegel 1956) showed a significant difference in the abundance of Ga and Rb between the shales of fresh and marine water. The same test also revealed a significant difference in the B concentration between fresh-water and brackish-water shales. In contrast, none of the trace-elements was adequate for distinguishing between brackish-water and marine sediments.

A two-dimensional discrimination analysis based on the concentrations of two elements or on the concentration of one element and the illite: kaolinite ratio did not generally lead to any distinction between fresh-water and marine shales. Using such an analysis, only the contents of B and Ga are able to provide a discrimination between the fresh-water and marine samples (Fig. 2).

The B-Ga-Rb triangular diagram of Degens, Williams and Keith (1958) is a good means of discriminating between the clay sediments of fresh and marine waters (Fig. 3). In this diagram the clay fractions of limestone have also been analysed, since the origin of these limestones can be determined on the basis of their assemblage of fossils.

According to the results of their investigations, Degens, Williams and Keith maintain that, in the region studied, it is possible to draw a distinction between fresh-water and marine shales by the quantitative analysis of B, Ga and Rb. As regards

the studies of rocks from different regions and of different ages, they point out that it is misleading to compare the absolute abundances of the elements, since they may be due to many factors other than the salinity of the water during deposition. However, they assume that the abundance ratios of the above elements may lead to satisfactory results.

Degens, Williams and Keith (1958) also applied their method to certain sediments of the Pennsylvanian Allegheny series whose origin is uncertain due to the lack of fossils. In addition to the above-mentioned shales, determinations were also made on the clays underlying the coal beds as well as the sandstones. The clay fractions of the latter were analysed. The results were projected on a triangular diagram, Fig. 3. Most of the points fell on the fresh-water zone. As stated previously, the actual origin of these sediments was not definitely known due to the absence of fossils. However, on the basis of stratigraphic and petrographic criteria, different investigators agree very closely with the results by Degens, Williams and Keith concerning the environment during the deposition of the above formations. These workers state that, by determining B, Ga and Rb of shales and related limestones, an agreement was found in about 80 % of the samples with the origin known on the basis of the fossils. By using the same diagram for the underclays, sandstones and other clay sediments of the Allegheny series, results compatible with the stratigraphic and petrographic evidence were obtained. The above workers believe that it is possible, by means of trace-element studies, to classify argillaceous sediments even when of different ages into those formed in fresh and those formed in marine waters.

The studies of Keith and Degens (1959) were a partial continuation of the work of Degens, Williams and Keith (1957, 1958). In these studies, pertaining to geochemical indicators of marine and fresh-water sediments, the authors refer to the trace-element investigations of Keith and Bystrom (1959), likewise on the shales of the Allegheny series. The material comprised 15 marine and 15 fresh-water samples. These samples made up a part of the material underlying the study of Degens, Williams and Keith, described above, but Keith and Bystrom performed additional determinations. These analyses indicate that, in addition to the typical indicator elements of marine water, B, Rb and Ni, to some extent F and Sr and very strongly Li are concentrated in marine shales. The average content of lithium in fresh-water shales is 92 ppm and in marine shales 159 ppm. In a two-dimensional diagram of the B and Li contents (Fig. 4) the marine and fresh-water sediments are clearly separated from one another. According to these studies, a possible additional indicator of fresh water, besides Ga, is Cr. Its abundance in fresh-water shales is nearly double that in marine beds.

In addition to the above-described trace-element determinations, Keith and Bystrom (according to Keith and Degens 1959) made conventional silicate analyses both on marine and fresh-water shales. The analyses showed that in fresh-water shales  $MnO = 0.12\%$  and  $S = 0.15\%$ , while in marine shales  $MnO = 0.80\%$  and  $S = 0.92\%$ . Thus Mn and S may be quite worthy of consideration in determining the salinity of water at the time of deposition.



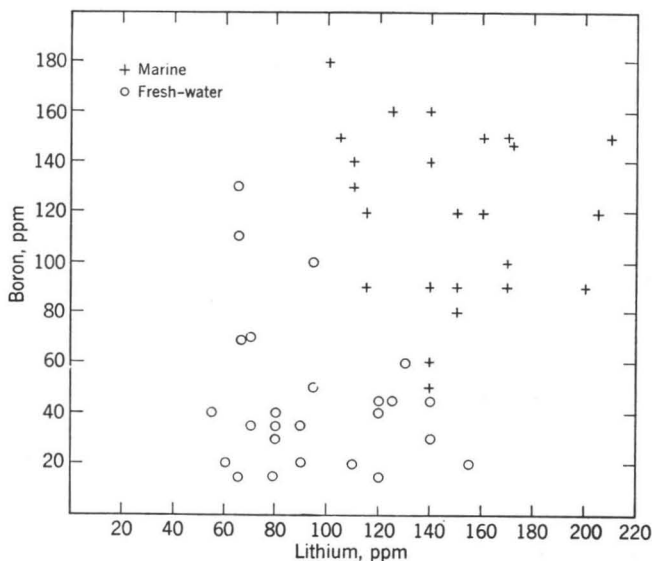


FIG. 4. Boron versus lithium content of a group of Pennsylvanian shales of fresh-water and marine origin. After Keith and Bystrom (1959).

The studies of Degens, Williams and Keith as well as those of Keith and Degens were based on beds of sediments of the same geologic age. Prompted by these studies, Potter, Shimp and Witters (1963) carried on investigations of clay sediments using trace-element determinations. Their selection of material, however, was different. They collected samples from clay sediments which differed as widely as possible as regards source area, tectonic environment, amount of deposition, climate and geologic age. A total of 66 samples were taken, of which 14 were from marine sediments from the Gulf of Mexico, the Caribbean Sea, the depths of the North Atlantic Ocean and the southern Pacific Ocean. There were 19 samples from modern fresh-water shales, taken from lakes and rivers in different parts of the U.S.A. The samples were all from U.S.A., ranging in age from Ordovician to Pliocene and comprising 20 marine and 13 fresh-water shales. All the samples were analysed for nine elements: B, Cr, Cu, Ga, Ni, Pb, V, Co and Zn. In making statistical comparisons of the results, additional confirmation was achieved by using both nonparametric and parametric methods. Moreover, the marine and fresh-water sediments were distinguished from each other by means of discrimination analyses made on their contents of B, Cr, Cu, Ga, Ni, Pb and V.

On the basis of their studies, Potter, Shimp and Witters (1963) came among other things to the following conclusions:

- Modern marine and fresh-water argillaceous sediments can be discriminated according to their trace-element composition. The amounts of B, Cr, Cu, Ga, Ni and V are considerably greater in marine shales than in fresh-water shales.

- No significant differences were found in the trace-element concentrations between older and younger argillaceous sediments of the same environment.
- The most efficient discriminant function was based on B and V and shows that those elements decisively discriminate between modern marine and fresh-water shales.
- By means of the above discriminant function based on B and V, it was possible to divide 85% of the 33 ancient shales into marine and fresh-water types. Similarly, 88 % could be classified graphically on the basis of their trace-element contents.

Investigations of sedimentary rocks based on trace-element determinations are not limited to the works of the above authors. Krauskopf (1955, 1956) studied the distribution of trace-elements in sedimentary rocks and their concentration in marine waters. The distribution of such elements between the shales of shallow and deep water was investigated by Wedepohl (1960). Determinations of the trace-element contents in the graywacke-like and slaty portions of turbidites were made by Weber and Middleton (1961 a, b). The manner of occurrence of boron in clay sediments has been discussed by, *e.g.*, Goldberg and Arrhenius (1958), Frederickson and Reynolds (1960) and Harder (1959, 1961). Investigations based on the boron contents in sediments have also been made by determining B solely from illite (*e.g.*, Reynolds 1965). The occurrence of trace-elements in the organic fraction of shales has been studied by Le Riche (1959) and Tourtelot (1964). The use of statistical methods in trace-element investigations has been discussed particularly by Shaw and Bankier (1954) and Ryabchikov (1961).

The investigations described above in detail were concerned chiefly with clays, shales, slates and phyllites. Furthermore, these studies pertained only to the differentiation between marine and fresh-water sediments on the basis of trace-element determinations made directly on the samples. This is due to the fact that the present investigation is concentrated on Precambrian phyllites from which trace-element determinations were likewise made directly without any fractionation.

## MATERIAL AND METHODS

### Collection of samples

A total of 174 samples were collected from Finnish Precambrian phyllites and mica-schists. Attempts were made to obtain material which was as homogeneous as possible. This aim would have been best achieved by, for example, limiting the material to the least metamorphosed phyllite samples. However, in this case the material would have been very limited; therefore, in addition to the best-preserved phyllites, fine-grained mica-schist samples were also collected. Thus minor variations occurred in the composition and grain size of the samples, and the material subsequently reflects small variations in metamorphism.

The samples were collected from 18 different areas in Finland (Fig. 1, p. 8). Three of these are located in southwestern Finland, representing the Tampere and Kalvola phyllites, and the Forssa mica-schists. Four areas, comprising the Jormua mica-schists, the Sotkamo and Kontiolahti phyllites, and the Pyhäselkä black schist, belong to the Sotkamo-Joensuu schist zone. The Kuhmo schist zone is represented by the phyllites and mica-schists of Hyrynsalmi and Kuhmo. In the Ostrobothnia schist zone, samples were taken from the mica-schists of Seinäjoki, and the phyllites and mica-schists of Central Ostrobothnia. Likewise, two areas in the Kemi zone were included: Taivalkoski and Tervola, from where phyllite samples were collected. The remaining five areas represent the mica-schists and phyllites of Vieremä and the mica-schists of Kolari, Kuopio, Ilomantsi and Ristiina.

The number of samples taken in each area varies from four to nineteen. In general, the samples were taken as series running perpendicular to the bedding either from surface outcrops or from drill holes. The distance between samples varies from a few metres to 1—2 kilometres, depending on the thickness of the beds and the extent of outcropping in the area. The samples from Vieremä and Central Ostrobothnia, however, do not form such series; there 1—2 samples have been taken from each outcrop.

The 19 samples collected in the Tampere phyllite zone (at Ylöjärvi, Siivikkalan-niemi) were all taken from a cut about 150 metres long. Some of them were taken from the dark (slaty) beds and some from the light (graywacke-like) beds, with the intention of studying the variations in trace-element content between the clay-rich and clay-poor beds of phyllite. These Tampere phyllites are probably the least metamorphosed Precambrian phyllites in Finland or at least this is how they appear in relation to all the specimens used in this investigation. A list of the samples and their locations is given in Table 4.

### Petrographic classification of samples

On the basis of field observations and microscopic examinations, the entire sampling material has been classified into two groups: phyllites and fine-grained mica-schists.

In this connexion, the phyllite group is considered also to include distinctly varved phyllites, relatively homogeneous rocks, which, on the basis of their mineral composition and grain size, consist of slaty as well as graywacke-like portions.

The slaty portions are made up chiefly of mica and quartz. There may also be a small amount of plagioclase occurring together with quartz as larger crystals. The graywacke-like portions contain the same minerals but have less mica and minor amounts of potassium feldspar. In both portions, small quantities of alteration products are found, such as chlorite, sericite and epidote. Accessory minerals are apatite, magnetite and in some places tourmaline. The grain size in the slaty portions is 0.01—

TABLE 4  
Type and location of samples

Sample number	Type of sample	Location
1	Mica schist	Kolari, Taporova, drill hole No 8 (depth 90 m) SMOY*, 1958
2	» »	» » » » No 8 ( » 100 m)
3	» »	» » » » No 8 ( » 125 m)
4	» »	Kajaani commune, Jormua, railroad cut
5	» »	» » » » » »
6	Phyllite	Ylöjärvi, Siivikkalanniemi
7	» »	» » » » » »
8	» »	» » » » » »
9	» »	» » » » » »
10	» »	» » » » » »
11	» »	» » » » » »
12	» »	» » » » » »
13	» »	» » » » » »
14	» »	» » » » » »
15	» »	Kalvola, Oikolankallio, quarry
16	» »	» » » » » »
17	» »	» » » » » »
18	» »	» » » » » »
19	Mica schist	Forssa, road cut 3 km from Forssa to Helsinki
20	» »	» » » » » » » » » »
21	» »	» » » » » » » » » »
22	» »	» » » » » » » » » »
23	Phyllite	Sotkamo, Naapurilampi, road cut
24	» »	» » » » » » » »
25	» »	» » » » » » » »
26	» »	» » » » » » » »
27	» »	» » » » » » » »
28	Black schist	Pyhäselkä, Hammaslahti, road cut
29	» »	» » » » » » » »
30	» »	» » » » » » » »
31	Mica schist	Kolari, Taporova, drill hole No 8 (depth 95 m) SMOY, 1958
32	» »	» » » » » » No 8 ( » 110 m)
33	» »	» » » » » » No 8 ( » 115 m)
34	» »	» » » » » » No 8 ( » 120 m)
35	» »	» » » » » » No 8 ( » 130 m)
36	» »	» » » » » » No 8 ( » 132 m)
37	Black schist	Pyhäselkä, Hammaslahti, road cut
38	» »	» » » » » » » »
39	» »	» » » » » » » »
40	» »	» » » » » » » »
41	» »	» » » » » » » »
42	» »	» » » » » » » »
43	» »	» » » » » » » »
44	» »	» » » » » » » »
45	» »	» » » » » » » »
46	» »	» » » » » » » »
47	Phyllite	Sotkamo, Naapurilampi, road cut
48	» »	» » » » » » » »
49	» »	» » » » » » » »
50	» »	» » » » » » » »
51	» »	» » » » » » » »
52	» »	» » » » » » » »
53	» »	» » » » » » » »
54	» »	» » » » » » » »
55	Mica schist	Kajaani commune, Jormua, railroad cut
56	» »	» » » » » » » »
57	» »	» » » » » » » »
58	» »	» » » » » » » »
59	» »	» » » » » » » »

\*SMOY (Finnish Prospecting Company)

Table 4 cont.

Sample number	Type of sample	Location
60	Mica schist	Kajaani commune, Jormua, railroad cut
61	Phyllite	Kalvola, Oikolankallio quarry
62	»	» » »
63	»	» » »
64	»	» » »
65	»	» » »
66	»	» » »
67	»	» » »
68	»	Ylöjärvi, Siivikkalanniemi
69	»	» »
70	»	» »
71	»	» »
72	»	» »
73	»	» »
74	»	» »
75	»	» »
76	»	» »
77	»	» »
78	Mica schist	Kuopio commune, Kuopio-Varkaus road cut 6 km from Kuopio to S
79	» »	» » » » » » 6 km » » »
80	» »	» » » » » » 7 km » » »
81	» »	» » » » » » 7 km » » »
82	» »	» » » » » » 8 km » » »
83	» »	» » » » » » 8 km » » »
84	» »	» » » » » » 10 km » » »
85	» »	» » » » » » 10 km » » »
86	» »	» » » » » » 11,5 km » » »
87	» »	» » » » » » 12 km » » »
88	» »	Seinäjoki, railroad cut, south border of railway yards
89	» »	» » » » » » » »
90	» »	» » » » » » » »
91	» »	» » » » » » » »
92	» »	» » » » » » » »
93	» »	» » » » » » » »
94	» »	» » » » » » » »
95	» »	Kälviä, Passoja crossroads
96	» »	Lohtaja, Vahtikallio
97	» »	» »
98	» »	» , Kungas
99	» »	» »
100	» »	Merijärvi, Pyhäla
101	» »	Ylivieska, Niemenkylä
102	» »	» »
103	Phyllite graywacke-like	By the road Sievi-Ylivieska, at the commune boundary
104	Phyllite in conglomerate	Rautio, Typpö
105	Phyllite graywacke-like	Alavieska, by the road 5 km from church towards Alakääne
106	Mica schist	Alavieska, by the road 5 km from church towards Tiivisperä
107	» »	Alavieska, by the road 5 km from church towards Tiivisperä
108	» »	Himanka, Pöntiö
109	» »	» , Ainali
110	» »	Kannus, Mutkalampi
111	» »	» , Peräjärvi
112	Phyllite	» , Hanni
113	»	» , »
114	Mica schist	Vieremä, Nissilä
115	Phyllite	» , Lähdemäki

Table 4 cont.

Sample number	Type of sample	Location
116	Phyllite	Vieremä, Lähdemäki
117	Phyllite in conglomerate	» , Luvejoki
118	Phyllite	» , »
119	»	» , »
120	»	» , » settled area
121	»	» , » » »
122	»	» , Salahmi
123	Mica schist	» , Kookomäki
124	» »	» , »
125	» »	» , »
126	» »	» , »
127	» »	» , »
128	» »	Ylistaro, Vittinki
129	Phyllite	Kontiolahti, Romppala
130	»	» »
131	»	» »
132	»	» »
133	»	» »
134	»	Tervola, Paakkola quarry
135	»	» » »
136	»	» » »
137	»	» » »
138	»	» » »
139	»	Kemi commune, Taivalkoski
140	»	» » »
141	»	» » »
142	»	» » »
143	»	» » »
144	»	» » »
145	»	Hyrnsalmi, Tapaninkylä
146	»	» »
147	»	» »
148	»	» »
149	»	» »
150	Mica schist	Ristiina, Puntala crossroads, road cut
151	» »	» » » » »
152	» »	» , Rahikkala crossroads, road cut
153	» »	» , » » » »
154	» »	» , from Rahikkala crossroads 2 km towards Savitaipale
155	» »	» , » » » 2 km » »
156	» »	» , » » » 4 km » »
157	» »	» , » » » 4 km » »
158	» »	» , » » » 7 km » »
159	» »	» , » » » 7 km » »
160	» »	» , » » » 8 km » »
161	» »	Iiomantsi, Huhus
162	» »	» »
163	» »	» »
164	» »	» »
165	» »	Kuhmo, Arola
166	» »	» »
167	Phyllite	» »
168	»	» »
169	»	» » drill hole No 7 (depth 120 m) SMOY, 1964
170	»	» » » » No 7 ( » 128 m)
171	»	» » » » No 7 ( » 127 m)
172	»	» » » » No 12 ( » 67 m) SMOY, 1964
173	»	» » » » No 12 ( » 82 m)
174	»	» » » » No 12 ( » 85 m)

—0.05 mm and in the graywacke-like portions 0.01—0.5 mm. The phyllite group also includes the Pyhäselkä black schists, which contain, in addition to quartz and mica, also sulphides and abundant graphite. Figures 5 and 6 show sections of fine-grained and coarse-grained samples respectively taken from the slaty beds, while Figures 7 and 8 show corresponding sections from the graywacke-like beds. The grain size of the samples classified as phyllites varies thus from 0.01 to 0.5 mm.

The mineral paragenesis of the mica-schists is mainly the same as that of the phyllites. However, in addition to mica and quartz, plagioclase is also slightly more abundant and, especially in the more coarse-grained samples, microcline occurs in considerable amounts. Accessory minerals in mica-schists are apatite, garnet, epidote and chlorite. Variations occur both in the grain size (perpendicular to the cleavage plain the range is 0.02—2.0 mm) and the intensity of foliation. The most coarse-grained mica-schist specimens are from the Kuopio and Ristiina areas. The variations in type and grain size of the mica-schists samples are seen in Figures 9—11.

Tourmaline is found in the samples from Tampere, Kalvola, Kolari, Forssa, Seinäjoki, Ilomantsi and Sotkamo, as well as in some of the Vieremä specimens. Staurolite occurs in the Kalvola phyllites and in some of the Central Ostrobothnia and Vieremä schists. Andalusite is likewise found in some of the samples from Central Ostrobothnia. Graphite, sulphide and oxide minerals are observed both in the Pyhäselkä schists and sparsely in some of the samples from Kuhmo and Kuopio. The Tervola phyllites contain weak impregnations of rutile <sup>1)</sup>, magnetite and ilmenite. Hornblende together with biotite occurs to a certain extent in some samples from Central Ostrobothnia and Seinäjoki as well as in most of the samples from Sotkamo.

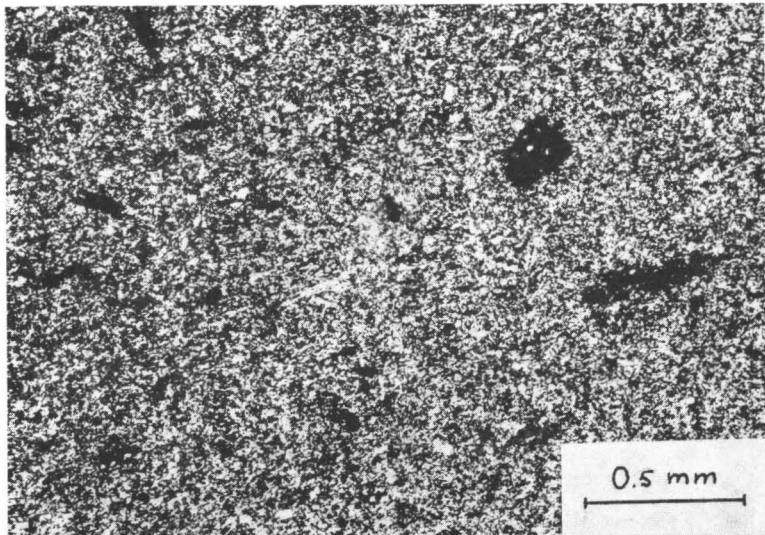


FIG. 5. Slaty portion of Tampere phyllite. Ylöjärvi, Siivikkalanniemi. Crossed nicols. Photo H. Papunen.

<sup>1)</sup> By microanalyzer (J. Siivola).

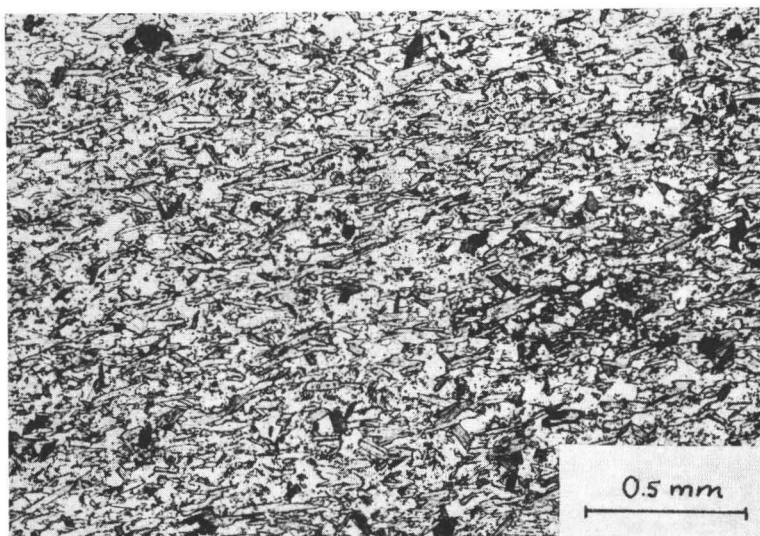


FIG. 6. Phyllite. Kannus, Hanni. Crossed nicols.  
Photo H. Papunen.

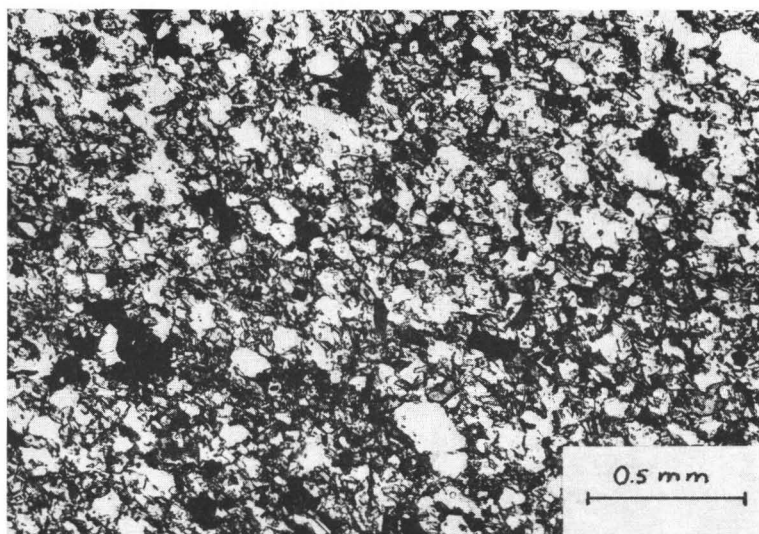


FIG. 7. Graywacke-like schist. Vieremä, Lähdemäki. One nicol.  
Photo H. Papunen.



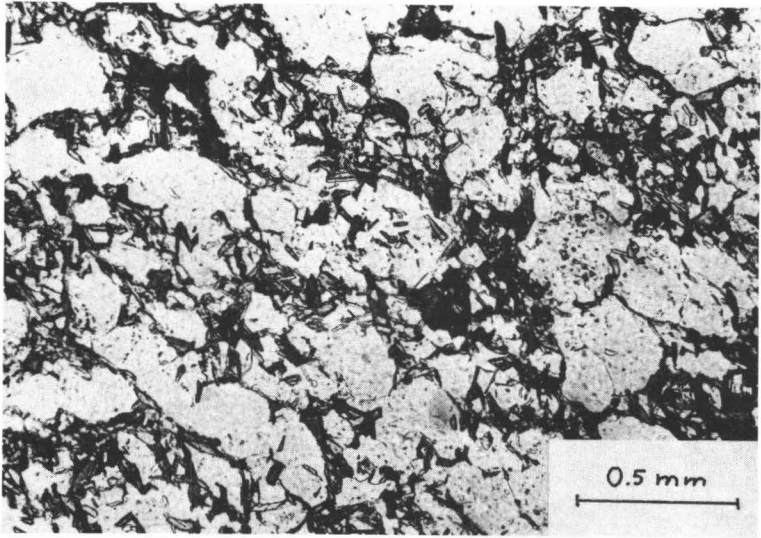


FIG. 8. Graywacke-like schist. Vieremä, Luvejoki, One nicol.  
Photo H. Papunen.

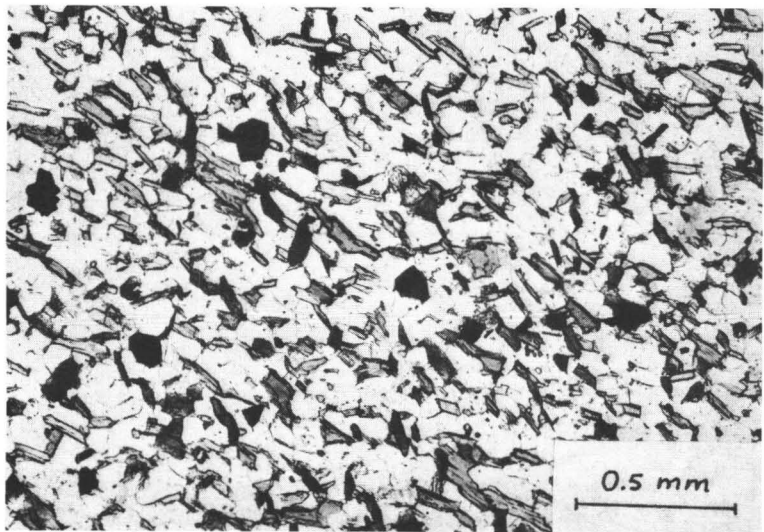


FIG. 9. Mica-schist. Alavieska. One nicol.  
Photo H. Papunen.

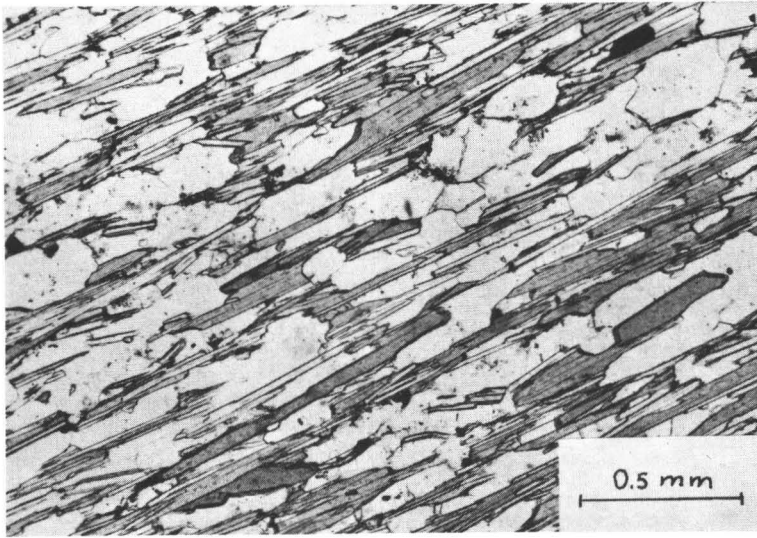


FIG. 10. Mica-schist. Forssa. One nicol.  
Photo H. Papunen.

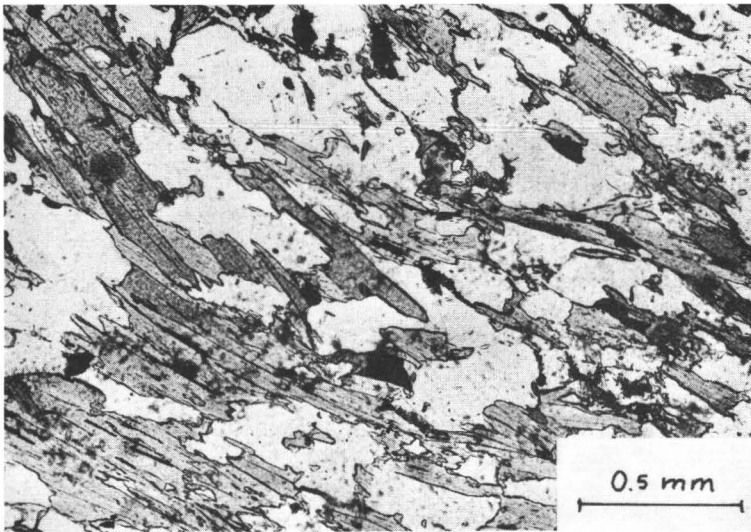


FIG. 11. Mica-schist. Kuopio. One nicol.  
Photo H. Papunen.

### Analytical methods

On the basis of results obtained by other investigators, the present study was especially concerned with the contents of B, Ga, Rb, Li and V. In addition to these, the contents of 14 further elements were determined, so that the total number of analysed trace-elements was 19. All 174 samples were analysed for Li, B, Ga, Ba, Be, Pb, Zn, Co, Cr, Cu, Ni, V and Zr. Rubidium was determined in 44 samples. The contents of La, Sc, and Y were analysed in 143 samples. In addition, determinations for Sr were made on 33 samples and for Mn on 16 samples.

Spectroscopic analyses were made according to the methods of O'Neil and Suhr (1960) with the following modifications: <sup>1)</sup>

- a. The internal standards used were Pd, Gd and Bi.
- b. A mixture of oxygen and argon (10 % O<sub>2</sub> + 90 % A) was used for the Stallwood jet arc.

The standard mixture consisted of 0.75 % Gd<sub>2</sub>O<sub>3</sub>, 0.51 % Pd, 0.51 % Bi, 23.22 % NaCl and 75.01 % CaCO<sub>3</sub>. The sample was mixed together with the standard mixture and graphite in a ratio of 1: 1: 2 (sample: standard mixture: graphite). The electrode used was Ultra Carbon Corp. Electrode Type No. 5790 (outside diam. 1/8", drilled to 0.4" depth); electric supply was 12 amp. D.C.; the spectrograph was a Bausch & Lomb Dual grating instrument; Eastman SA No. 1 plates were used. The analyses were made using the standard samples G<sub>1</sub> and W<sub>1</sub> of the U.S. Geol. Survey (Stevens and others 1960).

Pb, Zn and Ga were determined employing a conventional D.C arc (O'Neil and Suhr 1960).

Li and Rb were determined using the Stallwood jet arc, but with carbon dioxide instead of the O<sub>2</sub>-A mixture. The spectra were photographed on Eastman SA No. 1 plates. The composition of the standard mixture was 10 % BaCl + 90 % NaCl. It was mixed together with sample and graphite in a ratio of 1: 1: 2 (standard mixture: sample: graphite). The electrode was Ultra Carbon Corp. Type No. 5790.

The spectral lines used for the elements were as follows:

Element	Line	Internal standard	Line	Element	Line	Internal standard	Line
Ba	4554.04 Å	Gd	4342.00 Å	Cr	3132.59 Å	Gd	3102.55 Å
Sr	3464.45 »	Gd	3463.98 »	Be	3131.07 »	Gd	3102.55 »
Co	3453.50 »	Pd	3441.39 »	V	3102.29 »	Gd	3102.55 »
Ni	3414.76 »	Pd	3441.39 »	Rb	7800.23 »	Ba	7780.48 »
Sc	3353.73 »	Gd	3331.38 »	Li	6707.84 »	Ba	6693.88 »
La	3337.48 »	Gd	3331.38 »	Mn	2949.20 »	Ga	3102.56 »
Y	3227.87 »	Gd	3331.38 »	Pb	2833.07 »	Bi	2938.30 »
Zr	3273.04 »	Gd	3331.38 »	Zn	3345.02 »	Bi	3397.07 »
Cu	3273.96 »	Pd	3251.64 »	Ga	2943.64 »	Bi	2938.30 »
B	2497.13 »	Pd	2447.91 »				

The precision of the analyses was about  $\pm 10\%$  of the amount present.

The results of analyses are shown in Table 5. The table also gives the average trace-element contents, locations, averages and the standard deviations for the samples.

<sup>1)</sup> Based on the information given by Mr. Oiva Joensuu.

TABLE 5  
Results of analyses, ppm

Location	Sample number	Li	B	Ga	Rb	Ba	Be	Pb	Zn	Co	Cr	Cu	Ni	V	Zr	La	Sc	Y	Sr	Mn	
Kolari	1	35	70	15	160	800	3,5	20	35	45	125	320	55	100	110	—	—	—	—	—	
	31	40	20	20	—	1 500	—	11	40	25	170	140	95	90	140	50	15	17	—	—	
	2	35	90	22	105	200	2,7	20	45	20	140	70	65	130	120	—	—	—	—	—	
	32	52	10	16	—	750	—	10	40	22	130	45	140	130	230	15	15	35	—	—	
	33	65	50	15	—	600	4,0	10	50	15	160	80	70	90	180	30	12	22	—	—	
	34	60	10	16	—	570	—	6	40	15	145	60	85	115	220	35	15	22	—	—	
	3	25	55	15	65	310	2,7	180	155	10	90	40	30	60	155	—	—	—	—	—	
	35	45	30	17	—	700	—	6	120	13	130	90	70	105	150	35	15	25	—	—	
	36	45	15	18	—	570	—	8	40	25	125	130	80	120	135	60	20	25	—	—	
	Average	—	45	42	17,1	110	666	3,20	30	54	21	135	108	77	104	160	38	15	24	—	—
	Stand. dev.	—	12	27	2,3	—	347	0,6	53	41	10	22	82	29	21	40	14	2	6	—	—
Jormua	55	25	25	11	—	470	2,2	20	50	10	80	25	30	110	140	35	12	15	—	—	
	56	32	35	13	—	490	2,5	15	50	12	90	25	35	115	190	30	12	20	—	—	
	57	25	70	10	—	600	3,0	20	70	12	110	40	40	90	140	30	15	25	—	—	
	4	25	20	15	60	370	2,0	25	75	10	100	55	40	85	130	—	—	—	—	—	
	58	25	30	11	—	500	2,0	15	70	10	110	50	55	45	120	35	12	25	—	—	
	5	25	20	15	50	350	2,0	25	55	10	70	30	30	70	115	—	—	—	—	—	
	59	30	35	11	—	210	3,5	25	50	10	120	40	40	90	170	40	15	20	—	—	
	60	30	30	12	—	550	3,0	30	50	10	100	30	40	90	130	40	12	25	—	—	
	Average	—	27	33	12,3	55	442	2,53	22	59	9	98	37	39	87	142	35	13	22	—	—
Stand. dev.	—	3	15	1,8	—	118	0,6	5	10	0,3	16	11	7	20	24	4	1	4	—	—	
Sotkamo	23	60	70	12	85	220	2,5	25	84	20	130	60	40	80	60	—	—	—	—	—	
	47	65	160	12	—	330	3,0	35	40	17	120	50	50	145	120	25	20	20	—	—	
	48	55	110	10	—	300	3,0	20	40	20	95	65	45	100	150	22	15	25	—	—	
	49	55	90	10	—	320	3,0	40	30	15	90	40	45	90	80	30	12	18	—	—	
	50	55	95	10	—	350	2,5	25	40	15	100	45	45	90	95	20	15	18	—	—	
	24	35	65	14	60	250	3,0	30	80	15	95	55	27	75	80	—	—	—	—	—	
	51	30	40	8	—	200	2,5	20	40	20	60	60	45	60	190	25	10	20	—	—	

Table 5 cont.

Location	Sample number	Li	B	Ga	Rb	Ba	Be	Pb	Zn	Co	Cr	Cu	Ni	V	Zr	La	Sc	Y	Sr	Mn	
Sotkamo	25	40	90	16	120	370	3,0	55	75	12	105	10	35	90	70	—	—	—	—	—	
	52	45	120	10	—	520	3,5	40	40	15	110	20	35	110	125	45	17	15	—	—	
	26	90	60	15	190	250	3,0	35	85	10	100	20	30	85	60	—	—	—	—	—	
	53	50	90	10	—	320	2,5	40	40	10	60	20	30	70	90	25	10	15	—	—	
	54	70	100	10	—	390	3,0	35	50	15	110	20	40	110	120	25	17	20	—	—	
	27	80	90	15	130	310	2,5	40	100	15	115	15	35	90	110	—	—	—	—	—	—
	Average	—	56	91	11,7	117	317	2,8 <sup>5</sup>	34	54	15	99	37	39	92	104	27	15	19	—	—
Stand. dev.	—	17	29	2,4	—	79	0,3	9	23	3	20	19	7	21	36	7	3	3	—	—	
Pyhäselkä	37	70	25	16	—	450	4,0	12	130	20	195	150	160	230	135	35	20	22	—	—	
	38	85	30	16	—	400	4,0	17	150	20	200	140	170	195	130	30	15	22	—	—	
	39	70	45	18	—	500	3,0	15	150	25	230	125	160	190	130	32	25	22	—	—	
	40	65	45	16	—	500	2,5	17	150	25	200	130	140	190	130	35	25	25	—	—	
	30	45	60	20	80	250	2,5	20	220	30	250	125	150	180	110	—	—	—	—	—	
	41	70	40	15	—	600	2,5	17	150	25	220	130	160	175	125	45	27	25	—	—	
	42	70	40	11	—	470	2,5	40	130	30	230	110	150	190	125	40	25	25	—	—	
	29	50	60	20	120	450	2,0	20	190	30	290	140	140	210	110	—	—	—	—	—	
	43	65	45	13	—	350	3,0	12	120	30	210	100	120	205	125	40	25	22	—	—	
	44	60	40	13	—	550	2,5	15	120	35	200	160	140	175	125	35	25	25	—	—	
	45	65	40	13	—	340	2,0	15	140	25	180	90	150	175	120	25	22	20	—	—	
	46	65	50	12	—	350	2,5	25	140	20	170	80	150	180	130	25	22	20	—	—	
	28	160	60	15	180	300	2,7	40	150	30	320	150	160	200	110	—	—	—	—	—	
	Average	—	72	45	15,2	127	423	2,7 <sup>5</sup>	20	149	27	223	125	150	192	124	34	23	23	—	—
	Stand. dev.	—	27	10	2,8	—	99	0,6	9	27	5	41	23	12	16	8	6	3	6	—	—
Tampere	6	50	40	16	65	610	2,5	30	75	10	110	20	35	80	—	—	—	—	—	—	
	68	60	80	13	—	1 000	2,0	15	70	7	75	25	35	100	100	35	15	17	—	—	
	7	75	37	22	125	800	2,5	50	130	10	130	35	40	110	150	—	—	—	—	—	
	69	70	90	13	—	950	2,5	20	70	10	110	50	40	100	110	60	15	17	—	—	
	8	75	32	22	115	650	2,5	70	130	10	100	35	40	85	145	—	—	—	—	—	
	70	25	140	10	—	600	3,0	20	75	45	100	100	160	130	130	50	16	30	—	—	
	9	80	30	16	105	700	2,2	30	90	12	85	30	30	82	105	—	—	—	—	—	
	71	65	70	15	—	270	2,0	20	90	20	50	60	70	75	80	30	7	17	—	—	

Table 5 cont.

Location	Sample number	Li	B	Ga	Rb	Ba	Be	Pb	Zn	Co	Cr	Cu	Ni	V	Zr	La	Sc	Y	Sr	Mn	
Tampere	10	70	80	16	100	580	2,7	220	250	12	130	50	50	90	160	—	—	—	—	—	
	72	80	130	19	—	550	3,0	25	180	47	95	90	140	130	140	40	18	30	—	—	
	73	80	130	16	—	550	3,0	20	160	47	100	95	90	125	130	45	18	35	—	—	
	74	90	90	20	—	350	2,5	25	180	20	30	80	85	85	90	30	7	12	—	—	
	75	75	70	17	—	260	2,0	20	150	22	35	70	170	70	95	35	7	10	—	—	
	11	85	110	20	130	720	2,7	65	130	25	130	65	70	130	130	—	—	—	—	—	
	12	45	90	17	90	720	2,5	25	80	20	80	45	35	100	110	—	—	—	—	—	
	76	80	160	18	—	900	2,0	20	140	32	75	75	80	120	180	30	15	30	—	—	
	13	45	50	16	75	600	2,5	35	130	15	140	42	40	70	110	—	—	—	—	—	
	77	70	110	16	—	800	2,5	20	110	35	120	85	75	90	190	50	12	20	—	—	
	14	70	70	19	125	800	2,5	60	130	12	130	60	45	85	150	—	—	—	—	—	
	Average	—	68	85	16,9	103	653	2,48	42	125	21	96	59	70	98	128	41	13	22	—	—
	Stand. dev.	—	16	37	3,0	—	202	0,3	45	46	13	32	24	42	20	30	10	4	8	—	—
	Forssa	19	100	30	12	220	520	2,2	15	90	10	50	130	30	85	90	—	—	—	—	—
20		110	40	18	200	700	2,5	55	130	15	115	25	45	105	130	—	—	—	—	—	
21		100	35	15	130	480	2,5	15	100	10	50	90	25	85	90	—	—	—	—	—	
22		45	40	12	30	500	3,0	15	45	10	65	15	25	50	150	—	—	—	—	—	
Average	—	89	36	14,3	145	550	2,55	25	91	9	70	65	31	81	115	—	—	—	—	—	
Stand. dev.	—	26	4	2,5	—	88	0,3	17	30	2	27	47	8	20	26	—	—	—	—	—	
Kalvola	61	52	40	11	—	550	3,5	25	90	8	100	55	60	95	160	35	12	20	—	—	
	15	70	40	20	160	620	2,7	70	200	15	120	70	55	100	115	—	—	—	—	—	
	16	85	60	20	200	530	2,2	55	130	15	95	60	45	85	120	—	—	—	—	—	
	62	60	60	13	—	570	3,0	20	120	10	90	60	65	95	190	35	12	22	—	—	
	17	90	70	18	200	480	2,5	25	130	12	85	20	37	70	150	—	—	—	—	—	
	63	70	55	15	—	600	3,0	25	110	10	95	45	50	120	190	40	15	22	—	—	
	64	65	80	13	—	950	2,5	25	130	5	100	55	60	140	140	50	15	25	—	—	
	65	50	55	12	—	600	2,5	25	80	5	60	80	75	80	80	30	8	15	—	—	
	66	30	10	12	—	350	3,0	25	70	5	75	80	45	80	80	30	10	20	—	—	
	18	40	20	15	65	520	2,5	65	95	10	70	35	30	60	130	—	—	—	—	—	
	67	25	10	11	—	300	4,0	30	70	10	60	45	25	55	60	25	7	15	—	—	
	Average	—	58	45	14,5	156	551	2,85	36	111	10	86	55	50	89	129	35	11	20	—	—
	Stand. dev.	—	20	23	3,2	—	159	0,6	18	36	3	18	17	15	24	41	8	3	3	—	—

Table 5 cont.

Location	Sample number	Li	B	Ga	Rb	Ba	Be	Pb	Zn	Co	Cr	Cu	Ni	V	Zr	La	Sc	Y	Sr	Mn	
Kuopio commune	78	35	10	9	—	350	2,0	15	60	30	130	70	50	70	190	17	10	15	—	—	
	79	80	10	12	—	400	2,0	12	80	12	80	90	40	65	270	15	12	22	—	—	
	80	100	10	15	—	350	2,5	11	80	30	220	100	150	60	120	40	20	20	—	—	
	81	100	20	17	—	550	2,5	10	110	30	420	160	160	165	130	35	22	20	—	—	
	82	20	10	10	—	400	1,5	15	90	35	60	100	65	80	130	15	30	30	—	—	
	83	25	10	11	—	600	1,5	8	80	35	140	100	70	180	120	15	30	25	—	—	
	84	45	15	12	—	450	1,5	10	60	17	250	35	120	130	130	15	17	15	—	—	
	85	60	30	15	—	700	2,0	25	120	30	190	45	160	155	160	20	30	30	—	—	
	86	50	30	15	—	600	2,0	35	200	45	220	130	130	220	130	30	17	25	—	—	
	87	50	10	14	—	950	2,5	45	100	40	220	170	170	230	100	30	20	25	—	—	
Average	—	57	13	13,0	—	535	2,00	19	98	30	193	100	112	136	148	23	21	23	—	—	
Stand. dev.	—	27	8	2,5	—	179	0,5	12	39	9	97	42	48	61	47	9	7	5	—	—	
Seinäjäki	88	25	10	14	—	250	3,0	10	50	12	95	40	45	60	150	35	10	25	—	—	
	89	50	20	14	—	700	2,5	25	50	10	130	15	20	85	160	35	12	25	—	—	
	90	50	12	14	—	800	2,5	20	50	10	65	15	20	60	150	35	10	15	—	—	
	91	50	10	14	—	410	3,0	30	50	10	100	20	30	70	220	60	12	20	—	—	
	92	55	10	15	—	600	3,0	25	60	10	160	50	65	95	120	20	17	20	—	—	
	93	50	10	14	—	400	2,5	30	50	12	100	40	40	70	150	30	12	20	—	—	
	94	85	120	18	—	800	2,0	20	65	12	160	60	40	130	100	40	15	25	—	—	
	128	70	11	16	—	750	2,0	25	20	18	110	45	52	95	190	45	17	30	210	—	—
	Average	—	54	25	14,9	—	589	2,6	23	49	12	115	36	39	86	155	38	13	23	—	—
	Stand. dev.	—	16	36	1,4	—	197	0,5	6	12	3	31	16	15	22	35	11	3	4	—	—
Central Ostrobothnia	95	40	10	16	—	1200	3,0	20	45	10	90	25	40	80	170	50	15	30	—	—	
	96	45	35	13	—	850	2,0	30	40	10	95	20	25	80	150	35	12	20	—	—	
	97	45	10	12	—	330	2,0	30	50	10	95	25	25	85	155	30	15	20	—	—	
	98	45	12	12	—	300	3,0	20	50	7	90	25	25	75	110	35	10	20	—	—	
	99	60	15	14	—	300	2,5	50	80	7	75	20	25	75	110	35	10	20	—	—	
	100	60	15	14	—	350	1,5	30	80	15	110	35	40	100	110	25	12	20	—	—	
	101	30	15	10	—	350	2,5	20	40	5	60	20	20	60	300	20	5	20	—	—	
	102	40	20	14	—	550	2,5	30	50	8	100	20	22	65	140	35	12	22	—	—	
	103	20	30	14	—	700	2,5	10	60	8	120	100	35	110	160	25	12	22	—	—	

Table 5 cont.

Location	Sample number	Li	B	Ga	Rb	Ba	Be	Pb	Zn	Co	Cr	Cu	Ni	V	Zr	La	Sc	Y	Sr	Mn
Central Ostrobothnia	104	35	20	10	—	650	2,5	8	50	7	380	20	40	90	140	10	5	15	—	—
	105	30	30	14	—	650	2,0	15	60	10	190	25	20	130	130	35	15	22	—	—
	106	120	10	14	—	600	2,0	15	80	10	160	25	50	130	130	25	15	25	—	—
	107	90	10	14	—	600	2,0	20	80	15	120	50	75	90	110	30	15	20	—	—
	108	110	15	12	—	600	2,0	8	60	8	150	50	75	110	100	20	20	15	—	—
	109	65	80	18	—	750	2,5	20	110	8	100	60	85	95	130	30	15	15	—	—
	110	65	130	14	—	1000	2,0	20	60	10	110	30	40	110	135	35	17	20	—	—
	111	60	15	13	—	750	2,0	13	40	7	100	30	40	95	100	25	15	15	—	—
	112	65	10	14	—	700	2,0	25	200	5	130	25	80	190	120	30	20	25	—	—
	113	75	10	14	—	600	2,5	80	150	7	140	110	80	170	120	30	25	15	—	—
	Average	—	58	26	13,5	—	623	2,3	24	73	9	127	38	44	102	138	30	14	20	—
Stand. dev.	—	26	29	1,8	—	227	0,3	16	40	3	24	26	22	33	43	8	5	4	—	—
Vieremä	114	110	150	16	—	450	3,5	12	200	20	170	25	100	140	110	20	20	22	—	—
	115	40	45	10	—	220	3,0	35	65	10	150	25	90	85	190	15	10	15	—	—
	116	60	90	13	—	450	2,0	30	70	15	150	50	95	95	100	20	12	20	—	—
	117	30	10	9	—	250	1,5	10	40	8	90	25	35	60	90	15	5	10	—	—
	118	50	30	11	—	220	2,0	13	80	12	90	20	55	70	120	20	8	10	—	—
	119	100	140	18	—	800	3,5	40	100	22	350	70	150	220	150	40	30	30	—	—
	120	45	35	12	—	350	3,0	13	100	10	160	100	150	160	310	35	15	20	—	—
	121	55	55	15	—	550	3,5	40	100	15	220	20	160	200	280	15	10	25	—	—
	122	45	20	16	—	150	2,0	25	80	10	130	90	60	140	140	25	20	20	—	—
	123	50	10	15	—	550	3,0	30	60	7	110	20	35	90	220	50	12	25	—	—
	124	45	55	12	—	330	3,5	30	60	15	120	50	35	70	220	45	12	25	—	—
	125	45	25	14	—	650	3,0	20	120	18	120	25	60	90	150	40	15	25	—	—
	126	30	10	13	—	500	2,0	30	130	10	100	20	30	110	100	55	15	10	—	—
	127	50	160	18	—	550	2,0	30	100	20	140	90	80	120	130	40	7	10	—	—
	Average	—	54	59	13,7	—	430	2,68	26	92	14	150	45	81	118	165	31	14	19	—
Stand. dev.	—	22	52	2,7	—	179	0,7	10	38	5	65	29	44	47	67	14	6	7	—	—

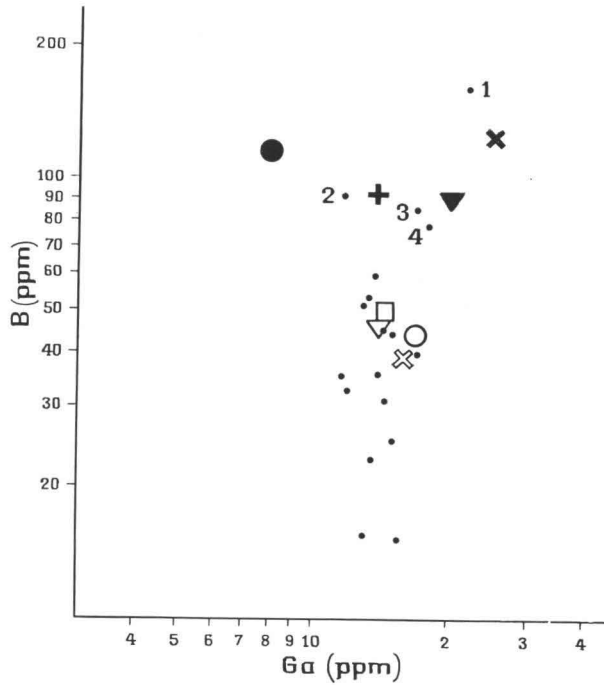


Table 5 cont.

Location	Sample number	Li	B	Ga	Rb	Ba	Be	Pb	Zn	Co	Cr	Cu	Ni	V	Zr	La	Sc	Y	Sr	Mn
Kontiolahti	129	90	30	15	—	360	2,0	20	50	25	160	75	95	130	130	27	17	30	120	—
	130	60	30	16	—	390	2,0	18	40	22	180	40	95	130	130	25	17	18	110	—
	131	60	40	14	—	350	1,5	15	15	17	140	22	70	110	150	18	15	20	110	—
	132	20	27	13	—	270	1,5	20	15	15	130	70	55	100	120	25	14	15	90	—
	133	50	30	14	—	320	1,2	15	35	15	110	80	65	100	130	25	15	15	70	—
Average	—	56	31	14,4	—	338	1,64	18	31	19	144	57	76	114	132	24	16	20	—	—
Stand. dev.	—	22	4	1,0	—	41	0,3	2	14	4	24	23	16	14	10	3	1	6	—	—
Tervola	134	60	50	14	—	270	2,0	35	40	22	180	100	90	130	90	28	17	12	110	—
	135	80	70	20	—	500	2,5	35	20	27	220	90	130	190	110	45	30	18	110	—
	136	65	90	18	—	480	3,0	20	90	27	240	80	127	200	120	22	30	25	100	—
	137	70	95	20	—	450	5,0	30	120	35	230	110	135	200	140	30	32	25	110	—
	138	65	90	18	—	520	2,5	18	80	30	210	65	120	200	130	27	30	20	70	—
Average	—	68	79	18,0	—	444	3,0	28	70	28	216	89	120	184	118	30	28	20	—	—
Stand. dev.	—	7	17	2,2	—	90	1,1	7	36	4	21	16	16	27	17	8	5	5	—	—
Kemi commune	139	60	85	18	—	520	3,0	22	90	25	200	62	110	150	150	27	25	25	120	—
	140	40	80	15	—	650	5,0	12	50	25	160	12	90	100	130	30	15	20	70	—
	141	40	37	12	—	550	1,0	12	50	30	160	70	70	100	150	16	15	20	70	—
	142	65	75	12	—	500	3,0	20	30	30	190	55	110	100	130	30	25	35	110	—
	143	30	15	10	—	950	1,0	17	70	11	100	6	40	80	130	16	7	20	70	—
	144	30	25	12	—	480	1,5	15	50	16	140	15	60	100	160	23	12	20	75	—
Average	—	44	53	13,2	—	608	2,42	16	57	23	158	37	80	105	142	24	17	23	—	—
Stand. dev.	—	14	28	2,6	—	162	1,4	4	19	7	33	26	26	21	12	6	7	6	—	—
Hyrynsalmi	145	25	220	20	—	1 200	4,5	15	10	5	190	22	20	110	95	40	15	21	120	—
	146	10	140	23	—	1 250	4,5	15	10	5	220	9	22	120	220	42	22	25	120	—
	147	12	130	23	—	1 100	4,0	20	10	5	210	8	28	110	190	65	20	25	110	—
	148	12	130	23	—	1 200	4,5	15	10	5	210	11	25	120	220	35	16	22	110	—
	149	20	180	22	—	1 200	5,0	20	20	5	240	17	40	130	230	10	16	30	110	—
Average	—	16	160	22,2	—	1 190	4,5	17	9	3	214	13	27	118	191	38	18	25	—	—
Stand. dev.	—	6	35	1,2	—	49	0,3	2	4	0	18	5	7	8	50	18	3	3	—	—

Table 5 cont.

Location	Sample number	Li	B	Ga	Rb	Ba	Be	Pb	Zn	Co	Cr	Cu	Ni	V	Zr	La	Sc	Y	Sr	Mn	
Ristiina	150	15	20	15	—	500	1,0	30	90	8	140	120	40	100	190	30	13	20	250	—	
	151	60	22	15	—	520	1,5	60	40	20	130	40	85	160	130	50	22	40	250	—	
	152	65	15	15	—	850	1,5	28	75	10	130	5	35	125	150	30	9	18	110	—	
	153	65	17	20	—	550	2,0	22	75	15	140	9	40	100	120	33	17	30	160	—	
	154	120	16	15	—	90	6,0	25	160	13	125	9	55	120	150	28	19	37	110	—	
	155	60	11	15	—	420	5,0	20	190	5	22	60	5	6	250	50	25	65	450	—	
	156	50	15	18	—	450	2,0	20	90	14	140	35	38	120	140	28	16	33	210	—	
	157	40	15	12	—	420	2,5	20	100	15	100	120	45	110	144	40	18	30	300	—	
	158	45	10	15	—	820	3,0	25	75	14	140	15	40	130	170	40	16	30	260	—	
	159	30	10	15	—	700	4,0	20	70	5	60	30	22	52	170	35	10	55	270	—	
	160	75	15	15	—	830	2,0	25	120	11	110	85	60	110	120	45	15	40	250	—	
	Average	—	57	15	15,5	—	559	2,77	27	99	12	113	48	42	103	158	37	16	36	—	—
	Stand. dev.	—	26	4	1,9	—	218	1,5	11	41	4	37	41	19	40	36	8	5	13	—	—
Ilomantsi	161	46	10	12	90	700	2,0	60	200	42	100	170	110	160	70	10	22	12	—	750	
	162	45	110	12	110	650	1,5	40	200	20	130	30	70	130	140	10	22	20	—	1 300	
	163	38	40	16	70	450	1,0	40	230	17	150	18	80	90	90	10	15	12	—	2 000	
	164	30	45	12	110	920	1,5	180	450	28	180	120	110	130	110	18	18	15	—	820	
Average	—	40	51	13,0	95	680	1,5	80	270	27	140	85	93	128	103	8	19	15	—	1 218	
Stand. dev.	—	6	36	1,7	—	167	0,3	58	105	10	29	63	18	25	26	3	3	3	—	—	
Kuhmo	165	31	15	12	90	1 120	1,5	30	130	8	100	17	35	75	130	18	9	6	—	700	
	166	45	65	15	130	900	1,2	30	170	10	100	12	35	70	120	20	10	8	—	600	
	167	20	65	11	80	600	1,0	25	85	20	430	55	70	65	90	10	7	3	—	480	
	168	20	10	11	80	450	0,7	20	65	4	350	16	20	55	130	10	6	3	—	430	
	169	45	50	10	90	620	2,5	25	100	20	170	70	230	90	140	10	12	12	—	3 100	
	170	45	65	10	110	180	1,5	25	180	95	450	85	270	140	130	20	18	10	—	1 400	
	171	35	25	9	112	500	1,0	60	120	20	450	70	130	75	220	15	8	9	—	450	
	172	30	17	12	90	700	1,5	30	130	24	400	120	170	70	120	10	8	3	—	850	
	173	45	40	14	120	600	1,5	30	100	16	300	35	70	95	130	20	17	12	—	500	
	174	30	22	12	100	450	1,2	25	160	33	140	33	55	65	140	12	8	12	—	350	
	Average	—	35	37	11,6	100	612	1,36	30	124	25	289	51	109	80	135	13	10	8	—	886
Stand. dev.	—	10	21	1,7	—	245	0,5	11	36	25	139	33	83	23	31	4	4	4	—	—	
Average of all samples	—	55	50	14,5	—	552	2,5	28	92	17	144	60	71	111	138	31	16	21	—	—	



Explanation:

- Average content of marine Pennsylvanian shales (Degens et al. 1957)
- ⊕ Average content of brackish-water Pennsylvanian shales (Degens et al. 1957)
- Average content of fresh-water Pennsylvanian shales (Degens et al. 1957)
- ▼ Average content of marine modern clays (Potter et al. 1963)
- ▽ Average content of fresh-water modern clays (Potter et al. 1963)
- × Average content of marine ancient shales (Potter et al. 1963)
- ⊗ Average content of fresh-water ancient shales (Potter et al. 1963)
- Average content of phyllites in each sample area in Finland
- Average content of phyllites in Finland

1 Hyrnsalmi, 2 Sotkamo, 3 Tampere, 4 Tervola

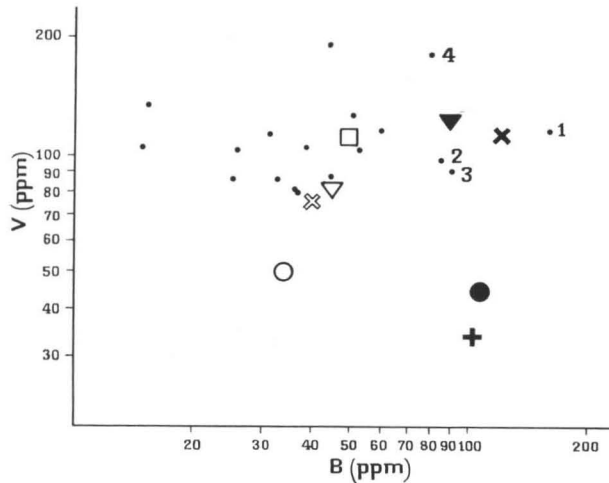
FIG. 12. Graph of boron versus gallium contents in Pennsylvanian shales (After Degens et al., 1957), in modern and ancient (Pliocene-Ordovician) shales (After Potter et al., 1963) and in Precambrian phyllites in Finland.

## GENERAL DISCUSSION OF MATERIAL AND ANALYTICAL RESULTS

### Comparison of trace-element contents with earlier results

Since Degens *et al.* (1957), Keith, Degens (1959) and Potter *et al.* (1963) were able to distinguish marine from fresh-water clay sediments in North America on the basis of their B, Ga, Rb, Li and V contents (*cf.* pp. 14, 15, 17), it may be useful to see first in a





## Explanation:

- × Average content of marine ancient shales (Potter et al. 1963)
  - ⊗ Average content of fresh-water ancient shales (Potter et al. 1963)
  - ▼ Average content of marine modern shales (Potter et al. 1963)
  - ▽ Average content of fresh-water modern shales (Potter et al. 1963)
  - Average content of marine Pennsylvanian shales (Degens et al. 1957)
  - + Average content of brackish-water Pennsylvanian shales (Degens et al. 1957)
  - Average content of fresh-water Pennsylvanian shales (Degens et al. 1957)
  - Average content of phyllites in each sample area in Finland
  - Average content of phyllites in Finland
- 1 Hyrnsalmi, 2 Sotkamo, 3 Tampere, 4 Tervola

FIG. 14. Graph of vanadium versus boron contents in modern and ancient (Pliocene—Ordovician) shales of marine and fresh-water origin (After Potter et al., 1963), in Pennsylvanian shales of marine, brackish- and fresh-water origin (After Degens et al., 1957) and in Precambrian phyllites in Finland.

1959). In this case, too, the overall average of the 174 samples as well as most of the 18 area averages lie close to the average of the Pennsylvanian fresh-water shales. The area of Hyrnsalmi diverges considerably from the others, although the divergence is not in the direction of the average marine shales from Pennsylvania. It has to be pointed out that, like the previous B-Ga diagram, the areas of Sotkamo, Tampere and Tervola differ in the same direction as Hyrnsalmi.

As regards the application of vanadium as an indicator of salinity at the time of deposition, the results are not consistent. However, Potter *et al.* (1963) observed that the vanadium content increased with a rise in the salinity of the water (*cf.* p. 16). The overall average found for the boron-vanadium contents of the Finnish Precambrian phyllites is seen in the diagram (Fig. 14) to lie approximately half-way between the marine and fresh-water averages of both the ancient and modern shales occurring in

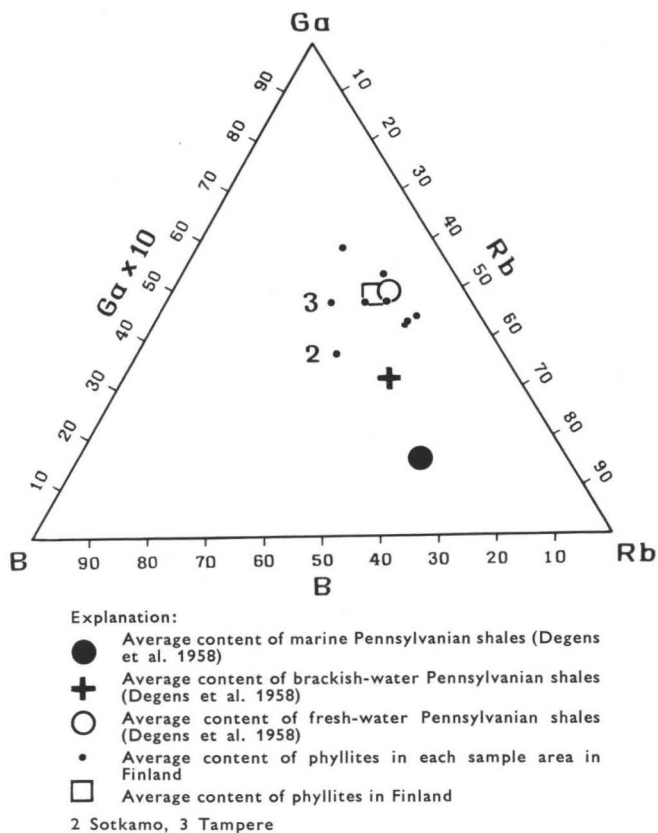


FIG. 15. Triangular diagram showing average abundance of boron, gallium and rubidium in Pennsylvania shales of fresh-water, brackish-water and marine origin (After Degens *et al.*, 1958) and in Precambrian phyllites in Finland.

America (Potter *et al.* 1963). If the 18 area averages are examined, it is seen that less than one-third are located closer to the average for marine shales. This diagram also shows the average contents of Pennsylvania shales as found in the studies of Degens *et al.* (1957). The values these workers found for marine and brackish-water shales differ considerably from the average for marine shales in the studies of Potter *et al.* (1963). On the other hand, the values for fresh-water shales are fairly close to each another. Although it is not possible to separate the Finnish phyllites clearly using this diagram, it can be observed that also in this case, the points representing the four areas of Hyrynsalmi, Tampere, Sotkamo and Tervola are located close to the averages of the known marine sediments of North America.

The salinity prevailing during deposition is also known to be reflected in the ratios between the contents of boron, gallium and rubidium (*cf.* p. 14). The average

points from nine sample areas, the overall average of the 44 samples in these 9 areas (Rb was determined only in 44 samples), as well as the average contents of marine, brackish-water and fresh-water Pennsylvanian shales are indicated in the B-Ga-Rb triangular diagram shown in Fig. 15. It is seen that the averages of both the Finnish Precambrian phyllites and the Pennsylvanian fresh-water shales are almost exactly at the same place in the diagram. Points 2 and 3, representing Sotkamo and Tampere, lie close to the marine zone determined from the studies on the Pennsylvanian sediments, depicted in Fig. 3 (*cf.* p. 14).

The diagrams showing the contents of boron-gallium, boron-lithium, and boron-gallium-rubidium (Figs. 12, 13, 15) demonstrate that the averages of the 18 Finnish Precambrian phyllite areas sampled are clearly located close to the averages found for known fresh-water shales of different ages. The dispersion in the vanadium-boron diagram (Fig. 14) is so great that no conclusions can be drawn from it.

The above comparisons must be interpreted with extreme caution. Possible differences in geologic factors (for example, differences in sedimentation conditions) as well as in the trace-element analyses may make it questionable whether direct comparisons can be made between the results obtained by different workers in different regions. It should be emphasised, however, that the contents of B, Ga, Rb and Li in the Precambrian phyllites, when projected on the boron-gallium, boron-lithium and boron-gallium-rubidium diagrams, lie in the fresh-water zone determined on the basis of results from earlier, quite independent studies.

### Variations in trace-element contents in different beds of phyllites

Weber and Middleton (1961 a, b) studied the variations in trace-element content between the sand-rich and clay-rich fractions of turbidites from Normanskill and Quebec in Canada. The results indicated that there were no appreciable differences in the contents of, *e.g.*, B, Ga, Ba, Be, Cu, Ni, Cr and V between these two fractions in the same bed (a bed comprises both a sandy and a clayey fraction). But, on the other hand, they did observe distinct differences in the concentrations of these elements between different beds. Li and Rb were not included in their studies.

On the basis of microscopic examinations, 8 samples representing slaty beds and 9 representing graywacke-like beds were selected from the Tampere varved phyllites. Table 6 shows the average contents of Li, B, Ga, Rb, Cu, Ni, Cr, V, Ba and Be and their standard deviations in both beds. Except for chromium and barium the contents of all these elements are lower in the graywacke-like than in the slaty beds. The greatest differences occur for boron, nickel and copper. It seems that all the above elements, excluding chromium, are associated with mica minerals and have thus become enriched in the slaty beds. The behaviour of chromium seems strange, since on the basis of a similar investigation made by Shaw (1954a) on banded gneiss (*cf.* p. 11), chromium was apparently more abundant in the most mica-rich portions.

TABLE 6

Average abundance of trace-elements in slaty and graywacke-like beds of Tampere phyllites (ppm)

Type	Li	B	Ga	Rb	Cu	Ni	Cr	V	Ba	Be
Slaty beds										
average .....	74	104	17,4	108	69	86	90	106	650	2,5
stand. deviation ..	12	38	1,4	17	21	45	27	22	184	0,44
Graywacke-like beds										
average .....	59	72	15,6	96	49	57	105	91	673	2,5
stand. deviation ..	15	30	3,3	23	22	38	27	17	220	0,45

According to the present results there are no wide differences in the trace-element contents between the slaty and graywacke-like beds. It should be noted, however, that the concentrations of the known indicators of salinity, Li, B, Ga and Rb, are slightly lower in the graywacke than in the slaty beds.

#### Effect of metamorphism on trace-element contents

The present material may be divided into two groups on the basis of its grade of metamorphism. The Tampere phyllites and some other samples represent the lower grade of metamorphism, while the coarse-grained phyllites and fine-grained mica-schists belong to the group of higher-metamorphosed samples. This latter group also contains small amounts of potassium feldspar. On the basis of field observations and microscopic examinations, 53 lower-grade and 43 higher-grade phyllite samples were selected. The lower-grade group is represented by the samples from Tampere, Kalvola, Sotkamo, Tervola and Kontiolahti. The higher-grade group comprises the samples from Forssa, Ilomantsi, Jormua, Kolari, Ristiina and Seinäjoki. Table 7 shows the average contents of Li, B, Ga, Rb, Cu, Ni, Cr, V, Ba and Be in both groups.

According to the studies of Gorlitskiy and Kalyayev (1962) metamorphism did not cause any redistribution in the contents of Ga, Cu, Ni, Cr and V (*cf.* p. 12). Their

TABLE 7

Average abundance of trace-elements in lower- and higher-metamorphosed phyllites in Finland (ppm)

Grade of metamorphism	Li	B	Ga	Rb	Cu	Ni	Cr	V	Ba	Be
Lower										
average .....	62	72	14,8	119	55	63	111	104	500	2,6
stand. deviation ..	18	36	3,5	44	25	36	45	34	205	0,60
Higher										
average .....	50	31	14,7	108	61	52	114	97	571	2,6
stand. deviation ..	24	26	2,6	55	57	28	34	31	258	0,99



analyses did not include lithium, boron or rubidium. Of the ten elements analysed in the present studies, the grade of metamorphism has a substantial effect only on the abundance of boron which tends to decrease with increasing metamorphism. The changes in contents of Li, Ga, Rb, Cu, Ni, Cr, V, Ba, and Be are so small that on the basis of this investigation, metamorphism apparently does not have any noteworthy effect on their amounts. Lithium shows a discrepancy in comparison with the studies of Shaw (1954a) who found a pronounced increase in lithium with the grade of metamorphism. Likewise in contrast with Shaw's studies, the contents of copper and chromium show a slight rise with the increase in metamorphism.

### **Consequences of the metamorphic and bedding variations**

According to trace-element analyses made on the Tampere phyllites, it appears that only boron shows a clear difference in abundance between the slaty and the graywacke-like beds, since the amount of boron is less in the graywacke-like than in the slaty beds. Similarly, boron appears to be the only trace-element investigated whose content has been substantially modified by the grade of metamorphism. With increasing metamorphism the boron content shows a distinct decrease. In this connexion, it should be pointed out that the highly metamorphosed phyllites studied generally contained slightly less mica than the lower metamorphosed group. Thus it is difficult to say whether the decrease in boron content in the highly metamorphosed phyllites is due solely to the grade of metamorphism or whether also partly to the lesser amounts of mica in these rocks.

Even at the outset of these investigations, it was expected that there would be variations in trace-element contents between the different beds of phyllites. For this reason, samples were collected, from all sampling areas both from the sandy and the clayey beds, providing there were such variations in the beds. In certain areas, for instance in the Kolari and Kontiolahti schists, variations occurred in every sample. Since the trace-element contents between the clay-rich and clay-poor beds of the Tampere phyllites showed variations, although generally not very large, it was considered desirable when making comparisons to use the areal average of each trace-element in order to eliminate this composition factor.

According to the above discussion, the abundance of boron varies clearly in the material studied as a function of the grade of metamorphism and the type of bed in the phyllites. This influence is seen clearly in the B-Ga-Rb diagram in Figure 16 which gives the average contents of these three elements in the case of the slaty and graywacke-like beds of the Tampere phyllites both in the higher and the lower-metamorphosed phyllites; the overall average for all samples studied is also depicted. If this diagram is compared with that made of the Pennsylvanian shales (Fig. 3, p. 14), it is seen that all of these averages remain in the fresh-water zone of the Pennsylvanian sediments. Moreover, they also lie within the same area as the averages of the different

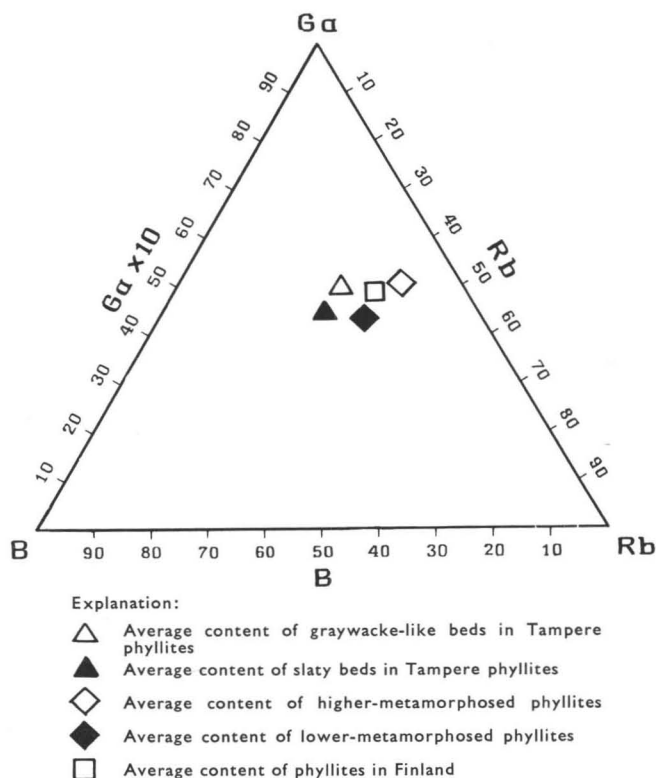


FIG. 16. Triangular diagram showing average abundance of boron, gallium and rubidium in slaty and graywacke-like beds of Tampere phyllites and in lower- and higher-metamorphosed phyllites in Finland.

areas in Finland (Fig. 15, p. 37). It can thus be stated that the metamorphic and bedding variations occurring in the material studied have no appreciable effect on the validity of making comparisons with the North American shales.

### Contents of boron and gallium

In comparing the Precambrian phyllites described above with known clay sediments of fresh-water and marine origin by means of their trace-element contents, boron is seen to be a common factor in all such comparisons. The preliminary results thus obtained suggest that, except for the Hyrynsalmi phyllites, all the Finnish Precambrian schists investigated have been deposited originally in fresh water. Consequently, it is considered essential to compare the present boron contents with those found in known fresh-water clay sediments in North America.

Since it is not justified to assume that the trace-element contents follow normal distribution, a nonparametric test has been selected in order to decide whether there is a significant difference in the amounts of trace-elements between the American fresh-water shales and the Finnish phyllites investigated.

The average boron contents from 17 sample areas (Hyrnsalmi not included) have been taken for this test and comprise one sample. The second sample consists of 19 boron determinations made of modern fresh-water clay sediments (Potter *et al.* 1963), while the third comprises 13 determinations of ancient fresh-water shales (Potter *et al.* 1963). The fourth sample includes the boron determinations made from 31 Pennsylvanian fresh-water shales (Degens *et al.* 1957).

The null hypothesis, that the averages of the different areas are the same, was tested by the nonparametric analysis of variance based on the Kruskal-Wallis ranking (Miller and Kahn 1962). The basis of this test is the assumption that the variable has a continuous distribution, but nothing is presumed about the form of the distribution.

The Kruskal-Wallis statistic is

$$H = \frac{12}{N(N+1)} \sum_{i=1}^K \frac{R_i^2}{n_i} - 3(N+1)$$

where N is the grand total of all the observations and n is the number of observations in each sample. K is the number of samples, and R is the sum of the ranked values in each sample.

Since there are more than five observations in each sample, the test function follows a  $\chi^2$ -distribution in which there are K—1 degrees of freedom.

The level of significance was chosen to be  $\alpha = 0.05$ . The value of the test function H obtained from the samples was 0.63. Since this value is smaller than the  $\chi^2$ -value 7.82 found in the table (Siegel 1956) with three degrees of freedom and  $\alpha = 0.05$  the null hypothesis can be accepted. In other words, at the significance level of  $\alpha = 0.05$ , the average boron contents of the samples tested do not differ significantly from each other.

The same test was also performed on the gallium contents and the test function value obtained was 1.82. Since this value is also smaller than  $\chi^2 = 7.82$ , the null hypothesis can be accepted for gallium as well. Consequently, the gallium contents of the Finnish Precambrian phyllites do not differ significantly from the Ga-contents of known fresh-water clay sediments.

The average boron abundance in the Hyrnsalmi phyllite samples is 160 ppm. The corresponding figure for the modern marine clay sediments investigated by Potter *et al.* (1963) is about 90 ppm and that for the ancient marine shales about 124 ppm. The average boron content of the Pennsylvanian marine shales is ca. 115 ppm (Degens *et al.* 1957). Accordingly, on the basis of their boron contents, the Hyrnsalmi phyllites form a separate group of their own.

The average abundance of gallium in the Hyrynsalmi phyllites is 22 ppm. The corresponding values of modern and ancient marine sediments was found by Potter *et al.* (1963) to be 20 and 25 ppm respectively. All three values can be regarded as being of the same order. A statistical test was not performed, however, since there were only five samples from Hyrynsalmi.

### Contents of manganese

According to the studies of Keith and Bystrom (after Keith and Degens 1959) the average MnO content of Pennsylvanian fresh-water shales is 0.12 %, while that of marine shales is 0.80 %. Converted to parts per million manganese, these values become 930 and 6 200 ppm respectively.

According to analyses of Finnish phyllites and mica-schists (Lokka 1950) the average abundance of manganese in schists taken from ten parts of the country is approximately 600 ppm. The highest value is found in the Tervola phyllites, about 2 100 ppm (Hausen 1936). The manganese content of the Tampere phyllites varies from 300 to 450 ppm (Simonen and Kouvo 1951). According to Sahama (1945) the average Mn content of alumina-rich schists in Lapland is 450 ppm. The average value found in the Ilomantsi mica-schists is 1 218 ppm and in the Kuhmo mica-schists 886 ppm (*cf.* Table 5, p. 33).

The manganese contents of the above-mentioned Finnish phyllites are all approximately the same as those of the Pennsylvanian fresh-water clay sediments.

## MULTIVARIATE ANALYSIS OF TRACE-ELEMENT CONCENTRATIONS

### Theory of principal component analysis

The concentrations of  $p$  trace-elements to be determined in the samples are stochastic variables. By principal components are meant the linear combinations of these variables  $X_1, \dots, X_p$

$$Y_i = \sum_{j=1}^p \alpha_{ij} X_j, \quad i = 1, \dots, p,$$

which are defined on the basis of their variances as follows: The coefficients  $\alpha_{ij}$  are chosen so that the first of the new variables,  $Y_1$ , has the maximum variance,  $Y_2$  is a variable uncorrelated with  $Y_1$  which again has the largest possible variance, and  $Y_i$  is in general a variable uncorrelated with the previously defined variables  $Y_1, \dots, Y_{i-1}$  having the maximum variance. This principle determines (except for a few rare cases seldom occurring in practice) the variables  $Y_i$  uniquely (excluding the sign). The coefficient  $\alpha_{ij}$  is called the loading of variable  $X_j$  on component  $Y_i$ .

It may happen that the variance of some of the first new variables, *e.g.*  $Y_1, \dots, Y_q$ , already accounts for most of the total variance. In this case the rest  $p - q$  variables  $Y_{q+1}, \dots, Y_p$  differ so slightly from one sample to another that they can be disregarded in studying the variation between the different samples. Accordingly, instead of the original  $p$  variables,  $q$  new uncorrelated variables ( $q < p$ ) suffice to determine the whole variance approximately. Such is also the case in the present investigation, as will be seen later.

It is possible that one or more of the principle components  $Y_i$  have a »natural explanation», though they, as a matter of fact, have been determined purely on mathematical grounds without regard to possible factors causing variance. Similarly, in the present investigation it is profitable to try to identify the prominent principle components together with some of the geological, mineralogical and other factors which obviously are involved.

When samples have been taken from  $n$  places, there are thus  $n$  observations from each  $X_i$ , say  $x_{i1}, \dots, x_{in}$ . Let the mean of variable  $X_i$  be  $\mu_i$  and the dispersion be  $\sigma_i$ . In place of  $X_i$ , consider the standardized variable

$$\tilde{X}_i = \frac{X_i - \mu_i}{\sigma_i}.$$

If we use as the value of  $\mu_i$  its maximum likelihood estimate

$$m_i = \frac{1}{n} \sum_{j=1}^n x_{ij}$$

and for  $\sigma_i$  its estimate

$$s_i = \sqrt{\frac{1}{n} \sum_{j=1}^n (x_{ij} - m_i)^2},$$

we obtain as the value of  $\tilde{X}_i$  the following:

$$\tilde{x}_{ij} = \frac{x_{ij} - m_i}{s_i}, \quad j = 1, \dots, n.$$

In the following, we shall assume that the  $X_i$  ( $i = 1, \dots, p$ ) are already standardized and that the matrix of observations,

$$X = \begin{pmatrix} x_{11} & x_{12} & \dots & x_{1n} \\ x_{21} & x_{22} & \dots & x_{2n} \\ \dots & \dots & \dots & \dots \\ x_{p1} & x_{p2} & \dots & x_{pn} \end{pmatrix}$$

is thus formed from the values of these standardized variables  $X_i$  which have been calculated from the measured trace-element concentrations as described above. The problem is now to determine the principle components of the standardized variables  $X_i$ .

The values of the variables  $X_1, X_2, \dots, X_p$  are interpreted as being the coordinates of  $n$  points in a  $p$ -dimensional Euclidean space  $E^p$ . The columns of the observation matrix  $X$  are thus these  $n$  points of  $E^p$ . In order to obtain the first principal component  $Y_1$ , the line  $l_1$  of  $E^p$  is constructed which has the following property of the least squares: the sum of the squares of the distances of  $n$  observation points measured from this line is a minimum. It is seen that the line  $l_1$  passes through the origin, that its direction is the direction of the eigenvector  $\alpha_1$  corresponding to the largest eigenvalue  $\lambda_1$  of the correlation matrix

$$R = \frac{1}{n} XX^T$$

( $X^T$  = transposed matrix of  $X$ ) belonging to the observation matrix  $X$ , and that the variance of  $Y_1$  is actually the above eigenvalue  $\lambda_1$ . The second principal component is obtained in the same way by constructing the line  $l_2$  at right angles to the line  $l_1$ ; and the line  $l_2$  again has the above-mentioned property of least squares. The further components are similarly obtained. Taken all together, by means of the above-described extreme properties of the principal components, the problem of determining these components can be reduced to the eigenvalue problem of the correlation matrix. The following holds:

Let the eigenvalues of  $R$  be  $\lambda_1, \dots, \lambda_p$ ,

$$\lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_p \geq 0,$$

and the corresponding eigenvectors of unit length

$$\alpha_i = (\alpha_{i1}, \dots, \alpha_{ip}), \quad i = 1, \dots, p.$$

Then the principal components are

$$Y_i = \sum_{j=1}^p \alpha_{ij} X_j, \quad i = 1, \dots, p$$

and the variance of the principal component  $Y_i$  is  $\lambda_i$ ,  $i = 1, \dots, p$ .

The probabilistic and mathematic details of this method are not discussed here. Reference can be made to the comprehensive account of Anderson (1958), as well as to Kendall (1961) and Krumbein and Graybill (1965).

### On factor analysis

In studying the structure of variance, the method of factor analysis can also be used. In this method, it is assumed that the standardized stochastic vector

$$X = (X_1, \dots, X_p)^T$$

has the structure

$$X = AF + U,$$

where the components  $F_i$  of the vector  $F = (F_1, \dots, F_m)^T$  are called common factors, the element  $\alpha_{ij}$  of the  $p \times m$ -matrix

$$A = \begin{pmatrix} \alpha_{11} \cdots \alpha_{1m} \\ \dots \\ \alpha_{p1} \cdots \alpha_{pm} \end{pmatrix}$$

is termed the loading of variable  $X_i$  on factor  $F_j$ , and vector  $U$  is the error vector:

$$U = (b_1 \varepsilon_1, \dots, b_p \varepsilon_p)^T.$$

The vectors  $F$  and  $U$  cannot be directly determined on the basis of the observations.

It is assumed that the theoretical means of both the factor variables  $F_i$  and the error variables  $\varepsilon_i$  are zero, and that for all  $i \neq j$  the factors  $F_i$  and  $F_j$ , the variables  $\varepsilon_i$  and  $\varepsilon_j$  are uncorrelated as well as  $F_i$  and  $\varepsilon_j$  for all  $i$  and  $j$ . In this case

$$\sum_{k=1}^m \alpha_{ik}^2 + b_i^2 = 1, \quad i = 1, \dots, p,$$

where

$$h_i^2 = \sum_{k=1}^m \alpha_{ik}^2$$

is the so-called communality of the  $i^{\text{th}}$  variable  $X_i$ , and  $b_i^2$  is its unreliability. The task is to determine the factor matrix  $A$  and the factors  $F_i$ . The number  $m$  of factors is not fixed beforehand.

The solution is not unique. In the factor analyses performed in this study, the value one has been taken preliminarily for the communalities, and the factor directions are determined by means of varimax rotation. Thorough descriptions of the principles and methods of factor analysis are given by Harman (1960). Reference can also be made to Seal (1964) and Vahervuo-Ahmavaara (1958).

In order to illustrate the structure of the observation material, a scatter diagram can be constructed, in which the projections of the observed vectors ( $x_{1i}, \dots, x_{pi}$ ),  $i = 1, \dots, n$  on the subspace spanned by some factors are indicated. In this subspace the factor directions form a rectangular coordinate system.

### Principal component analysis of observation material

Two principal component analyses have been made of the present observation material. In one of these, the contents of thirteen trace-elements were selected as variables, while in the others the variables consisted of only six trace-element concentrations. In both cases the number of observations was  $n = 174$ .

#### Analysis of thirteen variables

In the principal component analysis of thirteen variables, the variables chosen were the contents of the following elements: Li, B, Ga, Ba, Pb, Zn, Co, Be, Cr, Cu, Ni, V and Zr. Not included were Rb, Mn, Sr, La, Y and Sc, since considerably fewer determinations of these elements have been made than of the above thirteen.

The correlation matrix is shown in Table 8, and the eight principal components are given in Table 9. The contribution of the six main components to the total unit variance is illustrated in Fig. 17. This figure also shows as profiles the relative contributions of all the 13 original variables to the sum of the squared loadings. For convenience the signs of all loadings in the component  $Y_1$  have been changed.

It can be seen in Table 9 and Fig. 17 that in the first principal component, zinc, cobalt, chromium, copper, nickel and vanadium all have a strong negative loading. In the second principal component there is a strong positive loading for boron, gallium, barium and beryllium. The third component shows a similar loading for lead and zinc.

TABLE 8  
Correlation matrix of thirteen variables.

	Li	B	Ga	Ba	Be	Pb	Zn	Co	Cr	Cu	Ni	V	Zr
Li	9 999												
B	0 882	9 999											
Ga	2 369	3 392	9 999										
Ba	-1 256	2 400	3 593	9 999									
Be	1 060	3 531	2 020	-0 149	9 999								
Pb	0 273	0 526	0 631	0 112	0 112	9 999							
Zn	2 717	-0 025	1 211	-0 290	-0 398	5 017	9 999						
Co	1 349	1 506	-0 291	-1 297	-1 303	-0 400	3 100	9 999					
Cr	0 276	0 767	0 853	0 802	-0 706	-0 304	1 273	3 906	9 999				
Cu	1 647	-0 430	0 651	-0 436	-0 721	-0 134	2 851	5 663	2 568	9 999			
Ni	2 647	0 677	0 407	-1 122	-0 736	-0 491	3 660	6 995	5 693	5 477	9 999		
V	2 990	1 804	2 674	0 638	0 931	-0 339	2 649	4 476	4 535	4 603	6 460	9 999	
Zr	-1 820	-0 564	0 469	1 443	1 485	-0 652	-1 466	-1 454	0 375	-1 450	-0 311	-0 457	9 999



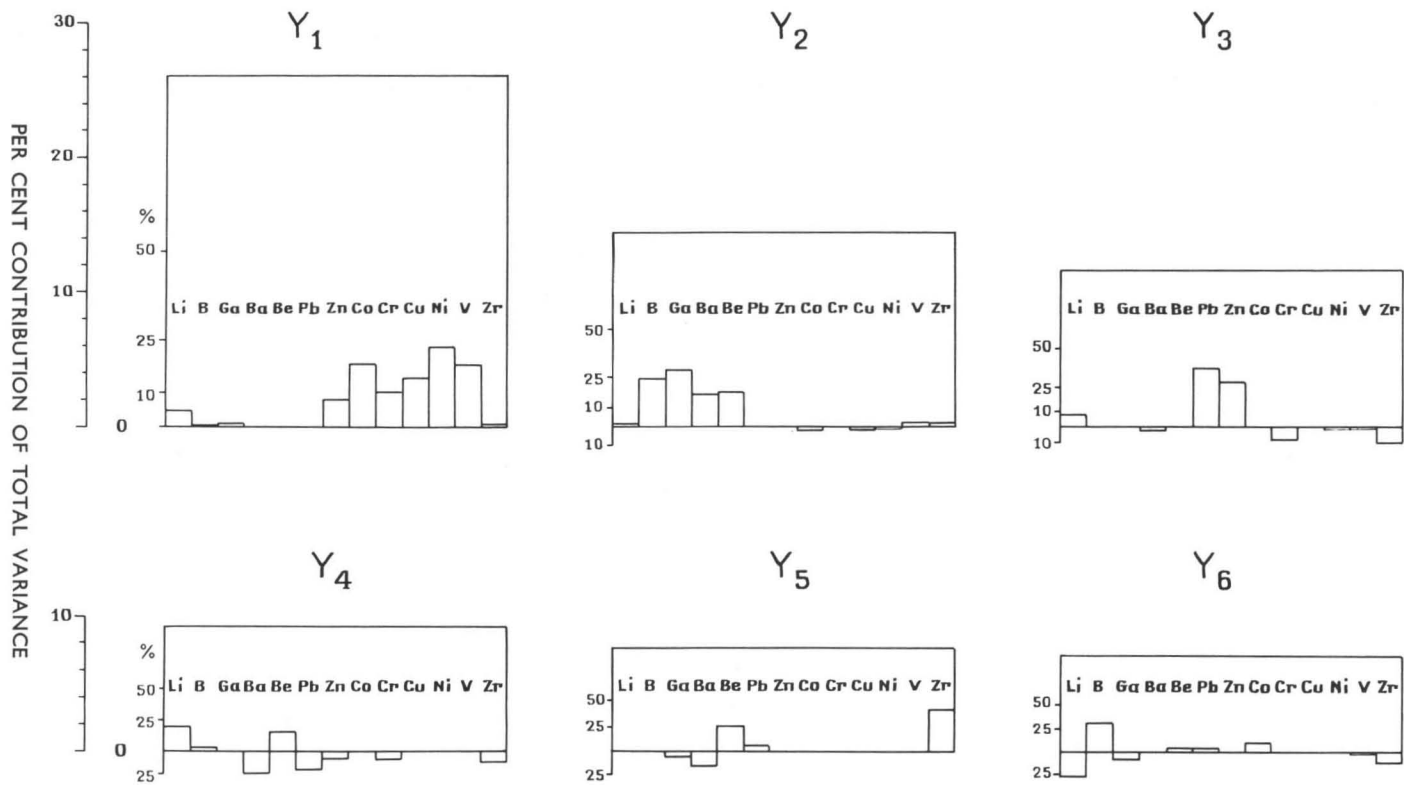


FIG. 17. Relative contributions and profiles of the 6 principal components for 13 variables.

TABLE 9  
Principal components of thirteen variables.

	Y <sub>1</sub>	Y <sub>2</sub>	Y <sub>3</sub>	Y <sub>4</sub>	Y <sub>5</sub>	Y <sub>6</sub>	Y <sub>7</sub>	Y <sub>8</sub>
Li .....	-.395	.171	.344	.497	-.109	-.496	-.196	-.236
B .....	-.180	.680	-.035	.176	-.072	.548	-.065	-.316
Ga .....	-.213	.737	.056	-.059	-.238	-.290	.057	.073
Ba .....	.042	.563	-.195	-.545	-.377	-.057	.130	-.005
Be .....	.035	.571	.006	.442	.510	.156	.140	.314
Pb .....	-.074	.111	.755	-.420	.248	.170	-.073	.071
Zn .....	-.521	0.000	.655	-.262	.148	-.056	.048	-.070
Co .....	-.780	-.221	-.120	.019	-.010	.280	.164	-.282
Cr .....	-.601	.002	-.360	-.276	.098	.068	-.524	.220
Cu .....	-.704	-.185	-.045	.004	-.087	-.028	.547	.186
Ni .....	-.879	-.142	-.171	-.007	.132	-.015	-.075	-.090
V .....	-.777	.195	-.159	.053	.027	-.137	-.051	.201
Zr .....	.175	.203	-.397	-.323	.645	-.340	.137	-.314
eigenvalues .....	3.390	1.876	1.521	1.205	1.013	.909	.719	.581
% contribution to total variance .....	26.08	14.44	11.70	9.28	7.79	7.00	5.53	4.47

### Analysis of six variables

The principal component analysis described above included thirteen variables. It is possible, however, that the mutual correlations among so many variables weaken the appearance in the principal component matrix of factors which are of interest in the present study. Therefore, the principal components were also calculated from the same material but by taking only six variables which were chosen on the basis of earlier investigations and which proved them to be salinity indicators. These six trace-elements were Li, B, Ga, Cr, Ni and V.

Table 10 shows the correlation matrix, while the principal components are given in Table 11 and Fig. 18 in the same manner as in the case of the previously described thirteen variables. It is seen that in the first principal component, chrome, nickel and vanadium have a strong negative loading. In the second component there is likewise a strong similar loading for boron and gallium. The third component shows a pronounced positive loading for lithium. In the fourth component boron and gallium have loadings with different signs, although they are not very strong.

It is seen that the first and second principal components in this analysis are to be identified with the corresponding components in the analysis of thirteen variables. In the third principal component the strong loading of lithium is conspicuous, while in the fourth component the different-signed loadings of boron and gallium are noteworthy.

### Factor analysis of observation material

In addition to the principal component analysis described above, a factor analysis has also been made of the same six variables as previously. These variables were thus

TABLE 10  
Correlation matrix of six variables.

	Li	B	Ga	Cr	Ni	V
Li .....	.999					
B .....	.088	.999				
Ga .....	.237	.339	.999			
Cr .....	.028	.077	.085	.999		
Ni .....	.265	.068	.041	.569	.999	
V .....	.299	.180	.267	.454	.646	.999

TABLE 11  
Principal components of six variables.

	$\bar{Y}_1$	$\bar{Y}_2$	$\bar{Y}_3$	$\bar{Y}_4$	$\bar{Y}_5$	$\bar{Y}_6$
Li .....	-.456	-.306	.769	.187	-.258	-.063
B .....	-.325	-.641	-.473	.505	-.046	0.000
Ga .....	-.400	-.712	-.068	-.557	-.004	.126
Cr .....	-.687	.395	-.343	-.152	-.454	-.149
Ni .....	-.819	.371	.042	.126	.103	.403
V .....	-.851	.068	.037	-.030	.427	-.293
eigenvalues .....	2.343	1.312	.941	.641	.469	.290
% contribution to total variance	39.06	21.88	15.69	10.69	7.82	4.85

TABLE 12  
Rotated factors of six variables

	Comm.	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>
Li .....	.8938	-.118	-.086	.933
B .....	.7424	-.080	-.850	-.109
Ga .....	.6732	-.039	-.763	.296
Cr .....	.7474	-.842	-.051	-.187
Ni .....	.8105	-.874	.045	.207
V .....	.7304	-.766	-.220	.307
variances of factors .....		2.084	1.368	1.144
% contribution to total variance .....		34.74	22.81	19.08

the concentrations of Li, B, Ga, Cr, Ni and V. Rotation was made with only three factors. The rotated factor matrix is shown in Table 12.

The first factor in Table 12 shows again strong negative loadings of chrome, nickel and vanadium. In the second factor boron and gallium have pronounced loadings with the same sign. In the third factor only lithium has a strong loading. These results are parallel to those found in the corresponding principal component analysis.

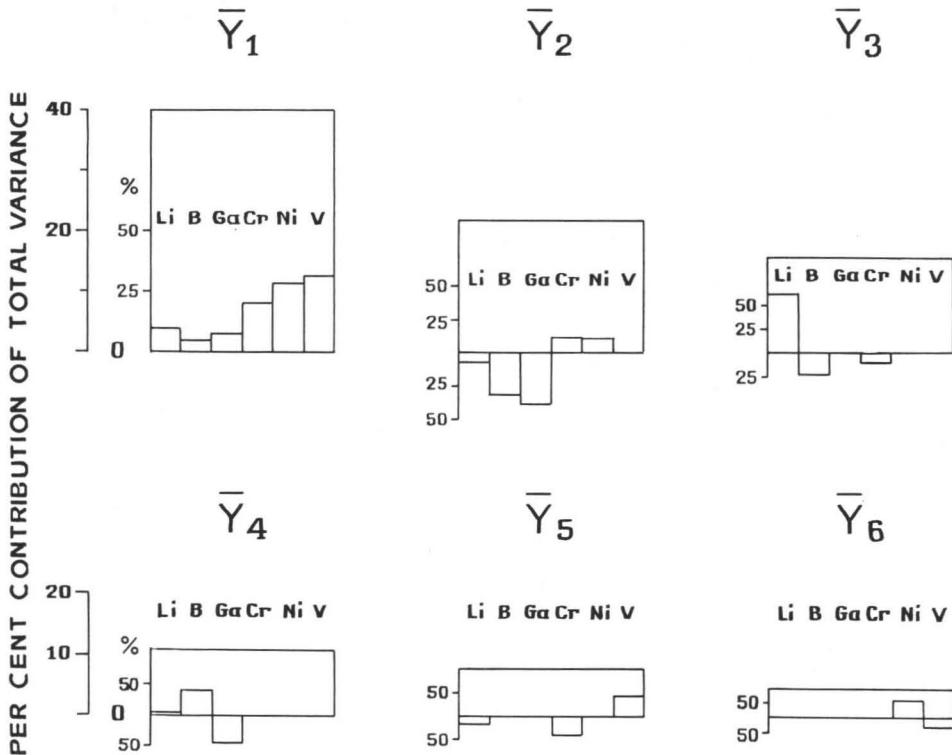


FIG. 18. Relative contributions and profiles of 6 principal components for 6 variables.

**Dispersion of observation points in  $F_1F_2F_3$  space**

By projecting the observation points in subspace spanned by certain components or factors, it is possible to ascertain which samples or sample areas are mainly responsible for causing the large loadings in the components or factors involved. The scatter diagram shown in Figs. 19—22 is based on the factor analysis described above. It could just as well have been made from the 6-variable principal component analysis, since in comparing the factor matrix (Table 12) with the 6-variable component matrix (Table 11), it is seen that the factors  $F_1$ ,  $F_2$  and  $F_3$  are in the main the same as the principal components  $\bar{Y}_1$ ,  $\bar{Y}_2$  and  $\bar{Y}_3$ . Consequently if the scatter diagram is constructed in either  $F_1 F_2 F_3$  or in  $\bar{Y}_1 \bar{Y}_2 \bar{Y}_3$  subspace, the result from the standpoint of interpretation is the same.

This scatter diagram has been constructed by projecting it on four planes perpendicular to the  $F_2$  axis, namely the four planes  $F_2 = +2$ ,  $F_2 = 0$ ,  $F_2 = -2$  and  $F_2 = -4$ . The points with  $F_2$  coordinate greater than +1 have been projected on the plane  $F_2 = +2$  (Fig. 19); the points with  $F_2$  coordinate between +1 and -1 have been projected on the plane  $F_2 = 0$  (Fig. 20); on plane  $F_2 = -2$  (Fig. 21) the points

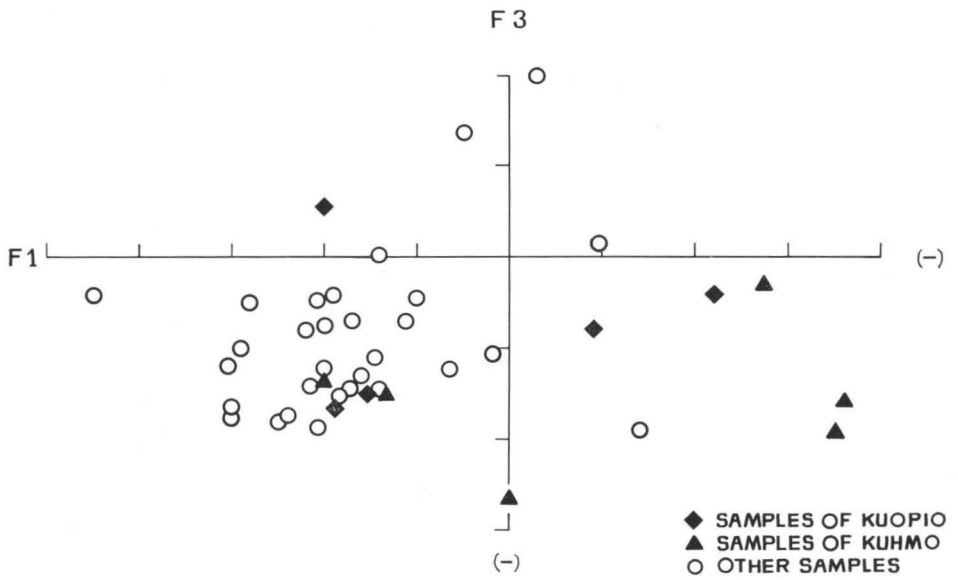


FIG. 19. Observation points projected on plane  $F_2 = +2$ .

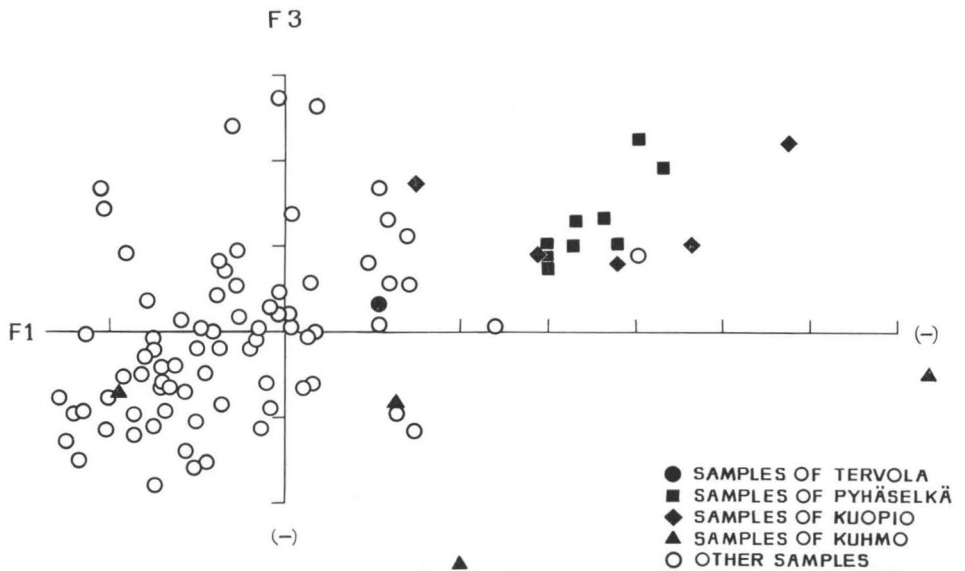


FIG. 20. Observation points projected on plane  $F_2 = 0$ .

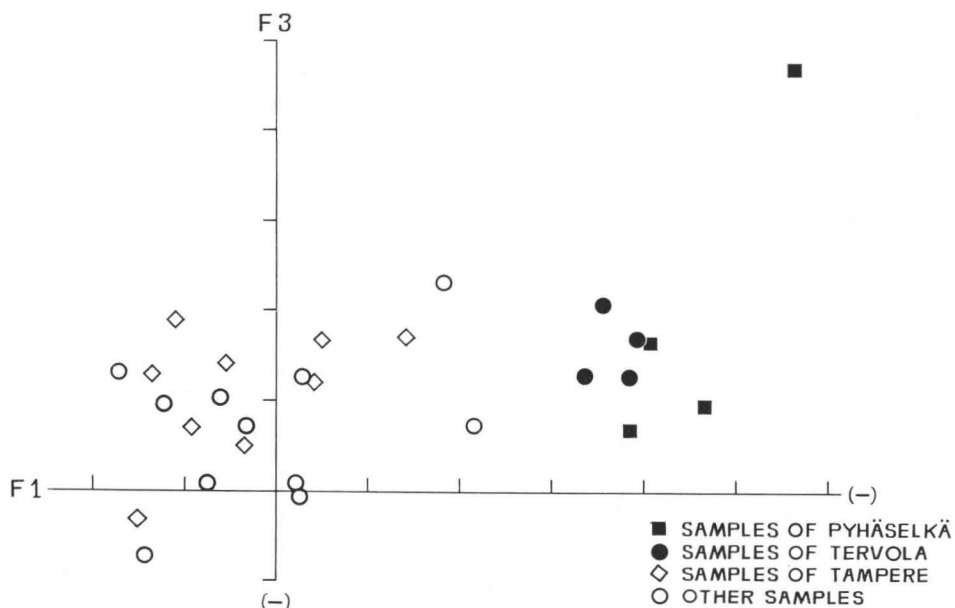


FIG. 21. Observation points projected on plane  $F_2 = -2$ .

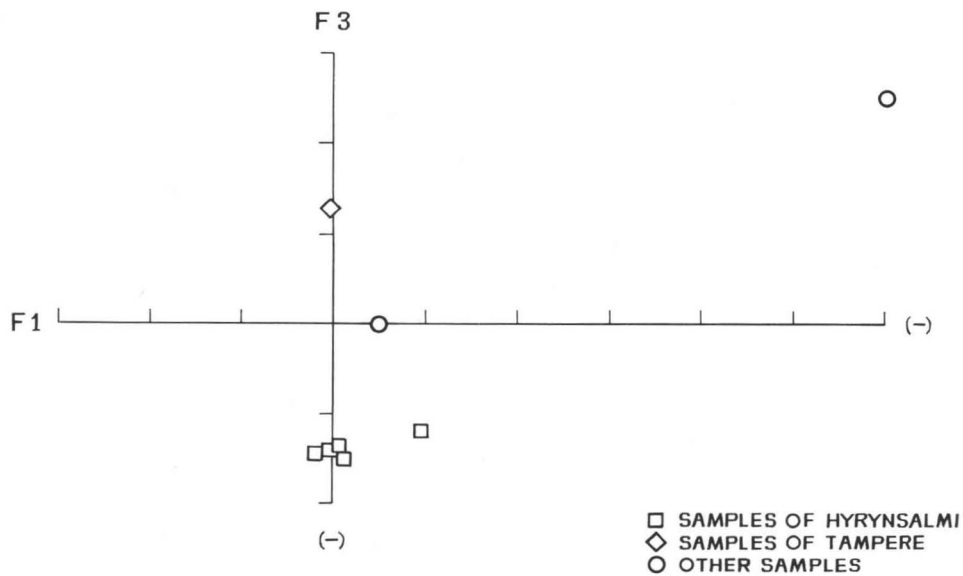


FIG. 22. Observation points projected on plane  $F_2 = -4$ .

having a  $F_2$  coordinate between  $-1$  and  $-3$ ; and on plane  $F_2 = -4$  (Fig. 22) the points whose  $F_2$  coordinate is less than  $-3$ .

In the direction along the  $F_1$  axis the samples are clearly divided into two parts (Figs. 20 and 21). The bulk of the points are grouped close to the origin or slightly to the left. The second, smaller part comprises samples with a strong negative  $F_1$  coordinate. With two exceptions, this latter part comprises the phyllites and mica-schists of Pyhäselkä, Tervola, Kuopio and Kuhmo. The points of the two latter areas, however, fall only partly in the above mentioned area of the diagram.

In examining the distribution of the points along the direction  $F_2$ , it can be seen that most of them lie on the plane  $F_2 = 0$  (Fig. 20). The plane  $F_2 = -4$  (Fig. 22) contains all the points of the Hyrynsalmi phyllites. The plane  $F_2 = -2$  (Fig. 21) includes all the points of the Tervola samples as well as half of the points of the Tampere phyllites. If the mean values of the coordinates of the points of each sample area are calculated, the points of the different areas, when projected in the above manner, fall on the four planes in the following way: plane  $F_2 = -4$  Hyrynsalmi, plane  $F_2 = -2$  Tervola and Tampere, plane  $F_2 = +2$  Jormua and Kuopio, and all the other areas on plane  $F_2 = 0$ .

No distinct grouping of the points is seen along the direction of factor 3 (Figs. 19–22).

### Discussion of results

As discussed previously, the factor matrix is essentially the same as the principal component matrix, so that an interpretation of the factors is analogous to that of the corresponding principal components. Consequently in the following section, only the results obtained from the principal component analyses will be dealt with.

In the analysis of the thirteen variables, attention is paid to the three first components  $Y_1$ ,  $Y_2$  and  $Y_3$ . In component  $Y_1$  the loadings of the trace-elements Zn, Co, Cr, Cu, Ni and V are substantial and of the same sign; in component  $Y_2$  the loadings of B, Ga, Ba and Be are similarly large and of the same sign, while in component  $Y_3$  the same holds true for the elements Pb and Zn. In the other components, whose variance makes up only a small part of the total variance, there are a few minor loadings. However, they are not of great interest from the viewpoint of this study and are in any case difficult to interpret.

In the analysis of the six variables comprising the trace-elements Li, B, Ga, Cr, Ni and V — which are known to be salinity indicators on the basis of earlier studies — it is reasonable to examine only the first four components. Noteworthy loadings occur in component  $\bar{Y}_1$  for the elements Cr, Ni and V, in component  $\bar{Y}_2$  for B and Ga, in component  $\bar{Y}_3$  for lithium and in component  $\bar{Y}_4$  for B and Ga. In components  $\bar{Y}_1$  and  $\bar{Y}_2$  the loadings have the same sign, but in the case of boron and gallium in component  $\bar{Y}_4$  they are of opposite signs.

Loadings of identical sign in the same principal component indicate that the trace-elements concerned are positively correlated in the direction of this component. In this case, the factor <sup>1)</sup> possibly representing the principal component affects the trace-element concentrations in the same direction. On the other hand, loadings of opposite sign in the same component indicate negative correlation.

According to the interpretation of the author, the principal components  $\bar{Y}_1$  and  $Y_1$  represent the same factor, and likewise components  $\bar{Y}_2$  and  $Y_2$ . Component  $\bar{Y}_3$  apparently corresponds to  $Y_4$  and component  $\bar{Y}_4$  to  $Y_6$ . The factor represented by component  $Y_3$  is probably not visible in the analysis of the six variables. The following names are given to the above-mentioned factors:

$\bar{Y}_1, Y_1$  = Cr-Ni-V-Co-Cu-Zn factor

$Y_3$  = Pb-Zn factor

$\bar{Y}_2, Y_2$  = B-Ga-Ba-Be factor

$\bar{Y}_4, (Y_6)$  = B-Ga factor

$\bar{Y}_3, (Y_4)$  = Li factor

### Cr-Ni-V-Co-Cu-Zn factor

In connexion with the petrographic description (p. 22) it was mentioned that the Pyhäselkä schists and some of the Kuopio and Kuhmo schists contain a larger than normal amount of pyrite and pyrrhotite as well as magnetite and ilmenite. The Tervola phyllites, on the other hand, contain weak impregnations of rutile, magnetite and ilmenite. As seen in the scatter diagrams (Figs. 19—22), the Pyhäselkä and Tervola samples as well as some of the Kuopio and Kuhmo samples differ clearly from the others in the direction of the Cr-Ni-V-(Co-Cu-Zn) factor.

Because of their chemical properties, the chalcophile elements, cobalt, copper and nickel, readily replace iron in the above sulphide minerals (Rankama and Sahama 1950, Häkli 1963). Chromium and vanadium generally replace ferric iron and also titanium in some oxide minerals. Zinc is able to replace ferrous iron in magnetite and ilmenite. Consequently, an increase or decrease in the amount of sulphides or oxides in the sample material causes a change in the contents of Cr, Ni, V, Co, Cu and Zn which proceed in the same direction. This change is seen in the strong loading of the same sign possessed by the above elements in the same principal component. On the basis of the above discussion, it can be concluded that the Cr-Ni-V-Co-Cu-Zn factor is the varying content — although only slight — of sulphide and oxide minerals in the sample material.

### Pb-Zn factor

Lead and zinc appear to be closely associated in geologic processes. In magmatic differentiation both remain in the residual melt during the whole period of the main

<sup>1)</sup> The term factor is now used in its general meaning, i.e. to represent an aspect affecting the trace-element content, etc.



crystallization and pegmatitic stage, and become enriched in the low-temperature hydrothermal minerals (Sahama 1947). During the time of weathering, lead and zinc are relatively easily dissolved and in sedimentation both are preferentially precipitated in *e.g.* carbonate sediments (Rankama and Sahama 1950). The similar transportation of lead and zinc during sedimentation is demonstrated by the Mansfeld copper schists for example, where lead and zinc appear in the same horizons (Rankama and Sahama 1950). For the above reasons, it is quite understandable that the contents of lead and zinc, also in the schists investigated, have been changed in the same direction. Such an effect is revealed by the similar signs of their loadings in the principal component concerned. Thus the Pb-Zn factor is apparently the similar geochemical behaviour of these two elements during the deposition of clay sediments.

### B-Ga-Ba-Be factor

The effect of metamorphism on the contents of B, Ga, Ba and Be in the material investigated is seen in Table 7 (p. 39). The abundance of Ga and Be remains about the same. With the increase of the grade of metamorphism the content of boron decreases while that of barium increases. Since, however, the above elements are positively correlated, the B-Ga-Ba-Be factor cannot be the variation in metamorphism.

The influence of differences between slaty and graywacke-like beds on the contents of B, Ga, Ba and Be in the samples is shown in Table 6 (p. 39). In both kinds of beds the beryllium content is the same. The amount of barium is slightly greater in the graywacke-like than in the slaty beds. On the other hand, the contents of B and Ga are highest in the slaty beds. Since, however, the loadings of B, Ga, Ba and Be in the principal component concerned all have the same sign, the B-Ga-Ba-Be factor consequently cannot be the difference between beds.

With the exception of the Hyrynsalmi phyllites, the boron and gallium contents of the samples investigated are of the same order as the corresponding contents of known fresh-water shales (cf. p. 42). The points representing the abundance of boron and gallium are distributed in the same manner as the corresponding saline and fresh-water points in the studies of Potter *et al.* (1963) (Fig. 12, p. 34). In Figure 12, however, only the average values of the marine and fresh-water points are plotted. The Hyrynsalmi, Tampere and Tervola phyllites are located in the zone of marine shales established by Potter *et al.* (1963).

In the scatter diagrams (Figs. 19—22, pp. 52—53) the Hyrynsalmi, Tampere and Tervola phyllites differ from the other samples in the direction of the B-Ga factor ( $F_2$ ). The areal distribution along the direction of this factor corresponds entirely to the distribution of the different sample areas in the boron-gallium diagram (Fig. 12, p. 34).

The experimental material of Potter *et al.* (1963), which is very extensive both in terms of its location and its age, was derived from known marine and fresh-water shales. The Precambrian schists in the present investigation are distributed on the

basis of the boron-gallium diagram in the same way as the shales of Potter *et al.* (1963). According to the scatter diagram, the sample areas are distributed along the direction of the B-Ga factor ( $F_2$ ) analogously to their distribution in the B-Ga diagram. Since the B-Ga factor ( $F_2$ ) corresponds to the principal components  $\bar{Y}_2$ ,  $Y_2$ , it can be considered as probable that the B-Ga-Ba-Be factor is the variation in salinity during the time of sedimentation.

### Ba-Ga factor

In the principal component analysis of six variables, pronounced loadings of boron and gallium also occur in the principal component  $\bar{Y}_4$  (Table 11). The loadings are of opposite sign, which means that in the direction of this component boron and gallium are negatively correlated.

Degens *et al.* (1957) likewise found a negative correlation between boron and gallium. However, as mentioned in the section dealing with the B-Ga-Ba-Be factor, the distribution of Finnish Precambrian schists on the basis of their boron and gallium contents is very similar to the corresponding distribution described in the studies of Potter *et al.* (1963). The opposite behaviour of gallium reported in the investigations of Potter *et al.* (1963) and Degens *et al.* (1957) is surprising, since both studies were made on known fresh-water and marine shales.

Figure 23 shows the boron-gallium diagram of the graywacke-like beds of the Tampere phyllites. The broken line indicates roughly the direction of maximum variance in these beds. The direction of the line demonstrates that as the amount of boron increases, so that of gallium decreases. These two elements are thus negatively correlated. A similar correlation is reported in the studies of Degens *et al.* (1957), according to which an increase in salinity during the time of sedimentation resulted in a rise in the amount of boron but a decline in the content of gallium. Fig. 23 shows, besides the observations of the graywacke-like beds of the Tampere phyllites, only the average contents of the marine and fresh-water shales in the investigations of Degens *et al.*

A similar boron-gallium correlation is also evident in the principal component  $\bar{Y}_4$ . This B-Ga factor, causing the variation in the direction of the component  $\bar{Y}_4$ , must apparently be considered as the variation in the graywacke-like samples brought about by salinity.

Figure 24 shows the boron-gallium diagram of the fine grained slaty beds of the Tampere phyllites. The broken line indicates roughly the direction of maximum variance in these slaty beds. According to the direction of this line, an increase in the boron content is accompanied by a corresponding increase in the gallium content. Consequently, boron and gallium are positively correlated. This is similar to the correlation found in the studies of Potter *et al.* (1963). Fig. 24 shows, in addition to the observations of the slaty beds of the Tampere phyllites, only the average contents of the marine and fresh-water samples of Potter *et al.* A similar boron-gallium correlation as described in the work of Potter *et al.* (1963) and as found in the slaty beds of the

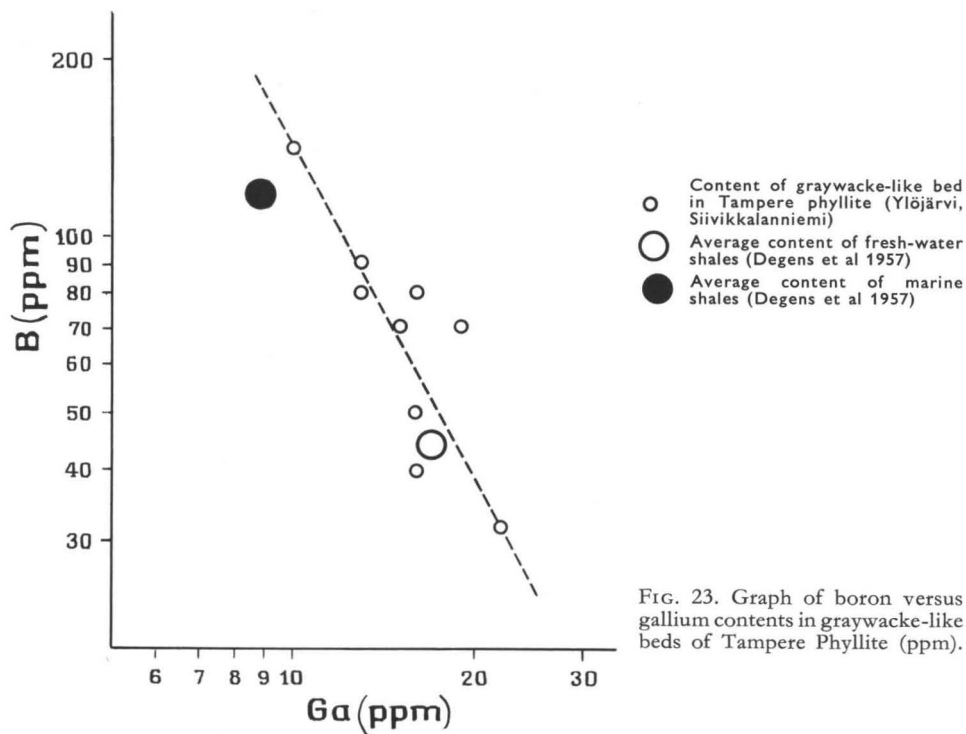


FIG. 23. Graph of boron versus gallium contents in graywacke-like beds of Tampere Phyllite (ppm).

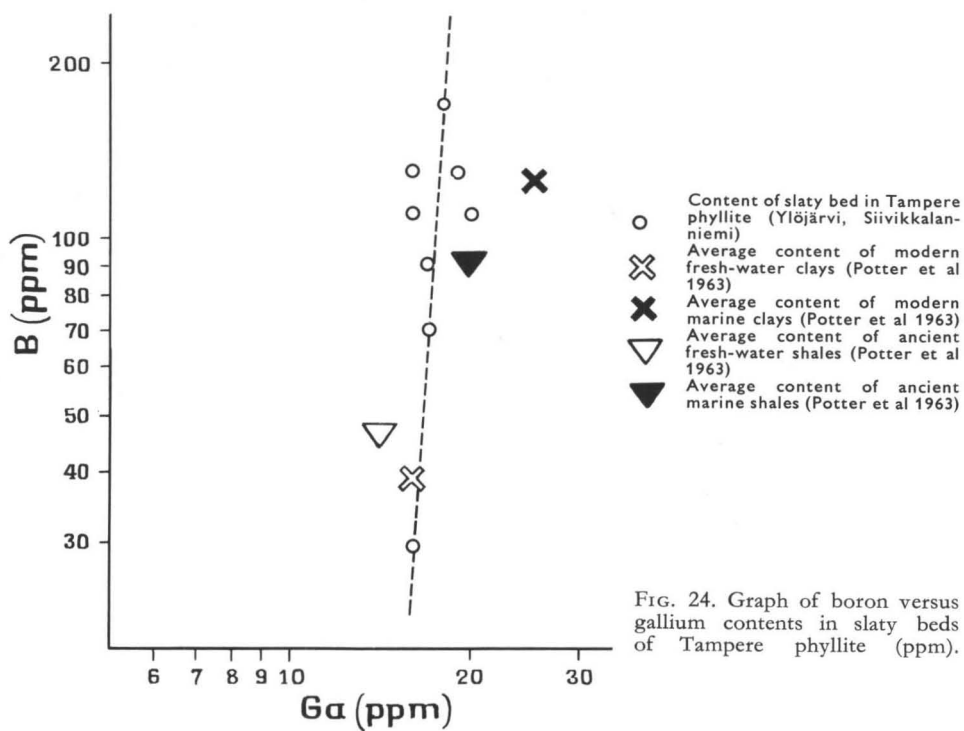


FIG. 24. Graph of boron versus gallium contents in slaty beds of Tampere phyllite (ppm).

Tampere phyllites also occurs in the principal components  $\bar{Y}_2, Y_2$ . The B-Ga-(Ba-Be) factor was previously considered (*cf.* p. 57) to be the variation in salinity during sedimentation. The correlations observed in Tampere phyllites show, however, that the salinity gives a positive B-Ga correlation in the slaty beds only, while a negative correlation is observed in the graywacke portions. This has caused variations in the present material in the direction of the two principal components. This is due to the fact that there are actually two different materials alternating with one another in the phyllites analyzed, namely a clay-rich and a clay-poor, graywacke-like material. The relative amounts of clay-rich and clay-poor portions in the sample material determine the value of the boron-gallium correlation. The results of Degens *et al.* (1957) and Potter *et al.* (1963) pertaining to gallium contents are consequently not contradictory (p. 57). The explanation is that the former workers probably studied beds which were lower in clay material than those studied by the latter workers.

It appears, therefore, that as salinity rises during the time of sedimentation, the boron content increases both in the slaty and in the graywacke-like beds. The gallium content, on the other hand, under the same conditions increases only in the slaty beds but decreases in the clay-poor graywacke-like beds.

### Li factor

According to the investigations of Keith and Degens (p. 15), the lithium content, similar to that of boron, rises with the increase in salinity. In the present material, the strong loading of lithium is accompanied by only a very weak loading of boron on the same principal component, and furthermore the signs of these two are opposite. It may well be that the behaviour of lithium found by Keith and Degens (1959) is due to variations in salinity during the period of sedimentation. In such a case, the lithium contents in the Precambrian schists of the present study have been influenced by some other factor, whose variance obscures the variance caused by salinity. Both the grade of metamorphism and the variation in composition between beds cause changes in the abundance of lithium (*cf.* Tables 7 and 6). Lithium occurs primarily in micas and potassium feldspar. The amounts of these minerals vary in the sampling material investigated. At least part of the potassium feldspar (the coarsest samples) appears to be produced by metasomatism. Consequently, on the basis of the discussion above it seems that the Li factor is the variation in the chemical composition of the sample material.

### SUMMARY

In the material taken from the Finnish Precambrian phyllite and mica-schist zones and studied in the present investigation, there are no essential differences in the boron and gallium contents as compared with the corresponding contents in known

fresh-water shales (p. 42) with the exception of the Hyrynsalmi phyllites. The gallium contents of the Hyrynsalmi phyllites are of the same order as those of known marine shales, and their boron contents are even higher.

The manganese contents of the Finnish Precambrian phyllites and mica-schists are found to be approximately the same as those of the known Pennsylvanian fresh-water shales (p. 43).

The grade of metamorphism and the variation between beds occurring in the sample material have a significant effect on the contents of boron only, and not on those of Li, Ga, Rb, Cu, Ni, Cr, V, Ba and Be (p. 40). The boron content decreases as the grade of metamorphism increases. Similarly, the abundance of boron is less in the graywacke-like than in the slaty beds. These variations in boron content, however, are smaller than the differences in the amount of boron occurring between known marine and fresh-water clay sediments.

The boron-gallium correlation in the bulk of the phyllites investigated is similar to that in known fresh-water shales and clays of different ages (Fig. 12). The B-Ga correlation in the Hyrynsalmi phyllites, on the other hand, resembles that of known marine shales. Likewise, the Tampere, Tervola and Sotkamo phyllites represent — in terms of their boron-gallium correlation — more marine sediments than in the other sample areas.

When the Finnish Precambrian schists are examined from the standpoint of their boron, gallium and rubidium contents, they are similarly found to lie in the zone of fresh-water shales (Figs. 3 and 15). Marine sediments are represented mainly by the Sotkamo and Tampere phyllites. Rubidium determinations are unfortunately not available from the samples from all of the areas, so that *e.g.* the Hyrynsalmi and Tervola phyllites cannot be located on the B-Ga-Rb diagram.

Principal component analysis reveals five factors which distinctly influenced the variations in trace-element contents.

The principal explanation for the variations in the abundance of Cr, Ni, V, Co, Cu and Zn is the varying — although to only a small degree — content of sulphides and oxides in the sample material (p. 55). According to Potter, Shimp and Witters (1963), the contents of Cr, Ni, Cu and V are higher in marine than in fresh-water shales (p. 16). Likewise, the studies of Shaw revealed positive correlations between Cr, Ni, V and partly Co (p. 12). The trace-elements Cr, Ni, V, Cu and Co, however, can hardly be regarded as indicators of salinity in general. On the basis of the present investigation, it is more than doubtful whether the abundance of the above elements in Finnish Precambrian phyllites can be considered as a reliable indicator of salinity at the time of deposition.

The parallel fluctuations in the Pb and Zn contents of the phyllites and mica-schists investigated are apparently a consequence of the similar geochemical behaviour of lead and zinc during sedimentation (p. 56).

Changes in salinity at the time of deposition most probably caused the differences in B, Ga, Ba and Be contents occurring in the Precambrian phyllites and mica-schists

studied. This conclusion has been reached on the basis of the fact that the trace-elements boron and gallium which previously were established as salinity indicators (Degens *et al.* 1957, Potter *et al.* 1963), are very conspicuous in the principal components  $Y_2$ ,  $\bar{Y}_2$  according to the principal component analysis (Figs. 17 and 18). If the interpretation of these components (p. 57) is correct, the contents of Ga, Ba and Be, on the basis of the entire material, change in the same way as that of boron, which is known to increase with the increase in salinity (*e.g.* Degens *et al.* 1957).

Furthermore it has been established in this investigation that, depending on the composition of the schists analyzed, the gallium content may also decrease as the salinity increases (p. 59). If the schists studied have a composition corresponding to the clay-rich beds of varved phyllites, the abundance of gallium rises with the increase in salinity (Fig. 24). If, on the other hand, the composition resembles that of the clay-poor, graywacke-like beds, the gallium content diminishes as the salinity increases (Fig. 23). This is probably the explanation for the contradictory results obtained by Degens *et al.* (1957) and Potter *et al.* (1963) concerning the behaviour of gallium as a salinity indicator during the time of sedimentation.

The variation in lithium content observed in the sample material is a consequence of the differing compositions of the schists investigated (p. 59). According to Keith and Degens (1959), the abundance of lithium in marine shales is considerably greater than in fresh-water shales (p. 15). In the Li-B diagram (Fig. 13) marine and fresh-water sediments are clearly separated. A high positive correlation between boron and lithium has not been found in the present investigation. For this reason, the use of lithium as a salinity indicator in ancient metamorphosed schists may be misleading.

On the basis of studies now performed there is no reason to assume that the Finnish Precambrian phyllites and mica-schists could have been deposited in very saline waters. The Hyrynsalmi phyllites, and to a lesser degree the Tervola, Sotkamo and Tampere phyllites, represent in the present material the sediments deposited in the water of the highest salinity.

Landergren (1945) was of the opinion that if the salinity of the ocean decreased during the passage of time, it must have happened before the Cambrian period. According to him, the salinity of the oceans has remained approximately the same ever since the Cambrian. Reynolds (1965) states that the salinity has been the same even since Precambrian times. On the basis of the present results obtained from studies on Finnish Precambrian phyllites and mica-schists, it appears that the salinity of the oceans during the Precambrian has been lower than at the present time.

## REFERENCES

- ANDERSSON, T. W. (1958) An introduction to multivariate statistical analysis. New York.
- DEGENS, E. T., WILLIAMS, E. G. and KEITH, M. L. (1957) Environmental studies of carboniferous sediments. Part I: Geochemical criteria for differentiating marine and fresh-water shales. Bull. Amer. Ass. Petrol. Geol., Vol. 41, pp. 2427—2455.
- DEGENS, E. T., WILLIAMS, E. G. and KEITH, M. L. (1958) Environmental studies of carboniferous sediments. Part II: Application of geochemical criteria. Bull. Amer. Ass. Petrol. Geol., Vol. 42, pp. 981—997.
- FREDERICKSON, A. F. and REYNOLDS, R. C. (1960) Geochemical method for determining paleosalinity. Proc. of the Eighth Nat. Conf. on Clays and Clay Min. 8, pp. 203—213 (Editor A. Swineford), Oxford.
- GOLDBERG, E. D. and ARRHENIUS, G. O. S. (1958) Chemistry of Pacific pelagic sediments. Geochim. et Cosmochim. Acta Vol. 13, pp. 153—212.
- GOLDSMITH and PETERS, C. (1932 a) Zur Geochemie des Bors. Nachr. Ges. Wiss. Göttingen, Math.-physik. Kl. III, pp. 402—407.
- »— and —»— (1932 b) Zur Geochemie des Bors, II. Nachr. Ges. Wiss. Göttingen, Math.-physik. Kl. III, pp. 528—545.
- GORLITSKIY, B. A. and KALYAYEV, G. I. (1962) The relation between trace element distribution and the conditions of formation of the upper part of the Krivoy Rog series. Geochemistry No. 12, pp. 1245—1250.
- HARDER, H. (1959) Beitrag zur Geochemie des Bors II. Bor in Sedimenten. Nachr. Akad. Wiss. Göttingen. Math.-physik. Kl., pp. 123—183.
- »— (1961) Beitrag zur Geochemie des Bors III. Bor in metamorphen Gesteinen und im geochemischen Kreislauf. Nachr. Akad. Wiss. Göttingen. Math.-physik. Kl., pp. 1—26.
- HARMAN, H. H. (1960) Modern factor analysis. Chicago.
- HAUSEN, H. (1936) The North-Bothnian downfold. Stratigraphical and tectonical studies in the sedimentary series between the lower course of the Torne river and the Kivalo ridge (Finland). Acta Acad. Aboensis. Math. et Phys. Vol. IX, No. 5.
- HÄKLI, A. (1963) Distribution of nickel between the silicate and sulphide phases in some basic intrusions in Finland. Bull. Comm. géol. Finlande No. 209.
- KEITH, M. L. and DEGENS, E. T. (1959) Geochemical indicators of marine and fresh-water sediments. Researches in geochemistry. (Editor P. H. Abelson). New York.
- KENDALL, M. G. (1961) A course in multivariate analysis. London.
- KRAUSKOPF, K. B. (1955) Sedimentary deposits of rare metals. Econ. Geol., Fiftietf Anniv. Vol., pp. 411—463.
- »— (1956) Factors controlling the concentrations of thirteen rare metals in sea-water. Geochim. et Cosmochim. Acta Vol. 9, pp. 1—32 B.
- KRUMBEIN, W. C. and GRAYBILL, F. A. (1965) An introduction to statistical models in geology. New York.

- LANDERGREN, S. (1945) Contribution of the geochemistry of boron. II. The distribution of boron in some Swedish sediments, rocks and iron ores. The boron cycle in the upper lithosphere. *Ark. Kemi, Min. Geol. Bd. 19 A, No. 26.*
- (1958) On the distribution of boron on different size classes in marine clay sediments. *Geol. Fören. i Stockholm Förh. Bd. 80, pp. 104—107.*
- Le RICHE, H. H. (1959) The distribution of certain trace elements in the Lower Lias of Southern England. *Geochim. et Cosmochim. Acta Vol. 16, pp. 101—122.*
- LOKKA, L. (1950) Chemical analyses of Finnish rocks. *Bull. Comm. géol. Finlande No. 151.*
- MILLER, R. L. and KAHN, J. S. (1962) *Statistical analysis in the geological sciences.* New York.
- O'NEIL, R. L. and SUHR, N. H. (1960) Determination of trace elements in lignite ashes. *Applied Spectroscopy. Vol. 14, pp. 45—50.*
- POTTER, P. E., SHIMP, N. F. and WITTERS, J. (1963) Trace elements in marine and fresh-water arcillaceous sediments. *Geochim. et Cosmochim. Acta. Vol. 27, pp. 669—694.*
- RANKAMA, K. and SAHAMA, Th. G. (1950) *Geochemistry.* Chicago.
- REYNOLDS, R. C. Jr. (1965) The concentration of boron in Precambrian seas. *Geochim. et Cosmochim. Acta. Vol. 29, pp. 1—16.*
- RYABCHIKOV, I. D. (1961) The application of nonparametric tests to geochemical data. *Geochemistry No. 9, pp. 891—896.*
- SAHAMA, Th. G. (1945) Spurenelemente der Gesteine im Südlichen Finnisch—Lappland. *Bull. Comm. géol. Finlande No 135.*
- (1947) *Geokemia.* Helsinki.
- SEAL, H. L. (1964) *Multivariate statistical analysis for biologists.* London.
- SHAW, D. M. (1954 a) Trace elements in pelitic rocks. Part I: Variation during metamorphism. *Bull. Geol. Soc. Amer. Vol. 65, pp. 1151—1166.*
- (1954 b) Trace elements in pelitic rocks. Part II: Geochemical relations. *Bull. Geol. Soc. Amer. Vol. 65, pp. 1167—1182.*
- and BANKIER, J. D. (1954) Statistical methods applied to geochemistry. *Geochim. et Cosmochim. Acta. Vol. 5, pp. 111—123.*
- SIEGEL, S. (1956) *Nonparametric statistics for the behavioral sciences.* New York.
- SIMONEN, A. and KOUVO, O. (1951) Archean varved schists north of Tampere in Finland. *Bull. Comm. géol. Finlande No. 154.*
- STEVENS, R. E. and other (1960) Second report on a cooperative investigation of the composition of two silicate rocks. *U.S. Geol. Survey Bull. 1113, pp. 1—126.*
- TOURTELOT, H. A. (1964) Minor element composition and organic carbon content of marine and nonmarine shales of the Late Cretaceous age in the western interior of the United States. *Geochim. et Cosmochim. Acta. Vol. 28, pp. 1579—1604.*
- VAHERVUO, T. and AHMAVAARA, Y. (1958) *Johdatus faktorianalysiin.* Porvoo.
- WEBER, J. N. and MIDDLETON, G. V. (1961 a) Geochemistry of the turbidites of the Normanskill and Charny formations—I. Effect of turbidity currents on the chemical differentiation of turbidites. *Geochim. et Cosmochim. Acta. Vol. 22, pp. 200—243.*
- and — (1961 b) Geochemistry of the turbidites of the Normanskill and Charny formations—II. Distribution of trace elements. *Geochim. et Cosmochim. Acta. Vol. 22, pp. 244—288.*
- WEDEPOHL, K. B. (1960) Spurenanalytische Untersuchungen an Tiefseetonen aus dem Atlantic.. Ein Beitrag zur Deutung der geochemischen Sonderstellung von pelagischen Tonen. *Geochim. et Cosmochim. Acta. Vol. 18, pp. 200—231.*





