

SUOMEN GEOLOGINEN TOIMIKUNTA

BULLETIN
DE LA
COMMISSION GÉOLOGIQUE
DE FINLANDE

N:o 126

SUOMEN GEOLOGISEN SEURAN JULKAISUJA
MEDDELANDEN FRÅN GEOLOGISKA SÄLLSKAPET I FINLAND
COMPTES RENDUS DE LA SOCIÉTÉ GÉOLOGIQUE DE FINLANDE

XIV

AVEC 60 FIGURES DANS LE TEXTE ET 4 PLANCHES



HELSINKI
JUN 1941

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Les auteurs sont seuls responsables de leurs articles.

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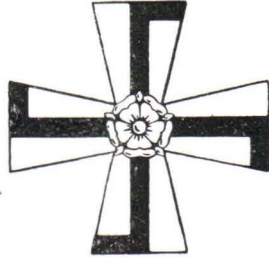
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IMPRIMERIE DE L'ÉTAT

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PRO PATRIA

1939—1940

JALO ANT-WUORINEN

GUNNAR BRANDER

ERKKI KUOSMALA

EERO MALMIVUO

ERKKI MIKKOLA

REINO UUSITALO



Jalo Ant-Wuorinen.

Unter den ersten Opfern des Krieges fand sich auch Dr. phil. Jalo Ant-Wuorinen, Lektor für analytische Chemie an der technischen Hochschule; er starb am 1. Dezember 1939 an den Verletzungen, die er sich am vorhergehenden Tage bei einem Luftangriff an seiner Arbeitsstätte im chemischen Laboratorium der Technischen Hochschule zugezogen hatte.

Dr. Ant-Wuorinen wurde am 24. August 1888 in Tampere geboren. Nach bestandener Reifeprüfung im Jahre 1906 widmete er sich dem Studium der Chemie an der Technischen Hochschule, und 1911 legte

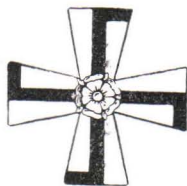
er das Ingenieurexamen ab. Um seine wissenschaftliche Ausbildung zu vertiefen, setzte Dr. Ant-Wuorinen seine Studien in Berlin fort, u. a. unter der Leitung des berühmten Forschers Ernst Beckmann. Im Jahre 1913 wurde seine Dissertation »Über die Reindarstellung und das Atomgewicht des Yttriums« fertig. In demselben Jahre erhielt er den Titel Doktor der Philosophie. Danach arbeitete er viele Jahre als Forschungs- und Lehrassistent sowohl an aus- als auch inländischen wissenschaftlichen Anstalten und im Dienste der Industrie, u. a. als Assistent am Kaiser-Wilhelm-Institut in Dahlem sowie als Prüfungsingenieur am Finnischen Patentamt. Staatlicher Alkoholchemiker war er in den J. 1923—32. Im letztgenannten Jahre wurde Dr. Ant-Wuorinen zum Lektor für analytische Chemie an der Technischen Hochschule ernannt, in welchem Amt ihn der Tod ereilte. Seit Anfang 1939 versah er neben seinem eigenen Amt auch die Professur für anorganische Chemie.

Dr. Ant-Wuorinen interessierte sich seit seiner Schulzeit für die Untersuchung von Sprengstoffen und veröffentlichte 1928 ein Lehrbuch über diese. Von seiten des Generalstabs des finnischen Heeres und auch anderswo wurde er in Sprengstofffragen seiner Sachkenntnis wegen oft zu Rate gezogen. Ausserdem wirkte er auch als Lehrer kriegstechnischer Kurse.

Seine eigentliche wissenschaftliche Forschungsarbeit wandte Dr. Ant-Wuorinen vorwiegend der Chemie seltener Metalle und der in ihnen enthaltenen Mineralien zu. Höchst wichtig unter den seltenen Metallen blieb die Lanthangruppe, zu deren analytischen und präparativen Fragen er stets zurückkehrte. Von diesen Untersuchungen seien die Arbeiten über Samariumsulfid und die Benutzung von Aziden bei der Trennung von Lanthaniden angeführt. Bedauerlicherweise sind viele der beabsichtigten interessanten Untersuchungen unvollendet geblieben.

Dr. Ant-Wuorinen war stets an den neuen Errungenschaften der Wissenschaft und vorwiegend seines eigenen Gebietes interessiert. Er war ein geschickter Lehrer, überwachte eingehend die Arbeiten und die Entwicklung seiner Schüler und sorgte dafür, dass die von ihm geleitete Laboratoriumsabteilung immer in mustergültiger Ordnung war. Die jüngere Generation der an der Technischen Hochschule ausgebildeten Chemiker wird sich stets an Dr. Ant-Wuorinen erinnern.

Olavi Erämetsä.



Gunnar Brander.

Gunnar Brander, Doktor der Philosophie, Untersergeant der Reserve, fiel bei Nisalahti in Säkijärvi am 11. März 1940, zwei Tage vor dem Friedensschluss. — Er war geboren am 8. Februar 1903 in Paimio als Sohn des verstorbenen Agronomen, Stationsinspektor Oskar Brander und seiner Gemahlin Sally, geb. Sjöberg. Im Frühjahr 1922 aus dem Schwedischen Realgymnasium in Helsinki ausgeschrieben, legte er im Frühjahr 1927 das Philosophiekandidatexamen an der Universität Helsinki ab, als Hauptfächer die Chemie und Geologie.

Zehn Jahre später (1937) erwarb er sich den Lizentiatgrad mit der Abhandlung »Ein Interglazialfund bei Rouhiala in Südostfinland« (Bull. Comm. géol. Finl., N:o 118).

Sein warmes Interesse für die Natur hatte Brander von seinem Vater geerbt, der während eines langen Lebens eifriger Botaniker war. Doch war es nicht die Botanik, der sich Gunnar Brander schliesslich hingeben sollte. Er liess sich bei der Technischen Hochschule einschreiben und studierte dort Chemie. Offenbar lag ihm aber die dortige Studienrichtung nicht recht, denn bald siedelte er zu der Universität Helsinki über. — Nach abgedienter Wehrpflicht arbeitete er in den Jahren 1929 und 1930 im Staatlichen Institut für Bodenforschung und danach bei der Geologischen Kommission als a. o. Geologe und stellvertretender Assistentgeologe. Die wissenschaftliche Tätigkeit bei der Kommission interessierte ihn in hohem Grade, und es war sein heisser Wunsch, seine dort angefangenen Arbeiten fortsetzen zu dürfen. Nur nach starkem Zögern entschloss er sich daher, zur Industrie überzugehen, und im Frühjahr 1938 begegnen wir ihm als Geologen der Kalkwerke in Lohja, wo er also nahezu zwei Jahre tätig gewesen war, als der Tod ihn seiner Familie und einer vielversprechenden wissenschaftlichen Forscherbahn entriss.

Schon vor der Ausführung der Revisionsuntersuchungen für das »Bodenkartenblatt Kuopio C 3« war er sich der Bedeutung der Diatomeen für die Quartärgeologie bewusst, und er beschloss, ihnen ein Spezialstudium zu eignen. Mit der ihm eigenen Energie und Gründlichkeit studierte er zunächst selbständig und verschaffte sich später all die Kenntnis, die auf dem besagten Gebiet im Norden zu erlangen war. Schon im Januar 1931 studierte er bei Dr. Carl Wilhelm Fontell in Turku, der während der letztvergangenen 20 Jahre als einziger bei uns systematische Diatomeenstudien betrieben hatte. Im Herbst des gleichen Jahres erhielt Brander die Gelegenheit während eines Monats seine Kenntnisse bei der hervorragendsten Diatomeenkennerin Skandinaviens, Dr. Astrid Cleve-Euler zu vertiefen. Mit reichsschwedischem Stipendium beteiligte er sich im Herbst 1933 (15. IX.—15. XII.) an dem von Professor Lennart von Post geleiteten Baltischen quartärgeologischen Kursus in Stockholm. Schliesslich unternahm er im Februar 1936 vermöge eines von der Nylands Nation (aus dem Kiseleffschen Donationsfonds) ihm zuerteilten Hilfsgeldes eine Studienreise zu Dr. Fr. Hustedt in Bremen.

Inzwischen hatte sich Brander bereits durch mehrere Veröffentlichungen als der vornehmste Kenner der vielförmigen Gruppe der Kieselalgen bei uns bewährt. Auch die Untersuchungsmethodik bezüglich des fossilen Materials hatte er zu einer weiten Vollendung

gebracht. Er hatte also die allerbesten Möglichkeiten, seine so erworbenen Kenntnisse für die quartärgeologischen Arbeiten zu verwerten, die schon von Anfang an ihn interessiert hatten. Es verdient erinnert zu werden, dass den Diatomeen seitens unserer Forscher bis dahin nur wenig Beachtung bei diesbezüglichen Untersuchungen geschenkt worden war — es sei denn, dass Harald Lindberg als einer der ersten bei uns die Aufmerksamkeit auf dieselben lenkte; in Skandinavien hatten die Kieselalgen schon seit den 1890er Jahren eine wichtige Rolle bei der Lösung einer Menge quartärgeologischer Probleme gespielt.

Einen grossen Teil seiner Zeit und seines Interesses widmete Brander in den Jahren 1930—38 der quartären Erforschung der Provinz Pohjanmaa. Schon früh sammelte er ein ansehnliches Material von Lehmprofilen in der Hoffnung, mit ihrer Hilfe den nacheiszeitlichen Verlauf der Landhebung klarlegen zu können. Die breit angelegte Untersuchung umfasste ganz Pohjanmaa von Karunki im Norden nach Isojoki im Süden, und es war seine Absicht, sie als Lizentiat-Abhandlung vorzulegen. Da traf es sich, dass er im Frühjahr 1936, gerade als er sich wieder zu seinen Feldarbeiten begeben wollte, von Dr. Thord Brenner einen Tonklumpen zur Ansicht erhielt, der aus einem Osausschnitt bei Rouhiala an den Tag gekommen war und den Verdacht aufkommen liess, dass er vielleicht interglazialen Ursprungs war. Im folgenden Winter gelang es ihm während einiger kurzen Wintermonate mit Hilfe des Mikroskops das Rätsel des Klumpens zu lösen. Das Resultat seiner Untersuchungen lag alsbald fertig vor, und im Mai 1937 disputierte Brander mit seiner schon eingangs erwähnten Abhandlung »Ein Interglazialfund bei Rouhiala in Südostfinnland«. Seine eigentliche Hauptuntersuchung, die zu ihrer Fertigstellung sicher noch die Feldarbeiten von ein paar Jahren erfordert hätte, geriet also dadurch gewissermassen zur Seite, und es ist heute leider unsicher, inwieweit das eingesammelte Material noch anderweitig verwertet werden kann. — Das von Brander für die Interglazialzeit gefasste Interesse veranlasste ihn später zu einer planmässigen Bestrebung, neues Material zur Beleuchtung der genannten Zeitperiode zu sammeln. Erfreulicherweise befindet sich in seinem Hinterlass auch ein Manuskript »Nya bidrag till kännedom om Finlands interglaciala bildningar«, welches voraussichtlich noch in diesem Winter im Druck erscheinen wird.

Branders zielbewusste Arbeitsweise und sein grosser Arbeitseifer beschränkten sich nicht einzig auf das Studierzimmer und das Laboratorium. Wer, wie der Verfasser der vorliegenden Zeilen, ihn bei seiner Arbeit im Felde sah, verwunderte sich über seine grosse Energie und

Ausdauer; er schonte sich nie. Es ist z. B. durchaus nicht leicht, sich während heisser Sommertage einsam ohne Hilfe mit einem schweren Torfbohrer nicht nur durch den Torf, sondern selbst durch eine 9 m dicke Lehmschicht hindurchzuarbeiten. Das kam aber bei ihm oft vor.

Seiner Natur nach war Brander ein stiller Mensch. Mit den Jahren machte sich allmählich auch eine gewisse Bitterkeit geltend, als er — über die Zukunft nachgrübelnd — die Möglichkeiten der Vollführung seiner vielen Pläne bezweifelte. — Als eifriger Sänger war er Mitglied der Akademiska Sångföreningen und Sällskapet M. M.

Gunnar Brander war Mitglied der Geologischen Gesellschaft in Finnland seit 1927, des Geologischen Vereins in Stockholm (1929), der Societas pro Fauna et Flora Fennica (1932), des Technischen Vereins in Finnland (1939) sowie der Geographischen Gesellschaft in Finnland (arbeitendes Mitglied seit 1937).

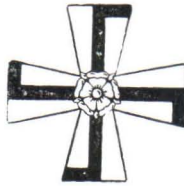
Gunnar Brander hinterlässt Frau, geb. Öberg, nebst zwei minderjährigen Söhnen, eine alte Mutter und Geschwister.

A. L. Backman.

VERZEICHNIS DER VON GUNNAR BRANDER VERÖFFENTLICHTEN
SCHRIFTEN:

1. Über die Petrographie von Degerö und Sandhamn. — Bull. Comm. géol. Finl., N:o 85, 1929. (2 S.)
2. Über den Dopplerit von Haapamäki in Finnland. — Ibid., 101, 1933. (20 S.)
3. Fredriksbergsmossen. (Zus. mit Thord Brenner.) — Fennia, 57, N:o 5, 1933. (31 S.)
4. Beiträge zur Kenntnis der Diatomeenflora Finnlands. I. — Memor. Soc. F. Fl. Fenn., 9, 1934. (4 S.)
- 5a. Suomen geologinen Yleiskartta. Lehti C 3, Kuopio. Maalajikartan selitys. 1934. (67 S.)
- 5b. D:o schwedisch mit franz. Zusammenfassung. 1934. (73 S.)
6. Om tilländningen och landhöjningen i Kronoby. — Terra, 46, 1934. (9 S.)
7. Die baltische Diatomeen-Succession des Bålen-Beckens. — Geol. Fören. i Stockholm Förh., 57, 1935. (23 S.)

8. Über das Einsammeln von Erdproben und ihre Präparation für die qualitative und quantitative Diatomeenanalyse. — Bull. Comm. géol. Finl., N:o 115, 1936. (14 S.)
 9. Jordskredet i Ingå. — Terra, 48, 1936. (7 S.)
 10. Ein Interglazialfund bei Rouhiala in Südostfinnland. — Bull. Comm. géol. Finl., N:o 118, 1937. (76 S.)
 11. Zur Deutung der intramoränen Tonablagerung an der Mga, unweit von Leningrad. — Ibid., N:o 119, 1937. (21 S.)
 12. Nya bidrag till kännedom om Finlands interglaciala bildningar (1939, Manuskript.)
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Erkki Kuosmala.

Am 17. Dezember 1939 fiel für die Freiheit Finnlands in Taipale Res.-Fähnrich Vilho Erkki Kuosmala (früher Forsberg).

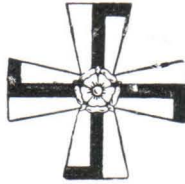
Res.-Fähn. Kuosmala wurde am 5. 8. 1914 in Helsinki geboren. Das Abiturientenexamen bestand er 1934 am Versuchslyzeum zu Helsinki, und in demselben Jahre begann er an der Universität Helsinki Geologie und Chemie zu studieren. Seiner Militärpflicht genügte er in den Jahren 1936—1937. Im Sommer 1938 nahm er teil an den von Professor Väyrynen geleiteten Felsgrundkartierungen in Pudasjärvi sowie in Nordkarelien.



Eero Malmivuo.

Am 27. Februar 1940 fiel für die Freiheit Finnlands im Luftkampf gegen einen zahlenmässig übermächtigen Feind der Jagdflieger Res.-Fähnrich Eero Aulis Malmivuo.

Res.-Fähnrl. Malmivuo wurde am 31. 7. 1915 in Helsinki geboren. Er bestand das Abiturientenexamen 1936 an der V. Gemeinschaft zu Helsinki. Danach erfüllte er 1936—1937 seine Wehrpflicht in der Reserveoffiziersschule der Luftwaffe. Im Jahre 1937 begann er an der Universität Helsinki sein Studium mit Geologie als Hauptfach. Im Sommer 1938 war er Assistent von Prof. Väyrynen bei den Felsgrund-Kartierungsarbeiten in Taivalkoski und Nordkarelien sowie im Sommer 1939 Assistent von Dr. Mikkola in Südwest- und Südfinnland.



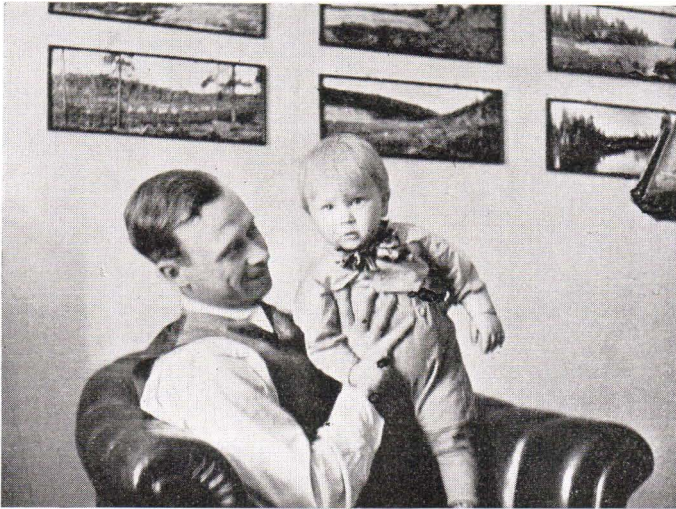
Erkki Mikkola.

The death of Dr. Erkki Mikael Mikkola was one of the most serious losses that Finnish science suffered during the country's war of defence against invasion in 1939—40. At the age of 35 years he had become a leading authority on Pre-Cambrian geology, and his life had just come to a stage when the fruits of his work began to ripen. His activity was cut off prematurely, but the results he had already attained amount to more than the lifework of many an aged man, while the plans and ideas left unfinished behind him clearly indicate what his loss has meant to Finnish geology. It is the duty of the survivors to do their best to preserve to posterity not only Mikkola's scientific legacy, but also the picture of his personality and the story of his life.

Erkki Mikkola's father, Juho Mikko Mikkola, born in 1875, was the son of a farmer in Laitila, West Finland; he became a clergyman in 1900 and was from 1902 to 1907 engaged as teacher of religion and Principal of a secondary school in Ikaalinen; later he became teacher of religion at the Training College for teachers in Jyväskylä, and was from 1926 to 1936 Principal of the College, from which post he was promoted to membership of the Department of Education. In 1903 he married Miss Anna Maria Sirén, a gifted woman and a teacher. Their home was the centre of intellectual activity in Jyväskylä, and their seven children all have unusual talents which are being developed in different careers.

Erkki Mikkola was born in Ikaalinen 18. 7. 1904, being the eldest child in the family. His great gifts and keen interest in nature appeared very early. Already at the age of three years he is said to

have been able to draw recognizable pictures of landscapes; at five he collected minerals and only a little later he first showed his keenness in drawing maps. During his first years at the secondary school in Jyväskylä he constructed a topographic map of an island by means of a self-made level. He undertook long excursions in order to observe animals and plants, soils and rocks and even geological phenomena. He also prepared an aquarium in which he kept water-nets, and during the very first summer after having learned some botany at school collected a herbarium containing several hundreds of plant species.



In 1922 Erkki Mikkola became a student at the University and started his studies in natural history. Botany was his first favorite subject, and he advanced so rapidly on the floristic line that, after a few years, his teachers regarded him as a thorough expert on the Finnish flora. One of his floristic studies was published (1927); it dealt with *Rubus humulifolius*, a species that was found by him for the first time in Finland near his home-town, Jyväskylä. Even after having specialized in geology he never forgot his interest in botany and during his field work in Lapland, on the Åland islands and in South Finland he made topographic floristic notes, and left in manuscript a study on the forest types in the Ivalojoeki valley in Lapland and a list of plant species occurring in the granulite area of Lapland, which was intended to be published in co-operation with

Dr. R. Kalliola. The dependence of the flora upon the underlying bed-rock was also the subject of his interesting article »On the influence of the ultrabasic rocks upon the flora in Lapland» (1938).

Mikkola's second subject that seemed natural to him was geography, which strongly attracted his imagination. In the summers of 1922 and 1923 he took part in an expedition sent out to Lapland by the Department of Forestry. He at once fell under the spell of Lapland's enchantment — life-long with him — and after that the greater part of his summers were spent in the high North. He was loath to leave the Northern wilderness in the autumn and only when the snow covered the fells and forests did he return south. In Lapland he got his practical training in geographical field work under the instruction of his teacher Professor J. G. Granö. Later he carried out an important geographic work as the editor of »Suomenmaa» (1929—31), a handbook of the geography of Finland, in which he wrote the chapters dealing with the parishes of Lapland. In writing these comprehensive descriptions he had a good opportunity of developing his stylistic talents, which later came into their right also when he was writing in other languages than Finnish. He possessed great richness of expression and could form sentences as artistically beautiful as were his drawings.

After botany and geography Mikkola commenced to study geology under the guidance of the late Professor Wilhelm Ramsay and the present writer.

It was very difficult for Mikkola to make his final choice between the three branches of natural science which all attracted him so greatly. Here he had little help from his teachers, who all competed for him, each being anxious to have the capable and industrious young man as a pupil and possible successor. His choice of geology matured during the summers of 1925—27 which he spent in geological field-work in Lapland. This work was primarily concerned with the Quaternary deposits of the Ivalojoiki valley and of the surrounding granulite area. Observations connected with the land-forms and the superficial deposits were of course close at hand in view of his earlier interests. The geological work of running water and deposition of sediments were things that he when a schoolboy had keenly observed in his home area, and in Lapland he now indulged in tracing in minute detail the work of the Late-Glacial waters upon the clean-washed rock surfaces and in the esker deposits; the results of his study were illustrated in a very original way by a splendid stereogram. Before the work was ended, however, Mikkola had finished his courses in tectonic geology, petrology, and Pre-Cambrian geology and had learned

much from the books of H. Cloos and from personal instruction by C. E. Wegmann, who in those years was active in Finland. In 1928 he published as a by-product of his Lapland work a study on the Nattanen granite south of the granulite area, in which he applied the magmatomic methods of H. Cloos. When the comprehensive memoir »On the physiography and Late-Glacial deposits in Northern Lapland» was presented as a thesis for the degree of Dr. Ph. (1932) it contained also an outline of the character of the bedrocks and tectonics of the area, and it is in fact a very deep study of superficial objects. He was able to demonstrate the great rôle played by fault movements of comparatively recent date in the land-forms and showed that it was especially the granulite massive that had been uplifted and split into tilted blocks. He did not hesitate to conclude that these late movements were a »posthumous» continuation of those orogenic movements that once had given rise to the granulite mass itself.

In 1928, the most productive among his earlier years as geologist, Mikkola passed his examinations for the degree of Cand. Phil. (=M.A.). It was not easy to persuade him to take that step, for he could never feel his knowledge sufficient. At last his teachers had to have recourse to the trick of arranging the examination unawares to him. After that he was more eager than ever to learn more. Plans were made for him to go abroad to work and study with some prominent geologist but, to the surprise of his teachers and friends, he was not willing to do this, saying that there was more than enough work to be done at home. He liked, however, to take part in excursions to foreign countries. In 1929 he visited Switzerland and the Alps with Dr. Wegmann. In the autumn of 1934 he participated in the excursions of the »International Association for the Study of the Pre-Cambrian and the Ancient Mountain Chains» and the »British Association for the Advancement of Science» in Scotland. In Finland he took part in the international excursions arranged by J. J. Sederholm in 1930 and by P. Eskola in 1936 *etc.*, and he himself led many excursions of foreign geologists to various parts of the country. Thereby he became acquainted with a great number of leading geologists from all over the world and won many personal friends. His last excursion abroad was that arranged by »Geologiska Föreningen i Stockholm» in Central and Northern Sweden in 1938.

In 1928 Mikkola was engaged as assistant to J. J. Sederholm, the late Director of the Geological Survey of Finland. This was the turning point that led Erkki Mikkola to his career as a Survey geologist, in which he in 1929 was appointed to the permanent position of »Junior», in 1935 of »Senior Assistant Geologist»; from 1938 he acted as State

Geologist. In 1928 he accompanied Sederholm to the Åland archipelago and prepared the geological map of the Enklinge area, of which Mikkola wrote, in the preface to Sederholm's memoir which he edited after the author's death, that it »is probably not surpassed by any other Pre-Cambrian area of corresponding size in the world for beauty and variety of rocks and the astonishing complexity of structure» (Sederholm 1934).



In the same summer 1928 Sederholm and Mikkola restudied parts of the Tampere district. Mikkola mapped in detail the important Suodenniemi area of breccias, conglomerates and diorites, and prepared a stereogram of the Bothnian area of Kankaanpää—Lavia—Suodenniemi, published by him in 1931. Sederholm (1931), writes about this work: »When the modern tectonic methods that have lately been developed in Switzerland and other Alpine countries were introduced into Finland by the activity of Dr. Eug. Wegmann, a new revision of the interesting areas in the neighbourhood of Tampere became necessary. This was entrusted to Mr. E. Mikkola who in the summer of 1928 mapped once more the areas N. W. of Tampere with

the special object of getting an idea of the tectonic structure of this interesting region. Mr. Mikkola performed this task in an able way». This was the beginning of their life-long co-operation and friendship. Sederholm wanted to have an assistant of independent ideas with whom to discuss questions of mutual interest. Sederholm's writings bear many evidences of their discussions, or »the dialectic method of developing ideas», as he expressed it. Thus in the Suodenniemi area Mikkola for a long time was opposed to Sederholm's explanation of the Suodenniemi breccias as products of weathering, but finally Mikkola became convinced by his chief's arguments and thus strengthened this conclusion, which meant that there exists a real unconformity in the Archaean formations — a very important thesis in Sederholm's doctrines. In general, Mikkola, although open to argument and gentle in manner, stubbornly defended his own opinion and trusted to his own judgment. This characteristic was just what Sederholm expected from his assistants in order to get real help. Mikkola, on the other hand, avidly absorbed the learning and experience of which the old Master in Pre-Cambrian geology had so much to offer, and it can rightly be said that he was Sederholm's pupil in a more strict sense than any other among the Finnish geologists. The following dialogue may prove how highly Sederholm valued his assistant. He once asked me (about 1932), who in my opinion ought to become his successor as Director of the Geological Survey. »Mikkola», I answered without hesitation. »Yes, I agree», he said, continuing after a pause: »It is a fact that whoever may become the Head, Mikkola will actually be the scientific leader, whatever position he may occupy in the Survey». After Sederholm's death (1934) Mikkola was mentioned as a candidate for the directorship, but he himself determinedly opposed the appointment. This was not alone because administrative activities were repugnant to him and would have impeded his scientific work, but more especially because he felt incompetent, as he understood that the activities of the Survey were to be concentrated more than before upon problems of practical geology and the utilization of the mineral resources. Also he was aware of certain personal deficiencies and therefore could not feel assured of success in practical leadership. I myself began to understand this during our common excursion to Scotland in 1934: Mikkola was too incommunicative and unable to let his thought easily shift into different matters, although he could discuss any scientific problem very intelligently or express his ideas in eloquent lectures, even unprepared. In bigger assemblies he was often a »silent Finn», and he himself felt this rather too seriously. Moreover, he had overworked himself during his college years and

suffered from insomnia and nervousness, which at that time greatly impaired his self-confidence.

During five summers, from 1931 to 1935, Mikkola performed his great field work on the Pre-Cambrian of Lapland, mapping the whole of Central Lapland, or the areas of the Muonio, Sodankylä and Tuntsa sheets, from the Swedish to the Russian frontier. It was officially a revision work, as all the area had been mapped earlier. The earlier work, however, had been mostly done by inexperienced surveyors who were not professional geologists, and the topographic basis had been very poor. Therefore Mikkola had to do almost the whole work anew, and alone. This work required an enormous physical endurance, and the excellent fulfilment was an achievement, of which only those who know the conditions in this very sparsely settled, for the greater part uninhabited and swampy country can have any idea. The three map sheets were printed in 1936—37 and they are at present by far the best geological maps in Finland. Mikkola's technical skill, his intuitive faculty of seeing through the geological formations and picturing them correctly in space and time come in these maps to their full right, although he was very careful in the classification of the rock formations according to their geological age and entirely abandoned the age grouping applied in the earlier mapping by Sederholm.

The common explanation of the Lapland sheets was not quite finished, when the the author was called to the defence of his country. On November 27th 1939, as it was believed in Finland that the menace of war had passed, Mikkola got ten days' leave of absence from his post as a lieutenant of the reserve on the Carelian Isthmus, intending during that time to finish his manuscript. But he had hardly returned to Helsinki when the unexpected attack came, and he went back to join his company, leaving the Geological Survey just one hour before it was destroyed during a bomb raid. Thereafter he spent all his time, two and a half months, in the front lines, taking a full share in the dangers of the heroic defence. The finishing touches to his Explanation to the Lapland sheets were carried out after his death by his colleagues, Dr. Th. G. Sahama and Mr. K. Rankama, and it is now ready to go into print.

This posthumous work of Mikkola consists of two parts, one in Finnish, being a description of the outcrops, and the other part in English, being a monographic geological and petrological treatise of Central Lapland's Pre-Cambrian rock-crust. Its contents will not be abstracted here, as this will be done in another place and as the memoir itself will soon be accessible. Happily, the work had proceeded

so far that the greater part of its contents could be published, but unfortunately some chapters were still lacking, the most important of these being the chapter dealing with the tectonics of Lapland. This is the more deplorable as Mikkola, among the Finnish geologists, had the best training as well as the best natural talent for tectonical research. As it is, the work will long remain a monograph of fundamental value to Pre-Cambrian geology and petrology.

Erkki Mikkola's college-studies were not planned as a basis for chemical and mineralogical petrology, as he had gone through no comprehensive courses in chemistry. He felt this as a lack in the beginning, but he made up for it by studying the necessary branches of chemistry by himself, and during his later work chemical petrology was greatly to the fore. An important contribution to this subject is his paper with Th. G. Sahama »On the region to the south-west of the »granulite series» in Lapland and its ultrabasics» (1936).

After finishing the field work in Lapland, Mikkola started the re-mapping of south-western Finland with the aim of publishing new map sheets on the scale 1 : 400,000. With a few student assistants he had already mapped numerous parishes with an exactitude similar to or, owing to better conditions of exposition, even greater, than that of the Lapland areas. In some regions, *e. g.* in the Mustio area, interesting geological and tectonical features were already revealed. Most important, however, were the results achieved in the Western part of the province Uusimaa just north of the Orijärvi region. The rocks of this region were found by Mikkola to present a mineral development, or to belong to a mineral facies so far unknown in the Archaean of Finland. Characteristic of this metamorphic formation are pyroxene-gneisses, partly such containing meionitic scapolite, and cordierite-almandite-gneisses or kinzigites. The study of this area, which promises new aspects for Archaean geology and petrology, is now being continued by Mr. K. Parras, who has worked in the said area every summer since 1936 as an assistant of Mikkola.

During his service in the Geological Survey Mikkola had to finish and edit, besides the third migmatite volume of Sederholm, still another posthumous work, *viz.* the explanation to the mapsheet Kuopio by W. W. Wilkman who died in 1937. To this end Mikkola did some revision work in the Kuopio region and arrived, in contrast to Wilkman's opinion, at the conclusion that the quartzites and schists of the Kuopio area probably belong to the Karelidic zone and not to the older Pre-Cambrian. He mentioned this only orally in a lecture before the Geological Society of Finland, letting Wilkman's text in this point remain unchanged. This, like many other shorter surveys

in different parts of Finland widened Mikkola's views — though the progress of his very important main work was hereby delayed — and it would soon have been possible for him to arrive at an improved picture of Finland's geological structure as a whole. Mikkola already took part, on behalf of Finland, in the composition of the synoptical geologic map of North Europe by A. Gavelin and N. Magnusson, and prepared in 1937 a new geologic map of Finland.

In 1935 Erkki Mikkola married Miss Toimi Teittinen, who also had studied geology. During his last years Erkki Mikkola seemed to be personally very happy, his health had improved, and he was full of the joy of work. In his letters from the front to his wife, he mostly wrote about their little son Tapani, whom he had not much hope of seeing again. Thus in a letter of 29. 1. 1940 he says: »My last wish would be that the young life of this my dear only son should be protected by all means and that care be taken of his education in community with western civilization, in freedom of the human spirit, in knowledge and appreciation of all our common values and of his Finnish descent, and in the consciousness of his father's life ideals and aims». With his stubborn will Erkki Mikkola could not retreat in the fight. His companions in arms have told that he had not rested for weeks, day or night, and that he had given leave of absence to his men, whom he had believed to be more fatigued than himself. Such men saved the freedom of their country, and their sacrifice cannot have been made in vain. — Erkki Mikkola fell in action at Taipale on February 12th 1940.

Pentti Eskola.

LIST OF THE PUBLISHED WORKS OF ERKKI MIKKOLA:

1. *Rubus humulifolius* löydetty Jyväskylästä. Luonn. Yst. 1927, pp. 23—27. (Finnish).
2. Ueber den Nattanengranit im finnischen Lapplande. *Fennia* 50, N:o 12, 1928, 22 pages.
3. Suomenmaa, maantieteellis-taloudellinen ja historiallinen tietokirja, IX, 2, Oulun lääni, pohjoisosa. Porvoo 1931, 472 pages. (Finnish; the greater part of this book has been written by Dr. Mikkola).
4. Explanation of the Section through the Area of Bothnian Schists and Intrusive Rocks W. of Tampere in Finland. *C. R. Soc. géol. Finl.* N:o 4; *Bull. Comm. géol. Finl.* N:o 93, 1931, pp. 9—11.

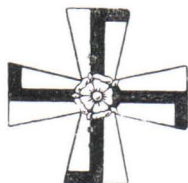
5. Inarin-Lappi ja Petsamo. Suomen Matk. yhd. Vuosik. 1932, pp. 9—27. (Finnish).
6. Enare-Lappmark och Petsamo. Turistför. Finl. Årsbok 1932, pp. 9—28. (Swedish translation of the foregoing article).
7. On the Physiography and Late-Glacial Deposits in Northern Lapland. Bull. Comm. géol. Finl. N:o 96, 1932, and Fennia 57, N:o 1, 1932. 88 pages. (Thesis for the degree of Ph. D.)
8. Karjalan kallioperä sekä hyödylliset kivilajit ja mineraalit. Karjalan kirja, 2 p., Porvoo 1932, pp. 12—20. (Finnish).
9. Keski-Suomen kallioperästä ja sen vaikutuksesta alueen luonnonsuhteisiin. Keski-Suomi I, Keski-Suomen Museoyhdistyksen julkaisuja I, Jyväskylä 1935, pp. 9—17. (Finnish).
10. The Region to the South-west of the »Granulite Series» in Lapland and its Ultrabasics. (Together with Th. G. Sahama). C. R. Soc. géol. Finl. N:o 9, Bull. Comm. géol. Finl. N:o 115, 1936, pp. 357—371.
11. Suomen Geologinen Yleiskartta, Kivilajikartta, Tunttsajoki (lehti D 7) — General Geological Map of Finland, Pre-Quaternary Rocks, Tunttsajoki (Sheet D 7), 1936.
12. Suomen Geologinen Yleiskartta, Kivilajikartta, Muonio (lehti B 7) — General Geological Map of Finland, Pre-Quaternary Rocks, Muonio (Sheet B 7), 1937.
13. Suomen Geologinen Yleiskartta, Kivilajikartta, Sodankylä (lehti C 7) — General Geological Map of Finland, Pre-Quaternary Rocks, Sodankylä (Sheet C 7), 1937.
14. Kainuu kuvissa—Kainuu i bilder—Kainuu in Pictures. Kainuun Sanomain kirjapaino O.Y. 1938.
15. Suomen Geologinen Yleiskartta — General Geological Map of Finland, Lehdet — Sheets B 7- C 7- D 7, Muonio—Sodankylä—Tunttsajoki, Kivilajikartan selitys — Explanation to the Map of Rocks, 1941.

Dr. Mikkola has also edited and brought into their final condition the following papers by the late Professor J. J. Sederholm and by the late Dr. W. W. Wilkman. He co-operated with Professor Sederholm during the field-work for the study of parts of the Tampere district cited below.

J. J. Sederholm: On Migmatites and Associated Pre-Cambrian Rocks of Southwestern Finland. Part III. The Åland Islands. Bull. Comm. géol. Finl. N:o 107, 1934.

W. W. Wilkman: Suomen Geologinen Yleiskartta. Lehti C 3. Kuopio. Kivilajikartan selitys. (With an English Summary). 1938.

J. J. Sederholm: On the Sub-Bothnian Unconformity and on Archaean Rocks Formed by Secular Weathering. Bull. Comm. géol. Finl. N:o 95, 1931.



Reino Uusitalo.

Am 1. Dezember 1939 fiel, mit einem Bomber vom Feindflug zurückkehrend, für die Freiheit Finnlands Res.-Fähnrich Reino Johannes Uusitalo.

Res.-Fähn. Uusitalo wurde am 2. 11. 1910 in Vähäkyrö geboren. Das Abiturientenexamen bestand er 1930 am Finnischen Lyzeum zu Vaasa, und in demselben Jahre wurde er in der Universität Helsinki immatrikuliert. Im Sommer 1939 nahm er teil an den Erzuntersuchungsarbeiten der Aktiengesellschaft Petsamon Nikkeli O.Y.

1.

ON THE COMPOSITION OF THE RESIDUE FROM
SILICA IN ROCK-ANALYSIS

BY
KALERVO RANKAMA

ABSTRACT.

By the aid of optical spectrography sixteen Finnish rocks and the silica residues obtained from them have been investigated. Quantitative determinations for a number of rarer oxides are presented together with qualitative records concerning the main constituents of the rocks, and also other elements. The causes of the presence of contaminants in the silica are discussed with especial reference to the theory of ionic potentials introduced by Cartledge and applied to geochemical problems by Goldschmidt. In addition some analytical and geochemical conclusions are given.

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INTRODUCTION.

Several investigations have been carried out in order to correlate the composition of the residue left from silica when this constituent is determined in the course of silicate analysis by driving it off by hydrofluoric acid. In nearly every handbook of silicate analysis one can find data concerning the qualitative composition of these residues. The facts presented in the manuals are summarized below.

According to Hillebrand and Lundell (1929, p. 725) the variations in quantity of the residues obtained from different rocks are greater than those in quality. The constituents of the residues are Al, Fe, Ti, and P, which are invariably present if the rock contains them. Other constituents are Zr, Th, Nb, and Ta when these are present in the rock. Ba and Ca are rarely components of the residue. Occasionally Mg is found to be present. The residue is not likely to contain alkalis. In silica residues obtained from minerals even Sn, W, and Sb can be present, depending upon the composition of the mineral. The amount of the residue ranges from less than one milligram up to 2 or even 3 per cent in basic rocks rich in titanium and phosphorus.

Washington (1930, p. 163) states that the weight of the silica residue in granites and other very salic rocks is only a few milligrams, and up to 0.5 per cent in more basic rocks. In rocks high in titanium and iron the residue amounts from 0.5 to 1 per cent, and occasionally even more. The main constituents present in the residues are Al_2O_3 , Fe_2O_3 , TiO_2 , and P_2O_5 .

According to Dittler (1933, p. 10) the following elements are present in the residue: Ti, P, Al, Fe, Zr, and traces of Ba, Mn, Mg, and Ca. The amount of the residue in basic rocks ranges up to 1 per cent.

Further studies on the composition of the silica residues have been made by Bloor, Kuzirian, Lenher and Truog, and Cissarz.

Bloor (1907, p. 1604) has studied residues from clays and argillaceous limestones. His results are therefore not entirely comparable with those of rock analyses. The residue was found by him to contain ferric and aluminium oxides, lime and magnesia, which are the main bases present in the clays. The residue averaged about 1 per cent of the separated silica.

According to Kuzirian (1914) the residue may contain Fe, Al, Mn, Ti, Mg, Na, K, Cr, Ca, and Ba. Mg, Ca, and Ba are thought in large degree to be present as sulfates.

Lenher and Truog (1916) have fused calcium, magnesium, and ferric oxides with silica and sodium carbonate. Their results show that the residue invariably contains ferric oxide. Lime was found to be present, but not always. As for magnesia, they state that silica becomes contaminated with this constituent at higher temperatures than are obtained when the dehydration of silica is carried out on a steam-bath. Potash and soda were never detected in the residues.

More recently, Cissarz (1930) has studied the influence of the separated silica upon the determination of very small amounts of various metals in the rocks. His results are, however, based on only one spectrographic analysis made of a certain copper-bearing shale («Kupferschiefer») of Mansfeld. According to Cissarz much of the following elements was carried away by the silica: V, Ti, P, W, Mo, and Mn. This effect was weaker for Ag, Au, Pb, Zn, Cd, As, Sb, Co, and Ni, and no quantitative relations could be established for Cu, Ba, Zr, Sn, Cr, Fe, and platinum metals. The presence of Zr, Sn, and Cr in the silica seems, however, to be evident.

The method used by Cissarz is an indirect one. The material was treated in three different ways: 1) solution by hydrofluoric and sulfuric acids, 2) digestion by *aqua regia*, and 3) fusion by sodium carbonate and borax (in a porcelain crucible) with subsequent solution of the melt in nitric acid, evaporation down to dryness and repeated removal of the now insoluble silica by filtering it off from the solution of the salts in nitric acid. The spectra of the three solutions were photographed and the concentrations of the various elements compared. The spectra obtained from the third solution showed fewer lines and lower concentrations than those from the other two.

The quantitative composition of the silica residues has been studied by Aourousseau (1923) and by Beger (1928). According to them titania predominates in the residues. The other oxides determined are Al_2O_3 , Fe_2O_3 , MgO , CaO , and P_2O_5 . MnO was not found to be present. Accordingly lime and magnesia seem to be regular constituents of the residue.

Our present knowledge of the quantitative amounts of the main constituents contained in the silica residues of rocks is established by the studies by Aourousseau and by Beger mentioned above. As for the minor constituents of the rocks, no data except those presented by Cissarz (1930) are available. It therefore seemed advisable to study

the rarer elements contained in the residues by a series of analyses made of different rocks, and since here the ordinary analytical methods, and even those of micro-analysis, fail in most cases, the highly sensitive methods of spectrum analysis were applied as the most suitable ones.

MATERIAL.

The material for this study consists of a number of Finnish rocks, whose chemical compositions are presented in Table I¹. One of the

NOTES ON TABLE I.

¹ The quartz diorite, No. 5 has been analyzed twice (Väyrynen, 1938, pp. 101, 102). Here the first analysis has been quoted.

The result of the determination of phosphorus in the basic vein, No. 10, has through a mistake been omitted in the analysis published by Väyrynen (1938, p. 131.)

For analysis No. 15 the sum 100.09 has erroneously been reported by Eskola and Sahlstein (1938, p. 79); cf. Lokka (1934, p. 42, Analysis No. 191).

TAB- CHEMICAL ANALYSES OF

	1.	2.	3.
	Light gray aplitic granite. Juurikkamäki, Saamaskylä, Leppävirta. Analyst: Lauri Lokka.	Granite. Lauttasaari, Huopalahti. Analyst: H. Lönnroth.	Granite. Near Sukkulajärvi, Nattasunturit, Sodankylä. Analyst: E. A. O. Nordensvan.
SiO ₂	75.48	74.13	72.82
Al ₂ O ₃	13.24	13.63	13.66
Fe ₂ O ₃	0.04	0.16	1.30
FeO	1.19	1.44	1.22
MnO	0.01	0.02	0.03
MgO	0.10	0.09	0.39
CaO	1.25	0.88	1.10
Na ₂ O	4.07	2.50	3.45
K ₂ O	3.61	6.43	5.00
TiO ₂	0.07	0.14	0.55
P ₂ O ₅	0.13	0.00	0.14
H ₂ O+	0.58	0.48	0.35
H ₂ O-	0.09	0.12	0.06
S	n. d.	n. d.	n. d.
Total	99.86	100.02	100.07
Published by	Wilkman (1938, p. 110)		Mikkola (1928, p. 9)

rocks, No. 15, is a nephelite syenite gneiss which has been found only as a boulder.

The author was fortunate enough to secure a number of suitable hand specimens which had been analyzed previously in the Chemical Laboratory of the Geological Survey of Finland. All the determinations presented here are based on this material. The only exception is the Nattanen granite, No. 3, of which the originally analyzed powdered sample was available.

As may be seen by comparing the silica percentages presented in Tables I and IV, the correspondence between the values is fairly good in many cases. It must be kept in mind, however, that the silica percentages presented by the author in Table IV are not the true ones, since a part of silica, though small, can still be recovered from the ammonia precipitate.

Anyway, the connection between the rock powders analyzed and those used in this study is thought to be close enough to allow of some general conclusions.

LE I.

THE ROCKS INVESTIGATED.

4.	5.	6.	7.	8.
Granodiorite. Soliskylä, Viitasaari.	Quartz diorite. Kaulatunturi, Petsamo.	Quartz diorite. W. of Pylkäs, Pylkönmäki.	Gabbro. Virnikkasokka, Moskuvaara, Sodankylä.	Pigeonite dolerite. Near Lake Suolampi, Varnaisjärvi.
Analyst: Lauri Lokka.	Analyst: Lauri Lokka.	Analyst: Lauri Lokka.	Analyst: Lauri Lokka.	Analyst: Lauri Lokka.
67.23	56.89	56.85	48.31	51.00
16.07	16.88	17.64	17.16	11.79
0.54	0.62	1.45	1.12	1.77
3.38	9.07	5.76	7.99	14.62
0.09	0.16	0.14	0.14	0.23
1.19	0.98	4.12	8.43	5.26
3.98	2.20	6.78	13.27	9.76
3.91	5.68	3.10	1.70	1.91
2.42	3.23	2.35	0.23	0.58
0.55	1.39	1.15	0.79	2.48
0.00	0.09	0.00	0.17	0.19
0.63	2.39	0.41	0.83	0.64
0.16	0.07	0.13	0.12	0.08
n. d.	0.61	n. d.	n. d.	n. d.
100.15	100.26	99.88	100.26	100.31
	Less O for S ₂ 0.15			
Wilkman (1938, p. 91)	100.11 Väyrynen (1938, p. 101)	Wilkman (1938, p. 84)	Lokka (1934, p.56 No. 281)	Wilkman (1938, p. 145)

TABLE I
CHEMICAL ANALYSES OF

	9.	10.	11.
	Pyroxenite. Vehkalahti, Leppävirta,	Basic vein. Kaulatunturi, Petsamo.	Perknite. Sattasvaara, Sodankylä.
	Analyst: Lauri Lokka.	Analyst: H. Lönnroth.	Analyst: H. Lönnroth.
SiO ₂	48.75	45.10	41.19
Al ₂ O ₃	2.96	6.53	6.59
Fe ₂ O ₃	2.21	2.00	4.00
FeO	7.15	12.17	6.05
MnO	0.14	0.11	0.25
MgO	17.54	16.51	26.55
CaO	17.96	9.89	6.04
SrO	n. d.	n. d.	n. d.
BaO	n. d.	n. d.	n. d.
Na ₂ O	0.59	1.36	0.24
K ₂ O	0.14	0.37	0.15
TiO ₂	0.68	2.80	0.88
ZrO ₂	n. d.	n. d.	n. d.
P ₂ O ₅	0.18	0.00	0.00
F	n. d.	n. d.	n. d.
Cl	n. d.	n. d.	n. d.
CO ₂	n. d.	n. d.	1.47
H ₂ O+	1.81	2.67	6.16
H ₂ O-	0.10	0.17	0.17
S	n. d.	0.01	n. d.
NiO	n. d.	0.06	n. d.
Total	100.21	99.75	99.74
Published by	Wilkman (1938, p. 61)	Väyrynen (1938, p. 131)	

METHODS.

CHEMICAL TREATMENT.

A pair of preliminary analyses, each made of one gram of rock powder, yielded residues too small to allow even a spectrographic analysis to be carried out. In order to secure sufficient amounts of the different residues and to maintain the working conditions as constant as possible throughout the work, for all analyses exactly 3 g. of the rock powder were weighed out into a capacious platinum crucible and intimately mixed there with 15 to 20 g. of anhydrous sodium carbonate (analytical reagent). The carbonate fusion was accomplished in the usual way, and the flux was finally blasted until the reaction was complete. In some few cases more sodium carbonate was added

(continued).

THE ROCKS INVESTIGATED.

12.	13.	14.	15.	16.
Syenite. Island in Lake Jerisjärvi, Muonio.	Syenite. Saenhariu. Nilsä.	Syenite. Lakkavaara. Kolari.	Nephelite syeni- te gneiss. Heinävaara, Kiihtelysvaara.	Keratophyr. Orshoaiivi, Petsamo.
Analyst: H. Lönnroth.	Analyst: Lauri Lokka.	Analyst: H. Lönnroth.	Analyst: Lauri Lokka.	Analyst: H. Lönnroth.
59.40	58.75	57.29	55.31	55.52
15.24	13.86	15.70	19.56	16.05
2.76	1.76	3.24	1.92	5.84
3.82	1.73	4.00	3.17	2.74
0.09	0.06	0.14	0.28	0.12
2.65	2.06	2.98	0.76	0.47
4.80	7.01	5.18	1.53	4.90
n. d.	n. d.	n. d.	0.00	n. d.
n. d.	n. d.	n. d.	0.06	n. d.
4.37	2.00	4.66	10.32	7.01
3.74	8.10	4.32	4.67	2.85
1.68	0.14	1.10	1.18	1.38
n. d.	n. d.	n. d.	0.31	n. d.
0.37	1.15	0.59	0.19	trace
n. d.	n. d.	n. d.	0.33	n. d.
n. d.	n. d.	n. d.	0.00	n. d.
n. d.	2.90	n. d.	n. d.	2.31
0.54	0.55	0.47	0.55	0.62
0.11	0.09	0.06	0.09	0.07
n. d.	n. d.	n. d.	n. d.	n. d.
n. d.	n. d.	n. d.	n. d.	n. d.
99.57	100.16	99.73	100.23	99.88
	Wilkman (1938, p. 118)		Eskola and Sahl- stein (1930, p. 79)	Väyrynen (1938, p. 126)

and the melt blasted again, when still insoluble particles were found to be present in the flux. The cake was removed and transferred to a platinum dish. 50 ml. of pure concentrated hydrochloric acid and 2 ml. of ethanol were added, and the solution was evaporated down to dryness on a steam-bath. 15 ml. of concentrated hydrochloric acid were then added. The insoluble silica was decanted several times with warm water to which some drops of hydrochloric acid were added, filtered off, and carefully washed with warm acidified water as before. After the second evaporation 15 ml. of concentrated hydrochloric acid were added again, and the small amount of silica washed as described before. The platinum dish was cleaned with pieces of filter paper moistened with water.

The silica was ignited to constant weight in a clean platinum cru-

cible over a Meker burner. After weighing, the silica was moistened with some drops of distilled water. 2 ml. of dilute (1 : 1) sulfuric acid and 30 ml. of hydrofluoric acid¹ were added and the whole evaporated down on a steam-bath. The impurities of the silica were now contained in the few drops of sulfuric acid left after evaporation.

van Tongeren (1938, p. 20), when determining the amount of impurities in a sample of quartz, scraped off the material left in a platinum crucible after the volatilization of silica and sulfuric acid. Applied here this method, however, seems to be inadvisable, because the residue adheres strongly to the bottom and the lower parts of the walls of the crucible. Accordingly, a big part of the residue will be left in the crucible, and one has to welcome impurities from the tool used in scraping. Further, the effect of this process on the platinum crucible is by no means beneficial.

In order to remove the residues from the crucible in an easy way the following procedure was adopted.

To the sulfuric acid solution left in the crucible was added 500 to 1 100 mg. of very pure carbon powder made from the carbon electrodes, or enough to make a thick paste with the liquid. The crucible was placed on a sand-bath and heated till no more white fumes were driven off. The carbon was then carefully burnt off over a Meker burner in an oxidizing atmosphere and the residue ignited for half an hour. After weighing, the whole residue could easily be removed with a soft, clean hair-pencil.

SPECTROGRAPHIC WORK.

For the investigation of the silica residues the methods of optical spectrography were used. The spectra were photographed with the Zeiss Three Prism Spectrograph, using the wave range from 3 900 to 4 800 Å and with the Zeiss Quartz Spectrograph Model Qu 24. The work was based on the carbon arc cathode layer or »Glimmschicht» method developed by Mannkopff and Peters (1931). A sharp image of the arc was focussed on to the spectrograph slit. Using this arrangement a series of six fractions of every sample was photographed on the same photographic plate in the visible region. In the ultra violet range five fractions were photographed on each plate.

¹ In order to get to the residues equal amounts of impurities contained in hydrofluoric and sulfuric acids, the amounts of these reagents given here were added to every portion of silica.

The width of the spectrograph slit was 0.01 mm. for both visible and ultra violet wave range.

The first exposure on each plate was made with 127 V and 5 A. The time of exposure was 40 seconds in the visible range and one minute in the ultra violet. For the other exposures the value of the current was raised to 9—10 A. Now the time of exposure was 20 seconds in the visible region and 30 seconds in the ultra violet.

Due to the scarcity of the material only one series of exposures was made of each sample.

Very pure carbon rods were used as electrodes. The diameter of the rods was 5 mm. The cathode bore was 6 mm. deep and 0.8 mm. in diameter with about 2.8 mm. outside diameter as described by Strock (1936 a, p. 175).

For the visible range Perutz Perchromo B plates and for the ultra violet Perutz Reproduktionsplatte Hart plates (photomechanical plates) were used. The developer was one for maximum contrast recommended by the maker of the plates.

The residues obtained from the rocks Nos. 9, 12, and 16 spat badly in the arc. The samples were therefore diluted with pure quartz, an amount equal to two times their weight being added, and the mixtures were homogenized by grinding in small agate mortars. Accordingly the concentrations obtained from their spectra are multiplied by three.

For the standard mixtures quartz was used as a base, to which the various elements were added in the form of oxides. The concentration steps were 1 %; 0.3 %; 0.1 %, *etc.* The mixtures were homogenized by grinding for 2 hours in clean, smooth agate mortars. When preparing the standard mixture of Ga_2O_3 the homogenization of each step mixture was carried out in a mortar of its own.

The spectrum lines used in the quantitative determinations are listed in Table II.

For the present purposes the accuracy obtained by visual estimation of the absolute intensities of the spectrum lines was considered to suffice. The comparison of the intensities was in most cases made by the aid of a Greenough type binocular microscope.

Notes concerning Table II.

G a l l i u m. Goldschmidt and Peters (1931, p. 168) report 0.0005 % as the lowest concentration of Ga_2O_3 determined in quartz or aluminium oxide base.

TABLE II.
LIST OF SPECTRUM LINES USED IN THE QUANTITATIVE
DETERMINATIONS.

Element	Line used in Å	Lowest concentration of element determined	Coincidences	References
Be	2 348.62	0.001 % BeO	none	Goldschmidt und Peters (1932, p. 363). Preuss (1935, p. 389).
Zn	3 345.00	0.01 % ZnO	none	Preuss (1935, p. 390).
Ga	2 943.65	0.001% Ga ₂ O ₃	none	Goldschmidt und Peters (1931, p. 168). Preuss (1935, p. 390).
Ge	2 651.18	0.001% GeO ₂	none	Goldschmidt und Peters (1933a, p. 144). Preuss (1935, p. 390).
Sn	3 034.12	0.001% SnO ₂	Cr 3 034.20	Goldschmidt und Peters (1933b, p. 281).
	2 421.70	0.1 % SnO ₂	none	—
Pb	2 833.07	0.001% PbO	none	Preuss (1935, p. 390).
V	4 379.24	0.001% V ₂ O ₅	none	van Tongeren (1938, p. 78).
Cr	4 254.34	0.0001 % Cr ₂ O ₃	none	Strock (1936b, p. 52). van Tongeren (1938, p. 83).
Mo	3 208.88	0.003% MoO ₃	none	Ernst und Hörmann (1936, p. 205).
W	2 896.44	0.01 % WO ₃	none	—
Co	3 453.51	0.003% Co ₃ O ₄	none	Strock (1936b, p. 52). Preuss (1935, p. 390).
Ni	3 414.77	0.0003% NiO	V 3 414.77 (?)	Ernst und Hörmann (1936, p. 205). Preuss (1935, p. 390).

Tin. The line 3 034.12 was used except in samples containing 0.3 %, or more Cr₂O₃. The coinciding chromium line at 3 034.20, however, was found to be very weak at 0.3 % Cr₂O₃, and to disappear at 0.1 % Cr₂O₃. Therefore the tin line mentioned above could be used in most cases.

Goldschmidt and Peters (1933 b, p. 281) report 0.0005 % SnO₂ as the lowest concentration obtained by the line 3 034.12 in a base of aluminium oxide with 30 % ferric oxide.

The SnO₂ percentages of the samples 9, 10, 11, and 12 were determined by the aid of the tin line 2 421.70, which can be followed down to 0.1 % SnO₂. The other tin lines given by Goldschmidt and Peters could not be used here, due to coincidences arising from the strange

composition of the residues, markedly differing from the composition of the rocks.

V a n a d i u m. For the line 4 379.24 van Tongeren (1938, p. 78) has reached the limit of determination at 0.00003 % V_2O_5 in samples diluted by half their weight of sodium carbonate.

C h r o m i u m. The end member of the series of standard mixtures used for this study contained 0.0001 % Cr_2O_3 . In this the chromium line 4 254.34 was still visible. Strock (1936 b, p. 52) gives 0.00002 % Cr_2O_3 as the lowest concentration obtainable with this line, according to unpublished results by Goldschmidt, Witte, Bauer, and Hörmann. van Tongeren (1938, p. 83) has determined concentrations as low as 0.00003 % Cr_2O_3 in samples diluted with sodium carbonate.

M o l y b d e n u m. Ernst and Hörmann (1936, p. 205) give 0.005 % MoO_3 as the lowest concentration determinable by the line 3 208.88.

T u n g s t e n. The line 2 946.98 has been used by Preuss (1935, p. 390) in analyses of tectites. The lowest concentration obtained by this line lies at 0.03 % WO_3 . As for line 2 896.44 used here, no data are given in literature concerning the limit of concentration reached.

C o b a l t. According to unpublished results by Goldschmidt, Witte, Bauer, and Hörmann the lower limit of determination for the line 3 453.51 lies at 0.005 % Co_3O_4 (See Strock, 1936 b, p. 52).

N i c k e l. Ernst and Hörmann (1936, p. 205) give 0.0005% NiO for the line 3 414.77 as the lower limit of determination.

In a list of the lines of the vanadium spectrum Meggers and Russell (1936, p. 161) present a strong line at 3 414.77, explaining that the vanadium line is masked by nickel. This probably means that the presence of a vanadium line at 3 414.77 cannot be established, due to the coinciding nickel line which arises from the nickel contained in the vanadium sample investigated. A coincidence of vanadium therefore is not to be feared here.

IMPURITIES CONTAINED IN REAGENTS AND IN FILTER PAPERS.

Blanks were run of the reagents and filter papers used in this study. The amounts of the quantitatively determined oxides are shown in Table III. These values have led to corrections for the percentages of the different oxides, obtained in the analyses of the rocks and residues. Accordingly, the corrected percentages of the oxides are given in Table V.

The carbon electrodes and carbon powder were found to contain none of the oxides of which quantitative determinations are presented in Table V. The carbon powder contained 0.015 % of non-volatile constituents. The elements determined qualitatively in the electrodes were Al (trace), B, Ca, Mg (trace), and Si (trace). In addition Fe was found to be present in the carbon powder.

The quartz base contained the following elements: Al, Ca, Fe, and Mg.

In order to study the impurities contained in the filter papers, 200 Schleicher und Schüll »Weissband» quantitative filters of 11 cm. diameter were incinerated in a platinum crucible. The residual ash weighed 14 mg. It was found to be partly molten, due to its content of salts, probably chlorides and fluorides. The spectra of the ash showed the presence of the following elements determined qualitatively in addition to the quantitative determinations of Table III: Al, Ba, Ca (much), Cu, Fe, K, Mg (much), Mn, Na, Pt (from the crucible), Sb (trace), Si, Sr, Ti, and Zr (trace). Of the lanthanides Sc, Y (much), and La were present. As for Ce, Pr, and Nd, their lines were not visible, due to covering strong neighbouring lines.

Preuss (1935, p. 380) gives a list of the easily volatile impurities contained in the filter papers. The presence of K and Pb in the filters has, however, not been established by him. As an explanation of this the differences in composition of filter papers are to be considered as well as the minute amounts of elements contained in only one filter paper. Accordingly the determination of some elements fails, except when a sufficient amount of filter ash is investigated.

In order to study the impurities contained in hydrochloric acid and ethanol, 2 ml. of ethanol and 80 ml. of concentrated hydrochloric acid were evaporated down nearly to dryness in a platinum crucible. Carbon powder was added, the evaporation completed, and the excess of carbon burnt off. After this procedure the impurities were contained in a small amount of carbon powder, nearly corresponding to the biggest amounts of the residues obtained.

The corrections arising from these impurities are legitimate, assumed that the silica really retains all the metals contained in hydrochloric acid and ethanol. The removal of the excess of carbon powder was carried out in order to treat the impurities in the same way as the silica is treated. Therefore the easily volatile compounds originally contained amongst the impurities are thought to be lost, at least partly.

The elements qualitatively determined in hydrochloric acid and ethanol were: Al, Ca, Fe, Mg, Na (trace), (Pt), and Si.

The impurities contained in hydrofluoric and sulfuric acids were determined by evaporating 2 ml. H_2SO_4 (1:1), 30 ml. distilled water, and 30 ml. hydrofluoric acid (40 %) down to dryness in a platinum crucible together with carbon powder. The excess of carbon was burnt off. The impurities were now concentrated in a small amount (35 mg.) of carbon powder.

Table III gives the quantitative determinations of the impurities. The elements determined qualitatively were: Al, Ba, Ca, Fe, K, Mg (much), Mn, Na, (Pt), Sr, Ti (trace), and Zr. In addition, Sc, Y, La, Ce, and Nd were found to be present.

TABLE III.

PERCENTAGES OF IMPURITIES CONTAINED IN THE REAGENTS.

	PbO	ZnO	Ga ₂ O ₃	GeO ₂	SiO ₂	PbO	Y ₂ O ₃	Cr ₂ O ₃	MnO ₂	WO ₃	Co ₂ O ₄	NiO
Quartz base..	≪ 0.001	0	0	0	0	0	0	0	0	0	0	0
Ash from filter papers	0	0.3	0	<0.001	0.3	1	0.03	0.06	0	0	0	0.01
Residue from HCl and C ₂ H ₅ OH	0	0.03	0	0	<0.001	0.01	0	0.0001	0	0	0	0.001
Residue from H ₂ O, H ₂ F ₂ , and H ₂ SO ₄	0	0.1	0	0	0.001	0.03	0.001	0.003	0	0	0	0.003
Anhydrous sodium carbonate	0	0	0	0	0	0	<0.001	0	0	0	0	0

The anhydrous sodium carbonate used as flux was found to contain the following elements qualitatively determined: Ba (trace), Ca, Fe (trace), and Sr.

RESULTS FROM CHEMICAL TREATMENT.

The amounts and percentages of the silica residues obtained from different rocks are shown in Table IV. This table also contains certain facts concerning the amount of recovered silica.

TAB-

AMOUNTS AND PERCENTAGES OF RECOVERED

	1.	2.	3.	4.	5.	6.	7.
	Light gray granite, Loppjärvi.	Granite, Huopalahti.	Natanson granite, Sodankylä.	Granodiorite, Vitasaari.	Quartz diorite, Peksauro.	Quartz diorite, Tykkimäki.	Gabbro, Sodankylä.
Silica recovered in g.	2.2883	2.2367	2.1844	1.9141	1.7153	1.6835	1.4289
Recovered silica per cent of the rock	76.28	74.56	72.81	63.80	57.18	56.12	47.63
Residue recov- ered in g.	0.0130	0.0143	0.0161	0.0339	0.0211	0.0451	0.0128
Residue per cent of silica	0.57	0.64	0.74	1.77	1.23	2.68	0.90
Residue per cent of the rock ...	0.43	0.48	0.54	1.13	0.70	1.50	0.43
Color of the re- sidue	brown	pale brown	dirty brownish yellow	dirty brownish yellow	dirty yellowish	grayish brown	brownish yellow

The residual sulfuric acid solution from quartz diorite, No. 6, contained white insoluble particles, probably due to its content of alkaline earth sulfates. The residual solution from basic vein, No. 10, was green. The color arises from the high chromium content of the separated silica.

RESULTS FROM SPECTROGRAPHIC WORK.

The spectrographic study of the material was carried out in two divisions, the first of which covers quantitative analyses of a number of oxides, many of which are not usually determined in the course of routine rock analysis. The second part deals with elements whose presence only is established. At the same time the intensities of the lines in the rocks and their residues are compared. Amongst the elements of this group are all those, whose oxides belong to the main constituents of the rocks. Due to their high percentages, which in most cases exceed the upper limit of concentrations determinable by the aid of optical spectrography their quantitative determination was not even attempted.

LE IV.

SILICA AND OF THE SILICA RESIDUES.

8. Pyroxenite, dolerite, Värpönsaari.	9. Pyroxenite, Leppävirta.	10. Basis yelm, Peksauro.	11. Perkante, Sodankylä.	12. Syenite, Muonio.	13. Syenite, Miesä.	14. Syenite, Kolari.	15. Nephelite, sye- nite gneiss, Kittiläsvaara.	16. Keratoklyf, Peksauro.
1.5338	1.4879	1.3190	1.2623	1.7678	1.8039	1.7332	1.6958	1.6638
51.13	49.60	43.97	42.08	58.93	60.13	57.77	56.53	55.46
0.0339	0.0164	0.0197	0.0195	0.0324	0.0160	0.0246	0.0312	0.0239
2.21	1.10	1.49	1.54	1.83	0.89	1.42	1.84	1.44
1.13	0.55	0.66	0.65	1.08	0.53	0.82	1.04	0.80
pale brownish yellow	dirty yellow	yellowish brown	dirty yellowish	pale brownish yellow	brownish yellow	yellowish brown	dirty brown	dirty brownish white

QUANTITATIVE RESULTS.

The corrected percentages (cf. p. 13) for the different oxides determined quantitatively in the rocks and residues are presented in Table V. Where the intensity of a line was found to be intermediate between two steps of the concentration series, the average concentration was chosen, *e. g.* 0.2 between 0.3 and 0.1, 0.06 between 0.1 and 0.03.

Notes on Table V.

Since it lies beyond the scope of this work to discuss the actual percentages of the elements in different kinds of rocks, no attention is here paid to such considerations. Of more importance is here the determination of the ratio of concentration for an oxide when a given rock and the silica residue obtained from it are considered. When the percentage of an oxide is decidedly greater in the residue than in the rock we are dealing with a case of enrichment. One percentage is here considered to be decidedly greater than another when there is a difference in the order of magnitude of the percentages.

TAB-

PERCENTAGES OF QUANTITATIVELY DETERMINED

No.	Rock	BeO	ZnO	Ga ₂ O ₃
1	Light gray granite. Leppävirta.	0	0.01	0.01
	Residue	0.001	0	0.1
2	Granite. Huopalahti	« 0.001	0.02	0.01
	Residue	0.001	0	0.1
3	Nattanen granite. Sodankylä	« 0.001	0.03	0.01
	Residue	0.001	0	0.03
4	Granodiorite. Viitasaari	< 0.001	0.1	0.003
	Residue	0.001	0.2	0.01
5	Quartz diorite. Petsamo	« 0.001	0.1	0.001
	Residue	< 0.001	0.2	0.01
6	Quartz diorite. Pylkönmäki	0.001	0.03	0.003
	Residue	0.01	0.2	0.01
7	Gabbro. Sodankylä.	0	0.1	0.003
	Residue	« 0.001	0.2	0.001
8	Pigeonite dolerite. Varpaisjärvi	« 0.001	0.1	0.003
	Residue	« 0.001	0.2	0.001
9	Pyroxenite. Leppävirta.	0	0.3	0.001
	Residue	< 0.001	∞	0.001
10	Basic vein. Petsamo	« 0.001	0.03	0.001
	Residue	< 0.001	0.2	0.003
11	Perknite. Sodankylä	0	0.03	0.003
	Residue	< 0.001	0.2	0.003
12	Syenite. Muonio	< 0.001	0.3	0.003
	Residue	< 0.001	∞	0.003
13	Syenite. Nilsjä	< 0.001	0.01	0.003
	Residue	0.001	0	0.1
14	Syenite. Kolari	« 0.001	0.1	0.001
	Residue	0.001	0.2	0.03
15	Nephelite syenite gneiss. Kiihtelysvaara	< 0.001	0.1	0.01
	Residue	0.01	0.2	0.03
16	Keratophyr. Petsamo	« 0.001	0.3	0.003
	Residue	< 0.001	∞	0.003

¹ If present, less than 0.1 %.

LE V.

OXIDES IN ROCKS AND IN THEIR SILICA RESIDUES.

GeO ₂	SnO ₂	PbO	V ₂ O ₅	Cr ₂ O ₃	MoO ₃	WO ₃	Co ₃ O ₄	NiO
0	0	0	0.003	0.0003	0	0	0	≪ 0.0003
0.03	0.02	1	0.004	0.03	0.003	0	≪ 0.003	0.03
0	0	0.003	0.01	0.001	0	0	0	< 0.0003
0.003	0.02	1	0.001	0	0	0	0	0.006
0	0	0.001	0.03	0.001	0	0	0	≪ 0.0003
0.01	0.1	0.3	0.02	0.006	0.003	0	0	0.006
0	< 0.001	0	0.1	0.006	0	0.01	≪ 0.003	≪ 0.0003
0.01	0.003	0	0.06	0.006	0	0.01	0	0.006
0	< 0.001	0	0	< 0.0001	0	0	≪ 0.003	≪ 0.0003
0.01	0.1	1	0	0.06	0	0	≪ 0.003	0.1
0	< 0.001	0	0.3	0.06	0	0.02	< 0.003	0.0003
0.01	0.03	1	0.1	0.006	0	0.02	≪ 0.003	0.03
0	< 0.001	0	0.3	0.1	0	0.02	< 0.003	0.003
0.03	0.02	1	0.3	0.03	0	0.02	0	0
0	0	0	0.2	0.03	0	0.03	< 0.003	0.003
0.01	0.02	0.3	0.3	0.03	0	0.02	0	0
0	n. d. ¹	0	0.3	0.3	0	0.06	0.003	0.01
0.01	< 0.1	0.3	0.6	0.3	0	0.01	0	0.03
0	n. d. ¹	0	0.3	∞	0	0.02	0.003	0.3
0.01	< 0.1	0.3	0.3	∞ ²	0	0.01	≪ 0.003	0.03
0	n. d. ¹	0	0.3	∞	0	0.03	0.003	0.1
0.01	< 0.1	1	0.3	∞ ²	0	0.01	0	0.03
0	0	< 0.001	0.3	0.06	0	0.01	≪ 0.003	0.001
0.03	< 0.1	1	0.3	∞	0	0	0.003	0.02
0	< 0.001	0	0.06	0.001	0	0	0	< 0.0003
0.02	0.1	1	0.1	0.006	0	0	0	0.03
0	0	< 0.001	0.2	0.03	0	0.02	≪ 0.003	0
0.03	0.1	1	0.1	0.03	0	0	0	0.03
0	0.001	0	0.1	0.0003	0	0	0	0.0003
0.01	0.06	0.3	0.03	0	0	0.01	0	0.002
0	0	0	0.2	0.0003	0	0.02	< 0.003	0
0.01	0.06	1	0.2	0.006	0	0	0.003	0.03

² Line stronger than that from the rock.

In the following, each of the elements is discussed separately.

Beryllium. Decided enrichment only in a few cases. There seems to be, however, a general tendency towards enrichment of beryllium in the separated silica.

Zinc. Decided enrichment is found in six residues, a tendency towards an enrichment in as many cases. The other residues, from rocks containing small percentages of ZnO, show impoverishment in zinc.

Gallium. Enrichment in seven and impoverishment in two residues.

Germanium. All the residues are very decidedly enriched in germanium.

Tin. In all but one of the residues a marked enrichment is found to be present, the residues rich in chromium (9—12) being left out of consideration.

Lead. A strong enrichment of lead is found in the residues.

Vanadium. Enrichment is present only in a single case. The general tendency seems to be against an enrichment of the residues in vanadium.

Chromium. Positive enrichment is found in as many cases as an impoverishment. There seems to be a slight tendency towards enrichment of chromium in the residues.

Molybdenum. No conclusions can be drawn, due to the lack of an adequate amount of facts.

Tungsten. The results are against an enrichment of tungsten in the silica residues.

Cobalt. No enrichment of cobalt is present in the residues.

Nickel. Impoverishment is evident in four residues. The others show an enrichment of nickel in the residues.

QUALITATIVE RESULTS.

Rare Earths (including scandium and yttrium). Lanthanum was found to be present in the rocks, excepting in Nos. 7, 8, 9, 10, and 11. When there were lanthanum lines present in the spectra of the residues they were weaker than those in the spectra of the original rocks. Cerium was present in the rocks, excepting in Nos. 4, 5, 8, 9, 10, 11, and 16. In No. 7 the presence of the Ce line at 4222.62 Å could not be established, due to covering strong neighbouring lines. In the residues Nos. 5, 8, 9, and 16 no cerium lines were present. The residues

Nos. 10, 11, 12, and 15 showed Ce lines. In the last two the lines were weaker than in the corresponding rocks. Praseodymium was detected only in rock No. 15. The corresponding residue contained none of this element. The other residues were either free from praseodymium or there were strong neighbouring lines present by which the place of the Pr line used ($4\ 223.00\ \text{\AA}$) was hidden. Neodymium was found in the rocks Nos. 2—6, and 12—16. Due to strong neighbouring lines the presence of a Nd line at $4\ 325.77\ \text{\AA}$ could be traced only in residues Nos. 12, 14, and 16. These residues, however, were found to be free from Nd. Scandium was invariably found to be present in the rocks. The Sc lines from the residues were weaker than those from the rocks. Only one residue, No. 15 was free from scandium. All the rocks except Nos. 10 and 11 showed yttrium lines. In every residue yttrium was present. In six residues the lines were stronger than in the corresponding rocks; in four cases they were weaker. In many cases, however, the lines of scandium and yttrium might be due to the impurities contained in the reagents.

According to the above, the rare earths do not seem to be willing to enrich in the silica residues, though some of them may be found present therein.

Aluminium. The lines of this element were present in the spectra of each residue, being usually weaker than in the corresponding spectra of the rocks. In three cases the intensity ratio was about the same.

Barium. This element was present in every rock except No. 11. All the residues showed Ba lines, but in some cases their Ba content arises from the impurities of the reagents. According to the intensities Ba is not likely to enrich in the silica residues.

Calcium. Every one of the residues showed stronger Ca lines than those obtained from the rocks.

Iron. This element invariably contaminated the residues.

Potassium. Present in each residue. Due to the strong ignition of the residues this element must partly have been volatilized.

Magnesium. Present in each residue. In some cases the lines in the spectra of the residues are decidedly stronger than those in the spectra of the rocks, but no general idea can be gained as to the enrichment due to the magnesium content of the reagents.

Manganese. Every residue showed manganese lines, in many cases stronger than in the corresponding rocks. Manganese therefore regularly seems to be a constituent of the silica residues, even with regard to the manganese content of the reagents.

Sodium. Present in every residue, but its amount must have been diminished during the ignition.

Strontium. Present in each residue. Usually the intensities of the lines in a residue and in the corresponding rock are similar. The presence of Sr in the silica residues is without doubt regular.

Tellurium was found neither in the rocks nor in the residues.

Thallium. The rocks and their residues were invariably free from this element.

Titanium. Strong Ti lines were present in each residue. The lines were always stronger than those obtained from the rocks. By this fact the well-known enrichment of titanium in the residues is once more confirmed.

Zirconium. This element was found in every rock and every residue. The intensities of the zirconium lines from the residues were either superior to those from the rocks, or they both showed the same values. Accordingly we deal with an enrichment of zirconium in the residues left from silica.

Platinum. Lines due to contamination from platinum vessel, were present in each residue. In the rocks no platinum was found since the percentage of Pt in the rocks usually is too small to be determined without a microdokimastic pre-enrichment.

Antimony. Lines of this element were not found in any of the spectra of the rocks. Every residue, on the contrary, showed weak Sb lines, but these were due to the antimony content of the filter papers.

The determination of sulfur and phosphorus in the residues had to be passed over owing to the lack of suitable arc lines situated in the wave ranges used. For the same reason also columbium and tantalum, though interesting elements, were left out of consideration.

CAUSES OF THE PRESENCE OF CONTAMINANTS IN THE SILICA.

As an explanation of the presence of impurities in the silica it is very commonly assumed that from the chloride solution basic salts formed by hydrolysis are thrown down and carried away by the silica. The property of silica of carrying down such metals as titanium, aluminium, and iron is attributed to the fact that the negatively charged gelatinous silica, being a hydrogel of silicic acid, possesses rather strong adsorptive powers. As stated, *e. g.*, by Kolthoff and Sandell (1937, pp. 381—384) small amounts of basic salts of the metals mentioned

above, and even of other metals, are tenaciously held by the hydrous silica. These salts cannot be removed entirely by washing with dilute hydrochloric acid. On the other hand, the alkaline earths and the alkalis are not likely to be present in the silica in significant amounts, »chiefly because the salts of these metals do not hydrolyze to form slightly soluble basic salts».

Still another group of substances found in the silica is presented by Kolthoff and Sandell. To this group belong the substances which are insoluble *per se*. As an example titanium phosphate is given. This compound is only slightly soluble in dilute acids. Another example is furnished by calcium sulfate, which is left in the silica, due to insufficient washing.

The forming of basic salts by hydrolysis has been discussed already by Lenher and Truog (1916, p. 1 055). They state that ferric chloride by hydrolysis partly changes to oxide and oxychloride which contaminate the silica. Hydrolysis is, however, assumed to be only one cause of the contamination, but adsorption as a cause would hardly seem plausible according to these authors.

Beger (1928, p. 244), when discussing the causes of the presence of contaminants in the silica states that there might be possibilities of a strong adsorption by the gelatinous silica. This would cause enlarging of the residue with increasing amounts of silica. As is well-known, the silica from the second or third evaporation always contains more impurities than that from the first. The amount of the late silica is very small, however, (usually a few milligrams only), and accordingly the possibilities of adsorption are excluded.

Hydrolysis during the evaporation might, according also to Beger 1928, p. 247), represent a possible cause of contamination. Here one has to allow for the temperature, concentration of the acid, and other factors involved.

None of the causes referred to above is assumed to suffice alone to explain the presence of the impurities in the silica. Evidently there must be several factors co-operating. Two of these factors have been mentioned before: contamination of the silica 1) by compounds insoluble *per se*, 2) by adsorption of slightly soluble substances produced during hydrolysis. In addition the presence of 3) ionic sorption controlling the presence of many a rarer element in the silica is suggested.

Compounds Insoluble *per se*. The presence of zirconium and phosphorus in the silica is explained by the fact that zirconium is quantitatively precipitated by the phosphate ion in the form of secondary phosphate even in solutions containing a large excess

of concentrated hydrochloric acid. Since the oxychloride of zirconium is readily soluble it might well be possible that the zirconium is quantitatively retained as secondary phosphate in the silica. This is further supported by the fact that only a part of the phosphorus of the rock is present in the silica according to Aourousseau (1923, p. 331) and Beger (1928, p. 242).

Also a small part of titanium might be retained as titanium phosphate in the silica as presented by Kolthoff and Sandell (1937, *l. c.*). If much titanium were carried away by phosphorus, the P_2O_5 content of the residues ought to enlarge, but this is not the case.

The presence of Ba and Sr in the residues can be explained assuming that these elements are precipitated in the form of insoluble sulfates which are retained by the silica. Hillebrand and Lundell (1929, p. 726) communicate that barium is rarely present in the residues since it is a very minor constituent of most rocks and since $BaSO_4$ is appreciably soluble in hot hydrochloric acid.

The average amounts of barium and strontium present in the eruptive rocks are, according to Goldschmidt (1937 b, p. 100): Ba 250 g./ton and Sr 150 g./ton. When these numbers are compared with the average amount of sulfur in the eruptive rocks: 520 g./ton, the conclusion can be drawn that both Ba and Sr are quantitatively precipitated as sulfates contaminating the silica. As for their solubilities, strontium sulfate, being the more soluble, is leached out from the silica in a greater degree than the corresponding barium compound. The amounts of barium and strontium deposited in the silica are still large enough to allow them to be detected in the residues by the highly sensitive spectrochemical methods.

A part of the calcium present in the residues may be attributed to calcium sulfate contaminating the silica, due to insufficient washing. The greater part of calcium most probably is retained by the silica as calcium chloride when the washing of the silica has been defective, especially when the silica rendered insoluble partly consists of small lumps. From the inner parts of these lumps the impurities escape only with difficulty.

Adsorption of the Products Formed by Hydrolysis. This explanation has already been discussed (cf. p. 22). We find here a cause of the presence of titanium, iron, and aluminium in the residues from silica. Relatively large amounts of these elements have been found to be present in the residues by Aourousseau (1923, p. 331) and by Beger (1928, p. 242). The greater part of these impurities is retained by the silica from the first evaporation. The silica

residue from the second and third evaporation seems to contain mostly ferric oxide.

Another explanation lies in the mutual coagulation of two oppositely charged colloids. Silica is always negatively charged. The colloid hydroxides of aluminium, ferric iron, trivalent chromium, titanium and even of zirconium show a positive charge. According to the studies by Schwarz and Brenner (cf. Noll, 1931, p. 560) silica and aluminium hydroxide are coagulated already from a solution containing about 0.1 per cent of both Na_2SiO_3 and AlCl_3 . As trivalent chromium is present in the chloride solution, its presence in the residues could be explained in this way.

Ionic Sorption. The presence of most of the minor constituents in the silica residues is assumed to be controlled by ionic sorption.

The ionic sorption discussed here is a purely physical surface attraction termed adsorption. Several factors ruling over the adsorption of the ions are given by Noll in an important paper (1931) to which the reader is referred. As essential for this study ionic charge is mentioned here. According to Schultze's law (cf. Noll, 1931, p. 563) the adsorption increases with enlarging ionic charge.

In physical chemistry a function called ionic potential has been found to be of great importance by Cartledge (1928, p. 2855). This function is obtained by division of ionic charge (Z) by ionic radius (r). Thus,

$$\text{Ionic potential, } \phi = \frac{Z}{r}.$$

The importance of the ionic potential for geochemical considerations has been discussed by Goldschmidt (1937 a, pp. 664—668) with especial reference to the cycle of sediment formation in nature. With respect to ionic potential the elements are divided into three groups. Cations with low ionic potential remain in true ionic solution in the processes of weathering and transportation. Metals with intermediate ionic potential are precipitated by hydrolysis, and elements with still higher ionic potential form complex anions containing oxygen and being usually again soluble. To the second group belong many elements which are found concentrated in hydrolysate sediments, such as clays, bauxites and mudstones.

Since some of the rarer elements are enriched in the silica residues as well, it was thought to be worth while trying to consider the enrichment on the basis of ionic potential of the different impurities. To illustrate the ionic potential, Figure 1 is presented.

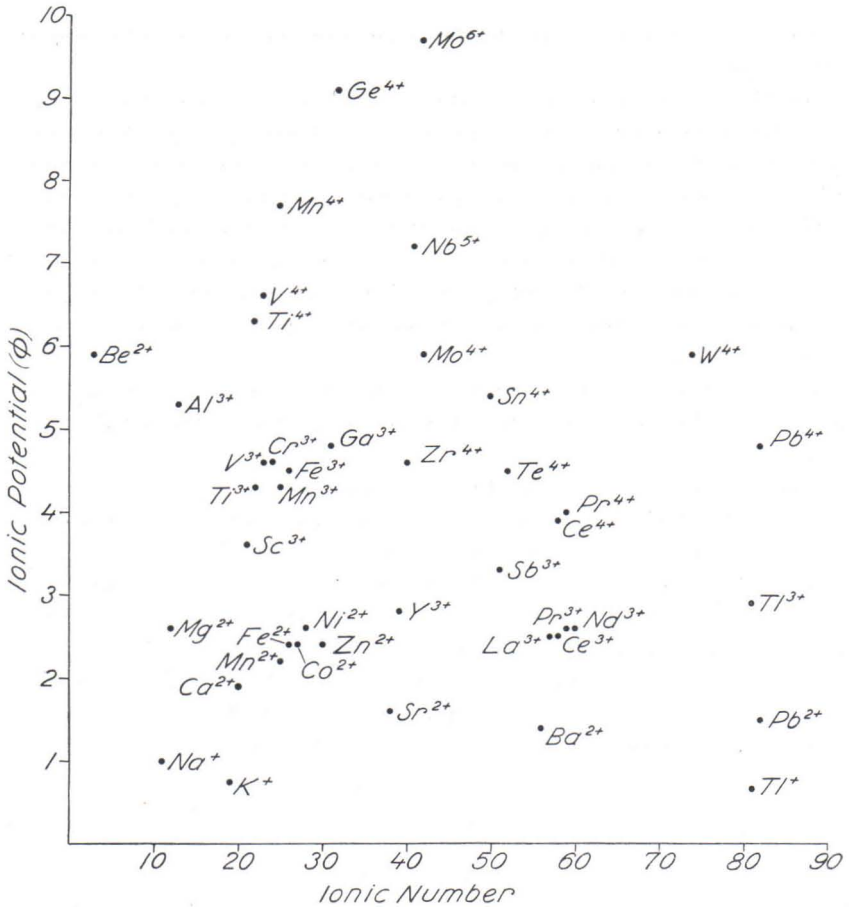


Fig. 1.

Of the impurities discussed in a previous chapter (pp. 16—22) the following were found to be especially enriched in the silica residues: Ge, Sn, Pb, Ti, and Zr. A tendency to enrich in the residues is present by Be and Ga. Under some circumstances even Zn, V, Cr, Sc, Y, Al, Mg, Ni, and Mn might be enriched. No enrichment is found for W, Co, La, Ce, Pr, Nd, Ba, Ca, K, Na, and Sr. The causes of the presence of some of these elements have been already discussed.

The ionic potential of the quadrivalent elements Ge, Sn, Pb, Ti, and Zr is high enough to cause a very strong enrichment of these elements in the silica. In rocks high in zirconium and low in phosphorus, where the amount of the latter is insufficient to throw the former

completely down as phosphate, the enrichment of zirconium in the residues is explained by the ionic potential. According to Goldschmidt (1937 b, p. 100) the average amounts of these elements in eruptive rocks are: Zr 220 g./ton and P 800 g./ton, and accordingly the amount of phosphorus is in excess over that of zirconium. For most rocks the formation of zirconium phosphate therefore seems to be plausible.

The ionic potential of bivalent lead is too low to cause a quantitative precipitation. The lead can, however, be assumed to be present in the sodium carbonate melt as plumbate¹. By the presence of quadrivalent lead the strong enrichment in the silica is easily explained.

Quadrivalent tin is present in the chloride solution. The strong enrichment of this element is well explained by its high ionic potential.

With further reference to Fig. 1 one can find explanations also regarding the enrichment of beryllium and gallium. The ionic potentials of trivalent Cr, V, and Sc are still high enough to allow them to enrich in the silica. Even for aluminium and ferric iron the ionic potentials lie in a favourable range.

Of the elements which are not enriched in the silica K, Na, Ba, Sr, and Ca have ionic potentials falling below 2, by which the behaviour of these elements can be explained.

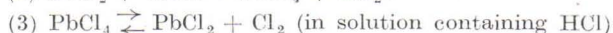
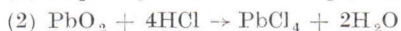
Molybdenum has been found present in two residues only. Both these cases show an enrichment. According to its ionic potential molybdenum is able to enrich in the silica. This also agrees with the grouping of the elements presented by Goldschmidt (1937 a, p. 665).

Tungsten, most probably, is present in the chloride solution in the form of sodium tungstate, and as such escapes from the silica.

No attention has as yet been paid to the elements Mg, Mn, Co, Ni, Zn, and the lanthanides. With regard to the ionic potential these form an intermediate group between the cations and the elements of hydrolysates. The limit between these two last mentioned groups is thought to lie at an ionic potential of about 2.6. The ions situated in the border region due to their position are thought to be able to enrich or not to enrich in the silica. The limit of enrichment, in addition, seems to be unstable, as is illustrated below.

It is a well-known fact that when the dehydration of the chlorides

¹ Assumed that calcium orthoplumbate is present in the melt the following reactions take place during the solution of the cake:



in the determination of silica is carried out in temperatures above 100°C , the amount of the impurities in the silica is increased. Lenher and Truog (1916, p. 1055) state that if the temperature of dehydration exceeds 115°C the silica becomes contaminated by lime and magnesia. According to Bloor (1907, p. 1604) dehydration at 125°C does not materially increase the amounts of alumina and ferric oxide in the silica. The amounts of lime and magnesia, on the other hand, are enlarged.

Also other factors evidently have influence upon the ionic sorption, and, especially, upon the limiting cases discussed above. Such factors are concentration of hydrochloric acid in the solution, that of the other salts present, and the contemporaneous presence of many ions in the same solution. In matters concerning these factors the reader is referred to the paper by Noll (1931) cited above. We may here only note that there are ions showing privileged sorption and that when there are several ions present at the same time, their sorptivity decreases (cf. Noll, 1931, pp. 566—567).

Still another factor might have influence upon the composition of the silica residue. Some of the oxides discussed above are apt to volatilize already at comparatively low temperatures. Thus molybdenum trioxide, MoO_3 , volatilizes at a temperature of 610°C . Also vanadium pentoxide, V_2O_5 , is found to volatilize when chlorides of alkalis or alkaline earths are present. If vanadium volatilizes it must escape from the silica before the chlorides contained therein are converted into sulfates by sulfuric acid.

The presence of alkalis in the residue has been discussed by Kuzirian (1914, p. 61) with the result that sodium and potassium may be present. On the contrary, Lenher and Truog (1916, p. 1063) state that no sodium is present in the residue, and according to Hillebrand and Landell (1929, p. 726) the residue is free from sodium chloride. Kolthoff and Sandell (1937, p. 385) find the presence of alkali chlorides very objectionable except when the washing after a sodium carbonate fusion has been incomplete.

According to the results of the spectrum analyses presented before, the silica, even after very careful washing, contains traces of both sodium and potassium, evidently in the form of chlorides. Therefore the possibility of volatilization of a part of vanadium might not entirely be excluded.

A natural cause for the presence of sulfur in the silica residue lies in the treatment by sulfuric acid. On the other hand, this element is present already in silica in the form of the insoluble sulfates referred

to above. According to Kuzirian (1914, p. 63) the refractory alkali sulfates, and those of Mg, Ca, and Ba by blasting in a large degree remain in the state of sulfates. The volatilization of a part of the alkali sulfates is thought to be possible.

ANALYTICAL CONCLUSIONS.

It is generally assumed that the amount of the nonvolatile residue is very much higher in basic than in acidic rocks, as stated, *e. g.*, by Lenher and Truog (1916, p. 1 056). On the other hand, the quantitative studies by Arousseau (1923, p. 330) and Beger (1928, pp. 241—243) show that the residues obtained from the same rock by different fusions are unlike in quantity and appearance, even under conditions of work kept as constant as possible. In accordance with this is the statement by Hillebrand and Lundell (1929, p. 725) that with different rocks the qualitative composition of the residues varies less than the quantity.

In order to illustrate the amount of the residues as a function of the chemical composition of rocks, Figures 2 and 3 are presented¹.

As is shown by Fig. 2, the amount of the residue neither increases nor decreases parallel to the silica percentage. This is in accordance with the statement by Beger (1928, p. 246). The explanation hereof

¹ In Figs. 2 and 3 the numbers refer to Table I. In addition the andesite analyzed by Arousseau (1923, p. 332) is presented (No. 17) as well as the rocks analyzed by Beger (1928, p. 240): Proterobase XXII (No. 18), and Proterobase XXIV (No. 19).

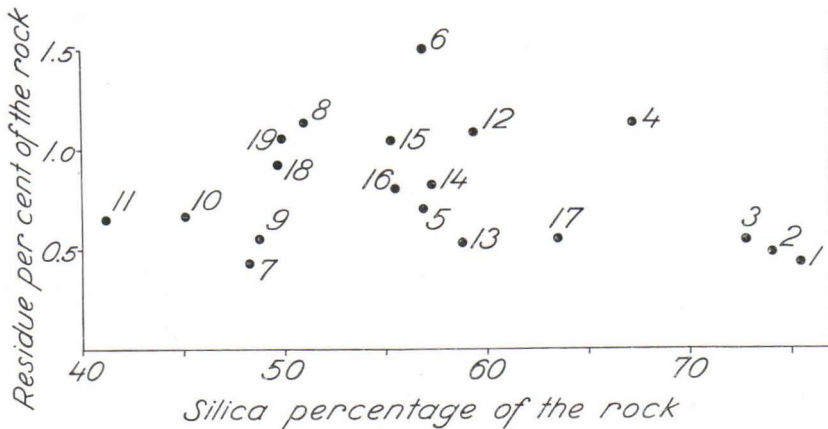


Fig. 2.

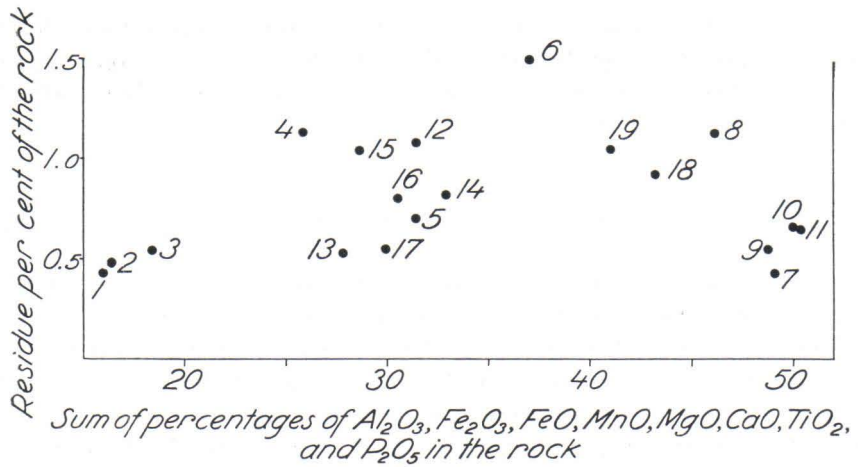


Fig. 3.

is that from this point of view alkalis and the volatile constituents of a rock are included amongst the basic ones. The conditions might be better represented by Fig. 3, in which the sum of the main constituents of the residues, *i. e.* those quantitatively determined by Aurousseau and Beger, is used as a basis instead of silica.

Even Fig. 3 shows no evident relation between the general chemical composition of a rock and the silica residue obtained from it. Not even for the main constituent of the residues, titania, can a relation between the percentage and the amount of the residue be established.

According to Beger (1928, p. 246) there might be evidence of a relation between the amount of the residue and the chlorides present in the solution rather than between the amount of the residue and that of separated silica. The results of the spectrum analyses presented before do not allow of any pros and cons in regard to Beger's theory.

As for the subsequent treatment of the silica residue in the course of analysis, the residue should be fused with sodium carbonate and added to the filtrate from silica if great accuracy is called for. In this respect the opinions of the various authors coincide (*cf.* Bloor, 1907, p. 1 606; Lenher and Truog, 1916, p. 1 062; Aurousseau, 1923, p. 332; Beger, 1928, p. 248).

As a summary concerning the constituents found in the residues from silica we may state that the presence of the following elements has been established, some of which have not previously been reported as constituents of the silica residue: Al, Ba, Be, Ca, Ce, Co, Cr, Fe,

Ga, Ge, K, La, Mg, Mn, Mo, Na, Ni, Pb, (Pt), Sc, Sn, Sr, Ti, W, V, Y, Zn, and Zr.

When these results are compared with those obtained by Cissarz (1930, p. 333) the following is to be taken into consideration. According to Cissarz vanadium is strongly retained in silica. This effect is here weaker, probably due to the partial volatilization of V_2O_5 . For tungsten the sorption in silica noticed by Cissarz is high. The author's analyses show contrary results. As for lead, only moderate amounts are carried away by silica in the analyses by Cissarz. Strong enrichment in silica is, however, noticed here.

GEOCHEMICAL CONCLUSIONS.

The results of this piece of work seem to provide examples somewhat analogous to those presented by Goldschmidt (1937 a, p. 667) concerning the removal of some elements from sea water. According to Goldschmidt beryllium, gallium, tin, titanium and zirconium are found to be concentrated in bauxites. An analogous tendency for these elements to enrich in silica is shown by the results of the present study. Also vanadium is found by Goldschmidt to be somewhat concentrated in some bauxites. Assumed that the vanadium pentoxide partly has volatilized from silica, a corresponding tendency to enrich might be present also in the separated silica.

The lanthanides, including scandium and yttrium, are as a rule not found to be concentrated in typical bauxites as stated by Goldschmidt. As for the lanthanides, concordant results have been obtained from the present study. Yttrium and, especially, scandium might, however, under some circumstances tend to enrich in the silica.

As a possible explanation of this deviation the influence of temperature can be brought forward. According to Goldschmidt (1937 a, pp. 665, 666) calcium, strontium, and magnesium remain in sea water in true ionic solution due to their low ionic potential. The temperature in which the sorption in the hydrolysate sediments takes place is a comparatively low one. In this temperature range yttrium, and even scandium, also remain in solution. According to these facts the limit between cations and the elements of hydrolysates at this temperature seems to lie at an ionic potential of about 3.8.

When the dehydration of the silica is carried out on a steam-bath, *i. e.* in a temperature of 90° — 95° C, the limit between the two groups of ions is thought to lie at an ionic potential of about 2.6 as has been

supposed before (cf. p. 27). Support for this value might be found in the cases of enrichment of nickel and, further, by the almost regular presence of Mg, Co, Mn and Zn in the separated silica. At 115° C the limit, according to the contamination caused by lime, would lie at 1.9.

Still another explanation could be provided supposing that the sorption is controlled by the different hydrogen ion concentrations present in the chloride solution and in sea water. A difference also lies in the electric charge of the colloids, silica being negatively charged, and the aluminium hydroxide of the hydrolysates showing a positive charge.

According to Goldschmidt (1937 a, p. 668) lead has been removed from sea water by adsorption on hydroxides of iron. Here the removal of lead evidently is effected by adsorption on silica.

For gallium and germanium the results of Goldschmidt and Peters (1931, p. 165; 1933 a, p. 141) concerning the enrichment of these elements in silica deposited from hot springs are of interest. In such deposits of amorphous silica there are notable amounts of these elements present. On the contrary, germanium was not detected in silica deposited at low temperatures. It might not be too bold to assume that the actual processes effected by hot springs are found to be reproduced here *in vitro* during the separation of silica from the chloride solution.

In a chapter dealing with the geochemical consequences of the ionic sorption Noll (1931, p. 573) gives for some bivalent cations the order of the relative enrichment in clays as



If the theory of ionic potential is applied here, we see from Fig. 1, that this order is fully concordant with the order of the values of ionic potentials.

In this connection regard may further be paid to recent investigations in chromatography concerning the separation of cations from each other by adsorption on aluminium oxide pillars. The order of separation of the more common ions in aqueous solution as presented by Schwab and Joekers (1937, p. 547), however, differs from the order of separation based on the ionic potential. These authors (*op. cit.*, p. 543) have also used silica pillars with the result that the adsorption properties of the ions then develop changes due to the low hydrogen ion concentration obtained.

ACKNOWLEDGMENTS.

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Geochemical Laboratory, The Mineralogical and Geological Institute of the University, Helsinki, June 1939.

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ZUR CHROMATOGRAPHIE SELTENER ERDEN.
(VORLÄUFIGE MITTEILUNG).

VON
OLAVI ERÄMETSÄ

INHALT.

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EINLEITUNG.

Vor ein paar Jahren haben Lange und Nagel (1936) auf Grund theoretischer Darlegungen den Vorschlag gemacht, dass man zur Trennung der auf chemischem Wege bekanntlich äusserst schwierig reindarzustellenden seltenen Erden das chromatographische Arbeitsverfahren prüfen sollte. Später haben jedoch Schwab und Mitarbeiter, die die Chromatographie anorganischer Stoffe in mehreren Arbeiten behandelt haben, die Anschauung ausgesprochen, dass dieser Methode für seltene Erden höchstens eine geringere Bedeutung zukomme. Diese Ansicht legen Schwab und Jockers (1937) etwa wie folgt dar: »Nur einmal wurde rein theoretisch der Vorschlag gemacht, die seltenen Erden chromatographisch zu trennen. Die Inangriffnahme unserer auf breiterer Basis stehenden Untersuchungen war hiervon unbeeinflusst, auch glauben wir nach unseren jetzigen Erfahrungen, dass gerade auf dem Gebiet der seltenen Erden die Chromatographie nur als Hilfsmethode anwendbar sein dürfte.«

Bei einigen vor ein paar Jahren ausgeführten Versuchen des Verfassers, die ausschliesslich optisch-spektrographisch kontrolliert worden waren, wurde beobachtet, dass die Adsorption der Lanthaniden sehr stark durch gewisse organische Zusätze sowie durch die Wasserstoffionenkonzentration beeinflusst wird. Vor allem macht sich dieser Umstand bei Anwendung von u. a. Weinsäure, Zitronensäure und Schleimsäure bemerkbar. Es schien nun wünschenswert, diese Versuche zu erneuern und die erhaltenen Präparate röntgenspektrographisch zu prüfen. In der vorliegenden Arbeit sollen aber nur die Resultate von drei unter verschiedenen Bedingungen ausgeführten Versuchen gegeben werden.

METHODISCHES.

Der Chromatograph. Als Adsorptionsmittel wurde in dem Chromatographen Aluminiumoxyd (nach Brockmann) der Firma E. Merck, Darmstadt, gebraucht. Eine Glasröhre, die aus mehreren etwa 10 mm dicken und 50 mm. langen zylindrischen Stücken zusammengesetzt worden war, wurde mit diesem Adsorptionsmittel gefüllt. Das unterste von diesen Stücken war am unteren Ende etwas schmaler ausgezogen und unten mit einem Filtrierpapierstopfen geschlossen. Am oberen Ende des Chromatographen befand sich eine etwa 30 cm lange Glasröhre zur Aufnahme der zu behandelnden Lösung. Der Chromatograph wurde in einer Höhe von etwa 20 cm mit dem Adsorptionsmittel gefüllt. Diese Anordnung des Chromatographen hat für den vorliegenden Zweck den Vorteil, dass man nach jedem Versuch die Röhre in ihre Teile zerlegen und von einer beliebigen Stelle eine Probe zur Kontrolle des Vorgangs entnehmen kann.

Die Lösung, die durch die mit dem Adsorptionsmittel gefüllte Röhre langsam hindurchgeflossen war, wurde in kleinen Dekantiergläschen fraktionsweise gefangen und der Reihe nach numeriert. Nach Zerlegung der Röhre wurde das Adsorptionsmittel entfernt, in der Reihenfolge von unten nach oben numeriert und der weiteren Behandlung unterzogen.

Bei einigen Versuchen wurden gewisse organische Stoffe zugesetzt. Zur Entfernung dieser Verbindungen aus den spektrographisch zu behandelnden Endpräparaten wurden die Fraktionen zur Trockne eingedampft sowie mit konzentrierter H_2SO_4 und HNO_3 behandelt und die Erden mit Ammoniak ausgefällt. Weil die gebrauchten tartrat- bzw. zittrathaltigen Lösungen das Adsorptionsmittel in geringen Mengen lösen, gelangten in die durchgeflossenen Endpräparaten oft bedeutende Mengen Aluminium, das jedoch die spektrographische Bearbeitung nicht stört.

Das aus dem Chromatographen entfernte Aluminiumoxyd wurde zuerst optisch-spektrographisch im Kohlebogen aufgenommen. Auf Grund der optischen Aufnahmen wurden einige der Fraktionen für die röntgenspektrographische Analyse ausgesucht. Diese ausgewählten Fraktionen wurden mit konzentrierter Salzsäure behandelt, mit Wasser

verdünnt, filtriert und mit heisser konzentrierter Oxalsäurelösung versehen. Nach dem Stehen einer Zeit wurde filtriert und die Fällung gegläht. In vielen Fällen war die filtrierte Lösung, aus der die Erden mit Oxalsäure gefällt werden sollten, mehr oder weniger trübe. Dadurch erhielt man auch hier zu den Endpräparaten oft sogar bedeutende Mengen Aluminiumoxyd. Bei denjenigen Fraktionen, deren Gesamtmenge an Oxalaten ziemlich klein war, hatte dies zur Folge, dass die röntgenspektrographisch ermittelte Summe der seltenen Erden unter 100 % gefunden wurde. In solchen Fällen, in denen das Vorhandensein des Aluminiums auch optisch-spektrographisch kontrollierbar war, wurde die röntgenspektrographisch gefundene Summe der Erden auf 100 reduziert. Bei den Versuchen gelangten Erdenmengen von 100—400 mg in Nitratform zur Anwendung.

Die optisch-spektrographischen Aufnahmen von dem erdenführenden Adsorptionsmittel wurden in dem Kohlebogen unter Anwendung der von R. Mannkopff und Cl. Peters beobachteten kathodischen Anreicherung der Metalle gemacht, eine Methode, die u. a. von Strock (1936) beschrieben worden ist. Die gebrauchten Kohleelektroden waren erdenfrei. Die geglähten Oxalatfällungen wurden im Kupferbogen aufgenommen. — Die Aufnahmen wurden mit einem Drei-Prismen-Glasspektrographen von Zeiss gemacht.

Die Röntgenaufnahmen wurden mit einem Vakuum-spektrographen gemacht. Der Kalkspatkristall wurde für die Lanthaniden zwischen 14.5° und 27.5° geschwenkt und der Film zwei Stunden belichtet sowie für Yttrium zwischen 6° und 9° geschwenkt und 20 min. belichtet. Die Spannung betrug 40 KV und der Strom 8—10 MA. Für die Aufnahmen wurden Ilford Ilfex Filme gebraucht. Von den Röntgenfilmen wurden mit einem selbstregistrierenden Photometer Regisgramme hergestellt und diese auf die von Minami (1935) angegebene Weise ausgewertet. Den Präparaten waren vorher bekannte Mengen einer Eichmischung zugefügt und die Mischungen durch zweistündiges Rühren in kleinen Achatmörsern homogenisiert worden. Die Eichmischung sowie die benutzten Spektrallinien waren dieselben, die Sahama und Vähätalo (1939) angewandt hatten.

DIE EINZELVERSUCHE.

Als Ausgangsmischung bei den chromatographischen Versuchen diente ein altes technisches Y-Er-Nitrat der Firma Riedel-de Haën. Das Präparat wurde in Oxydform röntgenspektrographisch analysiert.

Das Resultat der Analyse geht aus Tab. I und Fig 1 hervor. Von dem Zirkonium konnten optisch-spektrographisch keine Linien gefunden werden.

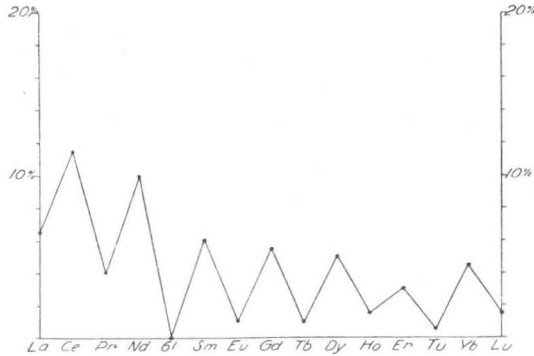


Fig. 1.

Tabelle I. Ausgangsmischung der chromatographischen Versuche.

La ₂ O ₃	6 1/2 %
Ce ₂ O ₃	11 1/2 %
Pr ₂ O ₃	4
Nd ₂ O ₃	10
Gd.....	—
Sm ₂ O ₃	6
Eu ₂ O ₃	1
Gd ₂ O ₃	5 1/2
Tb ₂ O ₃	1
Dy ₂ O ₃	5
Ho ₂ O ₃	1 1/2
Er ₂ O ₃	3
Tu ₂ O ₃	1/2
Yb ₂ O ₃	4 1/2
Lu ₂ O ₃	1 1/2
Y ₂ O ₃	32
ThO ₂	4
Summe	97 1/2 %

Versuch I. 1 %ige Nitratlösung ohne Zusätze. P_H 7.

Von den durchgeflossenen Fraktionen konnten weder durch Hydroxydfällung noch durch Oxalatfällung Erden erhalten werden. Das Adsorptionsmittel war in den untersten Fraktionen erdenfrei, die oberen Fraktionen von 3 an aufwärts dagegen reichlich erdenführend. Auf Grund optischer Aufnahmen scheint das Lanthan in den oberen

Fraktionen bedeutend schwächer vorhanden zu sein als in den mittleren. Die unterste erdenführende Fraktion 3 zeigt folgende Zusammensetzung (Tab. II und Fig. 2):

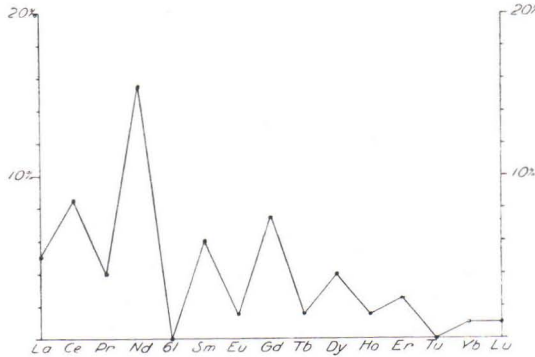


Fig. 2.

Tabelle II. Versuch I, Fraktion 3.

La ₂ O ₃	5	%
Ce ₂ O ₃	8 1/2	%
Pr ₂ O ₃	4	
Nd ₂ O ₃	15 1/2	
61.....	—	
Sm ₂ O ₃	6	
Eu ₂ O ₃	1 1/2	
Gd ₂ O ₃	7 1/2	
Tb ₂ O ₃	1 1/2	
Dy ₂ O ₃	4	
Ho ₂ O ₃	1 1/2	
Er ₂ O ₃	2 1/2	
Tm ₂ O ₃	—	
Yb ₂ O ₃	1	
Lu ₂ O ₃	1	
Y ₂ O ₃	46	
ThO ₂	—	
Summe		105 1/2 %

Versuch II. 1 %ige Nitratlösung mit 10 % K-Na-Tartrat. P_H 7.

Die durchgeflossenen Fraktionen waren erdenfrei. Die Fraktionen des Adsorptionsmittels Nr. 1—4 waren ebenfalls frei von Erden. Die Zusammensetzungen der Fraktionen 5, 6 und 9 sind aus Tab. III und Fig. 3—5 ersichtlich.

Tabelle III. Versuch II, Fraktionen 5, 6 und 9.

	5 ¹	6	9
La ₂ O ₃	0 %	0 %	10 %
Ce ₂ O ₃	7	5	13
Pr ₂ O ₃	2 1/2	2 1/2	5
Nd ₂ O ₃	9	17	15
61	—	—	—
Sm ₂ O ₃	3	8 1/2	6 1/2
Eu ₂ O ₃	1	1	2
Gd ₂ O ₃	2 1/2	9	7
Tb ₂ O ₃	1	1	2
Dy ₂ O ₃	4	6	5
Ho ₂ O ₃	1/2	1/4	1/2
Er ₂ O ₃	4	2 1/2	2 1/2
Tu ₂ O ₃	1	1/4	1/2
Yb ₂ O ₃	6 1/2	4	4
Lu ₂ O ₃	1 1/2	1	1 1/2
Y ₂ O ₃	57	38	30
ThO ₂	—	4	—
Summe	100 %	100 %	103 1/2 %

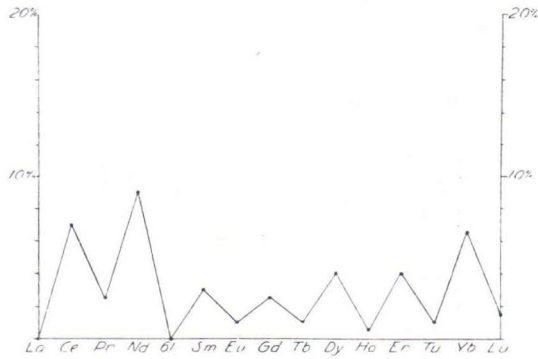


Fig. 3.

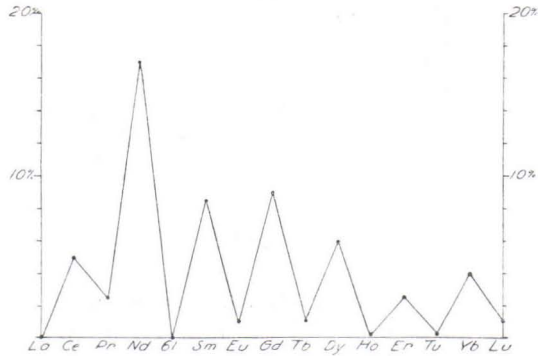


Fig. 4.

¹ Die Fraktion war stark von Aluminiumoxyd verunreinigt. Daher wurde das Resultat auf 100 umgerechnet.

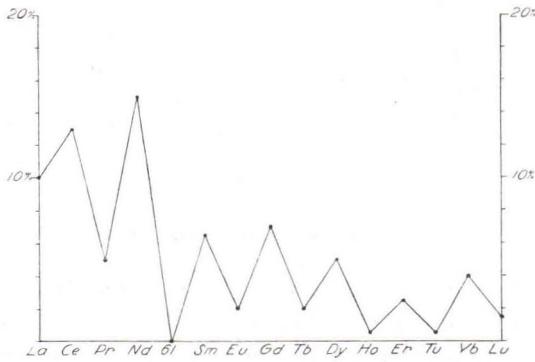


Fig. 5.

Versuch III. 1 %ige Nitratlösung mit 10 % K-Na-Tartrat. P_H 9.

Die durchgeflossenen Fraktionen sowie die Fraktionen des Adsorptionsmittels Nr. 1—4 waren erdenfrei. Tabelle IV und Fig 6 zeigen die Zusammensetzung der Fraktion 5.

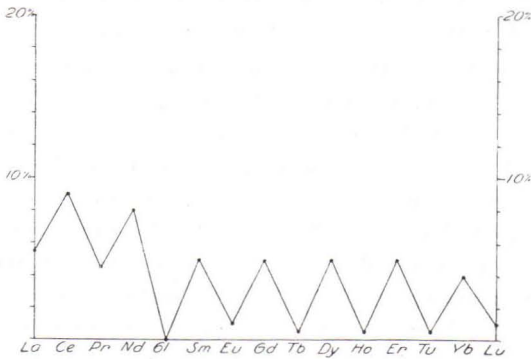


Fig. 6.

Tabelle IV. Versuch III, Fraktion 5.¹

La ₂ O ₃	5 1/2 %
Ce ₂ O ₃	9
Pr ₂ O ₃	4 1/2
Nd ₂ O ₃	8
61	—
Sm ₂ O ₃	5
Eu ₂ O ₃	1
Gd ₂ O ₃	5
Tb ₂ O ₃	1 1/2
Dy ₂ O ₃	5
Ho ₂ O ₃	1 1/2
Er ₂ O ₃	5

Tu ₂ O ₃	1/2
Yb ₂ O ₃	4
Lu ₂ O ₃	1
Y ₂ O ₃	33 1/2
ThO ₂	12
	Summe 100 %

DISKUSSION DER RESULTATE.

Bei Betrachtung der weiter oben gegebenen Analysen, etwa auf Grund der beigefügten graphischen Darstellungen, ist nun erstens festzustellen, dass tatsächlich durch chromatographische Behandlung der angewandten Ausgangsmischung gewisse Verschiebungen in der relativen Erdenzusammensetzung zustandegebracht worden sind. Dass aber diese Verschiebungen verhältnismässig klein sind und nicht etwa zu reinen Erdpräparaten geführt haben, ist auch zu erwarten, denn die Lösungen waren nur einmal durch die Chromatographenröhre durchgeflossen. Die Herstellung reiner Erdpräparate war aber auch nicht der Zweck der vorliegenden Untersuchung, es kam nur darauf an, zu zeigen, dass das Adsorptionsvermögen einzelner Erden in dem betr. Adsorptionsmittel gewissen Variationen unterliegt.

Vergleicht man erstens Fig. 2 aus Versuch I mit der Ausgangsmischung, so fällt in erster Linie eine starke Zunahme bei Nd und in geringerem Masse bei Gd in die Augen. Dagegen haben aber La und Ce sowie Yb etwas abgenommen. Vor allem ist aber beim Versuch eine Zunahme des Yttriums von etwa 32 auf 46 % zu beachten. Im Gegensatz dazu sieht man bei Versuch III, der in einer tartrathaltigen alkalischen Lösung ausgeführt wurde, bei der entsprechenden untersten Fraktion (Fig. 6) keine stark hervortretenden Verschiebungen in der relativen Lanthanidenzusammensetzung ausser in dem Fall von Er, wo eine deutliche Zunahme zu spüren ist. Eine Zunahme von Th ist aber merkbar.

Die Veränderungen der Lanthanidenzusammensetzung bei den beiden Versuchen I und III sind ferner in Fig. 7 und 8 veranschaulicht worden. Dabei ist als Ordinate das Verhältnis des betr. Elements in der zu analysierenden Fraktion und in der Ausgangsmischung eingezeichnet worden. Wenn demgemäss das Element in der betr. Fraktion von der ursprünglichen Lösung angereichert worden ist, liegt der Punkt im Diagramm oberhalb der stark gezogenen horizontalen Linie, die ein Verhältnis von 1 : 1 zwischen Fraktion und Ausgangsmischung andeutet. Wie aus der Figur ersichtlich, ist Yttrium, das durch eine mit Y markierten horizontalen Linie in der Figur angedeutet worden

ist, merklich angereichert. In Fig. 8 sind die entsprechenden Verhältnisse für Tab. IV ausgerechnet. Die Anreicherung des Erbiums ist deutlich zu erkennen.

Am deutlichsten ist die Verschiedenartigkeit der Adsorptionsvermögen der seltenen Erden aus Versuch II ersichtlich. Die Erdenge-

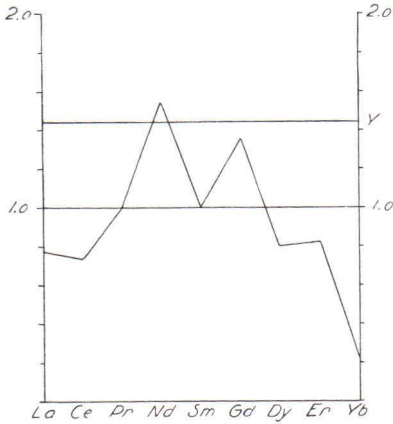


Fig. 7.

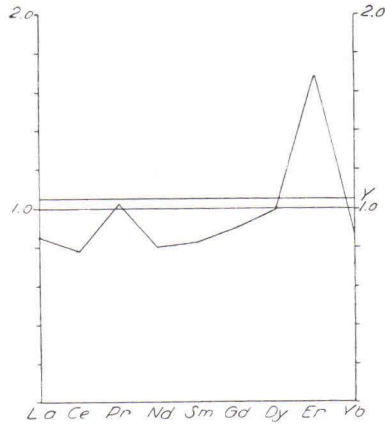


Fig. 8.

halte der analysierten Fraktionen sind im Verhältnis zu der Ausgangsmischung in Fig. 9 graphisch dargestellt. Bei der obersten Fraktion des Chromatographen (Nr 9) sind, wie aus der Figur ersichtlich, die Erden La, Ce, Pr, Nd, Sm, Gd mehr oder weniger deutlich angereichert, während Er und Yb etwas abgenommen haben. Bei der Fraktion 6 haben dagegen die mittleren Erden Nd, Sm, Gd, Dy zugenommen und nur die Erden La, Ce, Pr sowie andererseits Er und Yb abgenommen. Bei der untersten erdenführenden Fraktion Nr. 5 haben nur die Gehalte an Er und Yb zugenommen, diejenigen der übrigen Lanthaniden sind dagegen mehr oder weniger stark zurückgetreten. Die Erden Eu, Tb, Ho, Tu, Lu sind in so geringen Mengen vorhanden, dass sichere Schlüsse über ihr Verhalten nicht gezogen werden konnten. Bezüglich des Yttriums ist bei Fraktion 5 vor allem eine starke Zunahme zu beachten.

Als Zusammenfassung ist über den Versuch hervorzuheben, dass in den obersten Teilen der Chromatographenröhre vermöge der selektiven Adsorption der Lanthaniden von La bis Gd eine gewisse Anreicherung stattgefunden hat. In den mittleren bis unteren Teilen der Röhre ändert sich dieses Verhalten in der Richtung, dass die Lanthaniden mit niedrigsten Ordnungszahlen in der relativen Zusammensetzung zurück-

treten und das Maximum der Anreicherung sich gegen die mittleren Erden verschiebt. In den alleruntersten Teilen der Röhre treten auch diese zurück und verursachen eine relative Anreicherung der am wenigsten basischen Yttererden.

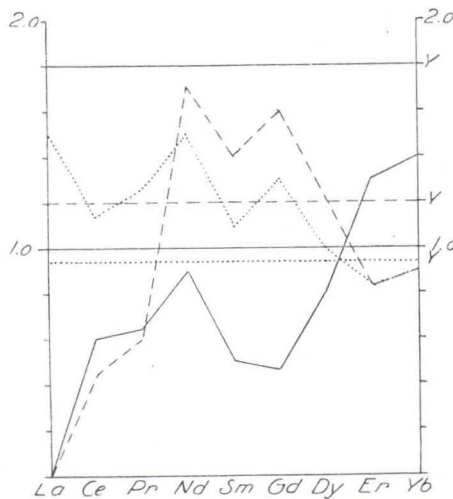


Fig. 9.

Fraktion Nr. 9
 » Nr. 6 - - - - -
 » Nr. 5 —————

Es scheint demgemäss, dass bei Versuch II die Adsorptionsfolge vom La nach Yb verläuft, und zwar in dem Sinne, dass das Lanthan zuerst, das Ytterbium aber zuletzt durch das Adsorptionsmittel gefangen wird. Ob aber diese Ordnung bei der Adsorption auch tatsächlich streng der Basizität der Erden folgt, ist auf Grund der vorliegenden Daten nicht mit voller Sicherheit zu beurteilen. Vielmehr scheint es gar nicht ausgeschlossen zu sein, dass unter geeigneten Bedingungen einzelne Erden gewisse Abweichungen zeigen konnten. Die Beantwortung der Frage sei aber vorläufig der Zukunft überlassen.

Neben den eigentlichen Lanthaniden ist aber hervorzuheben, dass das Verhalten des Yttriums nicht der Basizität des Elements in der Lanthanidenreihe zu folgen scheint. Wie man in dem Fall von Fraktion 5 sieht, hat das Dysprosium, das hinsichtlich des Ionenpotentials dem Yttrium am nächsten steht, schwach abgenommen, während die Zunahme des Yttriums bei der gleichen Fraktion am stärksten hervortritt.

Bei der vorliegenden Frage würde es nun von erheblicher Bedeutung sein zu erfahren, in welchem Masse die weiter oben gegebenen Versuche überhaupt reproduzierbar sind. Es ist wohl zu vermuten, dass der Vorgang der Adsorption von mehreren äusseren Faktoren stark abhängig sein wird. Die Frage ist besonders wichtig, wenn man die Brauchbarkeit der Methode zur Reindarstellung der Erden prüfen will. Jedenfalls ist schon auf Grund der gegebenen Versuche festzustellen, dass die Möglichkeiten dazu gegeben sind, besonders wenn man die chromatographische Behandlung der zu untersuchenden Lösung mehrere Male wiederholt. Auch für kleinere Materialmengen scheint die Methode ebenso gut wie für grosse Mengen brauchbar zu sein. Ebenfalls scheint es nicht ausgeschlossen zu sein, dass man das Adsorptionsmittel durch geeignete Substanzen aktivieren und den Vorgang durch geeignete Entwicklung verdeutlichen kann.

Die Versuche werden fortgesetzt.

ZUSAMMENFASSUNG.

1. Es wurde eine röntgenspektrographisch analysierte Mischung seltener Erden chromatographisch behandelt und die erhaltenen durchgeflossenen Lösungen sowie die verschiedenen Teile des Adsorptionsmittels der Chromatographenröhre optisch-spektrographisch und im Falle von drei Versuchen z. T. röntgenspektrographisch untersucht. Als Adsorptionsmittel wurde Aluminiumoxyd nach Brockmann gebraucht.

2. Das Adsorptionsvermögen des Yttriums scheint schwächer als dasjenige der eigentlichen Lanthaniden zu sein. In den relativen Lanthanidenzusammensetzungen wurden bei den verschiedenen Versuchen gewisse Verschiebungen festgestellt.

3. Ein Zusatz von gewissen organischen Verbindungen scheint einen starken Einfluss auf die Adsorption auszuüben.

BEKANNTMACHUNGEN.

An dieser Stelle möchte Verf. Herrn Prof. Dr. Pentti Eskola, Direktor des Mineralogisch-Geologischen Instituts der Universität Helsinki, seinen Dank aussprechen für die Erlaubnis, die vorliegende Arbeit im Geochemischen Laboratorium des erwähnten Instituts ausführen zu dürfen. Für die Überlassung des gebrauchten Erdenpräparats, das der analytischen Abteilung des Chemischen Laboratoriums der Technischen Hochschule Finnlands gehörte, schuldet Verf. dem

Direktor der betr. Abteilung, Herrn Dr. Jalo Ant-Wuorinen seinen Dank. Zum Schluss möchte Verf. Herrn Dr. Th. G. Sahama, aus dem Geochemischen Laboratorium, für die Unterstützung bei der Arbeit danken.

Geochemisches Laboratorium, Mineralogisch-Geologisches Institut
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X-RAY SPECTROGRAPHIC STUDY OF THE RARE EARTHS IN SOME FINNISH ERUPTIVE ROCKS AND MINERALS

BY

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ABSTRACT.

19 X-ray spectrographic analyses of the rare earths from Finnish eruptive rocks and minerals are given. In connection therewith the abundance of the earths, as compared with the data presented in literature is discussed, together with the observed variations in the relative concentration ratios of single earths.

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INTRODUCTION.

The results of the X-ray analyses given by various authors already give an idea of the average concentration ratios of the rare earths in the lithosphere (Minami 1935, Landergren 1936 and others) and in the silicate meteorites (Noddack 1935). More recently the data available about the abundance of the lanthanides together with yttrium, scandium, and thorium have been collected from literature by Goldschmidt, who compared them with one another and with his own unpublished results (1937 a und b). As one of the most prominent results of modern geochemical research dealing with the rare earths, Goldschmidt states that the concentration ratios of the elements from lanthanum to lutecium — the »lanthanides» — are very similar in different rocks. Thus, according to him the lanthanides with the exception of europium form a most coherent group of elements. They always follow one another in nature and are »wenig oder nicht beeinflusst von rein chemischen oder physikalischen selektiven Stofftrennungen» (Goldschmidt 1937 a, p. 36).

Further, as pointed out by the same author (Goldschmidt 1930), the lanthanides together with yttrium and thorium are especially enriched in the products of late magmatic crystallization. This behaviour is found to be in good agreement with the ionic sizes of the lanthanides obtained by Goldschmidt. In the more acid rocks which predominate in the uppermost parts of the lithosphere these »rare» earths therefore are more abundant than is indicated by their name. As a matter of fact, they are very common constituents of, *e. g.*, granitic rocks. In this connection, reference is made only to a recent paper by van Tongeren (1938), in which the percentages of the most common rare earths: yttrium, cerium, neodymium, lanthanum, and scandium in a big number of rocks of the East Indian Archipelago are presented. van Tongeren has made his study with the aid of optical spectrography without any chemical pre-treatment.

As to the occurrence of the rare earths in the Finnish Archaean rocks our knowledge is at present very slight. Excepting for some lanthanide minerals analyzed chemically by, *e. g.*, Wuorinen (1916),

Ant-Wuorinen (1936), and Lokka (1928 and 1935), and with the aid of X-ray spectrography by Sahama and Vähätalo (1939) the reader is solely referred to the qualitative notes concerning the presence or absence of lanthanide minerals in rocks and sand deposits found in the regional descriptions of the Finnish rock-ground. More recently, however, Sahama (1936) has given some spectrographic determinations of La, Ce, Eu, Y, and Sc in rocks and minerals mostly from the granulite belt of Finnish Lapland, which have been made in Göttingen under the guidance of Professor V. M. Goldschmidt and Dr. H. Bauer. Further on, we may note that according to a preliminary communication Sahama and Rankama (1938) have in Finnish granites found some of the rare earths very often though not regularly in amounts determinable by optical spectrography. Finally, Rankama (1939) has given a few qualitative data of the content of the rare earths in the rock specimens serving as basis for a study of the silica residue in rock-analysis.

The present authors have determined the rare earth content of a number of Finnish rocks and minerals with the aid of X-ray spectrography. In the present paper the results obtained during their work will be given. They fully understand, however, that the data available at present are in no way sufficient to allow of any conclusions concerning the regional distribution of the rare earths in Finland. In this paper therefore only some ruling principles are discussed in hopes that the results may be helpful in forthcoming regional investigations.

METHODICS.

When all of the rare earths — including the odd lanthanides — in a certain rock are to be determined with the aid of spectrographic methods, two different ways of treatment are to be mentioned. In both cases a chemical pre-enrichment is necessary because the amount of the odd yttrium earths, *e. g.* terbium, holmium, thulium, and lutecium in most rocks and minerals is too low to allow them to be determined spectrographically from the powdered sample. The first possibility is to use a 10- to 100-fold pre-enrichment by chemical means, which allows a determination of the rare earths with the aid of optical spectrography. The degree of enrichment necessary for a certain rock can often be estimated from the abundance of the most common earths which can be determined without enrichment (*e. g.* La, Ce, Nd, Y). The enrichment, on the other hand, can be extended until the earths at last form the principal part of the final product.

From such a precipitate containing even the most uncommon earths in amounts of a few tenths of one per cent, an X-ray spectrographic analysis can be carried out.

Of the two methods mentioned above the latter apparently is able to give a more accurate picture of the relative concentration ratios of the rare earths than the former, assuming, of course, that the chemical pre-enrichment has really given quantitative results. On the other hand, however, the risk of incompleteness increases parallel to the degree of enrichment. In other words, we may state that extending of the enrichment tends to enlarge the complexity of the chemical procedure demanded. A complicated procedure also enlarges the possibility of getting rare earths into products where they are unwanted.

In the present study all the rare earth analyses have been made by the latter method. A 1 000—10 000-fold enrichment was first made in the rock sample and the product thus obtained was analyzed by X-ray spectrographic methods.

CHEMICAL PRE-TREATMENT.

For a chemical pre-enrichment of the rare earths preceding an X-ray spectrographic analysis, two methods are given in literature. In both of these much attention is paid to the removal of the excesses of iron and aluminium. According to Ida Noddack (1935) the aluminium and iron hydroxides precipitated with ammonia are washed with a cold dilute sodium hydroxide solution, containing not more than 0.5 per cent NaOH, until aluminium quantitatively is gone into solution. The remaining precipitate is dissolved in hydrochloric acid and from this solution iron is extracted with ether. The rare earths remain quantitatively in the aqueous phase.

According to Minami (1935), silica is removed from the sample with concentrated hydrofluoric acid and the residue digested with very diluted hydrofluoric acid. The residue is dissolved and precipitated with strong KOH solution, dissolved in hydrochloric acid, and reprecipitated with ammonia. The precipitate is dissolved, the solution evaporated to a very small volume and the earths contained in it precipitated with oxalic acid. After standing for 12 hours or still more the rare earth oxalates are filtered off and ignited.

In the present paper the latter of these two methods, as given by Minami, has been used. According to this method the final isolation of the rare earths is accomplished by a precipitation with oxalic acid. In literature there are, however, communications indicating

that the oxalates of the lanthanides, including yttrium and scandium, in solutions containing free mineral acid are soluble to a noticeable degree. In this connection the reader is referred only to the reviews presented by von Hevesy in his book »Die seltenen Erden vom Standpunkte des Atombaues» (Struktur der Materie, Berlin 1927) and by Friedheim and Peters in Gmelin-Kraut's »Handbuch der anorganischen Chemie» (7th Ed., 1932, Vol. 6, Part 2). There appears to be danger of the incomplete precipitation of the rare earths especially if the evaporation of the solution of the chlorides is not extended long enough.

We may further note that the solubility of the lanthanide oxalates is, throughout the series, not a constant one. Investigations dealing with the cerium earths presented by Sarver and Brinton (1927) show that in this respect there exist certain differences between the members of the cerium earths in solutions saturated with oxalic acid and containing free mineral acid. For the yttrium earths our knowledge seems to be somewhat incomplete. The determinations by, *e. g.*, Bodländer referred to by v. Hevesy (*op. cit.*), however, seem to indicate that also the group of the yttrium earths might show a fixed order in the solubility of their oxalates.

The case referred to above seems to be of importance for the purpose in question. Therefore some experiments with known mixtures of rare earths were arranged. This was done in order to find out whether the selectivity in the solubilities of the rare earth oxalates had any effect upon the geochemical conclusions based on the analyses. The results of these experiments, however, are neither new in principle nor to be regarded as wholly exhaustive. The aim of the experiments is only to find out the direction possibly indicated by the errors.

From the rare earth compounds available, partly bought from Messrs. Adam Hilger, Ltd. (London) and Messrs. Dr. Fraenkel und Dr. Landau (Berlin-Oberschöneweide) and partly obtained through the courtesy of Dr. Dr.-Ing. Wilh. Feit (Berlin-Zehlendorf-West) from his private collections, mixtures of known composition were prepared and homogenized by grinding for two hours in small agate mortars. Since all of the lanthanide compounds used were not quite pure, the mixtures were analyzed by X-ray spectrographic methods before their use in any chemical treatment. From the material known amounts were brought into solution, precipitated with oxalic acid from a solution slightly acidified with free mineral acid under the same circumstances as in the treatment of the rocks investigated. The precipitates and the filtrates evaporated down to dryness were analyzed by X-ray spectrographic methods.

Fig. 1 illustrates one of the experiments carried out. The oxalic acid precipitate from the original mixture (Diagram I) is shown by Diagram II and the corresponding filtrate by Diagram III.

From Diagrams I—III of Fig. 1 we first see that in the case of incomplete precipitation of the earths as oxalates, the yttrium earths show a very strong tendency to enrich themselves in the filtrate in

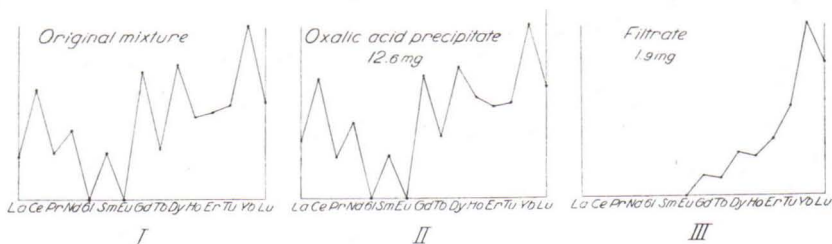


Fig. 1.

relation to the cerium earths. In his review on the solubilities of the earth oxalates cited above, v. Hevesy states that the solubility in water of yttrium earths is greater than that of cerium earths, while, on the other hand, according to the same review, solubility in mineral acid solutions of some 3—4-fold normality, appears to show an opposite behaviour, most remarkable in the case of lanthanum. In the practical extraction of rare earths from rocks, the oxalic acid precipitate is always obtained by means of a solution containing very little free mineral acid. As explained above, the procedure adopted here consists of evaporation of the commonly hydrochloric acid solution down nearly to dryness, whereupon the residue is taken up in a little water and hot, almost saturated oxalic acid solution in large excess is added. By the use of such a method it may be expected in advance that, should the precipitation on the whole be incomplete, the earths of weaker basicity will to a greater extent remain in the solution.

The circumstance discussed above in the precipitation of the earths is now especially important, as it is always accompanied by the risk that the yttrium earths will be underestimated in the final result. When therefore an X-ray film of an earth precipitate shows that the yttrium earths are found to be either altogether missing or at least very insignificant in relation to the figures given, *e. g.*, by Minami, it lies near at hand to assume that the divergency is merely to be attributed to a selective enrichment of the earths. When, however, the yttrium earths on the contrary preponderate in a greater

or lesser degree, this appears, according to the above, as being not a consequence of the enrichment, but rather an actual characteristic of the rock. To this it may of course be remarked that, as indicated above, according to the aforesaid work of v. Hevesy, the yttrium earths just in mineral acid solutions are less soluble than are the cerium earths. Such behaviour in the test conditions now in question was, however, not observed during the experiments carried out, one of which is reproduced in Fig. 1.

A control of the fact that the earths actually are present in the enrichment product in the correct ratio of quantity was recently brought about by Lux (1938), by adding known amounts of praseodymium and thulium to the experiment material and again determining these two earths in the enrichment product.

In this connection reference should be made to another phenomenon of the enrichment, observed, *i. a.*, by Minami (1935) and specially stressed by Goldschmidt (1937 a and b). According to the said authors the fact is that in the precipitation of the earths as hydroxides, one has to take into account that the cerium in the shape of a quadrivalent ion is not precipitated quantitatively, but remains partly in solution.

In addition to the above discussed possible irregular behaviour of various earths in the chemical enrichment, mention should further be made of the fact that it does not appear impossible that the oxalate precipitate gives too low values also in respect of the total amount of the earths.

X-RAY SPECTROGRAPHIC METHOD.

The X-ray exposures were made with a vacuum spectrograph. The exposure data and the standard mixtures used were similar to those given by the authors in an earlier work (Sahama and Vähätalo 1939). Photometric records were made from the spectrograms. This was in part done by Mr. Lars E. Lindfors, M. A., at the Institute of Physics of the Helsinki University with the big Zeiss recording micro-photometer, and in part by the first author in the geochemical laboratory of the Mineralogical and Geological Institute of the said University. The last-mentioned work was carried out with a likewise recording micro-photometer, built for the purpose by Mr. Lindfors, an apparatus which he will describe more particularly in the near future. The photometric records were utilized mainly in the manner indicated by Minami (1935).

MATERIAL.

On scrutinizing the results of the X-ray spectrographic analyses given below, it should be observed, that the results for those earths which are present in smallest amounts obviously show the greatest relative errors. This circumstance is due to the fact that the galvanometer deflections for the lines in question in the photometer curves are the smallest and accordingly are burdened with the greatest errors in the determination of the blackening of the background. For this reason, and particularly in the case of the odd earths from Eu to Lu, the values given are not to be regarded as exact, but should rather be dealt with in accordance with the order of magnitude. — For the earths of more abundant occurrence, however, also the errors peculiar to X-ray spectroscopy have to be taken into consideration. — The results of the analyses are given also in the form of diagrams, and this with $Ce_2O_3 = 100$.

ACID DIKES AND PEGMATOIDS IN THE DIABASES OF SÄPPI AND WALAMO.

On Säppi Island, in the neighbourhood of the town of Pori in south-west Finland, peculiar formations in the Post-Jotnian diabase are found. These formations have been investigated by Eskola. He has published a preliminary information of the same (Eskola 1932 and 1936), and is to deal with them in detail in the near future. At a place which Eskola has named Piippukallio, there appear in the diabase which occasionally shows a plane-parallel orientation of the plagioclase laths lying in a flat position, apparently nearly vertical pipe-like bodies of a diameter generally about ten meters. Petrographically these bodies are alkali-felspar-bearing pegmatites, or pegmatoids, of the diabase. The chemical composition of the rocks appears from the tables of analyses given by Eskola (1936), here quoted as Table I. Other, mostly smaller pipes occurring near the Pilot Station of Säppi, consist of coarse-grained or »mega-ophitic» varieties of ilmenite-magnetite-rich diabase.

The interpretation of these tubular bodies has been conceived as follows by Eskola (1936) (in translation): »At least in their present condition the diabase pegmatites must be regarded as products of crystallization differentiation, *i. e.*, crystallizations from the residual solutions of the diabase magma. The mega-ophitic diabase represents an earlier stage, when the residual magma had not yet noticeably altered its composition, but had simply become somewhat

Table I. Chemical composition of the rocks of Säppi according to Pentti Eskola. Analyst Kalervo Rankama.

	Normal olivine diabase	«Mega- ophitic» diabase	Alkali felspar pegmatite	Grano- phyre
SiO ₂	47.59	46.41	54.53	74.99
TiO ₂	2.01	5.00	2.38	0.28
Al ₂ O ₃	17.03	10.59	11.06	10.04
Fe ₂ O ₃	2.41	4.11	4.89	0.91
FeO	11.72	10.91	10.64	2.44
MnO	0.16	0.23	0.25	0.12
MgO	5.38	5.50	1.36	0.76
CaO	8.45	11.18	4.16	0.48
SrO	0.00	0.00	0.00	trace
BaO	0.00	0.00	0.00	0.00
Na ₂ O	3.30	2.73	4.19	2.24
K ₂ O	1.04	0.78	4.23	6.79
H ₂ O	0.95	2.60	2.08	0.93
P ₂ O ₅	0.09	0.13	0.28	0.09
Cl	—	—	0.07	—
Total	100.13	100.17	100.10	100.07

enriched in water and other volatile constituents, whereas the alkali felspar pegmatite belongs to the last stage of differentiation under the existing conditions».

The observation of the authors, that the alkali felspar pegmatite shows a remarkable enrichment of, *i. a.*, beryllium, agrees well with this interpretation by Eskola, as according to Goldschmidt and Peters (1932) beryllium belongs to the typical elements of the magmatic late-crystallization. The content of BeO in the alkali felspar pegmatite amounts to 0.001 per cent, determined by the Zeiss Quartz Spectrograph Qu 24, whereas the normal olivine diabase and the mega-ophitic diabase are free from Be.

All three types of rock — the normal olivine diabase, the mega-ophitic diabase and the alkali felspar pegmatite — were first optically tested for rare earths by means of the Zeiss Three Prism Glass Spectrograph. The result was negative, as regards both the normal olivine diabase and the mega-ophitic diabase; in the alkali felspar pegmatite on the contrary, the earths were easily detected. A chemical concentration of the rare earths in samples of all three rocks was now carried out. In the case of the normal olivine diabase, no earths were found to be present by X-ray spectrograph, not even in the concentrated product. Starting with about 10 g. of the mega-ophitic diabase, a final preparation of about half a milligram in weight was obtained, in which the rare earths could be determined by X-ray

spectrograph. Owing to the very small amount of material, this final product was photographed without any admixture of comparison substances, and accordingly only the relative concentration ratios of the lanthanides could be determined. The lanthanides of the alkali felspar pegmatite were determined quantitatively. The results of the analyses are set forth in Table II.

Table II.

	Säppi					Grano- phyre, Sorkka	
	Alkali felspar Pegmatite		«Mega- ophitic» Diabase	Grano- phyre			
Y ₂ O ₃	n. d.	n. d.	n. d.	0.013	185	0.008	89
La ₂ O ₃	0.01	32	40	0.002	29	0.004	45
Ce ₂ O ₃	0.031	100	100	0.007	100	0.009	100
Pr ₂ O ₃	0.005	16	18	0.001	14	0.002	22
Nd ₂ O ₃	0.018	58	95	0.003	43	0.005	55
61	—	—	—	—	—	—	—
Sm ₂ O ₃	0.008	26	45	0.001	14	0.001	11
Eu ₂ O ₃	0.002	6	12	0.0001	1 1/2	0.0002	2
Gd ₂ O ₃	0.010	32	50	0.001	14	0.002	22
Tb ₂ O ₃	0.003	10	12	0.0001	1 1/2	0.0002	2
Dy ₂ O ₃	0.013	42	55	0.0007	10	0.001	11
Ho ₂ O ₃	0.004	13	n. d.	0.0002	3	0.0003	3
Er ₂ O ₃	0.013	42	34	0.0004	6	0.0007	8
Tm ₂ O ₃	0.003	10	10	0.0001	1 1/2	0.0001	1
Yb ₂ O ₃	0.013	42	36	0.0005	7	0.0006	7
Lu ₂ O ₃	0.002	6	13	0.0002	3	0.0002	2
ThO ₂	n. d.	n. d.	n. d.	n. d.	n. d.	0.004	45
Total	0.135	—	—	0.0303	—	0.0383	—
Ignited oxalic acid precipitate	0.38	—	—	0.034	—	0.045	—

The final product of the alkali felspar pegmatite examined by X-ray spectrograph was found furthermore to contain a large amount of Ca, Ba, and Sr, as was shown by an optical exposure in the visible wave range. The X-ray film also proved the presence of Ba. The total of the rare earths determined by X-ray spectrograph therefore amounts to only about a third of the earth precipitate obtained by chemical means.

In the case of the mega-ophitic diabase, it was not possible to measure the HoL β_1 -line in the very weak film and the amount of material was not sufficient to allow of a second exposure being made. As the HoL α_1 -line could not be used owing to coincidence with the very strong GdL β_1 -line, it was not found possible to determine the holmium. In the diagram on Fig. 3 its amount has been only estimated as equal to that of terbium.

Besides those types of rock to which reference has already been made, still another rock occurs on Säppi Island, penetrating the diabase in the form of narrow dikes and according to Eskola representing a granophyre. The chemical composition of this rock is given in Table I. The earths of this granophyre, as well as of another analogous granophyre from Sorkka, were determined by X-ray spectrograph and the results annexed to Table II. Eskola has personally informed the first author that these granophyres are not to be regarded as differentiation products of the diabase, but that they more probably represent veins of a foreign matter penetrating the diabase. As shown below, this interpretation by Eskola stands in good agreement with the lanthanide composition of the granophyre.

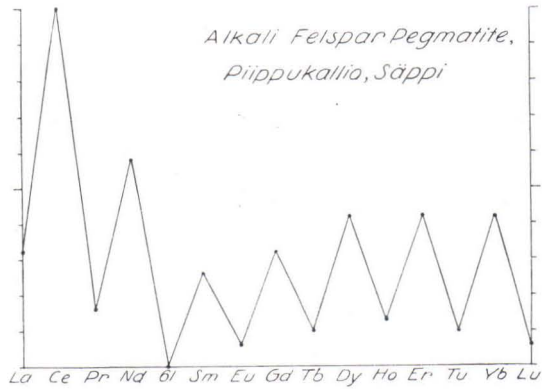


Fig. 2.

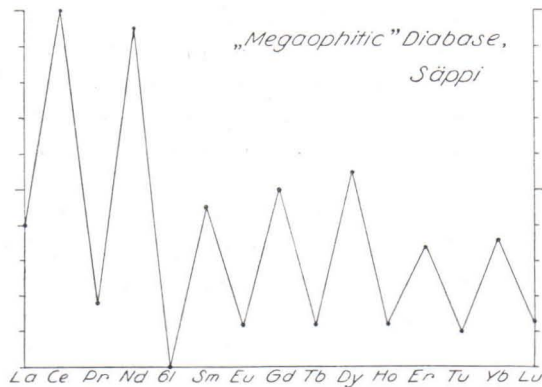


Fig. 3.

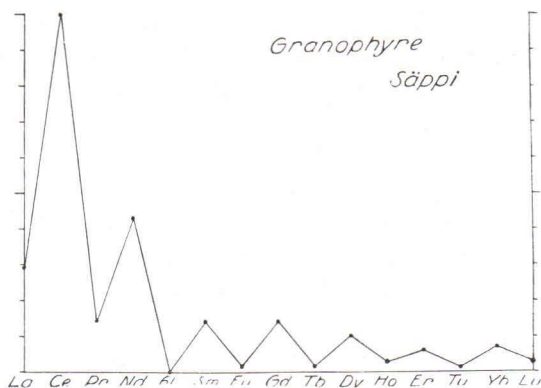


Fig. 4.

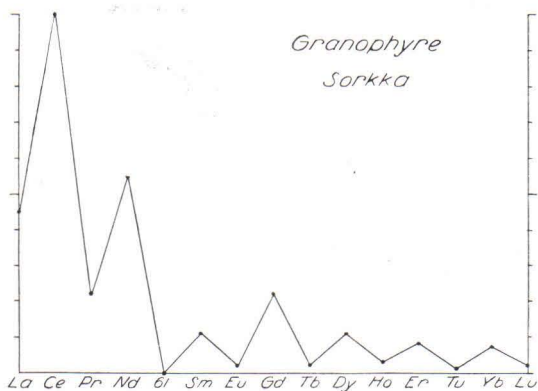


Fig. 5.

The analyses given in Table II are graphically represented by Figs. 2—5.

Judging by their mode of occurrence, the granophyres from Säppi and Sorkka appear to be formations analogous to the so-called walamite in the diabase region of Walamo. These rocks have been petrographically examined in detail by Wahl, who has, however, not yet published his results. In the explanation to the map sheet Savonlinna (Sheet D 2, General Geological Map of Finland, published by the Geological Survey of Finland), Hackman (1933) gives a description of the rocks based upon the results of Wahl. According to this description the walamites belong magmatically to the diabase, representing the last crystallization products of the diabase magma.

Three samples of these rocks — in which rare earths were recognizable already by the means of optical spectrography — were subjected to a complete X-ray spectrographic analysis. The films from the yttrium determinations of the products of the chemical enrichment showed, however, no $\text{ThL}\beta_1$ -line.

In the case of the walamite No. 17 from Rantaveräjänkallio, the difference between the total of the rare earths as determined by X-ray spectrograph and chemically, is due to the high content of iron and barium in the enrichment product as can be seen in the respective film.

The analyses by X-ray spectrograph are set forth in Table III and Figs. 6—8.

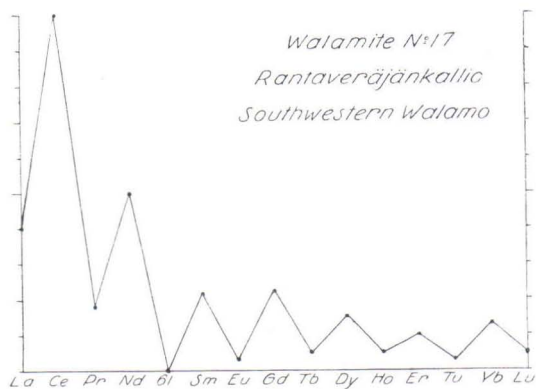


Fig. 6.

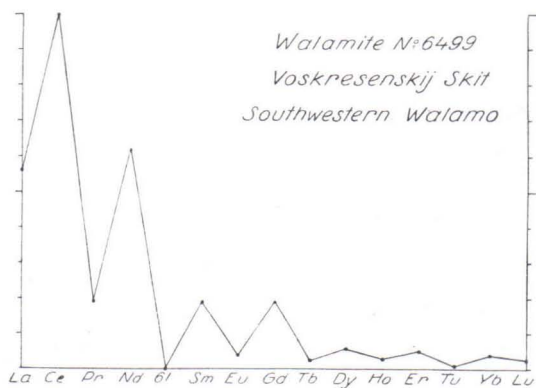


Fig. 7.

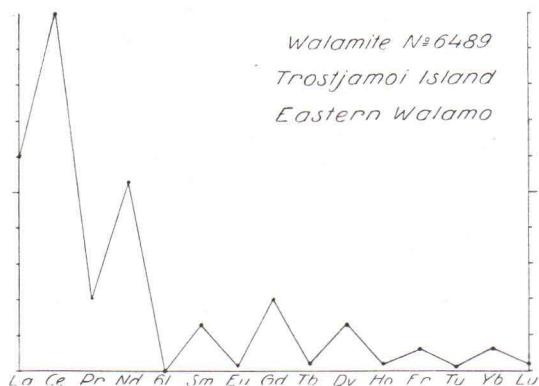


Fig. 8.

Table III.

	Walamite, No 17, Rantaveräjän- kallo, Southern Walamo		Walamite, No 6499, Voskresenskij Skit, Southwestern Walamo		Walamite, No 6489 Trostjamo Island Eastern Walamo	
Y ₂ O ₃	0.003	75	0.007	44	0.01	67
La ₂ O ₃	0.0016	40	0.009	56	0.009	60
Ce ₂ O ₃	0.004	100	0.016	100	0.015	100
Pr ₂ O ₃	0.0007	18	0.003	19	0.003	20
Nd ₂ O ₃	0.002	50	0.010	62	0.008	53
61	—	—	—	—	—	—
Sm ₂ O ₃	0.0009	22	0.003	19	0.002	13
Eu ₂ O ₃	0.0001	3	0.0006	4	0.0002	1 1/2
Gd ₂ O ₃	0.0009	22	0.003	19	0.003	20
Tb ₂ O ₃	0.0002	5	0.0004	2 1/2	0.0003	2
Dy ₂ O ₃	0.0006	15	0.001	6	0.002	13
Ho ₂ O ₃	0.0002	5	0.0005	3	0.0003	2
Er ₂ O ₃	0.0004	10	0.0008	5	0.001	7
Tu ₂ O ₃	0.0001	3	0.0001	1	0.0002	1 1/2
Yb ₂ O ₃	0.0005	13	0.0007	4	0.001	7
Lu ₂ O ₃	0.0002	5	0.0004	2 1/2	0.0003	2
Total	0.0154	—	0.0555	—	0.0553	—
Ignited oxalic acid precipitate	0.030	—	0.051	—	0.051	—

YOUNGEST ARCHAIC GRANITES.

Five samples of the youngest Archaic granites of Finland were examined. The results arrived at are shown in Tables IV and V, and in Figs. 9—15.

The first of these samples was taken from a small quarry near the estate of Juva, in Espoo, some 20 kms. WNW of Helsinki. The

rock belongs to the Bodom-massif, of which a short description is given by Sederholm (1926). The real carrier of the rare earths in this rock is orthite, although Sederholm made no mention of this mineral. Four thin sections were made of the rock and these were then analyzed planimetrically, using the integration stage of Leitz. The results show some 1 per cent of orthite.

An investigation of the distribution of the rare earths among the different minerals of the rock was found to be of interest. For this purpose hornblende, fluorite and orthite were separated from the rock with heavy liquids. It was found, however, that pure mineral fractions could be obtained only with considerable difficulty, as all fractions contained small amounts of orthite, visible under

Table IV.

	Granite, Quarry at Juva, Bodom		Orthite from Bodom Granite, Quarry at Juva		Granite, Onas		Granite, Obbnäs		Granite, Nattanen	
Y ₂ O ₃	0.03	38	< 1	< 10	0.008	80	0.02	40	0.003	33
La ₂ O ₃	0.06	75	7	78	0.004	40	0.03	60	0.003	33
Ce ₂ O ₃	0.08	100	9	100	0.01	100	0.05	100	0.009	100
Pr ₂ O ₃	0.02	25	2	22	0.002	20	0.007	14	0.002	22
Nd ₂ O ₃	0.03	38	4	44	0.008	80	0.02	40	0.005	55
61	—	—	—	—	—	—	—	—	—	—
Sm ₂ O ₃	0.01	13	3/4	8	0.002	20	0.006	12	0.001	11
Eu ₂ O ₃	0.002	2	—	—	0.0003	3	0.001	2	0.0002	2
Gd ₂ O ₃	0.012	15	1 1/2	16	0.002	20	0.008	16	0.001	11
Tb ₂ O ₃	0.002	2	—	—	0.0004	4	0.001	2	0.0002	2
Dy ₂ O ₃	0.006	8	1/5	2	0.0015	15	0.003	6	0.0005	5
Ho ₂ O ₃	0.002	2	—	—	0.0004	4	0.001	2	0.0002	2
Er ₂ O ₃	0.005	6	1/5	2	0.001	10	0.003	6	0.0003	3
Tu ₃ O ₃	—	—	—	—	0.0002	2	< 0.001	1/2	< 0.0002	< 2
Yb ₂ O ₃	0.005	6	1/10	1	0.001	10	0.002	4	0.0003	3
Lu ₂ O ₃	0.002	2	—	—	0.0004	4	0.001	2	0.0002	2
ThO ₂	0.02	25	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	0.003	33
Total	0.286	—	ca. 25	—	0.0412	—	0.154	—	0.0291	—
Ignited oxalic acid precipitate ..	0.29	—	23.7	—	0.035	—	0.142	—	0.040	—

the microscope. For this reason an enrichment of the rare earths was carried out only in the orthite fraction, and the enrichment product was examined by the X-ray spectrograph.

The second sample is from the Onas massif, near Porvoo, in South Finland. This granite region has been investigated by Borgström (1931). In respect of this granite he makes no mention of either orthite or monazite.

The third sample was obtained from a small granite massif in the parish of Kirkkonummi. This granite has been investigated by Sederholm (1926) who called it the Obbnäs granite. Neither as regards this granite has any mention of a content of earth minerals been made.

The Nattanen granite massif lies in Finnish Lapland, cutting through the granulite belt. This granite has been thoroughly investigated by Mikkola (1928), who has found orthite among the accessory minerals. The material used for the X-ray spectrographic analysis derives from the original sample used for a chemical analysis by Nordenswan, as given by Mikkola and analyzed by the means of optical spectrography by Rankama (1939).

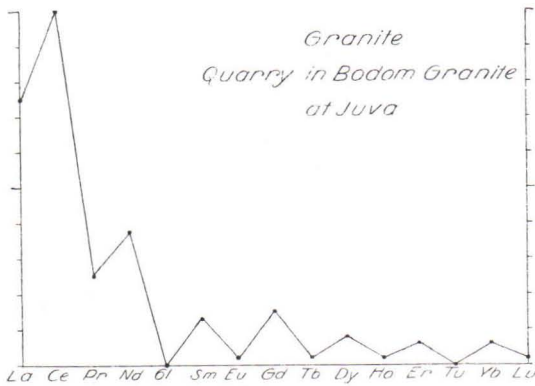


Fig. 9.

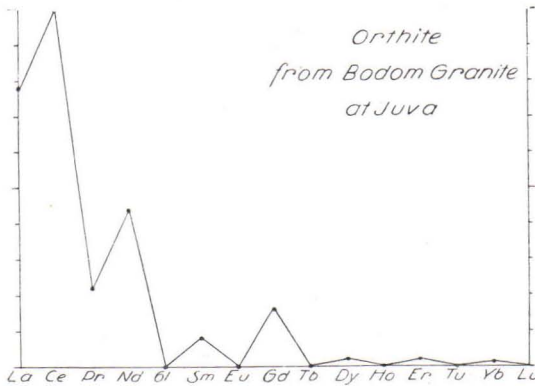


Fig. 10.

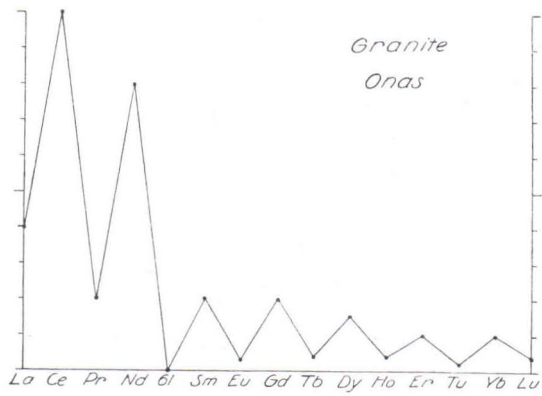


Fig. 11.

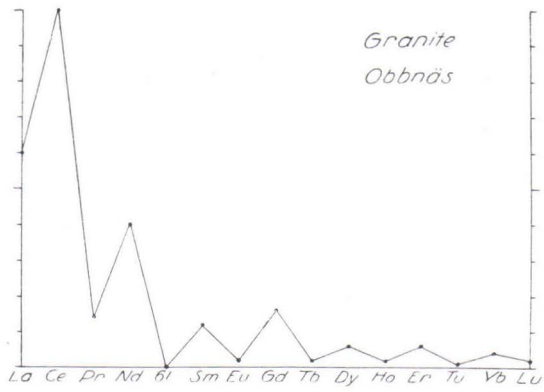


Fig. 12.

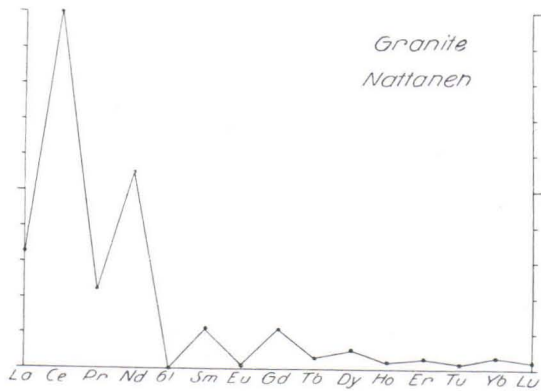


Fig. 13.

The granite of Maarianvaara in Northern Karelia has been subjected to a preliminary qualitative spectrographic investigation by Sahama and Rankama (1938). It was then found that this region is very poor in rare earths. A coarse-grained pegmatitic variety from Luikonlahti was selected among the samples from this region which were treated spectrographically, as the spectra taken in the visible wave-range had shown it to be one of the more rich in earths. This sample was twice subjected to a chemical enrichment (Table V, Fig. 14). In addition, a quartz-felspar fraction, a frac-

Table V. Granite Pegmatite, Luikonlahti, Maarianvaara Massif in Northern Karelia.

	I		II		Average from I and II		Monazite	
Y ₂ O ₃	0.005	250	0.005	250	0.005	250	1	4
La ₂ O ₃	0.001	50	0.001	50	0.001	50	14	60
Ce ₂ O ₃	0.002	100	0.002	100	0.002	100	23	100
Pr ₂ O ₃	0.0004	20	0.0006	30	0.0005	25	4	17
Nd ₂ O ₃	0.001	50	0.001	50	0.001	50	13 ^{1/2}	56
61	—	—	—	—	—	—	—	—
Sm ₂ O ₃	0.0005	25	0.0006	30	0.0006	30	4 ^{1/2}	20
Eu ₂ O ₃	0.0001	5	—	—	0.0001	5	—	—
Gd ₂ O ₃	0.0007	35	0.0008	40	0.0008	40	4 ^{1/2}	20
Tb ₂ O ₃	0.0002	10	0.0002	10	0.0002	10	< 1	< 4
Dy ₂ O ₃	0.0009	45	0.001	50	0.001	50	2	9
Ho ₂ O ₃	0.0002	10	0.0002	10	0.0002	10	—	—
Er ₂ O ₃	0.0007	35	0.0008	40	0.0008	40	1	4
Tu ₂ O ₃	0.0001	5	0.0001	5	0.0001	5	—	—
Yb ₂ O ₃	0.0006	30	0.0006	30	0.0006	30	< 1	< 4
Lu ₂ O ₃	0.0002	10	0.0002	10	0.0002	10	—	—
ThO ₂	0.0006	30	n. d.	—	0.0006	30	2	9
Total	0.0142	—	0.0141	—	0.0147	—	69—70	—
ignited oxalic acid precipitate	0.013	—	0.018	—	—	—	—	—

tion of biotite and one of garnet, and a very small one containing pyrite and monazite were all isolated from the rock by the aid of heavy liquids. Under the binocular microscope a couple of mg. of monazite were selected from the last-mentioned fraction with tweezers, mixed with comparison material and then subjected to X-ray analysis. The result is shown in Table V and Fig. 15. — No apatite was found to be present in the rock.

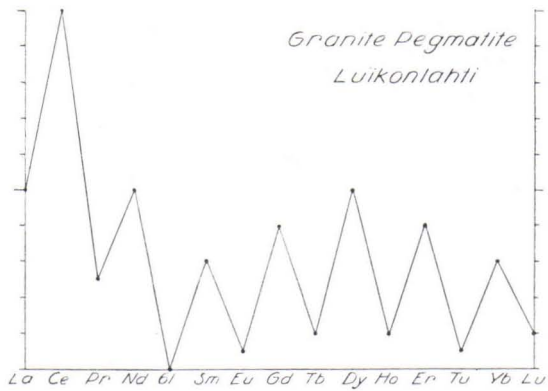


Fig. 14.

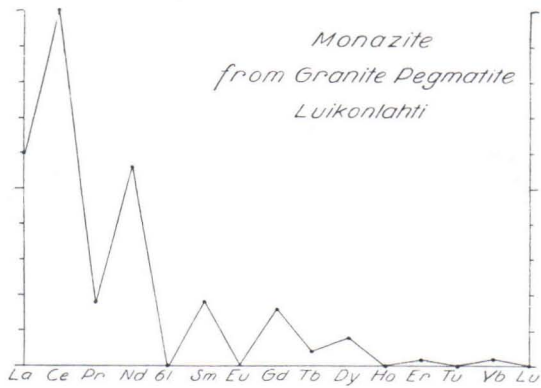


Fig. 15.

TWO EXAMPLES OF THE OLDER ARCHAEOAN GRANITES.

Besides making the above analyses of the youngest granites of Finland, two samples of older granites were investigated for comparison, both being remarkable for their relatively high earth content. For this purpose the granites from Unonen in Kalvola and from Astelsholm, Bällarby in Karjaa were selected. The results are shown in Table VI and Figs. 16—17.

Table VI.

	Granite, Unonen, Kalvola,		Granite, Astelsholm, Bällarby, Karjaa	
Y ₂ O ₃	0.005	71	0.003	60
La ₂ O ₃	0.004	57	0.003	60
Ce ₂ O ₃	0.007*	100	0.005	100
Pr ₂ O ₃	0.0015	21	0.001	20
Nd ₂ O ₃	0.005	71	0.003	60
61	—	—	—	—
Sm ₂ O ₃	0.0017	24	0.001	20
Eu ₂ O ₃	0.0003	4	0.0002	4
Gd ₂ O ₃	0.002	28	0.001	20
Tb ₂ O ₃	0.0003	4	0.0002	4
Dy ₂ O ₃	0.0015	21	0.0006	12
Ho ₂ O ₃	0.0003	4	0.0002	4
Er ₂ O ₃	0.001	14	0.0004	8
Tm ₂ O ₃	0.0001	1 1/2	0.0001	2
Yb ₂ O ₃	0.0007	10	0.0004	8
Lu ₂ O ₃	0.0003	4	0.0002	4
ThO ₂	0.002	28	0.001	20
Total	0.0327	—	0.0203	—
Ignited oxalic acid precipitate	0.031	—	0.029	—



Fig. 16.

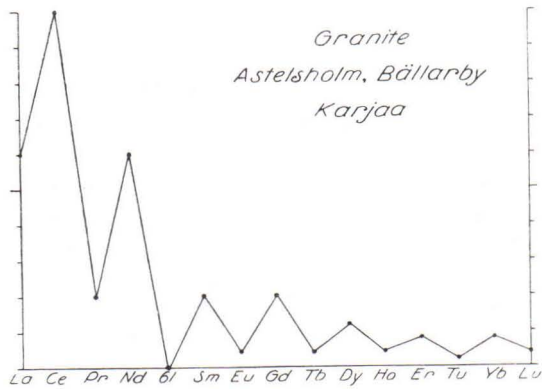


Fig. 17.

MINERALS.

One of the real lanthanide minerals, a monazite from the Kakola granite in Turku, was analyzed by X-ray spectrograph, in addition to the orthite from Bodom and the monazite from Luikonlahti. This mineral had been isolated from the rock by Laitakari (1934) and a sample of the monazite fraction was kindly placed at the disposal of the authors. By means of the binocular microscope fresh, inclusion-free grains of monazite were sought out from the monazite fraction — which was mainly contaminated by zircon and garnet — and were photographed without the admixture of comparison material (Table VII, Fig. 18).

Table VII. Monazite from Kakola Granite, Turku.

La ₂ O ₃	64	Gd ₂ O ₃	15
Ce ₂ O ₃	100	Dy ₂ O ₃	3½
Pr ₂ O ₃	20	Er ₂ O ₃	2
Nd ₂ O ₃	52	Yb ₂ O ₃	< 1
Sm ₂ O ₃	12		

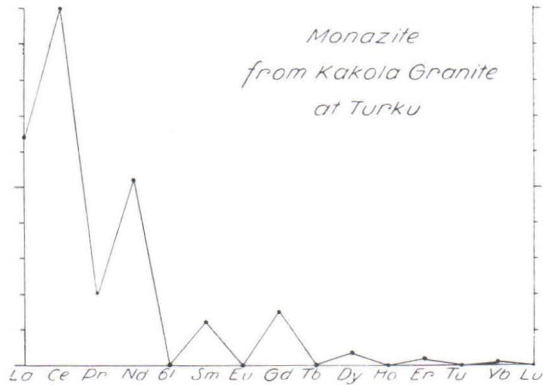


Fig. 18.

Among the rockforming minerals, which do not belong to the real earth minerals, but which, however, contain rare earths in fairly abundant amounts, mention must in the first place be made of apatite, titanite and fluorite. Of these a titanite from Pulmionniemi in Ristiina was isolated from placers and examined by X-ray spectrograph. (Table VIII, Fig. 19). A Mn-rich variety of apatite from the pegmatite granite of Uiharla in Eräjärvi was also examined (Table IX, Fig. 20).

Table VIII. Titanite Fraction from Sand, Pulmionniemi, Ristiina.

Y ₂ O ₃	0.1	125
La ₂ O ₃	0.03	37
Ce ₂ O ₃	0.08	100
Pr ₂ O ₃	0.02	25
Nd ₂ O ₃	0.06	75
61	—	—
Sm ₂ O ₃	0.02	25
Eu ₂ O ₃	0.004	5
Gd ₂ O ₃	0.02	25
Tb ₂ O ₃	0.005	6
Dy ₂ O ₃	0.02	25
Ho ₂ O ₃	0.005	6
Er ₂ O ₃	0.01	13
Tu ₂ O ₃	0.004	5
Yb ₂ O ₃	0.01	13
Lu ₂ O ₃	0.004	5
ThO ₂	0.02	25
Total	0.412	—
Ignited oxalic acid precipitate	0.39	—

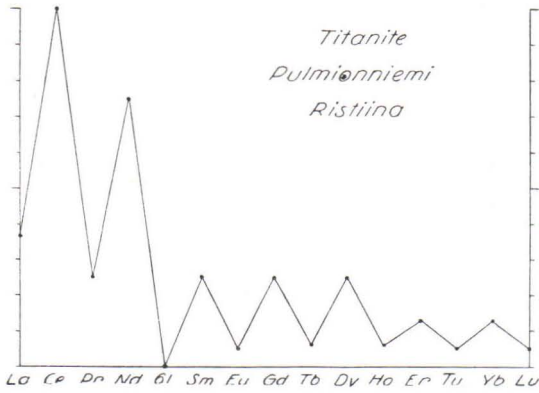


Fig. 19.

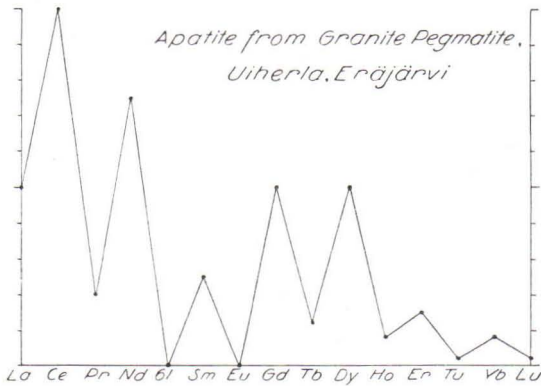


Fig. 20.

Table IX. Apatite (rich in Mn) from Granite Pegmatite. Uiharla, Eräjärvi.

Y ₂ O ₃	ca. 1	250
La ₂ O ₃	0.2	50
Ce ₂ O ₃	0.4	100
Pr ₂ O ₃	0.08	20
Nd ₂ O ₃	0.3	75
61	—	—
Sm ₂ O ₃	0.1	25
Eu ₂ O ₃	—	—
Gd ₂ O ₃	0.2	50
Tb ₂ O ₃	0.05	12
Dy ₂ O ₃	0.2	50
Ho ₂ O ₃	0.03	8
Er ₂ O ₃	0.06	15
Tu ₂ O ₃	< 0.01	< 2
Yb ₂ O ₃	0.03	8
Lu ₂ O ₃	< 0.01	< 2
Total	2.67	—
Ignited oxalic acid precipitate	2.57	—

DISCUSSION OF THE RESULTS.

As Goldschmidt and his co-workers have pointed out in several works, the rare earths in the periodic system undoubtedly represent one of the most beautiful examples of a very coherent group of elements, which in nature follow one another fairly far. As set forth by Goldschmidt and Thomassen (1924), the deviations in the relative concentration ratios of single earths in the real earth minerals are certainly very strong, but, as shown in the works of Minami (1935), Noddack (1935), and Landergren (1936) the corresponding disturbances in the rocks examined are considerably smaller in size.

The now available X-ray spectrographic data of the abundance of rare earths in rocks which are to be found in the above works by Minami, Noddack and Landergren, have been compared one with another by, *i. a.*, Landergren (*op. cit.*) and the observed differences have been discussed by him. He draws particular attention to the fact that in the iron ore derived from Blötberget the composition of the earths agrees very far with those relative earth concentrations, which have been found by Ida Noddack in the silicate meteorites, thus in an undifferentiated silicate magma. In contrast to this, the D-ore from Gällivare, according to Landergren, shows a different lanthanide composition, lying considerably nearer the abundance relation of the earths stated by Goldschmidt (1937 a), mainly on

the basis of data given by Minami. According to Landergren, the G-ore from Kiirunavaara lies between the two above-mentioned ores.

Seeing that literature contains no X-ray spectrographic data concerning the abundance relations of the rare earths in eruptive silicate rocks, it appeared to the authors to be of importance to discuss this side of the question on the basis of their material. As shown above, the rare earths are enriched especially in magmatic late crystallizations. It would, however, be of interest to ascertain in what concentration ratios the earths — though present in small amounts — occur in the intermediate and basic rocks. In this connection it is of special importance that according to Goldschmidt and Peters (1931) scandium in nature occurs enriched in more basic eruptive rocks. This circumstance is attributable to the scandium being captured particularly in the magnesium minerals. According to the cited authors (*op. cit.*, p. 271) it is also to be expected that when lanthanides and yttrium in very minute amounts occur together with scandium in basic, say, gabbroidic rocks, the earths of less basicity will be found to occur relatively enriched. In so far as the question can be judged by the aid of data given by van Tongeren (1938) from rocks of the East Indian Archipelago, this expectation seems to a certain extent to have received confirmation (*cf.* Table XI).

In order to throw some light on the subject, an attempt was made to enrich for quantitative determination the rare earths of some dioritic to gabbroidic rocks of the Finnish Archaean. Amounts of material up to 20 g. were treated. The earths were in no case discernible by means of X-ray spectrograph in the enrichment products in question. Neither were any earths discovered in the spectra of the chemically untreated material, taken in the visible region.

Included among the basic rocks in which the X-ray spectrographic methods failed to show any content of the rare-earth elements, was, *i. a.*, the normal olivine diabase from Säppi, of which a chemical analysis is given in Table I. Use was made of Eskola's interpretation, according to which the pegmatoids of Säppi really represent magmatic late crystallizations from the diabase magma. If rare earths are on the whole present in the original diabase magma, even though in very small amounts, it might well be thought that the earths would occur especially enriched in the pegmatoids, and, as already indicated above, such an expectation has actually received confirmation. Nature herself has here carried out an enrichment, thereby considerably facilitating the work. True, against such a train of thought the objection may be raised that hand in hand with the enrichment of the earths in pegmatoids, also a certain displace-

ment of the concentration ratios of single earths may become apparent. At all events it is nevertheless to be expected that these pegmatoids, although in a somewhat blurred form, will present a picture of the earth content of the diabase, more particularly when both the mega-ophitic diabase and the alkali felspar pegmatite are dealt with.

On comparing the X-ray spectrographic analysis of the two rocks in question, as given in Table II and Figs. 2—3, with the mean rela-

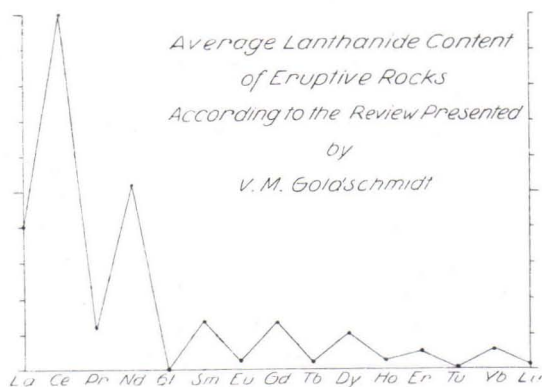


Fig. 21.

tive earth composition of the eruptive rocks shown in Fig. 21 — drawn on the basis of Goldschmidt's (1937 a) information — it will be found that the weaker basic yttrium earths actually are relatively enriched in the pegmatoids from Säppi. This phenomenon, which already qualitatively is plainly to be seen in the respective spectrograms, appears to be an indication that the earths with smaller ionic radii are somewhat more strongly represented in the diabase magma than in the average rare earth composition of the eruptive rocks. Further, as indicated above, in the account of the chemical pre-enrichment method (pre-treatment) this circumstance does not seem to be attributable to such causes as, *e. g.*, a selective enrichment of the earths, but really to represent a primary characteristic of the rock.

On the other hand, a comparison of these two rocks with the two granophyres from Säppi and Sorkka (Table II, Figs. 4—5) shows an appreciable difference. The two granophyres have an earth content which, within the limits of error, obviously corresponds to the mean earth composition of eruptive rocks as stated by Goldschmidt. Only yttrium content appears on the average to be somewhat higher. As pointed out above, in the discussion of the material, there is also

an obvious difference in the lanthanide composition of the pegmatoids proper on the one hand and of the vein-forming granophyres on the other. This difference exists in such sense that as regards their earth content the two granophyres are ranged alongside most of the granites investigated. This circumstance appears to indicate that also magmatically the granophyres do not correspond to the pegmatoids, but are of some other origin in the diabase.

As regards the walamite from the diabase region of Walamo, the relative concentration ratios of the rare earths agree fairly far with those of the granophyres from Säppi and Sorkka. As appears from Hackman's description (*op. cit.*) the genetic interpretation of these walamites, as hitherto given, differs from that of the granophyres referred to. However, it does not appear possible to the authors to take up a standpoint in this matter solely on the grounds of the given X-ray spectrographic determinations of the earths in the respective rocks. At any rate, this question, which has come up for discussion in connection with the earth composition of the walamite, seems worthy of consideration in the genetic interpretation of this rock.

The concentration ratios of the rare earths in the granites, which appear to represent the prevailing eruptive rocks of the upper lithosphere, have been presented above by several instances. In order to avoid misunderstandings it should at once be pointed out that the figures given for percentage must not be used in the discussion of the absolute abundance of the earths in the lithosphere, as granites which are comparatively rich in earths were purposely chosen when selecting the material. If the data given by Minami (1935) be compared with the existing contents of the granite, say, *e. g.*, on the basis of Tables IV and VI, it appears that the figures given by Minami are smaller on the average. This applies also to the data provided by van Tongeren (1938). In this connection only a quantitative confirmation of the regularity stated by Sahama and Rankama (1938) will be given, *viz.*, that the granite varieties most rich in earths in the Finnish Archaean are fairly often found in the youngest massifs.

So far as the relative concentration ratios of the earths are concerned, it must above all be pointed out that the major part of the samples examined show a pronounced cerium maximum. In the case of neodymium a chief maximum has not as yet been found. Further, the fact may be established, that the granites of Tables IV and VI, presented in Figs. 9, 11—13, and 16—17, show a far-reaching analogy with Goldschmidt's mean value in Fig. 21. With regard to the four most common lanthanides, La, Ce, Pr, and Nd, it should,

however, be stressed that their relative concentration ratios in the different granites are subject to certain deviations. These deviations, which are not, however, to be attributed to errors in the determination in the course of the analysis, are visible already qualitatively in the respective photometric records. As an instance of these deviations, reference may be made to the analyzed granites from Bodom (Fig. 9, Table IV) and Onas (Fig. 11, Table IV). The respective parts of the photometric records for these two granites are to be seen in Fig. 22. The exchange ratio between film and photometer curve is

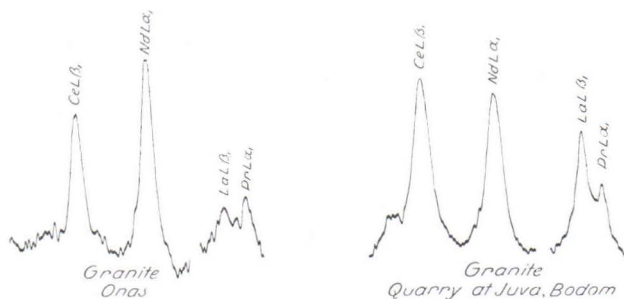


Fig. 22.

1 : 20 in the diagram. Heed should be paid to the galvanometer deflections for the given lines, as these differ from one another. These deviations in the concentration ratios between cerium and neodymium, observable in the Finnish granites are as a matter of fact also discernible from the data given by Minami (1935) for the three average mixtures of European and Japanese slates which he has investigated.

In analogy with Minami's statements, samarium and gadolinium are evidently the most frequent of the other even periodic number earths, while erbium and ytterbium are on an average those most rarely occurring. As already explained above, the figures given for the odd periodic number earths from europium to lutecium are much too inexact to allow of sure conclusions being drawn. It should only be pointed out that, as appears from the data of Minami (1935) and Ida Noddack (1935), and as specially stressed by Goldschmidt (1937 a and b) europium shows an abundance of about the same order of magnitude as Tb, Ho and Lu.

Among the samples of granite examined by X-ray spectrograph, there is, however, one with an earth composition distinctly differing from that of the others. This pegmatitic granite variety from Lui-

konlahti of the Maarianvaara massif in North Karelia shows a relative content of yttrium earths considerably higher than that of the other granite types investigated. This circumstance is plainly evident both from the film in question and from the photometric record, and was expected already beforehand, on the basis of the optical exposures. In the optical spectrum of the rock the strong line Y 4374.94 Å stated by Meggers (1928) is plainly to be seen and a test by V. M. Goldschmidt and H. Bauer, according to Strock (1936), shows that it can be traced to a concentration of 0.0005 %. Of the lanthanide lines the line La 4333.76 Å indicated by Meggers (1932) can be observed in extremely weak intensity.

The comparative abundance of yttrium earths in the granite pegmatite from Luikonlahti, shown in Table V and Fig. 14, is also very plainly to be seen in the annexed Table X. The relations between cerium and yttrium earths in the investigated granites are shown therein, gadolinium being reckoned as belonging to the latter.

Table X.

	Cerium earths / Yttrium earths
Granite, Bodom	3.2
Granite, Onas	1.8
Granite, Obbnäs	2.9
Granite, Nattanen	3.4
Granite Pegmatite, Luikonlahti	0.6
Granite, Unonen, Kalvola	1.8
Granite, Astelsholm, Bällarby, Karjaa	2.2

The circumstance discussed in connection with the granite pegmatite from Luikonlahti appears to be of a certain importance when judging of the distribution of the rare earths in eruptive rocks. It shows that there actually do exist granitic rocks differing in composition from the average earth content of the lithosphere. In this connection mention should be made of the fact that according to Goldschmidt (1930) the yttrium earths belong rather to the granite pegmatites than to the nephelite syenite pegmatites. Further, it is to be noted that in South Karelia, in the parish of Impilahti, pegmatites occur which contain wiikite on abundant amount, in addition to orthite and monazite. As the investigations of Lokka (1928) and of Sahama and Vähätalo (1939) agree in showing, wiikite is a pronounced yttrium earth mineral. Seeing, however, that the relation between

wiikite on the one hand and orthite as well as monazite on the other can scarcely be estimated with the requisite exactitude, the calculation of the total earth composition of these pegmatites in this manner is hardly possible. Neither are there, so far as is known to the authors, any similar calculations of single pegmatite occurrences to be found in literature. The calculations of Goldschmidt and Thomassen (1924) refer to the total abundance of the earths. At any rate, it does not seem to be impossible that just in the pegmatites of Impilahti a total earth content might be found in which the yttrium earths are present in relatively larger amount than in the lithosphere in general.

The circumstance already referred to above, that the relation between cerium and yttrium earths seems to be subject to certain deviations may further be assumed on the ground of the abundant data given by van Tongeren (1938) from rocks of the East Indian Archipelago. In the utilization of these data it should, however, be borne in mind that the respective spectrographic determinations have been made by means of visual comparison with comparison spectra. Accordingly the limits of error must be drawn correspondingly wide in dealing with the question. Further, the limits of sensitiveness for different earths given by van Tongeren must also be taken into account. In Table XI a few data from van Tongeren's work are given as instances. They show well the tendency in question.

Table XI.

Rock Name	Locality	No.	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Nd ₂ O ₃
Biotite granite	Djeboes	73	0.005	0.005	0.01	0.005
Granite	Gg. Bloeroe	83	0.003	0.005	0.01	0.01
Amph.-biot. granite	Bt. Barisan	37	0.001	0.0003	—	—
Biotite granite	Timor	249	0.003	0.0003	—	—
Amphibolite	Tg. Api	216	0.005	—	—	—
Uralite basalt	Djeboes	77	0.001	0.0003	—	—

As shown by Goldschmidt and Thomassen (1924) on the basis of numerous samples investigated by X-ray spectrograph, both monazite and orthite, which in rocks appear to be the most widely distributed of the real rare-earth minerals are quite pronounced cerium earth minerals, the yttrium earths having only a very small share therein. As regards pegmatite monazites this circumstance has later on been X-ray spectrographically demonstrated by Bearth (1924) and by Sahama and Vähätalo (1939), and has been confirmed by Matveyeff (1932) in respect of granite monazites from placers.

As a further confirmation reference may be made to the analyses given of the orthite from Bodom (Table IV, Fig. 10), and of the monazites from Kakola (Table VII, Fig. 18) and from Luikonlahti (Table V, Fig. 15).

If on the basis of the investigations referred to above a comparison be made between the earth content of orthite and monazite and the average relative earth composition of the eruptive rocks as stated by Goldschmidt, a definite regularity will be found. All the data referred to agree in indicating that in orthite and monazite the yttrium earths are subordinate in relation to the total earth content of the rock. This phenomenon is most clearly observable in the case of yttrium. According to Minami (1935) yttrium is certainly more abundantly present in the clay slates than either lanthanum or neodymium. In the orthites and monazites, of which quantitative X-ray spectrographic yttrium determinations are available, the observed content of yttrium is, however, far less than in the case of La and Nd. This circumstance is plainly to be seen in the turnerite from Tavetsch, examined by Bearth, as well as in the analysis of the orthite from Impilahti, previously published by the authors (1939), and also appears from the analyses of orthite, monazite and total rock from Bodom and from Luikonlahti, given in the foregoing.

The case of the granite pegmatite from Luikonlahti is very instructive in this respect. As monazite was the only earth-bearing mineral found in the rock, it was at first thought that the excess of yttrium earths in the total rock in relation to the monazite was perhaps to be found in the felspar. However, as shown by a spectrographic study of the pure, isolated felspar in the visible region, this expectation was not confirmed. Neither could any determinable amount of earths be chemically enriched from a felspar fraction of about 20 g. Further, there still remained the possibility that the excess of yttrium earths was to be found in the two dark constituents of the rock, *viz.*, garnet and biotite. An optical spectrum of the garnet, which had previously been carefully cleansed from all impurities, showed yttrium, but no La, Ce, or Nd. Unfortunately, a quantity of the mineral sufficient to allow of a chemical enrichment of the earths was not obtained. The fact, that garnets of different kinds are often yttrium-bearing was observed already by Goldschmidt and Peters (1931) and has later on been ascertained also by Sahama (1936) in regard to samples of several Finnish garnets.

According to the above it thus seems that an appreciable part of the yttrium earths in rocks remains outside the minerals orthite and monazite. Of those common rock-forming minerals, which

experience shows to contain rare earths in easily determinable amounts, fluorite, apatite and titanite are to be mentioned first of all. In so far as the data available in the literature allow of more general conclusions it may be said that the yttrium earths, taken on the average, are more strongly represented in all these minerals, than they are in monazite and orthite. This may be seen already from the fact that Goldschmidt and Thomassen (1924) have stated special apatite and yttrifluorite types for the relative earth content of the minerals in question, types which plainly differ from the monazite-orthite type as indicated above. The analyses of the titanite from Ristiina and of the apatite from Eräjärvi, given in Table VIII, Fig. 19 and Table IX, Fig. 20, point in the same direction.

In judging of the actual seat of the yttrium earths in rocks, it should not, however, be forgotten, that there exists a pronounced yttrium earth mineral, which may possibly be of a certain importance in this matter. It is a well-known fact that xenotime, the earth content of which has been published by Goldschmidt and Thomassen (1924) occurs in many, more especially pegmatitic and often muscovite-bearing granites. Unfortunately, however, in respect of its optical characteristics this mineral approaches zircon very closely. In thin sections, where perhaps only a couple of grains may be present, it is impossible to distinguish between the two minerals. Accordingly, it appears as if the possibility were to be reckoned with, that xenotime can be of a certain distribution in many rocks and represent one of the carriers of yttrium earths.

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CHALCOCITE FROM MERIJÄRVI, MIDDLE POHJANMAA

BY
KALERVO RANKAMA

INTRODUCTION.

The Geological Survey of Finland received in July 1937 from Mr. Teodor Hakala some rock specimens found by him in an outcrop on the bottom of the dried lake Tähjänjärvi in the parish of Merijärvi, Middle Pohjanmaa. Some of the specimens contained small dots of a green soft malachite-like material. A chemical analysis of one of the specimens gave 7 per cent of copper, and the copper mineral present was found to be chalcocite. During the summer of 1937 the outcrop and its surroundings were studied by Professor Aarne Laitakari, Director of the Geological Survey, and by Dr. Sampo Kilpi of the Geological Survey. In the summer of 1938 the present writer had an opportunity of paying a short visit to the area.

Since chalcocite has previously been found in Finland only at Pitkäranta (*cf.* Trüstedt, 1907, pp. 109, 112, 147; Laitakari, 1931, p. 56), it was thought to be not quite out of place to give a short account of this new miniature deposit.

GEOLOGY OF THE AREA.

The outcrop bearing chalcocite is situated about 1 km. to the north-west from the church of Merijärvi. The rocks of the area consist of granodiorite and quartz diorite. Their petrological and chemical character has been investigated by Mäkinen (1916, pp. 43—51, 58—62) and by Wilkman (1931, pp. 102—104, 107—113). The diorites form intrusive bodies in the Bothnian plagioclase gneisses which occur in the western parts of the region. Numerous resorbed inclusions of the gneisses are present in the diorites. In addition to these inclusions, the quartz diorite contains such of basic character. These have their origin in the pyroxene-bearing hornblendite and gabbro occurring east from the church of Merijärvi, as has been shown by Wilkman (1931, p. 85).

ALTERED QUARTZ DIORITE.

In places the normal quartz diorite is found to be somewhat altered, due to hydrothermal effects. The rock is cut by numerous quartz veins usually carrying a little pyrite. The gneiss fragments are often graphite-bearing, and graphite also occurs as small lumps of a few tens of cm. in diameter.

The color of the altered rock is greenish or reddish gray. The mineral grains measure up to 4.5 mm. The reddish color is due to the hematite inclusions contained in the feldspar. The main constituents of the rock, determined under the microscope, are plagioclase (ab. An₄₀), brown biotite, quartz, and yellowish green antigorite. Optically positive penninite (alteration product of biotite), almandite, thin needles of apatite, zircon, sillimanite, magnetite, pyrrhotite, graphite, and limonite are found as accessories. The texture of the rock is hypautomorphic granular. Antigorite occurs as veinlets penetrating the rock. In the neighborhood of these veinlets a few grains of microcline are occasionally found. Still another variety of serpentine is present, evidently replacing pyroxene: a pale grass green and weakly pleochroic chrysotile.

INCLUSIONS IN ALTERED QUARTZ DIORITE.

Three types of inclusions were found to be present in the altered quartz diorite:

1. Altered fine-grained biotite plagioclase gneiss. This type consists of biotite, plagioclase (An₃₅) filled up with chrysotile networks, graphite, limonite, and quartz with penninite, sericite, zircon, hematite, and opaque material in subordinate amounts. The penninite, which is optically negative, occurs as an alteration product of biotite. The inclusions are intersected by veinlets carrying graphite, antigorite, and ferric hydroxides. Veinlets of another kind carry chalcocite and, mostly, pyrite in the form of small grains and dust.

Some of the inclusions of this type are very rich in biotite whilst others, less altered, contain plagioclase as their main constituent.

2. Cummingtonite plagioclase rock. Besides these minerals, the other main constituents of this fine-grained rock are quartz and pyrite with a little chalcocite. Flaky antigorite, titanite, rutile, apatite, hematite, and limonite occur as accessories. The plagioclase is labradoritic with An₆₃₋₆₆. The pale-colored cummingtonite is faintly pleochroic with α nearly colorless, β very pale

yellowish, and γ very pale yellowish green. Absorption: $\gamma > \beta > \alpha$. The angle $c \wedge \gamma$ is $18^{\circ}5$, and the birefringence, measured by Berek compensator, is $\gamma - \alpha = 0.028$. The axial angle $2V$ is large. Sometimes there occurs twinning along the axis c . Antigorite is present as the alteration product of cummingtonite. The texture of these inclusions is granular, the components being present as anhedral or subhedral grains.

The biggest grains of the opaque material of the present rock measure up to 1.5 mm. Much of the pyrite and chalcocite, however, occurs in the form of very small particles, mostly together with a serpentine-like material, which obviously is of later origin than the other constituents of this rock. Sometimes the inner parts of serpentine develop a banding resembling the rhythmical precipitations of the colloids (Liesegang rings). A little microcrystalline quartz is found to be present inside these bubbles, giving the impression of a deposition as gel from colloidal solutions.

3. The third type of inclusions consists of granular medium-grained serpentine mica rocks, mainly composed of biotite (partly in an advanced state of alteration to chlorite), chrysotile, and quartz, with small amounts of microcline, muscovite, apatite, zircon, magnetite, and limonite. Hematite as thin scales is found included in the brown biotite. Quartz contains inclusions of sillimanite needles. Chrysotile is here pseudomorphous, most probably replacing hypersthene.

The shape of the inclusions of all types is lenticular.

CHALCOCITE.

Occurring in the form of small grains and, partly, as dust, pyrite and chalcocite are present in the biotite plagioclase gneiss and cummingtonite plagioclase rock inclusions. The stringers carrying the ore minerals evidently are later in their origin than the rock since they cut through and surround even the late serpentine.

The material for the chalcographic examination, carried out from a number of polished specimens by the aid of the Reichert Universal Microscope »MeF», was furnished by inclusions of Types 1 and 2 described above. The biggest inclusion of Type 1 was ab. 40 cm. in length and 15 cm. in width. In this inclusion the chalcocite was originally detected.

Under the reflecting microscope, chalcocite is seen to form bluish white anisotropic grains, the biggest of which display twinning. It also occurs as small stringers intersecting quartz and biotite. The grain size varies from 0.01 mm. to 0.4 mm. and is occasionally even more. The smaller grains are found to be intimately mixed with the pyrite grains whilst the bigger often are present as single ones, enclosed in quartz (Fig. 1). Malachite occurs as the alteration product of chalcocite.¹ The other minerals distinguishable in the polished specimens are biotite, quartz, and limonite, the latter as oxidation product of pyrite.

Big grains of chalcocite after etching with concentrated nitric acid develop etch cleavage directions (Fig. 3). In etching, also the twinning becomes more well developed, being in some instances present in two directions, at oblique angles to each other. Usually, the grains display an alternation of parallel blue and reddish white bands, thus resembling the twinning according to the albite law in plagioclase. The boundaries between the bands are straight and lie parallel to one of the orthorhombic cleavage directions of the chalcocite (Fig. 1).

Pyrite forms stringers penetrating the rock, or small grains and dust, the grains measuring from 0.04 up to several mm. In every section it is found to be surrounded and replaced by chalcocite (Fig. 2). In some cases pyrite develops textures comparable with the Liesegang rings due to rhythmical precipitation and referring to a forming from gels by crystallization at low temperatures (*cf.* Schneiderhöhn and Ramdohr, 1931, p. 160; Lindgren, 1928, p. 214) (Fig. 3). Here chalcocite replacing pyrite is of low anisotropy, after etching, however, growing blue and strongly anisotropic. Also »carietic» contacts between pyrite and chalcocite are present with chalcocite »bitten into» pyrite, which has been altered to limonite (Fig. 2).

GENESIS OF THE CHALCOCITE.

The chalcocite of Merijärvi, according to its properties and its mode of occurrence, is of the orthorhombic variety (β -chalcocite), and most probably has been deposited from descending aqueous solutions carrying cupric sulfate below 91°C in the oxidized zone

¹ According to Lindgren (1928, p. 950) the oxidation of chalcocite to malachite is relatively rare. Here, on the bottom of a lake, actually in water, it has easily taken place.

where there is a deficiency in oxygen (Lindgren, 1928, p. 942), and where the primary sulfides possess reducing powers (Schneiderhöhn and Ramdohr, 1931, p. 299). The chalcocite thus is supergene in its origin, the deposit belonging to the epigenetic ones.

Compared with each other, the Merijärvi chalcocite and one of those from Pitkäranta, described by Laitakari, present common features as to their mode of occurrence and origin. According to Laitakari (1931, pp. 57—58) the granular chalcocite replacing pyrite from the »New Tin Mine» in Pitkäranta has been formed from descending solutions by deposition on the earlier sulfides below 91°C.

As to the probable age of the Merijärvi chalcocite, it is thought to be identical in this respect with the lamellar white and blue chalcocite from southern Kiirunavaara, described by Geijer (1923, p. 9). According to Geijer (*op. cit.*, p. 11) this chalcocite is the product of a »secondary» enrichment of pre-glacial age.

Geological Survey of Finland, Helsinki, July, 1940.

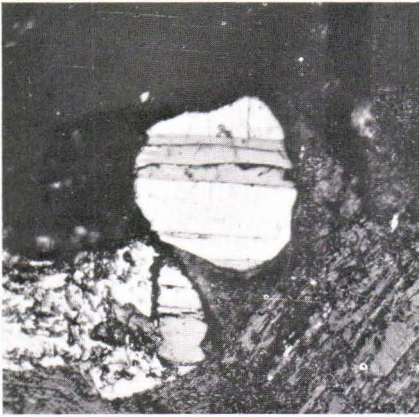


Fig. 1. Twinned chalcocite (gray) with pyrite (white, high relief) in a matrix of quartz and biotite. Etched (10 secs.) in concentrated HNO_3 . Ord. light. $\times 290$.



Fig. 2. Coating of chalcocite on pyrite due to peripheral replacement. Flakes of biotite at the sides. Etched (10 secs.) in concentrated HNO_3 . Ord. light. $\times 290$.

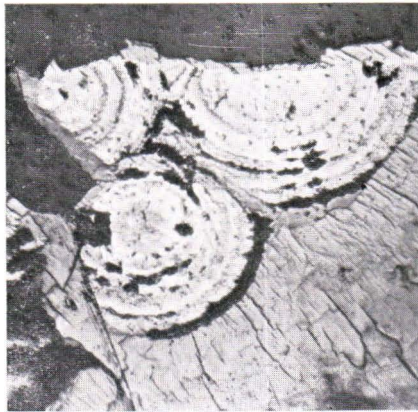


Fig. 3. Pyrite with concentric gel textures replaced by chalcocite. Chalcocite shows etch cleavages in two directions. The black areas around the pyrite shells consist of limonite. Etched (12 secs.) in concentrated HNO_3 . Ord. light. $\times 290$.



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ON THE USE OF THE TRACE ELEMENTS IN SOME
PROBLEMS OF PRACTICAL GEOLOGY.

BY
KALERVO RANKAMA.

ABSTRACT.

The enrichment of nickel in plant ashes from two nickel mining districts in Finland has been investigated by the aid of optical spectrography. The possibilities of the use of the minor elements in prospecting are discussed and a suggestion concerning their use as an aid in geological mapping is presented.

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INTRODUCTION.

Starting from the remarkable fact that the element germanium is found to be concentrated in certain coal ashes, the circulation from the soil to the surface of the ground during the cycle of plant growth and decay has been established for a large number of elements by Goldschmidt in three papers (Goldschmidt und Peters, 1933, p. 385; Goldschmidt, 1934, p. 425; 1937, p. 670). According to Goldschmidt, the solutions circulating in the soil dissolve and extract the inorganic compounds present in the sub-soil according to their solubility. These solutions, entering the plants through the roots, deposit the greater part of their burden at the places of strongest evaporation, especially in the leaves. It is also known that the highest concentrations of the trace elements in plants are found in the young parts which are in the state of strongest growth, and that in leaves turning yellow and withering the content of most of the minor elements decreases. From the decaying leaves the most soluble mineral constituents, such as sodium, potassium, magnesium, calcium carbonates and sulfates, and iron humates are washed away by the rain water, whilst the less soluble or insoluble compounds are retained in the humus layer. By such simple processes of a physical nature the following elements have been found to become concentrated in the uppermost humus layers of forest soils:

Ag, Au, Be, Zn, Cd, Sc, Tl, Ge, Sn, Pb, As, Mn, Co, and Ni.

This list thus covers many rarer elements of the most diverse groups of the periodic system.

Also biological processes may cause an enrichment, especially in the case of elements which show the greatest degree of concentration, such as boron, which in many cases is strongly enriched in the ashes of living plants (Goldschmidt, 1937, p. 671).

EARLIER FACTS ON THE GEOLOGICAL BACKGROUND OF ENRICHMENT.

The question of the possible application of these enrichment phenomena to some branches of practical geology, such as prospect-

ing and geological mapping, consequently lies very near at hand. As this at the first glance may seem rather speculative, a few citations from literature will be presented in the following to illustrate the facts so far known.

In a paper dealing with the spectroscopic detection of the Rare Earths in plants, Scribner (1939) presents the results of an investigation of the ash from hickory leaves from a tree growing on a pegmatite vein in Amelia, Virginia. The leaves were found to be very rich indeed in the Rare Earths, and the ashes from a number of other samples of plant material contained at least a few of these elements as well.

Contradictory results have been obtained by Sahama. For a study dealing with the Rare Earths in some Finnish eruptive rocks and minerals (Sahama and Vähätalo 1939) rather large samples of leaves were collected by Sahama from birch trees growing on the wilkite-bearing pegmatites at Hunttila and Nuolainniemi, parish of Impilahti. From these samples as well as from one from Koirinoja, Impilahti, with no pegmatites in the neighborhood, attempts were made to precipitate the Rare Earths by oxalic acid. The results, however, failed to show the presence of the lanthanides at all. The optical spectra of the samples showed only lanthanum lines of very doubtful character. In addition, a minute trace of yttrium was found in the Hunttila sample (Sahama, personal communication).

Bateman and Wells (1917) have investigated the presence of copper in plants of a copper tailing region near Anaconda, Montana. They found some plants to be dead or highly affected by the copper. On the other hand, several plants were found to be unaffected by the high copper content and still others were flourishing in spite of it, and thus showing a decided selective activity towards copper. In addition to copper, the plants growing in this region were found to contain arsenic, antimony, and zinc.

More recently, Prát and Komárek have established the presence of large amounts of copper in the ash of plants grown near the Slovakian copper mines (Sborník Masarykovy Akad. Práce, Tom. 8. p. 1. 1934). Unfortunately, this study is known to the present author only from an abstract (Chem. Zentralbl. 1935 II p. 870).

High percentages of zinc have been found in plants growing on ground rich in this element, *e. g.*, on the waste ore dumps of zinc mines. Some of these plants show a decided activity towards zinc, *e. g.*, *Viola calaminaria et zinci* from Belgium and the Rhineland, with a content of up to several per cent of ZnO in its ashes.

According to Dingwall, McKibbin, and Beans¹ molybdenum was found by spectrographic means in plant ashes from the Province of Quebec. All the plants investigated from a certain area in the Ottawa River Valley with known molybdenum deposits contained this element, while many of the plants grown outside this valley were found to be free from molybdenum.

The few examples cited above will perhaps suffice to give some hints as to the possible use of the trace elements in prospecting. No element, however, should be used without due attention to the fact that varying amounts of many of the minor elements are found normally in plants. In practice, the use of the Goldschmidt enrichment principle will find its most suitable realization in the use of spectrum analyses of the ashes from plants grown on the area investigated. So far as is known to the author, the recently developed Swedish Palmqvist-Brundin method of prospecting is based on this principle (*cf.* Landergren, 1939, p. 77). For this method the name »geochemical prospecting» is very commonly used.

SCOPE OF THE WORK.

With the exception of the very sparse facts presented by Landergren (1939, p. 77) and those contained in a report of a meeting of »Svenska teknologföreningens avdelning för Kemi och bergsvetenskap» (Tekn. Tidskr., Bergsvetenskap, 1939, pp. 55—56) no information concerning the application of the Goldschmidt principle to terrains once covered by the Quaternary land ice is available.²

In order to gain first-hand experience of the possibilities of prospecting based on the Goldschmidt principle, especially in Finland, the present author spent some time during his field-work in the summer of 1939 in collecting plant samples for the present study. Nickel was chosen as the reference element. In order to gain information as to the influence of the thickness of the glacial drift on the enrichment, samples were collected from three areas, *viz.*, from the vicinity of the outcrop of the Kaulatunturi nickel ore-body in Petsamo, from

¹ Canad. Journ. Res., Vol. 11, pp. 32—39, 1934; referred to in Chem. Zentralbl. 1935 I p. 2386 and in Chem. Abs. Vol. 28, p. 7299, 1934.

² A pamphlet »P. M. angående vår geokemiska prospekteringsmetod» published in 1939 by Svenska Prospekterings Aktiebolaget (The Swedish Prospecting Company Ltd.) explains shortly some of the results attained in Cornwall, Devonshire, and Wales; these areas, however, are situated outside the latest glaciation.

the adjoining Kolosjoki Town Area, and from the Makola Area in the parish of Nivala, where a deposit of nickel ore has been discovered by the Geological Survey of Finland. In addition, a few samples were collected from a small zinc and lead deposit at Pitkämäki, Leppäselkä, near Sortavala. Due to the Russo-Finnish war the laboratory work had to be postponed until the summer of 1940.

METHODICS.

COLLECTION AND PREPARATION OF THE PLANT MATERIAL.

The plant samples for the most part consist of birch leaves. A number of other plants were collected in addition, their names being given in the later descriptions of the areas investigated. As regards the choice of the plant species, the trees and the bushes in most cases seem to afford more suitable material for an investigation concerning the enrichment phenomena than is the case with grass and flowers, seeing that their roots reach deeper layers and cover larger areas of the ground. In the end, however, the local flora will be the decisive factor in the matter. In this connection it may be noted that since the ash percentages are different for different plants, the factors of the enrichment of the elements in the plant ashes are not directly comparable with one another, the samples with small ash percentages showing a more decided enrichment than those with large ones, as has been pointed out by Goldschmidt and Peters (1933, p. 372). However, when ashes from a certain plant species from a given area are investigated, as is the case in Makola, the differences in the ash percentages ought to be small enough to allow of a direct comparison of the results of the various analyses.

The plant samples were collected between July 10th and August 10th. As a matter of fact, the summer is the best season for collecting, since the plants have then arrived at their most thriving state of growth, while the autumnal withering has not yet commenced.

Leaves or needles were taken from the trees, while the grass and the flowers were collected as whole plants, though without roots. The collection of the plants took place during or after a rainy period; the possibility of contamination by soil particles or by dust blown by the winds being thereby excluded.

The weight of the fresh samples was ab. 40 to 60 g. In order to avoid any contamination by nickel, the collection was carried out by hand picking, without the use of any metal tools. The samples

were dried by exposure to the open air and were thereupon stored in clean paper bags.

By preliminary experiments vessels made of porcelain or silica were found to be attacked during the incineration. Therefore, after a few unsuccessful attempts to use a gold dish, the incineration was carried out in platinum crucibles of a capacity of 100 ml. The crucibles were heated over a very small flame of chromium plated Meker burners in order to avoid introducing nickel either from the burner material or from the coal gas with its possible content of nickel carbonyl. Due to their content of hygroscopic salts, the ash samples, after a thorough homogenization, were stored in well stoppered glass tubes. The weight of the samples was usually 0.1 to 0.3 g.

When there are easily volatile compounds to be determined, *e. g.*, Pb, Ge, Mo, and V, in the presence of chlorides of alkalis or alkaline earths, a sufficiently low incineration temperature (not exceeding 450° to 500°C) must be provided by the aid of an electric muffle furnace. In the present case, attention being paid only to nickel, no especial precautions were needed, due to the low volatility of the nickel oxides.

However, another source of error is supposed by Goldschmidt (Goldschmidt und Peters, 1933, p. 382) to be present during the incineration, *viz.*, the partial volatilization of nickel in the form of nickel carbonyl. In order to study the possibilities of the formation of this compound in the present case, the following experiment was carried out. A few grams of a sample of birch leaves with 0.006 % NiO were coarsely powdered and homogenized. Two portions were weighed out. The first portion was incinerated in a platinum crucible in the usual way, the second portion being treated twice by a mixture of concentrated nitric acid and of hydrogen peroxide (30 p. ct.) in a capacious platinum crucible in order to destroy all the organic material. Any nickel carbonyl possibly formed is decomposed here by the nitric acid (Abegg, Auerbach und Koppel, 1937, p. 809). The solution was evaporated down to dryness on a steam-bath and cautiously heated over a Meker flame in order to destroy the nitrates. When the spectra of the ashes were compared, it was found that the nickel line of the sample from the wet treatment was weaker than that from the sample subjected to the ordinary incineration. The amounts of NiO in both cases were close to 0.006 per cent. Accordingly no losses of nickel owing to the formation of carbonyl are to be feared here.

According to the facts presented in the handbooks, $\text{Ni}(\text{CO})_4$ is formed from nickel compounds and carbon monoxide at a temperature

of appr. 250°C under a pressure of 200 to 350 atm. (Abegg, Auerbach und Koppel, 1937, pp. 801—802). Favorable conditions for the formation of metal carbonyls from the oxides are elevated temperature and high pressure in combination with high purity of the carbon monoxide used, as the degree of formation of the carbonyls suffers greatly from the presence of gases such as oxygen, water vapor, and carbon dioxide (Abegg, Auerbach und Koppel, 1934, p. 553). During the incineration an oxidizing atmosphere is provided inside the crucible with the cover slipped a little to one side to allow the air to enter, and thus the possibilities of the formation of nickel carbonyl are too small to produce any noticeable losses of nickel.

Still one question lies beyond this discussion, namely, that of the rate of the election of cations by plants. According to Freeland¹ an increase in the water absorption of plants is accompanied by an increase in mineral intake, different ions being absorbed at different rates. The rate for each ion varies with the plant species. According to Collander (1937, pp. 78—79) the grouping of some elements (K, Rb, Cs, Mg, Ca, and Sr) according to their intake by plants can possibly be based on the mobilities of the ions. The indispensability of the ions to the plants plays no rôle during the intake and, accordingly, facts such as the poisoning of the plants by copper (Bateman and Wells, 1917) or by selenium (Strock, 1935, p. 11) can be explained.

SPECTROGRAPHIC TECHNIC.

Fast and sensitive methods of analysis being requisite owing to the large number of the samples to be investigated for the present study, the methods of spectrum analysis were chosen as being the most suitable. Compared with the methods of the ordinary chemical or microchemical analysis, their pre-eminence also lies in the fact that in many cases the ashes can be analyzed as such, without any preceding solution, which is connected with a possible source of error lying in the addition of impure chemicals. However, the possibilities of spectrographic analysis of solutions are not excluded, being, on the contrary, even recommended for some elements, *e. g.*, zinc, for reasons accounted for on p. 102.

The spectrographic examination of the ash samples was carried out by the aid of a Zeiss Quartz Spectrograph Model Qu 24, using

¹ Amer. Journ. Botany, Vol. 24. pp. 373—374. 1937; abstract in Chem Abs., Vol. 31. p. 6284. 1937.

the carbon arc cathode layer effect method developed by Mannkopff and Peters (1931). The cathode layer was projected diffusely on to the spectrograph slit, one of 0.01 mm. width being used. Five subsequent fractions were photographed on each plate. The other details of the technic are the same as those used by the present author in a previous study (Rankama, 1939, p. 11).

Specially purified carbon rods of a diameter of 5 mm. were used as electrodes. The cathode bore was 5.0 mm. deep with an inside diameter of 1.0 mm., and an outside diameter of 2.9 mm. The length of the thin nose of the cathode, provided with the bore, was 11.0 mm. These measures do not differ essentially from those used by Rost (1939, p. 3). Ernst and Hörmann (1936, p. 205) have used a bore with a depth of only 2.0 mm. and an inside diameter of 1.0 mm. These measures, however, were intended for samples smaller than those used in the present work.

The NiO percentages were determined by visually comparing the absolute intensities of the nickel lines in the spectra of the samples and in those taken of the concentration steps of the standard mixture series. The nickel line used, Ni 3414.77 Å, is that given by Ernst and Hörmann (1936, p. 205). As the plant ashes contain notable amounts of alkali carbonates, the steps of a previously used standard mixture (Rankama, 1939, p. 11) were diluted by anhydrous sodium carbonate free from nickel in order to ensure their being of a composition approaching those of the ash samples. The new mixtures, containing appr. 15 per cent of anhydrous sodium carbonate, were homogenized by grinding in small agate mortars.

The first comparison of the line intensities was carried out by the aid of a Zeiss Spectrum Projector. For the purpose the breadths of the nickel lines in the various concentration steps of the standard mixtures were traced side by side on a slip of paper. Using this master intensity series an estimation of the intensities of the nickel lines in the ash spectra was carried out.¹ The results were controlled by a comparison by the aid of a binocular microscope. When needed, corrections were made during that stage, but the results usually were concordant. The method of visual comparison of the line intensities introduced here combines ease to the eye with high rapidity. In an hour more than twenty determinations can conveniently be carried out.

No essential differences were found to exist between the intensities of the strongest nickel lines in the spectra of the steps of the

¹ This method of comparison has previously been used in the Geochemical Laboratory by Mr. Maunu Puranen, M. A.

concentration series diluted by sodium carbonate and the series with out additional alkali. Apparently, there is no difference between an exposure of an undiluted sample and of a diluted one after the evaporation of the alkalies in the arc as has been stated by van Tongeren (1938, p. 31). The only difference between the nickel lines in the two series of standard mixtures lies in the fact that the lowest concentration of nickel obtained by the addition of sodium carbonate is 0.001 % NiO, while the corresponding concentration in the series without additional alkali lies at 0.0003 % NiO (*cf.* Rankama, 1939, p. 12). Accordingly, the statement by van Tongeren (1938, pp. 89, 90) that the nickel lines in the visible region, being comparable with the cobalt lines in regard to their general character, show better without any addition of sodium carbonate has once more been confirmed as to the U. V. nickel line 3414.77 Å used in this study.

NICKEL IN PLANT ASHES FROM SOME NICKEL DEPOSITS.

KAULATUNTURI.

Some plants were collected from the immediate vicinity of the outcropping ore-body at the Kaulatunturi hill in Petsamo. The plants were growing on serpentinite at a height of 345 m. above sea level, 5 to 10 m. to the S. (downhill) of the largest part of the outcrop. Here the thickness of the morainic drift is negligible, and due to trenching the nickel-bearing waters from the outcrop have easy access to the roots of the plants. A large part of the drift consists of rocks belonging to the Lapland granulite belt and to the charnockites connected therewith. The source of the drift lies in the south part of the Petsamo Area (Väyrynen, 1938, p. 16).

The plant species and the nickel contents of their ashes are presented in Table I. The percentages of NiO are rather large, and a distinct and fairly uniform enrichment of nickel in the ashes due to the vicinity of the ore-body can be established.

TABLE I.

NiO PERCENTAGES IN SOME PLANT ASHES FROM KAULATUNTURI AND KOLOSJOKI.

Plant species	Kaulatunturi	Kolosjoki
<i>Betula tortuosa</i>	0.2	0.006
<i>Betula nana</i>	0.1	0.006
<i>Salix glauca</i> × <i>phylicifolia</i>	0.5	no sample
<i>Empetrum hermaphroditum</i>	0.1	< 0.001
<i>Cornus suecica</i>	0.1	no sample
<i>Deschampsia flexuosa</i> v. <i>montana</i>	0.03	no sample
<i>Cladonia alpestris</i>	0.1	= 0.001 ¹
<i>Vaccinium myrtillus</i>	0.02	< 0.001
<i>Pinus silvestris</i> ²	no sample	0.006

KOLOSJOKI.

From the Kolosjoki Town Area, situated at a height of 125 to 150 m. above sea level, and appr. 2.5 km. to the N.W. of the outcrop at Kaulatunturi, plants were collected for comparison with the Kaulatunturi samples. The prevailing rocks here consist of tuff schist covered, however, by a layer of morainic drift several metres in thickness. The composition of the drift is similar to that at Kaulatunturi. The results of the spectrum analyses are given in Table I. Compared with the percentages from Kaulatunturi, the NiO content is very decidedly lower, thus indicating the effects of the drift cover and of the watershed which hinders the nickel-bearing solutions reaching the country on the north slope of Kaulatunturi.

¹ The sample spluttered badly in the arc. Due to the scantiness of the material another spectrum could not be obtained.

² Young needles.

MAKOLA.

A comparatively large number of samples from the nickel deposits at Makola were analyzed, the material in its entirety consisting of birch leaves, whereby the obtaining of results well comparable with each other was guaranteed. In all, 63 samples of leaves were investigated. As to the different birch species, there were 4 samples of *Betula verrucosa* and 6 of *B. pubescens*, the other samples being of cross-breed types between the two pure species. No essential differences between the NiO percentages of the different kinds of birch could be established.

The collection of the samples was based upon a system of lines earlier made by the Geological Survey for the magnetic mapping at Makola. For this purpose the field had been divided into squares with sides 20 m. long. The sampling points together with some topographic features are presented in Fig. 1, Plate I. Unfortunately, the network of the sampling points is not very dense, due to the extensive trenching work carried out at Makola, owing to which the later location of the magnetometric survey points in many cases has become impossible.

The general character of the Makola Area is that of a wet swampy lowland with a little elevated dry terrain only in the east and south-east corners of the area illustrated in Fig. 1.

According to a communication which Dr. Sampo Kilpi of the Geological Survey very kindly put at the author's disposal, the thickness of the loose deposits overlying the bedrock at Makola is appr. 3 to 4 m. The topmost layer (0.3 to 1 m.) consists of peat, and under this a layer of fine-grained sand occurs (appr. 1 m.). Sometimes, however, the peat is found lying directly over the morainic drift. The thickness of the drift is 1.5 to 3 m. The composition of the morainic drift is characterized by the preponderance of boulders of gneissose granite, granite, and mica-schist with only small percentages of boulders consisting of gabbros and peridotites. The last-mentioned rocks are not of the local type. Only on the bottom of the drift do the local serpentine rocks of Makola occur.

According to investigations based on the striae and on the boulder trains, the principal transportation direction of the morainic material by the ice-sheet has been N.54°W. to N.60°W., with local movements during the stay of the ice-edge at Makola in the directions N.42°W. to N.54°W.

The first serpentine boulders of the local type found on the surface of the loose deposits are met with at a distance from the out-

crop of appr. 300 m. in the transportation direction. Accordingly, the influence of the ore-bearing serpentine bodies upon the composition of the surface layer of the morainic drift begins at an interval of not less than 300 m. from the outcrop in the directions N.54°W. to N.60°W.

The flow of the ground water most probably follows directions from the east to the west and from the south-east to the north-west.

The bedrock of the Makola area consists of biotite plagioclase gneiss closely resembling a mica-schist with intrusive bodies of serpentized peridotites carrying the sulfide minerals (Saksela ja Hackzell, 1938, pp. 73—79). An attempt was made to correlate the locations of the different rocks as indicated by the diamond drill holes and the trenching work to the nickel values found in the leaf ashes, but the result was unsatisfactory, evidently due to the many fluctuations in the geology of this small area.

The NiO percentages of the ash samples are presented in Fig. 1. As is shown by this figure, the highest percentages in many cases occur in the nearest vicinity of the ore-body, and also surround the area bounded by the curves of the magnetic vertical intensity. According to Fig. 1 the flow of the surface waters has no effect upon the distribution of nickel in the area investigated.

An attempt is given in Fig. 2, Plate I to present the local changes in the NiO contents of the ashes by curves of equal NiO percentages. In the construction of the curves the effect of the incompleteness of the sampling point network had to be taken into account, the location of the curves accordingly at some places being a result of rather wide extrapolation. The general tendency of the curves to surround the ore-body is, however, indicated by Fig. 2.

The NiO percentages of the ashes as such are not very high. The areal changes, however, are large enough to show the presence of nickel ore at Makola, the influence of an ore-body through 3 m. of morainic drift being here manifested. It cannot be suggested that the morainic drift would contain other nickel-bearing boulders, alien to the Makola area, in sufficient quantity to cause all the nickel indications of the ashes. Such a suggestion would presuppose the deposition of these boulders by chance exactly on top of the ore-body.

APPENDIX: PITKÄMÄKI.

For the sake of comparison a few samples were collected from a small blende and galena deposit at Pitkämäki, lying in the village

of Leppäselkä, appr. 23 km. to the N.W. of Sortavala. The sulfides occur in a layer of impure limestone which lies intercalated between amphibolite and mica-schist. During the summer of 1939 prospecting work was carried out here by the Prospecting Company Suomen Malmi Osakeyhtiö. The leaf samples were collected from a point situated ab. 5 m. to the W. (downhill) from the downmost part of trench No. 4. The results of the analyses of the ashes are presented in Table II. In addition, this table contains the results from the zinc determinations of the ashes. Here plant ashes are present containing no nickel at all or, at least, nickel in amounts small enough to escape

TABLE II.

NiO AND ZnO PERCENTAGES IN SOME PLANT ASHES FROM PITKÄMÄKI.

Plant species	NiO	ZnO
<i>Vaccinium vitis-idaea</i>	0.003	> 1
<i>Betula verrucosa</i>	0.001	> 1
<i>Oxalis acetosella</i>	< 0.001	> 1
<i>Fragaria vesca</i>	0	> 1
<i>Geranium silvaticum</i>	0	> 1

detection. The comparison series used for the zinc determination was one containing no sodium carbonate. In such a series the lowest concentration detected was 0.01 % ZnO (Rankama, 1939, p. 12) while in a series diluted by sodium carbonate the limit lies at 0.3 % ZnO. The zinc line at 3345.00 Å of a mixture with 1 % ZnO is already very weak. The present results are concordant with those obtained by van Tongeren (1938, p. 47) who states that the sensitivity of the zinc lines is lowered by the addition of sodium carbonate to the sample, and that zinc accordingly should be determined, whenever possible, in the absence of substances having this effect, as otherwise the results obtained will probably be too low.

DISCUSSION OF THE RESULTS.

THE USE OF THE TRACE ELEMENTS IN PROSPECTING.

The possibilities of the application of the minor elements as an aid to prospecting in areas lying outside the latest glaciation have been referred to on p. 93. According to the results presented above it seems possible that prospecting according to the Goldschmidt principle can in some cases also be carried out in terrain once covered by the Quaternary land ice. We may state that during the thousands of years which have passed since the melting of the land ice there has occurred an upward circulation of metal solutions in the morainic drift, enabling some chemical features of the underlying rocks to be reflected in the composition of the plants grown on the moraine. However, there are layers too thick or impenetrable which may cause a failure of this method. The false results caused by erratic boulders present in the drift must also be taken into account.

As to the last-mentioned feature, the failures might well be avoided, at least partly, if proper attention be paid to the bulk minor element composition of the ash samples investigated. It lies very close at hand to assume that the ashes of plants influenced by single erratics will contain minor elements alien to or not regularly found in the ashes of plants to whose composition the solutions carrying the metals present in the bedrock will contribute.

The results obtained in Sweden by Palmqvist (*cf.* Tekn. Tidskr., Bergsvetenskap, pp. 55—56. 1939) show the importance of the composition of the morainic drift, the type of the flora, and the thickness of the soil.

The investigations carried out by The Swedish Prospecting Company Ltd. (*cf.* foot-note on p. 93) very clearly showed the fitness of this method for use in the prospecting of elements not easily detected by ordinary geological or geophysical methods, including Au, Pt, Sn, Mo, and W. The method is also claimed to be swift and applicable to the prospecting of a large number of elements at the same time.

If the above method be applied to the investigation of previously discovered ore-bodies, the plant material should be collected before any trenching on a large scale has been carried out. The construction of profiles showing the variations in the metal content of the ashes, and of equipcentage curves would under favorable conditions give information regarding the location of an ore-body or a mineral vein covered by loose deposits.

SUGGESTION ANENT THE USE OF THE MINOR ELEMENTS IN GEOLOGICAL MAPPING.

The use of the minor elements as index elements for the geochemical classification of rocks has been discussed by Sahama and Rankama (1938) with especial reference to the possibilities of the following elements: Sr, Ba, Cr, V, Zn, Pb, Ga, and the Rare Earths. The presence of the minor elements in the plant ashes might also provide means for the mapping of contacts hidden under loose deposits. For this purpose suitable index elements for both the rocks are chosen after a spectrographic study of a number of rock specimens, and several sampling lines are drawn from one rock to the other in order to cross the contact line, which is located according to the results of the spectrum analyses of the plants' ashes with due attention paid to the composition of the morainic drift.

ACKNOWLEDGMENTS.

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Geochemical Laboratory, Mineralogical and Geological Institute of the University, Helsinki, October, 1940.

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EXPLANATIONS TO PLATE I.

- Fig. 1: 1 Curves of magnetic vertical intensity.
 2 Trench.
 3 Border of the ore-body.
 4 Sampling point (the numbers indicate the percentages of NiO multiplied by 10³).
 5 Drainage ditch and creek.
 6 Path.
 7 Transportation direction.

- Fig. 2: 1 Equipercantage curves for NiO.
 2 Border of the ore-body.
 3 Curves of magnetic vertical intensity.

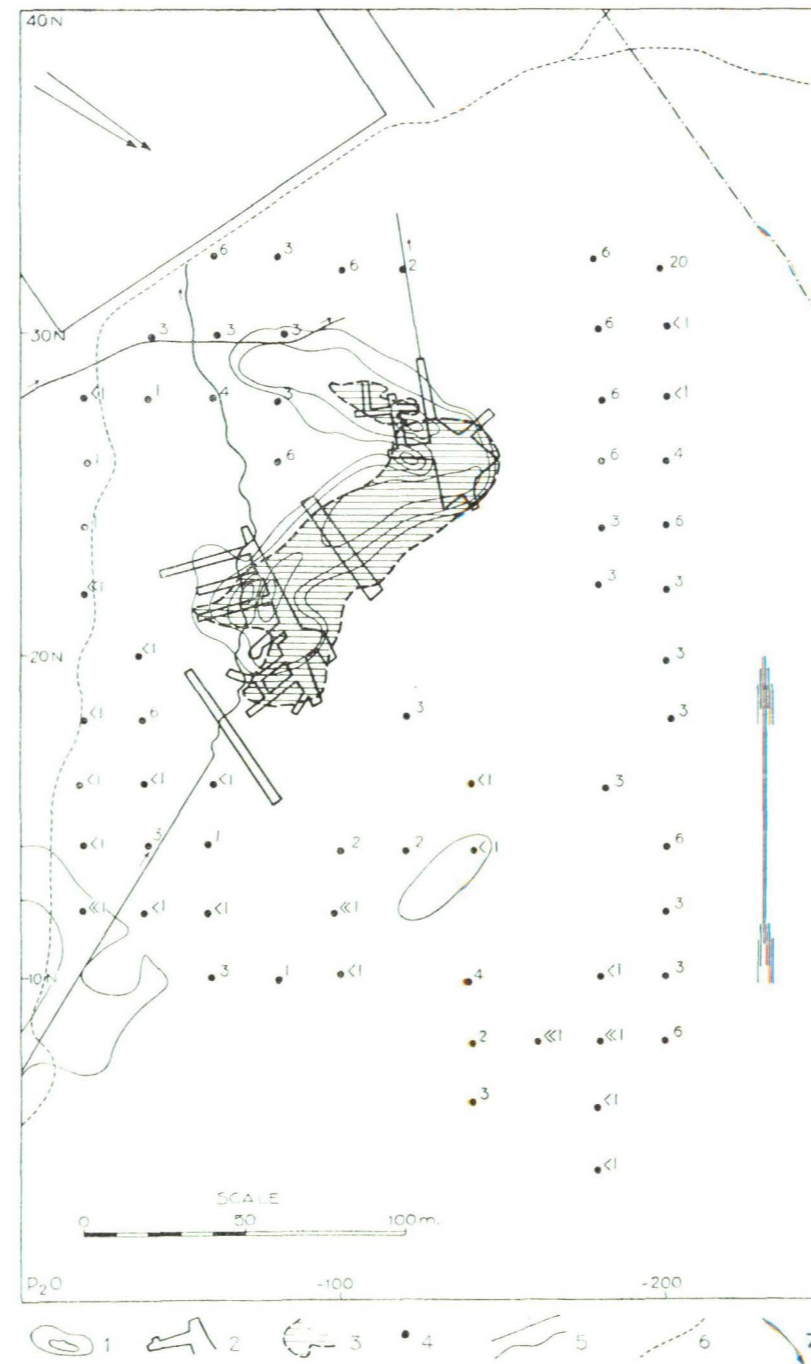


Fig. 1.

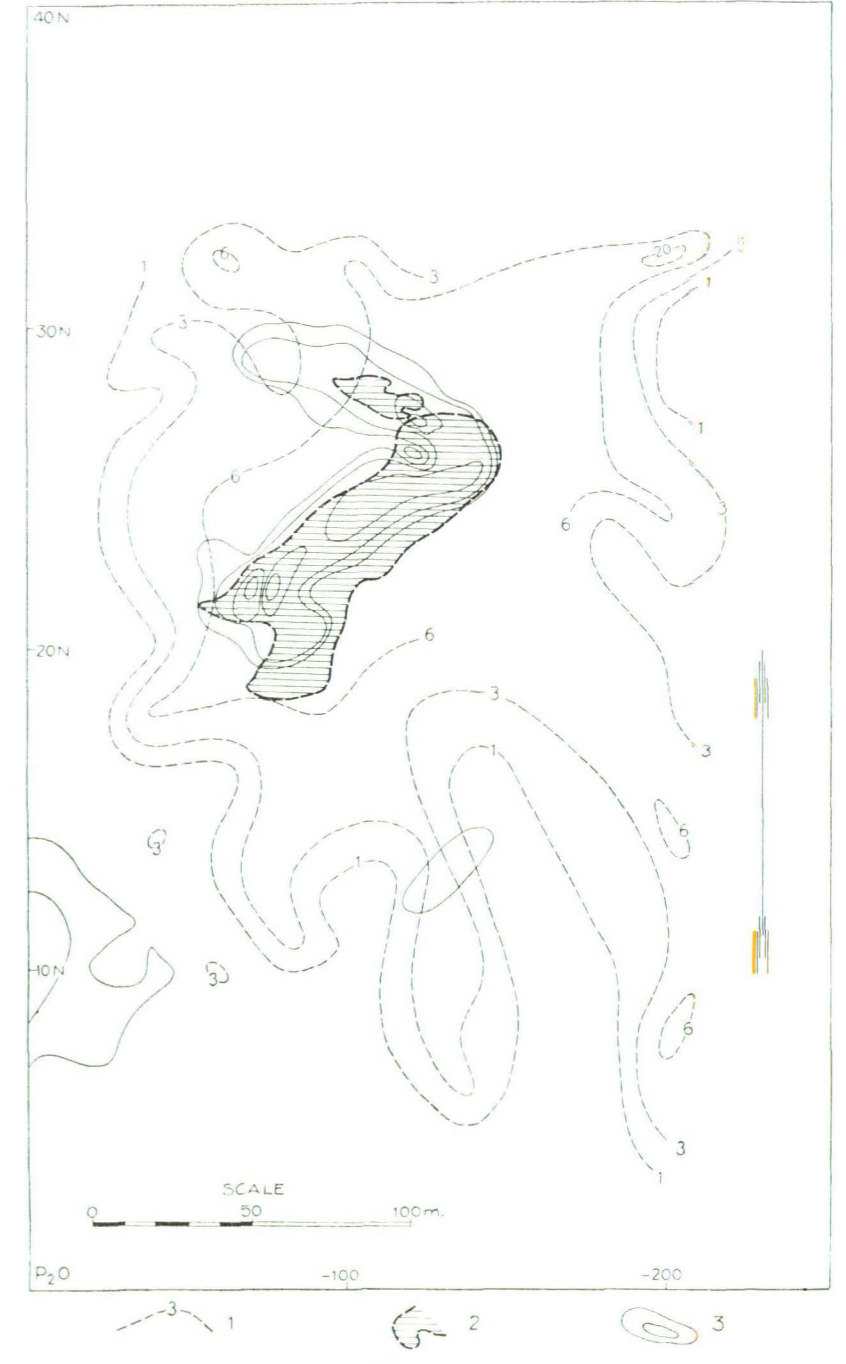


Fig. 2.

ORBICULAR ROCKS IN KEMIJÄRVI AND ESBO

BY

AHTI SIMONEN.

ABSTRACT.

A detailed description of the orbicular rock in Kemijärvi, with four analyses, is given. The origin of this rock by metamorphic differentiation in connection with granitization is discussed. New observations on the orbicular rock in Esbo, with one analysis, are presented. The Esbo rock seems to have been formed from a basic rock, presumably a basic pyroxene-gneiss, by a peculiar metasomatic process, or esboitization, which mainly consisted in an addition of soda with alumina and removal of $(Ca,Mg,Fe)O$. This rock has been but little affected by a later granitization involving addition of potash. In the case of the Kemijärvi rock, again, the metamorphic differentiation resulted in the crystallization of granitic material in oligoclasitic, or esboitic, inner parts and an outer microclitic shell of the orbicules. Some conclusions concerning the orbicular rocks and granitic rocks in general are discussed.

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INTRODUCTION.

The peculiar structure of orbicular rocks makes them one of the most interesting groups among the granitic rocks. Many investigators of the granite problems have pointed out the significance of the facts revealed by the study of orbicular rocks. The different theories of petrogenesis in general are reflected in the historical outlines of the study of these rocks.

On the basis of his study of the orbicular rock in Kortfors, H. Bäckström (1893, 1894) set forth his famous liquation hypothesis which has played a very remarkable rôle in the discussion of rock differentiation. According to Bäckström the orbicules are secretions formed as more basic magma drops from the silicate melt. Many investigators have shown, however, by physico-chemical studies, that liquation has no significance in the origin of silicate rocks (not even in the case of monomineralic rocks), and many petrologists have stressed the concretionary nature of the orbicules, which is evident from many structural features.

According to Frosterus (1892, 1896) and Chroustschoff (1894) the orbicular structure has originated in a primary concretionary crystallization of liquid magma. Chroustschoff points out that in most orbicular rocks there are, as nuclei of crystallization, either foreign inclusions, or single crystals or mineral aggregations crystallized out primarily from the magma. Frosterus (1896) describes in his classical study of the Kangasniemi rock a very good example of nuclei consisting of foreign gneissose inclusions, which have been changed by magmatic action into a granitic rock. These petrologists stress the hybridic nature of the orbicular rocks. Some investigators (Benedicks and Tenow, 1910) have gone so far as to look upon the orbicules as assimilated inclusions.

Other investigators of the problem have expressed the opinion that the orbicular structure has been formed by the primary crystallization differentiation of a liquid magma. According to Vogt (1906) the orbicular rocks are products of crystallization regulated by a tendency towards a eutectic composition of the magma. In some orbicular rocks one finds monomineralic spheroids, while the composi-

tion of the matrix is eutectic. There is an analogy with the origin of porphyritic structure in eruptive rocks which were supposed to have been similarly formed, although we now understand that even in this case the phenocrysts do not by far represent the part in excess over the eutectic mixture.

In his voluminous and important memoir Sederholm (1928) attributes to the orbicular rocks a paramount importance for the interpretation of the petrogenesis in general. He says: »We here meet with many of the main problems of granite petrology, almost literally in a nutshell». According to his opinion the spheroids of the orbicular rocks have been formed as concretions by fractional crystallization of a viscous magma. Sederholm deduces, however, his most remarkable result from a comprehensive chemical study; he demonstrates the peculiar, oligoclastic composition of orbicular rocks, characteristic of which is the high content of Al_2O_3 , Na_2O and CaO , while the K_2O -amount is in general very low. Sederholm designates this kind of rocks *esboites*.

Berg (1937) describes the orbicular rocks in the Riesengebirge, and concludes that crystallization of the orthoclase kernel has caused the enrichment of the surrounding magma in Na_2O , CaO , MgO and FeO . An albite-biotite zone has crystallized around that kernel from this new magma, where the diffusion of material has been very slow. Berg refers, however, to some cases, where the surrounding magma, rich in Na_2O , has caused the albitization of the orthoclase nucleus. Berg regards all the orbicular structures as magmatic. According to his opinion a similar explanation can be applied to all orbicular rocks as a consequence of oscillations in the concentration of salic and mafic components in the magma.

The most modern among the investigations concerning the orbicular structure is that by Eskola (1938) in which the *esboites* are described as products of granitization. Only a few of their more basic kinds may have been formed through crystallization differentiation of primary magma. In most cases the *esboitic* crystallization is supposed to be mainly a metasomatic process, which has proceeded outward from the nuclei of the orbicules.

The occurrence of orbicules showing different degrees of development and especially the occurrence of an embryonal stage is one of the best evidences of the concretionary nature of the orbicules. Further the warp and weft texture is also very good evidence. The tangential arrangement of hornblende prismatic perpendicular to (100), of biotite parallel to the c-axis, and plagioclase parallel to the a-axis is the result of crystallization pressure of the radially crys-

tallizing plagioclase. According to Eskola the crystallized plagioclase in the orbicules has pushed outward, in many cases purely mechanically, the previously existing mafic minerals. In the light of facts of this kind the concretionary nature of orbicules is very credible. Finally, as emphasized by Sederholm (1928), the orbicular granites of Virvik and a few other occurrences show unconformities between the different layers of some orbicules which have been partly resorbed before a new layer has grown around them, a phenomenon which is compatible only with the concretion, but not with the secretion hypothesis.

The matrix of the orbicules is in many cases clearly migmatitic and most occurrences of orbicular rocks so far known are in migmatitic surroundings. It seems that there is a genetic connection between the granitization and the development of the orbicular structure. In Finland eleven occurrences of orbicular rock are known. This great number certainly stands in connection with the fact that the rock crust is largely migmatitic. Most of the occurrences so far known have only been found as Quaternary, glacial boulders. Formerly only those of Kemijärvi, Esbo and Virvik were met with in place in the Pre-Cambrian rock crust of Finland. The present writer will in this investigation give a detailed description of his survey concerning the new find of orbicular rock in Kemijärvi and also some notes on the Esbo rock.

ORBICULAR ROCK IN KEMIJÄRVI.

During the prospecting work of Suomen Malmi O. Y. in the summer of 1937 the writer discovered, on the shore of Lake Kalliojärvi in the western part of the parish of Kemijärvi (in North Finland), a new occurrence of orbicular rock. This locality is easily accessible from the highroad between Rovaniemi and Kemijärvi near the farm Kalliosalmi from which the outcrop is about 1.5 km southeastward, on a hill sloping to the eastern shore of the lake.

In his paper Eskola (1938) has already given a short description of the Kemijärvi rock and he presents this as one of the best evidences of the ultrametamorphic nature of orbicular rocks. The writer (Simonen, 1938) has published earlier, as a preliminary report, a chemical study of the Kemijärvi rock showing clearly a migmatitic nature of the matrix and a granitic bulk composition of the orbicules similar to that of the migmatite-forming granite.

During the following summer (1938) the writer carried out a revision in the field and collected new specimens for microscopical investigation. In the present paper is given a detailed description of his survey in connection with this rock which shows, in a very instructive manner, many characteristic features of orbicular rocks.

ANCIENT ROCKS IN THE KALLIOJÄRVI REGION.

The prevailing rock in the region around the orbicular rock is migmatite, consisting mainly of microcline-granite (Fig. 1).

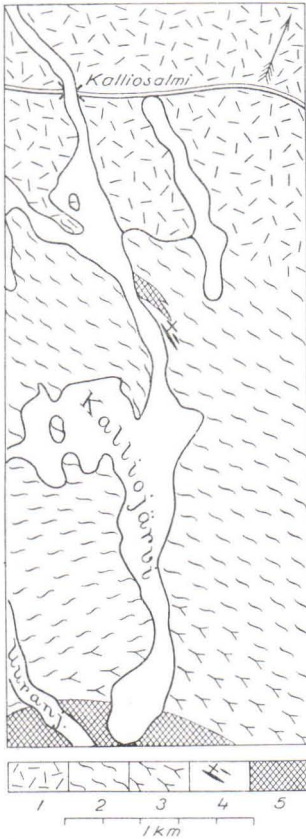


Fig. 1. Petrographic map of the Kalliojärvi region. 1. Microcline-granite. 2. Migmatite. 3. Plagioclase-gneiss with granitic bands. 4. Orbicular rock. 5. Gabbro.

Microcline-granite. — Pure microcline-granite occurs in a wide area northwards from the farm Kalliosalmi. It is coarse-grained, consisting chiefly of porphyritic microcline, quartz and plagioclase (An_{16}). The microcline-granite of Kalliosalmi is very similar to the so-called coast-granites in South-Finland and also to the granites penetrating the Karelidic schists in Eastern and Northern Finland. On the geological map of the sheet Rovaniemi by Hackman (1918) the microcline-granite of Kalliosalmi has been designated Post-Kalevian granite. Nowadays it is called either Postkarelidic or Karelidic granite. The former name is used if the Karelidic formation is spoken of as a series formed during the Karelidic orogenic cycle, while the latter name refers to an intrusion event that has taken place during the Karelidic orogeny.

Migmatites. — Southwards the above-mentioned, coarse-grained microcline-granite passes gradually over into more schistose and fine-grained varieties. It becomes inhomogeneous; foreign, more basic rocks are seen as corroded inclusions in the fine-grained microcline-granite. The rock is migmatitic.

The migmatite, consisting largely of microcline-granite, in the southern part

of Lake Kalliojärvi borders on plagioclase-gneiss. This rock is very inhomogeneous; there are in it grey, fine-grained, mica-rich as well as coarse-grained, gneissose granitic portions. On the geological map of Rovaniemi Hackman (1918) has called this rock a gneiss mixed with Post-Kalevian granite. The veins of microcline-granite penetrate the plagioclase-gneiss everywhere; alternating bands of grey plagioclase-gneiss and red microcline-granite can be seen in the rock. In some places again the migmatitization has gone so far that only dark, mica-rich schliers in the matrix consisting of red microcline-granite have been preserved. In the description of the geological map Hackman (1918) mentions already, as a characteristic feature, the following: »There are wide areas where the rock is mainly gneiss-granitic, but, at the same time, it is mixed up with Post-Kalevian granite — — — these rocks are most common near the boundary of the granite area and form the outer boundary-zones around it».¹⁾ Hackman certainly refers to formations similar to that in the Kalliojärvi region. On the boundary of the microcline-granite area the rock is migmatitic.

It is difficult to decide whether the plagioclase-gneiss, which occurs as inclusions in the migmatite of the southern end of Kalliojärvi, belongs to Karelidic or Prekarelidic formations. Hackman (1918) describes this kind of rocks mainly as Kalevian, but he mentions that there may exist among them remains of older rocks also. The present writer is inclined to look upon the gneissose granitic plagioclase-gneiss of the Kalliojärvi region as Prekarelidic.

The migmatites of the Kalliojärvi region may be interpreted as areritic rocks. In the vicinity of the outcrop of the orbicular rock there is a hill, where the microcline-granite quite clearly mechanically penetrates a medium-grained gabbro. In some places there occurs a beautiful breccia (agmatite according to Sederholm), where angular fragments of gabbro are embedded in a ground-mass of microcline-granite. The migmatitization has not, however, always taken place only by means of a mechanical intrusion. The study of structures in the migmatites (*e. g.* the occurrence of mica-rich schliers in microcline-granite) shows beyond doubt that a replacement process has played a prominent rôle in the origin of these rocks.

O r b i c u l a r r o c k. — The rock mass which shows an orbicular structure occurs as a worm-like strip in the migmatitic rock of the Kalliojärvi region (Map I). The elongation of this strip is parallel to the common strike of the region (N 60° W), and there are fairly big (10—15 cm in diameter), regular and undeformed orbicules em-

¹⁾ Translation from the Finnish text.

bedded in a migmatitic matrix consisting of granodiorite and microcline-granite. Inclusions of basic rock are seen in the outcrop of the orbicular rock, and the fine-grained, aplitic granite is injected into an older, basic rock.

B a s i c r o c k. — In the vicinity of the occurrence of orbicular rock medium-grained hornblende-gabbro underlies a small area. It is penetrated by microcline-granite in many places. This rock occurs in a wide area southwards from the southern end of Kalliojärvi. The basic rocks of this kind are described on the geological maps mainly as Kalevian metabasites, but surely a great part of them belong to Prekarelidic intrusions.

THE ORBICULES.

The orbicules of the Kemijärvi rock, as a rule, consist of three different parts. Coarse-grained plagioclase forms the light nucleus which passes gradually to the more fine-grained, grey-coloured zone of plagioclase. The plagioclase kernel is about 10 cm in diameter. The red-coloured outer zone of the orbicule consists of radially arranged microcline and the different development of this zone causes the most remarkable variation in the nature of the orbicules. In some places the microclitic outer zone forms about $\frac{2}{3}$ of the whole volume of the orbicules, the thickness of the outer zone being about 2.5 cm (Fig. 2). In some places, again, the microclitic zone is weakly devel-



Fig. 2. Orbicules with strongly developed microclitic zones in granodioritic matrix. The weathering has chiefly attacked the plagioclase; the microclitic rings are therefore standing in high relief. 1/10 natural size.

oped, appearing only as a narrow microcline shell, some millimetres thick around the plagioclase nucleus. Especially in the little, isolated occurrence (Fig. 3), which was found at the foot of the hill about

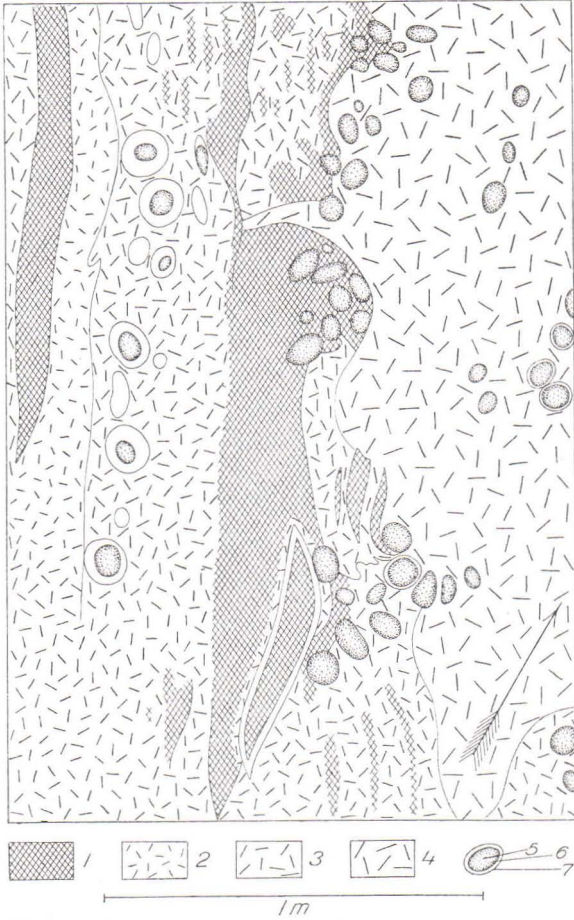


Fig. 3. Isolated occurrence of orbicular rock consisting mainly of embryonal orbicules. 1. Diorite. 2. Aplitic granite. 3. Migmatitic granite. 4. Pegmatitic granite. 5. Plagioclase nucleus. 6. Fine-grained plagioclase zone. 7. Microclitic outer zone.

6 m east of the larger mass showing orbicular structure, microclitic outer zones around the orbicules are in many cases entirely absent, and only the plagioclase nuclei with surrounding fine-grained plagioclase zones occur as separate groups in the migmatitic matrix. Spheroids of this kind are what may be called embryonal orbicules.

Nucleus of orbicule. — Besides the nuclei consisting of coarse-grained plagioclase three nuclei were observed to be formed by coarse-grained granodioritic rock (Fig. 4). It is interesting to note



Fig. 4. Fragment of granodiorite as nucleus of strongly developed microclinic zone. 1/10 natural size.

that the microclinic outer zone has been developed also around this kind of nucleus in a similar manner as around the nucleus consisting of plagioclase. The basic nuclei in the Kemijärvi rock are clearly fragments of the older, primary component of the matrix (isothrausmatic type of nuclei according to the terminology of Loewinson-Lessing and Olga Vorobjeva, 1929, originated by autobrecciation of the rock). In a single very small orbicule (3 cm in diameter) a quartz nucleus was observed in the middle of the microclinic shell.

This quartz nucleus consists of a single crystal in which are seen streaks of liquid inclusions. It may be a fragment derived from vein quartz. The plagioclase nuclei, again, are not at all like fragments of any kind. Apparently they have been formed as a first stage in the development of the orbicular rock (crystallothrausmatic type of nuclei according to Eskola, 1938).

Table I. The chemical composition of nucleus of orbicule in the orbicular rock of Kemijärvi. Analyst: A. Simonen.

	%	Mol. Prop.	Norm	Mode
SiO ₂	65.51	1.0864	Q	Quartz
Al ₂ O ₃	20.01	.1958	Or	10.4
Fe ₂ O ₃	0.67	.0042	Ab	Plagioclase { or 5.5 ab 64.9 an 16.1
FeO	0.52	.0072	An	
MnO	—	—	C	Magnetite
MgO	0.02	.0005	Σ sal	Ilmenite
CaO	3.24	.0578	Hy { MgSiO ₃ . 0.1	Chlorite
Na ₂ O	7.66	.1235	FeSiO ₃ . 0.1	98.4
K ₂ O	0.96	.0102	Mt	Al ₂ O ₃ in excess 0.3
TiO ₂	0.17	.0021	Il	98.7
H ₂ O+	0.41	—	Σ fem	H ₂ O
H ₂ O—	0.61	—	H ₂ O	1.0
			99.7	99.7
	99.78		Quantitative System: 1. 5. 2. 5 — No name. Or: Ab: An — 6.3: 75.9: 17.8	

The plagioclase nucleus is very similar to nuclei in many other orbicular rocks. The chemical analysis (Table I) carried out by the writer shows a typical esboitic composition.

The plagioclase of the nucleus gave, by the immersion method,

$$\begin{aligned}\alpha' &= 1.535; \\ \gamma' &= 1.544.\end{aligned}$$

The maximum extinction angle in the symmetrical zone is 4° . The plagioclase is oligoclase (An_{16}). The [or]: [ab]: [an] proportion calculated from the analysis seems to be very similar to the composition of plagioclases met with in granitic pegmatites.



Fig. 5. Graphic intergrowth structure in nucleus of orbicule. 10 x. One Nicol.

Quartz in a graphic intergrowth with the plagioclase (Fig. 5) is present in all the nuclei (10 pt according to the analysis).

Small amounts of magnetite and thin flakes of chlorite are observed. Sericite occurs as alteration inclusions in the plagioclase. Microcline can not at all be observed.

From the nucleus of the orbicules apophyses in some cases go into the granitic matrix; a similar phenomenon in the orbicular granite of Kangasniemi was described by Frosterus (1896). These apophyses show that replacement processes in the solid rock have taken place also after the crystallization of the orbicules.

Fine-grained plagioclase zone. —The coarse-grained plagioclase nucleus passes gradually to a more fine-grained, darker

grey zone of plagioclase which is pigmented and sericitized, and gave, by the immersion method,

$$\begin{aligned}\alpha' &= 1.537; \\ \gamma' &= 1.546.\end{aligned}$$

The maximum extinction angle in the symmetrical zone is 2° . The plagioclase is oligoclase (An_{18}).

Quartz is a minor component in the fine-grained zone of plagioclase appearing as small grains between the crystals of plagioclase.

As an accessory mineral iron ore is very common. It is mainly oxide, but grains of pyrite were also observed. Hornblende and apatite occur in trifling amounts. Chlorite and epidote are present as alteration products of the hornblende.

The structure of the fine-grained plagioclase zone is distinctly granoblastic.

The mineral composition of this zone is very similar to that of the nucleus, but the chemical composition is more basic, as the amount of the mafic minerals is larger and the plagioclase is more anorthitic than that of the nucleus.

Microclinic outer zone. — The red-coloured outer zone of radially arranged microcline borders sharply against the plagioclase zone (Fig. 6) as well as the matrix between the orbicules. A chemical analysis of the outer zone carried out by the writer shows a composition very rich in potash (Table II).

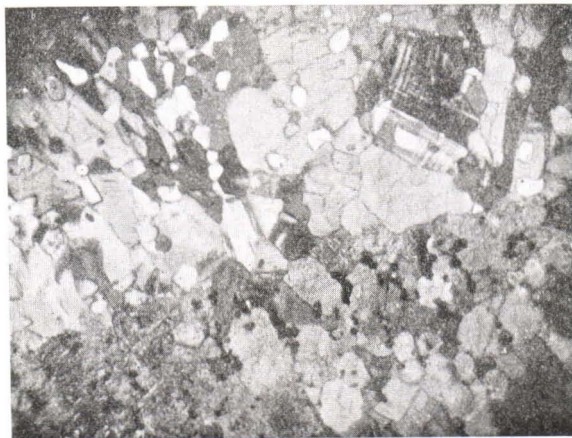


Fig. 6. Microclinic outer zone bordering sharply against the fine-grained zone of plagioclase.

12 x. Nicols +.

Table II. The chemical composition of outer zone of orbicule in the orbicular rock of Kemijärvi. Analyst: A. Simonen.

	%	Mol. Prop.	Norm	Mode
SiO ₂	73.91	1.2257	Q	Quartz
Al ₂ O ₃	13.55	.1326	Or	26.8
Fe ₂ O ₃	0.31	.0019	Ab	Microcline { or. 55.5
FeO	—	—	An	ab 16.1
MnO	—	—	C	an. 0.4
MgO	< 0.01	—	Σ sal	Magnetite 0.2
CaO	0.07	.0012	Mt	99.0
Na ₂ O	1.89	.0305	Σ fem	H ₂ O
K ₂ O	9.38	.0996	H ₂ O	0.8
TiO ₂	< 0.01	—		99.8
H ₂ O+	0.23	—		
H ₂ O-	0.57	—		
	99.91		Quantitative System: 1. 4. 1. 2 — Omeose.	
			Or: Ab: An — 76.2: 23.3: 0.5.	

The individual crystals of microcline are shuttle-like, 1—2 cm long, and elongated parallel to the crystallographic a-axis. A similar radial arrangement of feldspars has been observed in many orbicular rocks in which the a-axis, or the pseudotetragonal axis of the feldspar, is the axis of elongation. The structural investigations of the feldspars (W. H. Taylor, J. A. Darbyshire and H. Strunz, 1933) show that the rings formed by four [SiO₄]-tetrahedra are united in the direction of the a-axis as a band.

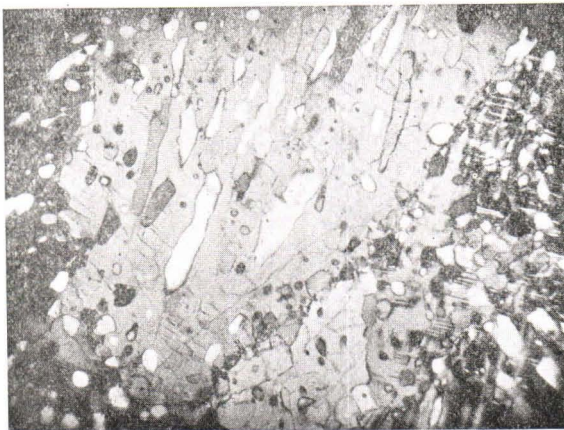


Fig. 7. Quartz inclusions in a shuttle-like crystal of microcline. 12 ×. Nicols +.

Perthite structure in the microcline is weakly developed. The [or]: [ab]: [an] proportion is very similar to that of microclines met with in granitic pegmatites.

Quartz is present as worm-like inclusions in the radially crystalline microcline (Fig. 7). No regular lattice orientation can be observed by means of a gypsum plate.

Between the crystals of microcline are seen small entirely sericitized grains which are remains of plagioclase.

Minute grains of magnetite and flakes of chlorite are observed in the microclitic outer zone.

THE MATRIX AND THE COUNTRY ROCK.

The matrix of the orbicular rock in Kemijärvi is distinctly migmatitic, consisting mainly of coarse-grained granodiorite with aplitic granitic portions. In some places the granitic rock may be the main component of the matrix, but in general it is distributed only as thin veins in the granodiorite. The migmatitic country rock again consists chiefly of aplitic granite with basic inclusions.

Granodioritic matrix. — The composition of the older, granodioritic part of the matrix is variable, due to the varying amounts of hornblende and plagioclase. In some parts it is rich in hornblende,

Table III. The chemical composition of granodioritic matrix in the orbicular rock of Kemijärvi. Analyst: A. Simonen.

	%	Mol. Prop.	Norm	Mode
SiO ₂	56.83	.9425	Q	Quartz 9.6
Al ₂ O ₃	16.62	.1626	Or	Microcline 3.6
Fe ₂ O ₃	3.20	.0200	Ab	Plagioclase { ab 38.2
FeO	5.11	.0711	An	
MnO	0.91	.0128	Σ sal	Hornblende ... 23.1
MgO	3.29	.0816	Wo	Biotite 6.9
CaO	5.36	.0956	Hy {	Magnetite 2.2
Na ₂ O	4.63	.0747		MgSiO ₃ .
K ₂ O	1.41	.0150	FeSiO ₃ .	Al ₂ O ₃ in excess 0.3
			MnSiO ₃ .	
TiO ₂	0.97	.0121	Mt	98.3
H ₂ O+	0.65		Il	H ₂ O 1.2
H ₂ O—	0.59		Σ fem	99.5
			H ₂ O	
			99.5	
	99.57		Quantitative System: II. 5. 3. 4— Andose. Or: Ab: An — 11.9: 59.2: 28.9	

but in other parts it consists of coarse-grained oligoclase with only occasional crystals of hornblende. The following analysis (Table III) shows the most typical composition of the granodioritic matrix in the Kemijärvi rock. In the analyzed specimen the microscope revealed, as is the rule in all thin sections of this matrix, a thin tissue consisting of quartz and microcline.

Plagioclase is the main component of the analyzed granodioritic matrix. It occurs as big, idiomorphic crystals; a determination by the immersion method gave as a result:

$$\begin{aligned} \alpha' &= 1.541; \\ \gamma' &= 1.550. \end{aligned}$$

The maximum extinction angle in the symmetrical zone is 8° . The plagioclase is oligoclase (An_{26}).



Fig. 8. Microcline antiperthite in homoaxial intergrowth with plagioclase. $12 \times$. Nicols +.

The grains of plagioclase contain regular-shaped antiperthitic inclusions of microcline (Fig. 8) in homoaxial intergrowth with the plagioclase. In some grains of microcline crosshatched twinning is well developed.

The hornblende is present as large crystals in the basic matrix. It is clearly idiomorphic and crystal faces are distinguishable. The hornblende is dark, strongly pleochroic, and the extinction angle is γ/c 20° .

On the boundary of the big crystals of hornblende biotite always occurs as minute flakes. This is an alteration product, representing the

first stage in the granitization of granodiorite. Chlorite and epidote are also present among the alteration products of hornblende.

Microcline, quartz, titanite, apatite and magnetite as minor components are observed.

The structure of the granodioritic matrix is granoblastic.

Granitic matrix. — The fine-grained aplitic granite forming parts of the matrix was analyzed by the writer (Table IV). Its granitic nature is apparent, and its composition is very similar to that of many microcline- and rapakivi granites in Finland.

Table IV. The chemical composition of aplitic matrix in the orbicular rock of Kemijärvi. Analyst: A. Simonen.

	%	Mol. Prop.	Norm		Mode	
SiO ₂	71.36	1.1834	Q	24.2	Quartz	27.3
Al ₂ O ₃	14.02	.1372	Or	30.9	Plagioclase { ab	31.4
Fe ₂ O ₃	0.56	.0035	Ab	32.4		
FeO	1.82	.0253	An	5.7	Microcline ...	26.7
MnO	—	—	Σsal	93.2	Biotite	6.4
MgO	0.59	.0146	Wo	0.6	Magnetite ...	0.6
CaO	1.39	.0248	Hy { MgSiO ₃	1.5		98.9
Na ₂ O	3.82	.0616		{ FeSiO ₃	2.6	H ₂ O
K ₂ O	5.21	.0553	Mt	0.8		100.1
TiO ₂	0.19	.0024	Il	0.4		
H ₂ O+	0.51		Σfem	5.9		
H ₂ O-	0.70		H ₂ O	1.2		
				100.3		
	100.17		Quantitative System: 1. 4. 2. 3 — Toscanose. Or: Ab: An — 43.6: 48.5: 7.9			

Microcline, quartz and plagioclase (An₁₆) are the main minerals of the granitic matrix. Dark biotite occurs only as thin flakes. Magnetite, apatite and epidote are visible as accessory minerals.

The aplitic granite penetrates the granodiorite as well as the orbicules, in which small apophyses of it are often observed. In the granitic matrix there are also some pegmatitic lenses which penetrate the spheroids. These phenomena show that the granitic material has given rise to replacement processes in the solid rock.

Country rock. — The country rock of the occurrence is similar to the migmatites of the Kalliojärvi region; basic rocks occur as inclusions in the microcline-granite (Fig. 9) which shows both aplitic and pegmatitic variations. The nature of the basic rocks is

very variable, including medium-grained and coarse-grained gabbros, diorites, and granodiorites.

The granitic material has been injected into the basic rocks, and at an incipient stage of the injection single porphyroblastic crystals of microcline are noticeable. In one place this structure is developed in the same way as the so-called eyed gneisses.



Fig. 9. Aplitic granite has been injected into the granodiorite. Basic inclusions are observed. 1/15 natural size.

THE ORIGIN OF ORBICULAR ROCK IN KEMIJÄRVI.

Eskola (1938) has shown that the origin of orbicules in many cases is due to a process of granitization and diffusion into a solid rock. Especially the composition of the plagioclase in different parts of orbicular rocks (Fig. 10) is contradictory to the laws of crystallization-differentiation; a clear exception is the orbicular gabbro of

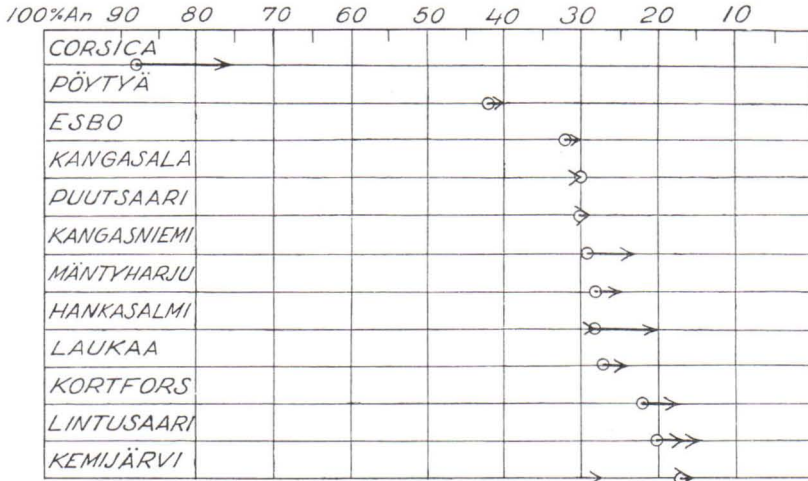


Fig. 10. The composition of plagioclase in orbicular rocks according to Eskola (1938). Ring = orbicule; arrowhead = matrix.

Corsica. In many cases the composition of the plagioclase in the orbicules is very similar to that of the matrix. In some orbicular rocks, again, in which the plagioclase in the matrix is more albitic than in the orbicule, the matrix is clearly migmatitic and the older, primary matrix contains a plagioclase nearly similar to that in the orbicule.

The orbicular rock in Kemijärvi is very interesting as regards the composition of the plagioclase in its different parts. A well preserved primary matrix contains a more anorthitic plagioclase than the orbicule, while the plagioclase of the orbicule agrees better with that of the migmatite-forming granitic matrix. In the light of this fact it seems credible that the orbicules in the Kemijärvi rock have originated in connection with the process of granitization.

Furthermore the chemical study of the orbicular rock in Kemijärvi carried out by the writer shows that the composition of the most typical orbicules is very similar to that of the granitic matrix (Table V). This result gives the impression that the orbicules have crystallized from the material added by granitization.

Table V. The chemical composition of orbicule and migmatite-forming granitic matrix in the orbicular rock of Kemijärvi.

	I	II
SiO ₂	71.11	71.36
Al ₂ O ₃	15.72	14.02
Fe ₂ O ₃	0.38	0.56
FeO	0.23	1.82
MnO	—	—
MgO	0.01	0.59
CaO	1.13	1.39
Na ₂ O	3.81	3.82
K ₂ O	6.57	5.21
TiO ₂	0.06	0.19
H ₂ O	0.87	1.21
	99.89	100.17

I. Average composition of orbicule (calculated).

II. Granitic matrix.

The field observations indicate that orbicules are mostly embedded in a granodioritic matrix injected with small aplitic, granitic bands, thus entailing a change of its bulk composition by addition of potash and silica. This mode of occurrence of the orbicules (Fig. 11) also

shows that their material has been mainly derived from the same granitic ichor which has caused the granitization.

The older granodioritic part of the matrix seems to be the product of metasomatism and recrystallization of medium-grained gabbro at an early stage of granitization. This process can be followed through different stages. The best preserved gabbroidic varieties have only been recrystallized and do not contain any potash feldspar. This appears, besides quartz, at the very first stage, as small grains between the plagioclase and hornblende grains, like the »mortar» in many mechanically deformed rocks. At subsequent stages the added mass begins to form veinlets and, at the same time, the homogenization of the rock proceeds, as the newly introduced minerals are incorporated in the fabric. The peculiar antiperthitic implication of microcline and plagioclase in the granodiorite seems to be also in connection with metasomatism caused by granitic ichor, rich in potash.

The occurrence of idiomorphic hornblende in the granodiorite is interesting; it is seen as big, idiomorphic crystals with crystal faces in many granodiorites of Finland. It is difficult, in such cases, to decide whether the hornblende is primary or secondary. In the Kemijärvi rock the idiomorphic hornblende is apparently secondary, formed by recrystallization.

The microcline-granite seems purely mechanically to penetrate—in some places as aplitic veins—the older granodioritic rock giving rise to an arteritic migmatite. In general, however, the migmatite-forming, arteritic silicate melt has imbued the granodiorite



Fig. 11. Boundary between granodiorite and granite. Orbicules are embedded in granodioritic matrix which is injected by granitic material. 1/10 natural size.

as intergranular pore magma. Everywhere in the granodioritic matrix there is observed a thin, aplitic granite tissue.

It is characteristic of the process of granitization that the older more basic material has been freed especially from FeO and MgO, while the amounts of K₂O and Na₂O have increased (Fig. 12). The

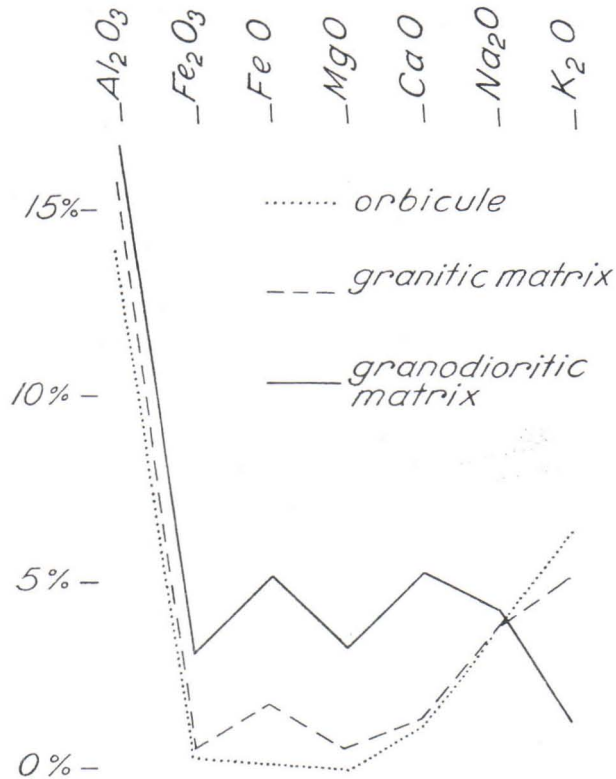


Fig. 12. The composition of different parts of the Kemijärvi rock. This diagram shows clearly that orbicules are impoverished in mafic components by granitization.

salic character of the orbicules is remarkable in the Kemijärvi rock as well as in many esboites; especially the nuclei formed by esboitic crystallization are quite poor in mafic minerals.

All the features just described corroborate Eskola's (1938) opinion about the origin of the orbicules in the process of granitization through the metamorphic differentiation by concretionary crystallization.

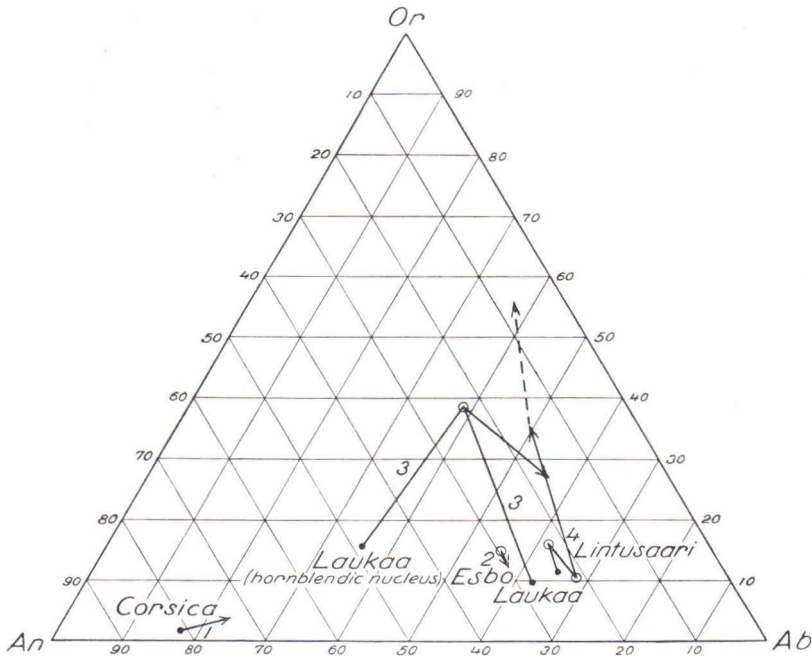


Fig. 13. Normative feldspars of some orbicular rocks according to Eskola (1938). Point = nucleus; ring = zone of orbicule; arrowhead = matrix.

In connection with the granitization the orbicules have been differentiated into different zones. Eskola (1938) plotted the [or]: [ab]: [an] proportions of different parts of orbicular rocks in the triangle diagram and classified them by this method of projection in the following five different groups (Fig. 13 and 14):

1. Orbicular rocks standing near the anorthite corner. In this case the orbicules are probably due to magmatic crystallization differentiation.

2. True esboites. All parts of the orbicular rocks are of esboitic composition.

3. Various nuclei, surrounded by narrow esboitic inner zones. Outer zones of orbicules are rich in mafic minerals and, at the same time, high in potash. The matrix is more esboitic than the outer zone.

4. Esboitic orbicules in granitic matrix.

5. Orbicules and matrix are mainly granitic in bulk composition. In the orbicules there are recurrent zones of esboitic and microcline composition.

The aforesaid groups are the most typical of orbicular rocks. There are, however, transitional types and in many orbicular rocks different orbicules belonging to several groups have been met with.

The Kemijärvi rock belongs to Eskola's group 5 (Fig. 14). The bulk composition of most orbicules is granitic and the orbicules are extremely sharply differentiated into an esboitic nucleus and a microclitic outer zone. The bulk composition of the orbicules, however, varies from granitic to esboitic, depending upon the different development of the microclitic outer zone. There are also, though very rarely, most typical esboitic orbicules in granitic matrix (group 4). Furthermore, the Kemijärvi rock shows two different kinds of matrix: the primary, well preserved, granodioritic matrix and the granitic matrix.

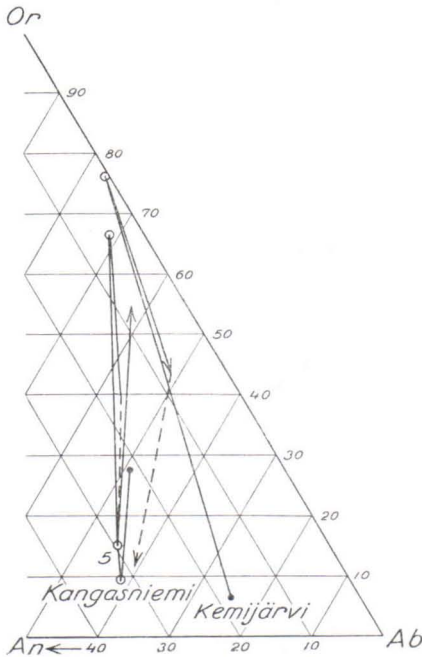


Fig. 14. Normative feldspars of Kemijärvi rock belonging to Eskola's group 5.

It seems that the development of all orbicules in the Kemijärvi rock has been similar in the beginning. Granitic, arteritic ichor has replaced the granodiorite. The nucleus has been impoverished especially in FeO, MgO and CaO; Na₂O and SiO₂ have come instead of these. A metasomatic albitization of the granodiorite, or a soda metasomatism, has proceeded, resulting in the formation of the esboitic nuclei. The composition of the material which has been added to the kernel by this addition of soda is approximately: 57.6% SiO₂, 22.4% Al₂O₃ and 20.0% NaO₂, making 15% of the primary, granodioritic rock.

The graphic intergrowth structure in the nuclei of the Kemijärvi rock, as well as in many other orbicular rocks, seems to have originated through a metasomatism. This result is in harmony with conclusions drawn by many American petrologists concerning the origin of pegmatites by replacement processes (Landes, 1933).

The esboitic crystallization of the nucleus has caused an outward diffusion of the femic components. According to Eskola (1938) the crystallizing plagioclase has in some cases purely mechanically pushed

aside the primary mafic minerals. In the Kemijärvi rock the fine-grained plagioclase zone is more basic than the plagioclase nucleus and there are some grains of hornblende in it. It seems plausible that the fine-grained plagioclase zone contains material which has diffused outwards from the nucleus. Thus the grains of hornblende can be remains of the primary, granodioritic rock; the crystallizing plagioclase has pushed them outward. We can not, however, find any kind of crystal orientation in the fine-grained plagioclase zone.

The radially arranged, microclincic zone has of course crystallized from the ichor very rich in K_2O , and its existence means that, at a certain stage, potash metasomatism came instead of soda metasomatism. The esboitic kernels and, in some cases, the isothraumatic fragments have been the crystallization nuclei of the outer zone. In general the spheroidic zones have formed around the kernels consisting of different rock fragments or nuclei originated by replacement processes. In some cases one single feldspar crystal may have served as crystallization nucleus of the spheroidal zone.

Not only feldspar but also many other minerals have under special circumstances been surrounded by radially crystallized zones of other minerals showing structures which closely recall and indeed are genetically analogous to the orbicular structures. In the pegmatite quarry of Paavo, in Kisko, »orbicular pegmatite» is met with, in which a radially arranged zone of pure albite occurs around single big, idiomorphic crystals of beryl. The a-axis of the albite is the axis of elongation, as is the rule in the spheroidal zones of feldspars.

During and still after the crystallization of the orbicules the magmatic ichor has caused replacement processes in the solid rock. The granitization of the primary, granodioritic matrix, the apophyses in the orbicules, and the aplitic and pegmatitic parts in the matrix have originated by these processes.

In the Kemijärvi rock, as well as in other orbicular rocks, many structures similar to those of granitic pegmatites are observed, and furthermore the compositions of feldspars are similar to those met with in pegmatites. These facts indicate that replacement processes have taken place in a very low temperature at which only a silicate ichor, especially rich in potash, has been able to be in a liquid state.

ORBICULAR ROCK IN ESBO.

The Esbo rock is one of the most famous orbicular rocks in the world. To this rock Sederholm (1928) attributes a remarkable signi-

ficance in his theory concerning the origin of the orbicular structure, owing to his, having been aware of its typically developed oligoclastic or esboitic composition. He considers all orbicular rocks as magmatic crystallization products of liquid, esboitic magma. According to the investigation by Eskola (1938) »esboite» does not mean a special magma type, but only a rock of oligoclastic composition. The term »magma type» is in many cases inappropriate, as several igneous-appearing rocks have originated by replacement processes in the solid state.

The present writer frequently visited Esbo during the years 1939 and 1940. Many new exposures were discovered, a petrographic map was outlined, and material was collected for microscopical studies. Here the writer will publish his new observations and briefly discuss the origin of the Esbo rock in the light of the new material. Concerning the chemical composition and many details in the structural development we refer to Sederholm's memoir, which also contains numerous excellent photographic pictures.

SURROUNDING ROCKS.

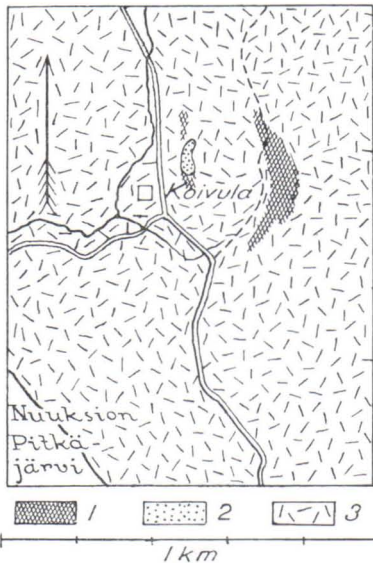


Fig. 15. Petrographic map of surrounding region of the orbicular rock in Esbo. 1. Pyroxene-gneiss. 2. Orbicular rock. 3. Microcline-granite.

The rock crust around the orbicular rock is largely granitic (Fig. 15). Migmatite-forming microcline-granite of the Hango type occurs in a wide area showing medium-grained, aplitic and pegmatitic varieties. Dark mica-rich schlieric portions may be seen here and there as remains from older rocks.

East of the orbicular rock as well as in the country rock all around the occurrence one meets with pyroxene-gneiss, consisting mainly of diopside, plagioclase (An_{40}), and biotite, as inclusions in the microcline-granite. This rock apparently represents a remainder from an oldest, Svecofennidic rock crust. A more detailed description of this peculiar rock is given in the chapter concerning the matrix and the country rock.

THE ORBICULES.

In the Esbo rock, as well as in other orbicular rocks, there are spheroids showing different stages of development. Sederholm (1928) already described embryonal small spheroids which »consist mainly of an aggregate of coarse feldspar grains surrounded by a dark cementing mass, rich in biotite». Especially interesting is a dark inclusion in the microcline-granite in which there are some aggregates of plagioclase (An_{26}) in a fine-grained matrix consisting mainly of plagioclase (An_{33}) and biotite (Fig. 16). This rock is distinctly migmatitic,



Fig. 16. Embryonal orbicules in fine-grained plagioclase matrix, rich in biotite. 1/8 natural size.

it is injected by granitic material. The plagioclase aggregates of this kind are similar to the esboitic nuclei of the orbicules. They are embryonal orbicules originated in a basic rock through replacement processes caused by magmatic ichor. This kind of rock seems to have a close analogy to eyed gneisses originated by injection metasomatism. In this case the component added must have consisted chiefly of soda.

The orbicules in the Esbo rock consist, in general, of a coarse-grained plagioclase nucleus and a fine-grained zone of plagioclase, rich in biotite. Sederholm (1928) has given in his memoir a detailed description of the orbicules. The new exposures of the rock show also orbicules with several recurrent zones. At the place shown in Fig. 17 the orbicules consist of the following parts:

- coarse-grained nucleus of plagioclase (An_{32});
- fine-grained zone of plagioclase (An_{34}), rich in biotite;

medium-grained zone of plagioclase (An_{33});
 fine-grained zone of plagioclase (An_{34}), rich in biotite;
 some orbicules have furthermore a coarse-grained outer zone of
 plagioclase which, however, borders, unsharply the esboitic
 matrix.

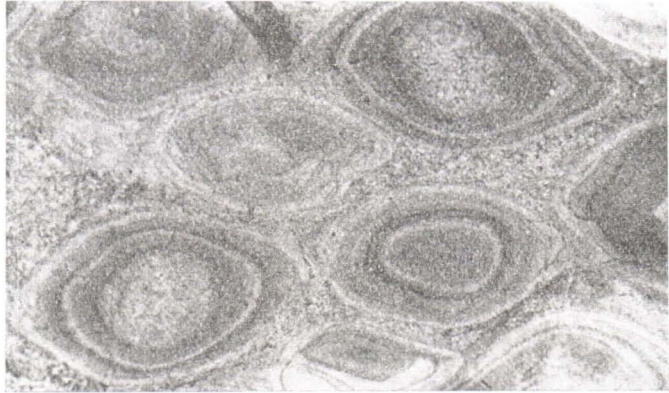


Fig 17. Esboitic orbicules with several zones in esboitic matrix. 1/8 natural size.

All parts of the orbicules are esboitic. Microcline occurs only as minor grains. The structure of the fine-grained zones is distinctly granoblastic. In the scarcity of microcline this variety differs from the orbicular granite of Virvik, to which it shows a structural resemblance, and it is more similar to the orbicular esboite of Kangasala.

THE MATRIX AND THE COUNTRY ROCK.

The matrix of the orbicular rock in Esbo consists mainly of a coarse-grained, esboitic rock. Microcline-granite occurs only locally as a secondary matrix. Similar granite with inclusions of pyroxene-gneiss also occurs as the country rock all around the orbicular rocks.

Esboitic matrix.—The chemical composition of the esboitic matrix is, according to Sederholm (1928), very similar to the bulk composition of the spheroids. Its main constituents are coarse-grained plagioclase (An_{34}) and biotite. Some small strips rich in biotite are observed here and there in the esboitic matrix; they may be remains from an older rock.

Granitic matrix. In the Esbo rock the esboitic, primary matrix is well preserved and only in some places a secondary, granitic matrix occurs, consisting mainly of microcline, plagioclase

(An₁₇), quartz and biotite. According to the author's microscopical studies, this rock seems to be quite identical with the microcline-granite in the surrounding region. The granitic material has been injected into the esboite on the boundaries of the orbicular rock and by replacement processes has caused some corrosion of the orbicules and the formation of small granitic bands in the primary matrix.

A sketch map (Fig. 18) made from the place, where the matrix is largely granitic, shows the orbicular rock with esboitic matrix as inclusions in the microcline-granite. Granitic material, rich in potash, has been injected into the esboitic matrix and the spheroids, in which are observed some porphyroblasts of microcline as a result of incipient granitization. The corroded orbicules in the granitic matrix illustrate the manner in which the processes have worked during the replacement of esboitic material by granitic material. It appears, among other things, that the orbicules have not been

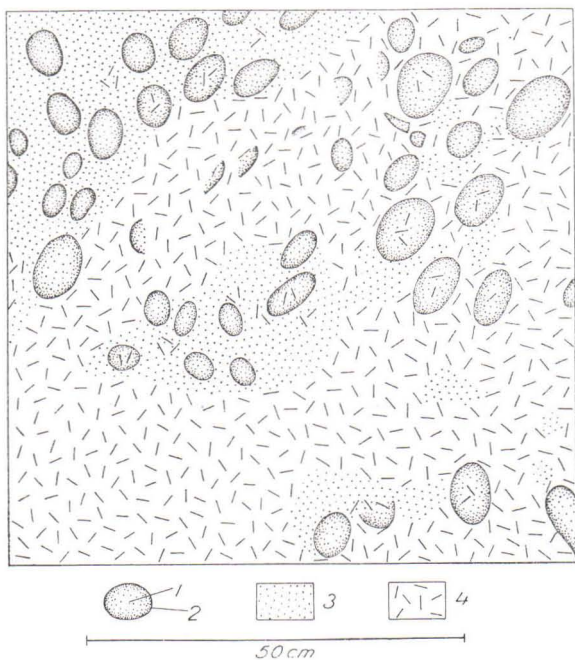


Fig. 18. Microcline-granite penetrates the esboite. 1. Coarse-grained plagioclase nucleus. 2. Fine-grained plagioclase zone, rich in biotite. 3. Primary, esboitic matrix. 4. Microcline-granite; these marks in the orbicules and matrix indicate porphyroblasts of microcline derived from granitic material.

much displaced, while large parts of them have disappeared. The esboitic matrix is granitized more easily than the orbicules. It seems that the fine-grained more basic zones of orbicules have been, in some cases, like an armour against the attack of the potash-rich material added by granitization.

The country rocks. Microcline-granite, diopside-gneiss. The country rocks of the Esbo rock consist chiefly of microcline-granite, the main characteristics of which were mentioned above (p. 130). There occur also basic rocks, especially rich in calcium, as inclusions in this granite (Fig. 19), consisting mainly of distinctly granoblastic diopside-gneiss of the following composition:



Fig. 19. Pyroxene-gneiss inclusions in microcline-granite. Esbo 1/15 natural size.

Table VI. Chemical composition of pyroxene-gneiss in Esbo. Analyst: Elsa Ståhlberg.

	%	Mol. Prop.	Norm	Mode
SiO ₂	53.22	.8826	Q	Quartz
Al ₂ O ₃	15.53	.1520	Or	Plagioclase { ab 23.8 an 17.3
Fe ₂ O ₃	1.52	.0095	Ab	
FeO	9.94	.1383	An	Biotite
MnO	0.17	.0024	Σsal	Diopside
MgO	4.78	.1185	Wo	Magnetite ...
CaO	8.90	.1587	Hy { MgSiO ₃ . 11.9 FeSiO ₃ . 14.9 MnSiO ₃ . 0.3	Apatite
Na ₂ O	2.90	.0468		
K ₂ O	0.54	.0057		H ₂ O
TiO ₂	1.24	.0155	Ap	100.2
P ₂ O ₅	0.04	.0003	Mt	
H ₂ O+	1.20		Il	
H ₂ O—	0.38		Σ fem	
			H ₂ O	
			100.4	
	100.36		Quantitative System: III. 5. 4. 4—Auvergnose. Or: Ab: An—5.6: 45.8: 48.6.	

Plagioclase with a zonal structure occurs as a main component of this rock. It is somewhat sericitized, most strongly in the middle of the crystal. The maximum extinction angles in the most calcic parts of the crystal kernels were 27° . This result indicates labradorite (An_{50}). Towards the margins the plagioclase gradually becomes more albitic, with the extinction angles as low as 22° , indicating andesine (An_{37}). According to the results of the chemical analysis the mean composition of the modal plagioclase conforms to the formula of about $Ab_{60}An_{40}$.

Diopside is observed in thin sections as rounded, colourless grains with no visible pleochroism. The crystals are optically positive with optic angle about 55° . Refractive index β_{Na} determined by the immersion method was found to be 1.700. $\gamma - \alpha = 0.024$.

Biotite is present as idiomorphic thin flakes growing through other minerals. It is not very dark, showing in thin sections γ and $\beta =$ brown, $\alpha =$ pale yellow. No pleochroic halos were observed.

As minor components there are observed quartz, magnetite and apatite.

In recent years rocks of this kind were mapped by Mikkola and Parras over a wide area of South-Finland. There occur many varieties of pyroxene-gneisses of magmatic and sedimentary origin belonging to a special formation of the Svecofennidic territory metamorphosed under conditions nearly similar to those in hornfels and granulite facies. The results of these studies are still unpublished.

Microscopical study of basic inclusions in the Esbo rock shows that in some places the diopside-gneiss, described above, has been partly amphibolitized. The bulk composition of the rock has remained unchanged during the process of amphibolitization, and only a recrystallization has taken place. Big individual crystals of hornblende have grown around and between the grains of diopside. The study of several thin sections revealed the existence of a continuous series with all gradations from pure diopside-gneiss to gneisses in which diopside occurs only in a minute amount besides hornblende. The basic inclusions in the orbicular rock, consisting mainly of hornblende and plagioclase (An_{42}), are of a chemical composition and structure similar to those of the diopside-gneiss. The mode of occurrence of hornblende in the amphibolite is also quite similar to that in the partly amphibolitized pyroxene-gneiss. It seems credible, therefore, that the basic inclusions in the orbicular rock have originally consisted of pyroxene-gneiss and have been entirely amphibolitized, so that diopside is now entirely absent.

Some thin sections of the granoblastic amphibolite show that these have been partly biotitized. It seems probable, therefore, that the fine-grained biotite-plagioclase-gneiss, the structure of which is similar to that of the pyroxene- and hornblende-gneisses, is a product of the recrystallization and metasomatism of amphibolite. A phenomenon like this has been recently described by Drescher-Kaden (1940) in the Forno-granite in Tessin, Switzerland, where a sedimentary pyroxene-quartzite passes gradually into a mica-rich gneiss. The embryonal orbicules of the Esbo rock occur just in this biotite-plagioclase-gneiss, which is chemically nearly esboitic and intermediate between the diopside-gneiss or the amphibolite and the typical esboite in the orbicular rock.

THE ORIGIN OF THE ESBO ROCK.

The fact that the orbicular rock bordering against diopside-gneiss contains residual inclusions of amphibolite, which differs from the pyroxene-gneiss only in containing hornblende instead of diopside, suggests the idea that both were formerly identical, while, on the other hand, the embryonal orbicules and consequently all the orbicules appear to have originated in the same rock. This reasoning leads to the following petrogenetic explanation:

The orbicular rock in Esbo has originated from a basic rock, rich in calcium, in the migmatitic rock crust of this region. Svecofennidic diopside-gneiss has been changed by the addition of soda to an esboitic rock, rich in biotite, and the metasomatism has given rise to a concretionary crystallization of the orbicules. The nuclei of the orbicules have been freed from the mafic minerals, and fine-grained plagioclase zones, rich in biotite, have originated by outward diffusion of feric material. Addition of soda connected with recrystallization has affected the rock almost throughout. The coarse-grained esboitic matrix has been formed, and in some cases new recurrent plagioclase zones are formed around the esboitic kernels. The origin of true esboite is, in this case, apparently a replacement process by the addition of soda to the basic rock, and the removal of lime and magnesia and ferrous oxide. Only as a secondary feature are there seen traces of granitization of the esboitic rock by magmatic ichors rich in potash.

CONCLUDING REMARKS.

Eskola's (1938) opinion about the origin of orbicular rocks by metamorphic differentiation is applicable both to the Kemijärvi and the Esbo rocks. The origin of an esboitic composition, in these cases, is mainly due to an addition of soda to basic rocks and a corresponding removal of $(Ca, Mg, Fe)O$, involving replacement processes. It seems credible that the esboitic parts of the orbicules are, in general, formed by concretionary crystallization in an esboitic or more basic rock causing outward diffusion of the femic components. The more mafic zones in the orbicules have been formed in connection with this diffusion. In most orbicular rocks a granitization of the earlier or primary matrix by ichors rich in potash has occurred. In connection with this process microclincic shells have crystallized. The soda metasomatism has given way to a potash metasomatism, and in some cases a repeated alternation of both processes has taken place, as in the orbicular granites of Kangasniemi and Virvik.

The above-mentioned processes in the origin of orbicular rocks are clearly manifested in the rocks of Lintusaari and Kemijärvi, in which the primary more basic matrix is well preserved, in addition to the secondary granitic matrix. Fig. 20. shows distinctly a high content of femic components in the primary matrix and impoverishment of the nuclei in FeO and MgO . In the diagram of the Lintusaari rock are plotted also the recurrent zones of the orbicules originated by outward diffusion of mafic components. This kind of projection seems to be well applicable in the study of diffusion in general.

The material added by the »esboitization» has been very rich in Na_2O , Al_2O_3 and SiO_2 . A concentration in the least soluble substances of the basic rock according to the principles of metamorphic differentiation proposed by Eskola (1932) seems to have occurred in the orbicules. The silicate material which has caused the partial albiti-

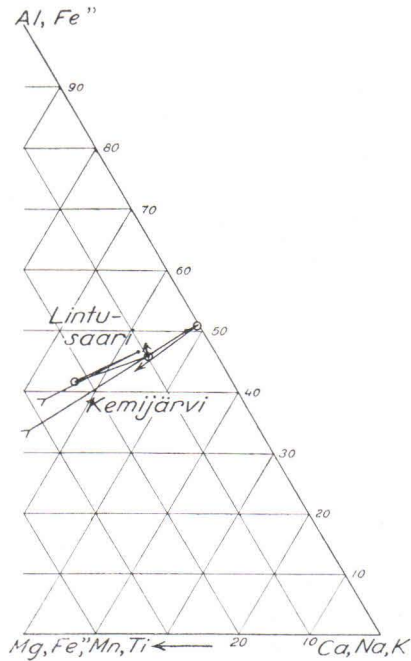


Fig. 20. Composition of different parts of orbicular rocks. The designations are the same as in Fig. 13.

zation as well as the origin of the orbicules may well be spoken of as magma originated by a differential anatexis (Eskola, 1933) of the primary rocks rich in sodium.

The «esboitization» of the orbicules stands in close connection with the granitization caused by arteritic silicate ichor rich in potash, which may be also spoken of as magma originated by differential anatexis. The granitization of the primary matrix and the origin of microclitic shells are the best evidences of replacement processes in a solid rock caused by this ichor.

Metasomatic granitic rocks consist of material originated from the silicate ichor, which has caused the granitization, and from the country rock, in which the replacement processes have taken place. It seems apparent, therefore, that the composition of this ichor is not a normal granitic one, but that it is still richer in alkalies, especially in potash, and quite poor in mafic components.

A concretionary crystallization similar to that in the orbicular rocks is met with also among granitic rocks in so-called eyed gneisses in which big «porphyroblasts» of alkali feldspars are embedded in a gneissose rock. The study of these rocks has shown that the origin of the eyes is due to granitization. According to Goldschmidt (1920) the eyed gneisses have originated in connection with igneous injection metamorphism. Recently Väyrynen (1939) considers the eyed gneisses in the Outokumpu area as migmatitic rocks owing their origin to pegmatitic and aplitic granitic injections in connection with tectonic movements. Erdmannsdörffer (1939) illustrates the crystallization of «eyes», or «migmatoblasts», in solid rock without destruction of earlier structures.

It seems credible that the origin of eyed gneisses is due to granitization through replacement processes by silicate ichor especially rich in alkalies. These rocks as well as the orbicular rocks may be considered as ultrametamorphic formations.

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To Professor Aarne Laitakari, Director of the Geological Survey of Finland, the writer presents his best thanks for information concerning the specimens of the orbicular pegmatite of Kisko.

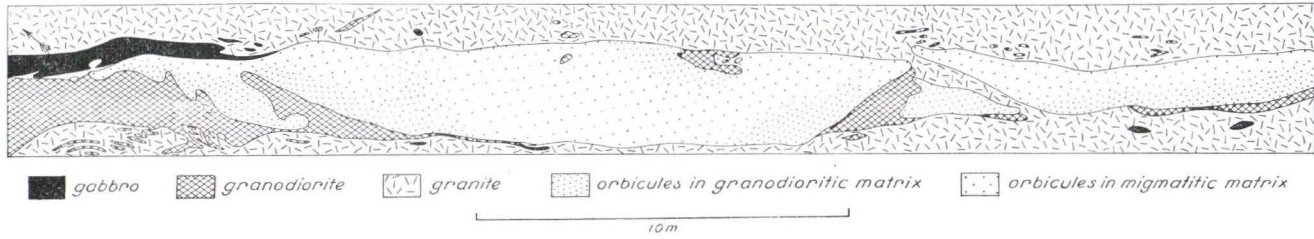
One of the chemical analyses was executed by Miss Elsa Ståhlberg and all drawings of maps and diagrams are the work of Miss Lyyli Dammert. The writer is very grateful for this valuable help.

The Mineralogical and Geological Institute of the University, Helsinki, July 1940.

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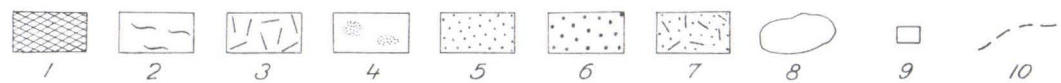
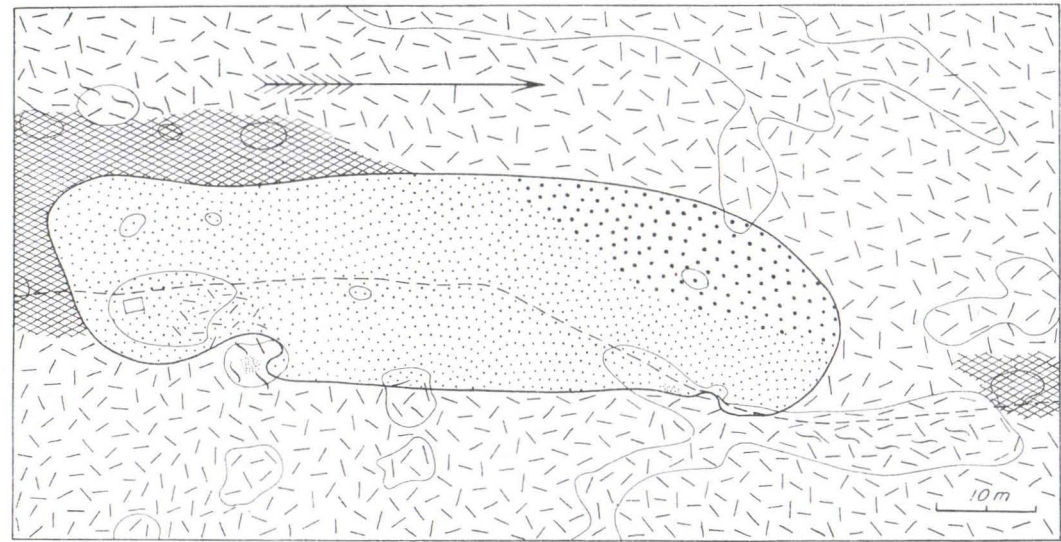
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ORBICULAR ROCK IN KEMIJÄRVI



Map II.

ORBICULAR ROCK IN ESBO



Legend: 1. Pyroxene-gneiss with granitic bands. 2. Mica-rich shapes in microcline-granite. 3. Microcline-granite. 4. Embryonal orbicules. 5. Esboitic orbicules with coarse-grained plagioclase nucleus and fine-grained outer zone in esboitic matrix. 6. Esboitic orbicules with several recurrent zones in esboitic matrix. 7. Esboitic orbicules in granitic matrix. 8. Outcrop. 9. Quarry. 10. Road.

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