GEOLOGINEN TUTKIMUSLAITOS

BULLETIN
DE LA
COMMISSION GÉOLOGIQUE
DE FINLANDE

N:o 138

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

XIX

AVEC 7 DIAGRAMMES, 13 TABLEAUX ET 9 FIGURES DANS LE TEXTE ET 1 PLANCHE

HELSINKI
AOÛT 1946

GEOLOGINEN TUTKIMUSLAITOS
BULLETIN DE LA COMMISSION GÉOLOGIQUE DE FINLANDE N:o 138

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

XIX

HELSINKI
1946
IMPRIMÊRIE DE L'ÉTAT

SISÄLLYSLUETTELO — CONTENTS

SUOMEN GEOLOGINEN SEURA

GEOLOGISKA SÄLLSKAPET I FINLAND

JÄSENLUETTELO 30. VI. 1946 LIST OF MEMBERSHIP

Kunniajäsen — Honorary Member

Eskola, Pentti, Prof.	Kauppiaankatu 8—10 B, Helsinki

Kirjeenvaihtajajäseniä — Foreign Corresponding Members

Cloos, Hans, Prof. Dr.	Geologisch-palaeontologisches Institut, Nussallee 2, Bonn. a. Rh., Deutschland
von Eckermann, Harry, Prof.	Linnégatan 75, Stockholm, Sverige
Flint, Richard F., Prof.	Dept. of Geology, Yale University, New Haven, Conn., U.S.A.
Goldschmidt, V. M., Prof.	Rothamsted Experimental Station, Lawes Agricultural Trust, Harpenden, Herts., England
Lougee, Richard J., Prof.	Colby College, Waterville, Me., U.S.A.
Magnusson, Nils H., Prof.	Valhallavägen 46, Stockholm, Sverige
Wegmann, C. Eugen, Prof.	Neuchâtel, Helvetia
Vendl, A., Prof. Dr.	Rezeda utca 7, Budapest, Magyarország
Öpik, Ar., Prof. Dr.	Aia t. 46, Tartu, U.S.S.R.

Jäseniä — Members

Aario, Leo, Prof.	Puutarhakatu 16 C, Turku
Aarnio, B., Prof.	Töölönkatu 14 B 6, Helsinki
Adamson, Olge J., Fil. Dr.	Mineralogisk Institutt, Blindern, Oslo, Norge
Alenius, P., Dipl. ins.	Lönnrotinkatu 15 A 2, Helsinki
Auer, Väinö, Prof.	Fredrikink. 66 B, Helsinki
Aulanko, Heikki, Dipl. ins.	Malmikaivos Oy., Luikonlahti
Aurola, Erkki, Fil. toht.	Malmikaivos Oy., Ratakatu 29, Helsinki
*Backlund, H. G., Prof.	Univ. Geol. Inst., Uppsala, Sverige
Backman, A. L., Fil. Dr., Docent	St. Robertsgatan 25 A, Helsingfors
*Barbour, George B., Prof.	33 Addison Road, London W 14, England
Blankett, Hugo, Industriråd	Myntg. 1 A 5, Helsingfors
Borgström, Leon. H., Prof.	Museig. 3, Helsingfors
Brenner, Thord, Fil. Dr., Docent	Grankulla
Brognon, Georges, Ingénieur Civil des Mines	68 Avenue Joseph Wanters, Cuesmes-lez-Mons, Belgique
*Bruce, E. L., Prof.	Dept. of Geology, Queens Univ., Kingston, Ont., Canada

*Bütler, H., Dr.	Rheinhaldenstrasse 105, Schaffhausen, Helvetia
Collet, Leon W., Prof.	Laborat. de Géologie de l'Université, Quai de l'École de Médecine, Genève, Helvetia
*Dahlström, Elis, Dr.	Addis Abeba, Ethiopia
*Du Rietz, Torsten, Fil. Dr.	Bolidens Gruv. A.-B., Boliden, Sverige
*Ebert, Heinz, Dr.	Sächs. Geol. Landesamt, Talstr. 35, Leipzig C. 1., Deutschland
Eigenfeld, Rolf, Dr.	Stadstrasse 14, Freiburg i. Br., Deutschland
Enkovaara, Antti, Fil. kand.	Rajasaarenkatu 9 E 66, Helsinki
Erämetsä, Olavi, Tekn. toht.	Lönnrotinkatu 45 A 15, Helsinki
Eskola, Salli, Fil. toht.	Huvilakatu 25 A 6, Helsinki
Friberg, Sven, Fil. maist.	Oy. Wilh. Schauman Ab., Jyväskylä
v. Gaertner, Hans Rudolf, Dr.	Preuss. Geol. Landesanst., Invalidenstr. 44, Berlin N 4, Deutschland
*Gavelin, Sven, Fil. Dr., Docent	Sveriges Geologiska Undersökning, Stockholm 50, Sverige
Gevers, T. W., Prof.	Geological Dept. of the University of Witwatersrand, Johannesburg, South Africa
Granö, J. G., Prof.	P. Rautatienkatu 11 A, Helsinki
*Grip, Erland, Dr., Chefsgeolog	Bolidens Gruv A.-B., Boliden, Sverige
Grönros, Y., Dipl. ins.	Vänr. Stoolinkatu 3 A 14, Helsinki
Haapala, Paavo, Fil. toht.	Malminrinne 2—4 A. Helsinki
Halinen, Vihtori, Vuori-ins.	Museokatu 30 A 8, Helsinki
Hall, A. Jean, M. A.	P. O. Box 60, Kitwe, Northern Rhodesia
Hausen, H., Professor	Åbo Akademi, Åbo
Heinonen, Leo, Fil. maist.	Pihlajatie 15, Helsinki
Heiskanen, V. A., Prof.	Messeniuksenkatu 10 A, Helsinki
Helkavaara, Eero K., Fil. maist.	Valtatie 20 A, Tikkurila
Hellaakoski, Aaro, Fil. toht.	Museokatu 34 A, Helsinki
Hietanen, Anna, Dr.	Dept. of Geology, Stanford University, Palo Alto, Calif., U.S.A.
Himmi, Reino, Fil. maist.	Outokumpu Oy., Tampere
*Hjelmqvist, Sven, Fil. Dr., Statsgeolog	Sveriges Geologiska Undersökning, Stockholm 50, Sverige
Holm, Caj, Dipl. ins.	Lohjan Kalkkitehdas Oy., Virkkala
*Homma, Fujio, Prof.	Institute of Petrology & Geology, Imperial University, Kyoto, Japan
Hyyppä, Esa, Fil. toht., dosentti, valtiongeologi	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Hämäläinen, Viljo, Ylioppp.	Pääskylänrinne 4 A 32, Helsinki
Härme, Maunu, Fil. kand.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Häyrynen, Matti, Dipl. ins.	Iso Puistotie 1 A 6, Munkkiniemi
Jalander, Holger, Dipl. ins.	Munkkiniemenkatu 7 A, Helsinki
*Janusson, Vladimir, Stud. rer. nat.	Paleontologiska Institutet, Uppsala, Sverige
Joensuu, Oiva I., Fil. maist.	Pieni Robertinkatu 10 as. 21, Helsinki
Jäntti, Olavi, Fil. maist.	Sotkankatu 18 A 2, Tampere
Järnefelt, Olai, Fil. maist.	Bernhardinkatu 5 A, Helsinki

Kahma, Aarno, Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Kaitaro, Simo, Fil. kand.	Runeberginkatu 48 A 13, Helsinki
Kalajoki, Reino, Fil. maist.	Töölöntorinkatu 9, Helsinki
Kanerva, Reino, Fil. maist.	Pohjoisranta 14 A 13, Helsinki
Keränen, Jaakko, Prof.	Topeliuskatu 1, Helsinki
Kivinen, Erkki, Prof.	Mariankatu 13 b B, Helsinki
v. Knorring, Oleg, Fil. mag.	Pohjolagatan 1 C 25, Helsingfors
Koponen, J. S. W., Lehtori	Kirkkokatu 25, Kajaani
Koponen, Olavi, Dipl. ins.	Kauppiaskatu 12 A 6, Turku
Kotilainen, Mauno J., Prof.	Korkeavuorenkatu 8 C, Helsinki
Kranck, E. H., Prof.	Institut de géologie, Neuchâtel, Helvetia
Kuenen, H., Dr. Ph.	Geol. Inst., Groningen, Nederland
*Kulling, Oscar, Fil. Dr., Docent	Östermalmsgatan 44, Stockholm, Sverige
Kulonpalo, Max, Fil. kand.	Töölöntorinkatu 4 B 46, Helsinki
Laakso, Perttu, Fil. toht.	Pengerkatu 13 A 39, Helsinki
Laaksonen, Martti I., Dipl. ins.	Västäräkki D, Riihimäki
*Laitakari, Aarne, Prof., Geologisen tutkimuslaitoksen johtaja	Bulevardi 29, Helsinki
Laitakari, Lauri, Kapt. evp.	Koivula, Korso
Landergren, Sture, Dr., Laborator	Sveriges Geologiska Undersökning, Stockholm 50, Sverige
Lehijärvi, Mauno, Fil. kand.	Pursimiehenkatu 9 A 15, Helsinki
Leiviskä, Iivari, Prof.	Museokatu 9, Helsinki
Linna, Antti, Dipl. ins.	Messukylä
*Lokka, Lauri, Fil. toht.	Mannerheimintie 35 A, Helsinki
Lukkala, O. J., Prof.	Aurorankatu 19 A, Helsinki
Lunnasvaara, Väinö, Fil. maist.	Puistolinna, Forssa
Lupander, Kurt, Fil. mag., Disponent	Mätäsvaara gruva, Mätäsvaara
Maijala, Paavo, Dipl. ins.	Mineral. laitos, Tekn. Korkeakoulu, Helsinki
Marmo, Vladi, Fil. maist.	Pukkimäenkatu B 312, Äänekoski
*Martna, Jüri, Stud. rer. nat.	Torsvikssvängen 16^{III}, Lidingö, Sverige
Matisto, Arvo, Yliopp.	Fredrikinkatu 58 A 12, Helsinki
Mattila, Jorma, Fil. maist.	Töölönkatu 36 B, Helsinki
*Meier, Otto, Fil. Dr.	Svenska Diamantbergborrnings A.-B., Kungsgatan 44, Stockholm, Sverige
Mellis, Otto, Dr., Priv. Doz.	L. U. Mineralogijas inst., Kronvalda bulv. 4, Rigā, U. S. S. R.
Metzger, A. A. Th., Fil. Dr., Docent	Pargas
Mikkola, Aimo, Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
*Mikkola, Toini, Fil. kand.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Mikkola, Toivo S. K., Fil. kand.	Temppelikatu 14 A, Helsinki
*Mineralogisch-petrologisches Institut d. Univ.	Bernoullianum, Basel, Helvetia
Mogensen, Fredrik, Tekn. Dr., Bergsingenjör	Ludvika, Sverige
Mäkinen, Eero, Vuorineuvos	Outokumpu Oy., Outokumpu
Mäntynen, Matti, Yliopp.	Mäenpää, Kärsämäki
Mölder, Karl, Fil. toht.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki

Neuvonen, Kalle, Yliopp.	Et. Hesperiankatu 28 B 30, Helsinki
Nisonen, Eino, Fil. maist.	Töölönkatu 36 B, Helsinki
*Noe-Nygaard, Arne, Prof.	Østervoldgade 7, København, Danmark
Nordenswan, Einar A. O., Fil. maist.	Runeberginkatu 17 A, Helsinki
Nordin, Walter, Dipl. ing.	Järnverket, Imatra
Nystén, Henrik, Dipl. ing.	Karlavägen 9—11 A, Drumsö
Ohlson, Birger, Fil. mag.	Grankulla
Ojanperä, Pentti, Fil. maist.	Valtatie 50—52, Marjaniemi
Okko, Veikko, Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Olson, E. O., Mining Engineer	Los Angeles, Calif., U.S.A.
Parras, Kauko, Fil. maist.	Museokatu 25 C 36, Helsinki
Pehrman, Gunnar, Prof.	V. Strandgatan 17, Åbo
Peltola, Esko, Fil. kand.	Outokumpu Oy., Outokumpu
Pilava-Podgurski N., Yliopp.	Hämeentie 39 B, Helsinki
*Popoff, Boris, Prof.	Popoffstr. 8, Rigā, U.S.S.R.
Puranen, Maunu, Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
*Pääkkönen, Veikko, Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Raiste, Helvi, Fil. maist.	Rauma-Raahe Oy., Rauma
Raja-Halli, Heikki, Dipl. ins.	Ahtiala, Kirkniemi
Rankama, Kalervo, Fil. toht., dosentti	Kalevankatu 16 A, Helsinki
Renvall, Åge, Fil. mag.	Esbo
Sahama, Th. G., Prof.	Yliopiston Geologian laitos, Snellmaninkatu 5, Helsinki
Saksela, Martti, Fil. toht., apulainen	Temppelikatu 21, Helsinki
*Salmi, Martti, Fil. toht.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Salminen, Antti, Fil. maist.	Pohjoisranta 4 A 3, Helsinki
Salminen, Kyllikki, Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Saraste, Ahti, Yliopp.	Kuusitie 9/47, Helsinki
Sauramo, Matti, Prof.	Tunturikatu 4, Helsinki
Savolainen, E., Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Seitsaari, Juhani, Fil. kand.	Kuusitie 6 A 23, Helsinki
Simola, Kaarlo, Yliopp.	Outokumpu Oy., Raivionmäki, Outokumpu
Simola, Torsti, Dipl. ins.	Fredrikinkatu 58 B, Helsinki
Simonen, Ahti, Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
*Sirén, Arne, Fil. Dr.	Ab. Airam Oy., Båtsmansgatan 29, Helsingfors
Soveri, Urpu, Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
*Stigzelius, Herman, Tekn. dr.	Handels- och industriministeriet, Mannerheimvägen 9, Helsingfors
Ståhlberg, Elsa, Fil. mag.	Fänrik Stålsgatan 11 B 28, Helsingfors
Sundell, I. G., Direktör	Kanalgatan 4. Helsingfors
Suominen Eero E., Fil. maist.	Tehtaankatu 1 A, Helsinki
Tanner, V., Prof.	Margaretapl. 2, Hälsingborg, Sverige

Toivonen, N. J., Prof.	Hallituskatu 3, Helsinki
Tuominen, Heikki, Fil. kand.	Liisankatu 21 B, Helsinki
Vaasjoki, O., Fil. kand.	Kammiokatu 15 D 29, Helsinki
Vahervuori, Teuvo, Yliopp.	Fredrikinkatu 14 A 6, Helsinki
Wahl, Walter, Prof.	Kyrkogatan 1 b, Helsingfors
Valtasaari, Lea, Fil. kand.	Vironkatu 5 A, Helsinki
Varma, Arno, Fil. kand.	Urheilukatu 46 A 8, Helsinki
Veltheim, Valto, Yliopp.	Fredrikinkatu 39 C 21, Helsinki
*Wenk, Eduard, Dr.	Mineralogisch-petrologisches Institut d. Univ., Basel, Helvetia
Wessman, Tor H., Fil. mag.	Dagmargatan 5 B 10, Helsingfors
*Wickman, Frans E., Dr.	Dalagatan 36, Stockholm, Sverige
Viento, Aimo, Johtaja	Mannerheimintie 55 a, Helsinki
Wiik, Hugo B., Fil. kand.	Koskelantie 56 B, Helsinki
Virkkala, Kalevi, Fil. maist.	Geologinen tutkimuslaitos, Bulevardi 29, Helsinki
Vuorjoki, Aarre, Fil. maist.	Untamontie 12 B 13, Helsinki
Vähätalo, Veikko, Fil. maist.	Outokumpu Oy., Outokumpu
*Väyrynen, Heikki, Prof.	Temppelikatu 13, Helsinki
*Zāns, Verners, Cand. rer. nat.	L. U. Geologijas institūts, Baznicas ielā 5—18, Rigā, U.S.S.R.
Zeidler, Waldemar, Dipl. ing.	Mätäsvaara gruva, Mätäsvaara
*Ödman, Olof H., Fil. Dr., Docent, Statsgeolog	Sveriges Geologiska Undersökning, Stockholm 50, Sverige

Vakinaiset jäsenet on merkitty tähdellä (*)
The Life Members are indicated by an asterisk (*)

SUOMEN GEOLOGISEN SEURAN TOIMINTA VUONNA 1945

Geologisella Seuralla on v. 1945 ollut 10 kokousta. Puheenjohtajana on toiminut toht. Martti Salmi, sihteerinä allekirjoittanut.

Uusiksi jäseniksi valittiin tohtorit Sven Gavelin, Sven Hjelmqvist, Oscar Kulling, Sture Landergren, Otto Meier, Frans E. Wickman ja Olof H. Ödman Ruotsista, insinöörigeologi Georges Brognon Belgiasta, fil. maist. Reino Kanerva, dipl. ins. Torsti Simola, tekn. yliopp. Caj Holm ja johtaja Aimo Viento. Seuraan kuului v. 1945 yksi kunniajäsen, 9 ulkomaista kirjeenvaihtajajäsentä sekä 150 muuta jäsentä, joista vakinaisia 32. Seurasta erosi v. 1945 4 jäsentä.

Vuoden 1945 aikana ilmestyi Seuran julkaisujen numero XVIII, jossa on 2 kirjoitusta ja XL + 67 sivua. Vakinainen valtionavustus on ollut mk 4 500: — ja lisäavustus mk 30 000: —.

ACTIVITIES OF THE GEOLOGICAL SOCIETY OF FINLAND IN 1945

During 1945 10 meetings of the Society were held. Dr. Martti Salmi acted as President and the duties of Secretary were attended to by the undersigned.

The following were elected Members of the Society: Dr. Sven Gavelin, Dr. Sven Hjelmqvist, Dr. Oscar Kulling, Dr. Sture Landergren, Dr. Otto Meier, Dr. Frans E. Wickman, and Dr. Olof H. Ödman, all of Sweden; Mr. Georges Brognon, Geologist, of Belgium; Mr. Reino Kanerva, M. A.; Mr. Torsti Simola, Mining Engineer; Mr. Caj Holm, Student of Engineering, and Mr. Aimo Viento. The List of Members included in 1945 one Honorary Member, 9 Foreign Corresponding Members, and 150 other Members, 32 of whom were Life Members.

Of the »Comptes Rendus» of the Society, the 18th volume containing 2 articles and totalling XL + 67 pages was published during the year. The ordinary Government subsidy was mks 4 500: — and the additional subvention mks 30 000: —.

Vuoden 1945 lopussa Seuran taloudellinen asema oli seuraava:
At the close of 1945 the financial position of the Society was the following:

Säästö vuodelta 1944 — Brought forward from 1944 ...	108 994: 65
Valtionavustukset — Government subsidies	34 500: —
Jäsenmaksuja — Membership fees	19 575: —
Ylipainoksista — Separate copies	5 485: —
Korkoja ja osinkoja — Interest & dividends	4 333: 75
Muita tuloja — Income not listed above	147: 30
Summa — Total mk	173 035: 70
Painatuskulut — Publishing costs	75 605: 30
Ulkomaiset esitelmöitsijät — Foreign lecturers	18 548: —
Toimistokulut — Office costs	5 699: 50
Sihteerin palkkio — Secretary's fee	3 000: —
Edustuskulut — Representation costs	112: —
Säästö vuodelle 1946 — Carried forward to 1946	70 070: 90
Summa — Total mk	173 035: 70

Helsinki 2. I. 1946.

In fidem:
Kalervo Rankama

KOKOUKSET — MEETINGS
1945

25. I.

Toht. Anna Hietanen: Naantalin seudun geologia. — On the Geology of the Naantali Area.

Esitelmöitsijä kuvasi Kalannin alueeseen geologisesti liittyvän Naantalin alueen kivilajeja. Esitelmän sisältö julkaistaan myöhemmin. — The lecturer dealt with the rocks of the Naantali area, geologically connected with the Kalanti area, described before (*cf.* Anna Hietanen, Über das Grundgebirge des Kalantigebietes im südwestlichen Finnland. Bull. Comm. géol. Finlande N:o 130. 1943). The lecture will be published later.

15. II.

Toht. Esa Hyyppä: Vihannin rikkikiisulohkareiden emäkallion etsinnästä glasiaaligeologisilla perusteilla. — The Search for the Source of the Pyrite Ore Boulders at Vihanti, Based on Principles of Glacial Geology.

Esitelmän sisältö julkaistaan sarjassa Bull. Comm. géol. Finlande. — The lecture will be published in the series Bull. Comm. géol. Finlande.

19. IV.

Prof. E. H. Kranck: Om Mätäsvaara molybdenförekomst. — On the Molybdenum Deposit at Mätäsvaara.

E. H. Kranck, The Molybdenum Deposit at Mätäsvaara in Carelia (E. Finland). Geol. Fören. Förh., Bd 67, p. 325, 1945.

Toht. Kalervo Rankama esitti havaintoja Outokumpu Oy:n Säätiön stipendiaattina Ruotsiin tekemältään matkalta. — *Dr. Kalervo Rankama* presented impressions of travel from a recent journey to Sweden.

3. V.

Prof. Mauno J. Kotilainen: Yhteistehtävistä ja -työstä kasvimaantieteen ja geologian aloilla. — On Common Problems and Cooperation in Phytogeography and Geology.

Esitelmöitsijä kosketteli geologian merkitystä kasvien kasvualustan ja niiden lajiston välisten suhteiden selvittämiselle kiinnittäen huomiota erikoisesti hivenalkuainetutkimuksen merkitykseen tässä yhteydessä. — The lecturer dealt with the importance of geology in elucidating the relations between plant species and soil, and specially stressed the study of minor elements in this connection.

27. IX.

Prof. Heikki Väyrynen: Pohjois-Suomen kallioperän tektonisesta rakenteesta. — On the Structural Geology of North Finland.

Esitelmän sisältö julkaistaan sarjassa Bull. Comm. géol. Finlande. — The lecture will be published in the series Bull. Comm. géol. Finlande.

26. X.

Dr. Sture Landergren (Stockholm): Några drag i järnmalmernas geokemi. — On the Geochemistry of Iron Ores.

Esitelmän sisältö julkaistaan Ruotsissa. — The lecture will be published in Sweden.

29. X.

Dr. Frans E. Wickman (Stockholm): Några atomistiska synpunkter på den magmatiska differentiationen. — Some Atomistic Aspects of the Differentiation by Crystallization.

Esitelmöitsijä loi yleiskatsauksen kuivissa silikaattisysteemeissä tapahtuvaan differentiatioon siirtyen sitten käsittelemään veden ja hydroksylin osaa mineraalien muodostumisessa ja kosketteli lopuksi vesiliuoksista tapahtuvaa kiteytymistä.— The lecturer dealt with the differentiation in dry silicate systems (*cf.* Frans E. Wickman, Some Aspects of the Geochemistry of Igneous Rocks and of Differentiation by Crystallization. Geol. Fören. Förh., Bd 65, p. 371, 1943), the role of water and hydroxyl in the formation of minerals, and the crystallization from aqueous solutions.

15. XI.

Dr. Thord Brenner: Lerornas vattenhalt. — On the Water Content of the Clays.

Thord Brenner, Om mineraljordarternas hållfastighetsegenskaper. Bull. Comm. géol. Finlande N:o 139, 1946.

Prof. Aarne Laitakari puhui geologisista hajahavainnoista korostaen niiden tallettamisen tärkeyttä muiden geologien käytettäviksi. — *Professor Aarne Laitakari* discussed incidental observations in geology and emphasized the importance of the collection and deposition of same for further use by other geologists.

29. XI.

Prof. Heikki Väyrynen: Havaintoja Etelä-Suomen kallioperän tektoniikasta. — Observations on the Structural Geology of South Finland.

Esitelmän sisältö julkaistaan sarjassa Bull. Comm. géol. Finlande. — The lecture will be published in the series Bull. Comm. géol. Finlande.

13. XII.

Valittiin Seuran toimihenkilöt vuodeksi 1946. Valituiksi tulivat: puheenjohtajaksi toht. Paavo Haapala, varapuheenjohtajaksi prof. Aarne Laitakari, sihteeriksi ja rahastonhoitajaksi toht. Kalervo Rankama uudelleen sekä tilintarkastajiksi dipl. ins. Matti Häyrynen ja maist. Eetu Savolainen, molemmat uudelleen.

The Ballot for the Officials was taken and the following functionaries were declared elected for the year 1946: President, Dr. Paavo Haapala; Vice President, Professor Aarne Laitakari; Secretary and Treasurer, Dr. Kalervo Rankama, re-elected; Auditors, Messrs. Matti Häyrynen, Civil Engineer, and Eetu Savolainen, M. A., re-elected.

Prof. Matti Sauramo: Rannansiirtymiset maankohoamisalueen reunavyöhykkeellä. — The Displacements of the Shore-Line on the Border Region of the Land Upheaval.

Esitelmän sisältö julkaistaan sarjassa Bull. Comm. géol. Finlande. — The lecture will be published in the series Bull. Comm. géol. Finlande.

Suomen Geologinen Seura. N:o 19. Geologiska Sällskapet i Finland.

1

ON THE COARSE-GRAINED GARNET-CORDIERITE GNEISSES OF SOUTH AND SOUTH-WEST FINLAND

BY

KAUKO PARRAS

CONTENTS

INTRODUCTION

The crust of South and South-west Finland is considered to be an ordinary and typical deeply eroded root zone of the Svecofennidic mountain chain with its leptites and amphibolites, represented by originally sedimentogeneous and volcanogeneous supracrustal rocks, from which quartzites in particular are almost entirely lacking, and, on the other hand, its infracrustal rocks, younger than the supracrustal series, the most widely distributed of which are the early orogenic gneissose and the late orogenic migmatite granites. The geological remapping carried out of late years and geological investigation in general have, however, shown that we ought to supplement and check, in many respects, the present opinions in regard to this classical region.

Besides the results already presented (Parras 1941) the investigations carried out by the author in South Finland have given rise to a number of more far-reaching questions, of which the author restricts himself to present in the following, in a condensed form, those points of view that refer to the garnet-cordierite gneisses.

DISTRIBUTION

Of supracrustal rocks the coarse-grained garnet-cordierite gneisses or kinzigites (kinzigite gneisses) have, according to the newest investigations, shown themselves to be surprisingly widely distributed in the Pre-Cambrian of South and South-western Finland. Those from the surroundings of Helsinki have been described by Kranck (1931, 1937) and Wegmann (1931), from the archipelago south of Turku and from the vicinity of Turku by Pehrman (1931, 1936), from West Uusimaa by Parras (1941) — the center of the region being about 60 km N.W. of Helsinki —, from the districts surrounding Uusikaupunki by Hietanen (1943) and those from the archipelago S.W. and S. of Turku by Hausen (1944) and Metzger (1945). The regions investigated are thus scattered over the Svecofennidic root zone.

It is, however, exceedingly probable that the distribution of kinzigites is not limited solely to South and South-west Finland but that they will also be met with elsewhere in the country, as the geological remapping progresses. In this respect the extensive schist and migmatite area of Central Finland becomes interesting. That kinzigites can be expected to be met with also here became apparent from the lecture on the rocks of the province of West Uusimaa, South Finland, held by the author in March, 1941 at the meeting of the Geological Society of Finland. The fact is that in the discussion following the lecture Professor Heikki Väyrynen mentioned having observed a quite extensively wide-spread rock type in the Mikkeli geological map-sheet area, the main characteristics of which coincided with the author's description of kinzigites. He also stressed the obvious association of the West Uusimaa and Mikkeli map-sheet areas with that of the Svecofennidic mountain chain. Besides, during the last couple of years, the author has had an opportunity of making scattered observations in the interior and eastern parts of the country and he has also personally been able to establish that, for instance, to the N.W. of Lake Laatokka, in the triangle Elisenvaara—Hiitola—Simpele, as well as near the town of Mikkeli, there undoubtedly are to be found rocks that can be said to be kinzigite.

In this connection the author cannot refrain from mentioning the well known so-called Sörmland gneisses (*cf.* Backlund 1937) of the Svecofennides on the Swedish side; there are at least as good grounds for associating them with the garnet-cordierite gneisses of South and South-west Finland as have been given for comparing the leptites on both sides of the Åland Sea.

NOMENCLATURE AND PETROGRAPHIC DEFINITION

The author first met with coarse-grained garnet-cordierite gneisses when he was in South Finland with Dr. Erkki Mikkola in the early summer of 1936. Already in the same year Dr. Mikkola began to use the name kinzigite as a descriptive term for this rock. Now it happens to be so that the conceptions kinzigite and kinzigite gneiss already appeared in German geological literature in the latter half of last century, since when they have been used and that by them are nearest meant the metasomatically produced garnet-cordierite gneisses (*cf.* Waldmann 1929, Wager 1938).

Kranck (1931) as regards the occurrences in the surroundings of Helsinki, as well as Pehrman (1931), in respect of those in the archipelago S. of Turku, have explained the origin of the rock in question in a similar manner. On the contrary again Pehrman (1936) re the rocks in the surroundings of Turku, considers resort to Mg metasomatism as being unnecessary and proposes that the rocks in question be regarded as corresponding to argillaceous sediments. The author himself has concurred in this opinion (Parras 1941) and on considering the question as a whole is more than ever inclined towards it. Hietanen (1943) and Metzger (1945) have later on come to the same result in their own areas. In using the name kinzigite with reference to garnet-cordierite gneisses, which correspond to an unaltered argillaceous sediment composition, one is thus being inconsistent.

As the already known distribution of the rock in question is rather extensive, with obvious signs of proving to be still more extensive, and as it, on being considered as a whole, in all probability has not been produced in a metasomatic manner from one or many other rocks but is, as such, nearest a highly metamorphic representative of a sediment corresponding to a clay composition, the author suggests for it the name lutogenite (= argillageneous, the root in Latin being *lutum*, = clay). The literal meaning of lutogenite, »argillageneous», cannot cause confusion with other rocks of the same origin such as, for instance, mica-schist, the meaning of which is already everywhere established and clear.

The author does not, however, in this connection intend to give a closer petrographic description of lutogenite, but limits himself to a rough definition of it: by lutogenite the author means a highly metamorphic — most nearly corresponding to the chemical composition of clay — coarse-grained, veined and banded gneissose rock, the main minerals of which are plagioclase (oligoclase), quartz, microcline, garnet (almandite), cordierite and biotite, accessory minerals being sillimanite, apatite, graphite, pyrite, oxidic iron ore, and zircon. An essential feature is the abundance of granite material which, besides the veins and bands, can form migmatites in which granite predominates, and even extensive parts of pure granite. The »normal» type, less mixed with granite material, is smallfolded, sometimes even straight banded, with a rather light rock in its weathering surface. The grey-blue tinge caused by the cordierite is clearly perceivable in a fresh surface. Among the Fe-Mg minerals garnet and cordierite predominate, while biotite occupies a secondary place. The abundance ratios existing between different minerals can naturally vary greatly and the phases given in the mineral list above need not necessarily appear together. Further, besides garnet, cordierite and biotite, one can also meet with antophyllite and muscovite. This variation, perceivable in the mineral composition, which variation is not to be confused with the veinedness and bandedness caused by the granite material, is thoroughly in accordance with the sediment character of lutogenite and it does not generally occur within the limits of centimeters but of meters and tens of meters, *i. e.*, the dimensions of the original strata, which in some definite way differ from one another in regard to composition, belong to an altogether different category than, for instance those in varved mica-chists. These original strata, however, are not always well defined.

In the definition of lutogenite by a clay composition is meant that, of the main oxides present, SiO_2 averages 60 %, Al_2O_3 14—20 %, total iron 6—10 %, MgO 2—4 %, CaO about 1 %, and as regards the alkalies, potassium predominates over sodium.

Due to understandable reasons, individual chemical analyses of such a rock deviate from one another within known limits, while also the preparation of an average mixture causes difficulties.

RESIDUAL-HYDROLYSATIC CHARACTER

Lutogenite's extensiveness of distribution alone demands such metasomatic processes as are difficult to conceive. But if we start with the idea that this rock represents a sediment, unchanged in its chemical composition, then the extensiveness of its distribution, as well as its great similarity of composition and structure will be more easily understood. The composition, structure and quantity of the original sediment, for their own part, signify conditions of weathering and sedimentation different to those considered as having existed, in adapting the actualistic principle to the Finnish Pre-Cambrian.

If the sedimentogeneous rocks of the Karelidic formation of East Finland are compared with those of the Svecofennidic zone of South Finland, then the distribution of mica-schists and quartzites in the Karelidic mountain chain is as typical as the appearance of lutogenite, and the conspicuous scarcity of quartzites and mica-schists in the Svecofennidic crust. As the stratification of the Karelian sediment proceeded, the exogeneous differentiation was to such an extent well defined that the separation of the hydrolysatic and residual sediments occurred almost completely (the conceptions hydrolysate and residua understood as given by V. M. Goldschmidt, 1937). On the other hand, in the stratification of the lutogenite sediment, the whole exogeneous differentiation occurred less clearly, so that separation had hardly taken place at all, or had remained incomplete. The strata, richer in residual or hydrolysatic material, in so far as these are perceptible in contemporary lutogenite, are characteristically thick and irregular, illustrating the impetuosity of the sedimentation and the instability of the conditions then prevailing. In short: the rhythm of geological processes during this »lutogenite period» has been essentially different from that prevailing during the formation of the Karelidic geosynclinal.

If, according to the afore-mentioned principle, we begin to examine the hydrolysate-richer extremity of the lutogenite sediment, there arises the question of the relations existing between lutogenite and mica-schist, and the possibility of their changing one into the other, *i. e.*, is it only a question of a different degree of metamorphism? The author has made no personal field observations concerning this relation, so that the question, in regard to this point, remains open to be cleared up later on. If we then transfer our attention to the residua-richer extremity of the lutogenite sediment, we have before us the old question: »where are the quartzites of the Svecofennides?» They have been explained as having either been granitized (Backlund 1937), or as having disappeared, due to the effect of erosion, prior to their getting into the Svecofennidic folding (Eskola and Nieminen 1938). According to the above-mentioned principle, however, they could hardly have formed to any extent, the residual material, arkose-like in its composition, appearing in the contemporary lutogenite and giving it the granite component typical of it. The total chemical composition of lutogenite is thus not to be considered as corresponding to that of clay, but most nearly to that of a mixture of sand with clay. However, it must be said that the quantity of quartz contained in the residual component seems to be rather small when compared to the ratio of Karelidic quartzites to mica-schists. This could, however, possibly be understood so, that the rock ground from which the lutogenite sediment originated, must have been more basic than that corresponding to Karelidic sediments, which explanation would thus be a step nearer to the prevailing conception of the total composition of the earth's original crust. Lutogenite could thus be considered as a highly metamorphic product of residual-hydrolysatic sediments, originating from an earlier rock ground, more basic than the present one.

CONCLUSION

The purpose of this paper has been the presentation of the lutogenite-conception in its main features without, however, attempting to prove anything more precisely. This especially refers to the residual-hydrolysatic character of lutogenite. Besides, several questions closely related to lutogenite have been left out altogether, while others, for instance that relating to the origin of its granite material, have been touched upon lightly. In stressing the bulk chemical composition of the sediment as being unchanged, the author by no means wishes to deny as an inner process of the rock the obvious circulation of substances and in general metamorphic differentiation. It is the intention to return to these matters later on. Finally, the author further desires to stress that the name »lutogenite» is not to be regarded as restricted to the garnet-cordierite gneisses of some fixed area, but that it can be suitably used as a general epithet in place of the name »kinzigite» for petrologically similar types of rocks met with all over our Pre-Cambrian territory. In this respect the petrographical definition given above cannot as yet be considered final and completely competent, wherefore its possible correction and expansion depend upon further observations.

REFERENCES

BACKLUND, H. G., Die Umgrenzung der Svecofenniden. Bull. Geol. Inst. Uppsala, Vol. 27, p. 119. 1937.

ESKOLA, PENTTI, and NIEMINEN, EERO, The Quartzite Area of Tiirismaa near Lahti. C. R. Soc. géol. Finlande N:o XII; Bull. Comm. géol. Finlande N:o 123, p. 29. 1938.

GOLDSCHMIDT, V. M., The Principles of Distribution of Chemical Elements in Minerals and Rocks. J. Chem. Soc. London, p. 655. 1937 (1937 b).

HAUSEN, H., Geologische Beobachtungen im Schärenhof von Nagu—Korpo, Südwest Finnland. Acta Acad. Aboensis, Math.-Phys. XIV, N:o 12. 1944.

HIETANEN, ANNA, Über das Grundgebirge des Kalantigebietes im südwestlichen Finnland. Bull. Comm. géol. Finlande N:o 130. 1943.

KRANCK, E. H., Beiträge zur Kenntnis der Svecofenniden in Finnland II. Petrologische Übersicht des Küstengebietes E von Helsingfors. Bull. Comm. géol. Finlande N:o 89, p. 67. 1931.

—»— Beiträge zur Kenntnis der Svecofenniden in Finnland IV. Über Intrusion und Tektonik im Küstengebiet zwischen Helsingfors und Porkala. C. R. Soc. géol. Finlande N:o X; Bull. Comm. géol. Finlande N:o 119, p. 69. 1937.

METZGER, ADOLF A. T., Zur Geologie der Inseln Ålö und Kyrklandet in Pargas — Parainen, S. W. Finnland. Medd. Åbo Akad. Geol. Min. Inst. N:o 27, p. 17. 1945.

PARRAS, KAUKO, Das Gebiet der Pyroxen führenden Gesteine im westlichen Uusimaa in Südfinnland. Geol. Runds., Bd. 32, p. 484. 1941.

PEHRMAN, G., Über eine Sulfidlagerstätte auf der Insel Attu im südwestlichen Finnland. Acta Acad. Aboensis, Math.-Phys. VI, N:o 6. 1931.

—»— Über Cordierit-führende Gesteine aus dem Migmatitgebiet von Åbo (S. W.-Finnland). Acta Acad. Aboensis, Math.-Phys. X, N:o 6. 1936.

WAGNER, RUDOLF, Studien im Gneisgebirge des Schwarzwaldes IX. Über die Kinzigitgneise von Schenkenzell und die Syenite vom Typ Erzenbach. Sitzungsber. Heidelb. Akad. Wiss., Math.-Nat. Kl., 4. Abh. 1938.

WALDMANN, LEO, Ein cordieritreicher Kinzigit vom Rieserferner Tonalit in Osttirol. Mitt. Wiener Geol. Ges., Bd. 22. 1929.

WEGMANN, C. E., Beiträge zur Kenntnis der Svecofenniden in Finnland I. Übersicht über die Geologie des Felsgrundes im Küstengebiet zwischen Helsingfors und Onas. Bull. Comm. géol. Finlande N:o 89, p. 1. 1931.

2

A SIMPLIFIED METHOD OF QUANTITATIVE SPECTROCHEMICAL ANALYSIS IN THE CARBON ARC CATHODE LAYER, BASED ON THE USE OF THE LOGARITHMIC WEGDE SECTOR

BY

KALERVO RANKAMA AND OIVA JOENSUU

ABSTRACT

A new method of quantitative spectrographic analysis in the cathode layer of the carbon arc *(»Glimmschicht»)* is described, based on the use of the logarithmic wedge sector, and on direct measuring, under a microscope, of the lengths of the lines used for analysis. The corresponding concentrations are found by a calibration curve constructed by plotting the lengths of the lines against the contents. Calibration curves for the quantitative determination of niobium (columbium) by the line Nb I 4 058.938 Å in titanium dioxide and quartz bases are presented, the use of safety and correction lines is introduced, and the application of the method in spectrochemical investigations discussed.

CONTENTS

INTRODUCTION

The most versatile of all spectrochemical methods based on the use of arc ist that developed by Mannkopff and Peters (1931) upon the carbon arc cathode layer effect. Nowadays, this method is most widely applied to geochemical investigations.

The high sensitivity of this method has made it exceedingly suitable in the search for trace elements, and, at the same time, quantitative methods have been developed, using the cathode layer effect. Of these, only the investigations carried out by Strock (1936 a and b, 1945), and those by Preuss (1938), and by Scott (1945) will be mentioned separately in this connection. The physical properties of the excitation in the arc in general are discussed by Rollwagen (1939) in an interesting paper.

The methods of spectrum analysis aiming at the determination of the amount of the compound to be investigated may, in general, be divided into the semi-quantitative and the quantitative ones. The former include the ocular estimation of the intensity of the spectrum lines, while in the latter the real blackening of the lines is determined by photometric means.

The simplest of the quantitative methods proper is the one using the logarithmic sector. The length of the spectrum line obtained by direct measurement in a sector spectrum is proportional to the logarithm of its photographic intensity.

Quantitative determinations based on the measurement of the length of lines have been first presented by Scheibe and Neuhäusser (1928) for the determination of metals in iron alloys with spark spectra. These authors used the ratio of the lengths of the lines as a mass for the concentration. A little later, Twyman and Simeon [1] (1929—30) published a paper on the use of the logarithmic sector for quantitative spectrum analysis, and Twyman and Fitch [1] (1930) dealt with the spectrographic steel analysis by the sector method. Twyman and Hitchen (1931) developed a method for the determination of metals in solution by their spark spectra, using the difference in the lengths of the lines in homologous pairs. A linear relationship was found to exist between the differences in the lengths of the lines obtained through the sector and the logarithm of the percentage content of the samples. Among other users of the sector methods mention may be made of Slavin (1933) who applied them to the determination of Cd, Pb, Tl, and Ge in the carbon arc, and Wilhelm (1937) who succeeded in increasing the accuracy in the reading of the lengths of the lines.

The general applicability of the sector methods to the measuring of the intensity of the spectrum lines is a matter of some controversy. On this subject the reader is referred to papers published, *e. g.*, by Kienle (1935 a and b), Strock (1939), and Kaiser (1941), which contain important contributions hereanent. As stated by Kaiser (*op. cit.*, p. 9), the logarithmic sector is a quite convenient aid in analyses by comparison where an entirely dependable measurement of the line intensities is not called for.

When searching for the ratio or difference of the lengths of the spectrum lines, two length measurements must be carried out to obtain a point on the calibration curve. Errors made in these measurements might, in some

---

[1] Unfortunately, these papers have not been available to the present authors.

cases, seriously affect the values of the length differences or ratios subsequently calculated, and hence the amounts of the elements involved in the analysis.

Leaving aside the complicated and time-consuming though accurate methods based on the use of a microphotometer, there exists a great body of problems, more especially in geochemistry, where no absolutely accurate results are needed. A method commonly applied to such investigations is the classical one of visual comparison as developed by A. de Gramont with its later modifications. All of these methods, however, cannot claim more than semi-quantitative value. An ideal solution of the problem in question would connect the speed and simpleness of the visual estimation with the higher accuracy characteristic of the photometric methods. As a possible method, the following procedure was anticipated by the first author to yield serviceable results, *viz.* (1) measuring the length of a suitable spectrum line of an element, produced by the logarithmic wedge sector, in a series of known standard mixtures; (2) plotting the length values against the logarithm of the concentration to obtain a concentration calibration curve for the analysis of unknown samples. This method has been investigated by the present authors in a series of Nb determinations in titanium dioxide and quartz bases. It was found that the excitation conditions in the carbon arc cathode layer could be made stable enough to allow a determination of the concentration of an element by the measurement of the length of spectrum lines produced by same. The results, which appeared quite satisfactory, will be presented in the following.

PRELIMINARY EXPERIMENTS

OPTICAL ARRANGEMENT

The Nb line Nb I 4058.938 Å, given by van Tongeren (1938, p. 80) as free from coincidences, was used for the present investigation. This line has been used previously by Sahama (1945, p. 28) when determining the Nb content in East Fennoscandian rapakivi granites. According to Sahama this line can be easily followed down to a little less than 0.001 % Nb_2O_5 in standard spectra in quartz base containing sodium carbonate. As a matter of fact, it was found that the line, however, can be traced down to 0.0005 % Nb_2O_5 in quartz base the mixtures containing as diluent 50 % Na_2CO_3.

The application of the carbon arc cathode layer for the present purpose is connected with more difficulties than any of the other excitation methods. The measurement of the absolute intensities as expressed by the length of the spectrum lines already demands a photographic emulsion of high and uniform quality. Of still more importance is the maintaining of constant exposure and working conditions throughout the work.

A Three Prism Glass Spectrograph of Zeiss with a dispersion of 5.6 Å/mm. in the range 4 027—4 060 Å was used in the present investigation. The optical system presented by Fig. 1 was finally accepted. It is based on the arrangement recommended by Messrs. Carl Zeiss, Jena [1] and gives a diffusely and uniformly illuminated slit of maximum intensity by the use of three double convex lenses. The lens C_1 is focussed on to the lens C_3 by means of C_2. A picture of the arc, E, is projected on screen, A, by C_1. The rectangular diaphragm in the screen allows only light from the cathode layer to pass, and a sharp picture of the diaphragm is projected on the collimator lens of the spectrograph, C_4. The logarithmic wedge sector, L, is placed right in front of the lens C_3, or, when space will not permit this arrangement, close to the spectrograph slit, S. — The maximum height of the opening in the sector used was 9 mm.

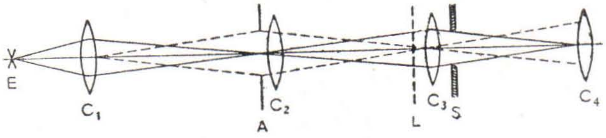


Fig. 1. Optical arrangement for photographing spectra through the logarithmic wedge sector.

The condensing lenses will usually project a diminished picture of high intensity of the light source on to the collimator lens. Accordingly, the spectrum lines thus obtained are strong and short, and well suited for the photometric measurement. Short lines are, however, ill applicable to the measurement of length since the relative error will increase due to the inaccuracy of the length determination. Accordingly, the differences in the lengths of the lines from the various steps of the concentration series will be found to be of the same order of magnitude as the error involved in the measurement. To obtain spectrum lines of maximum length the light source is projected diffusely on the collimator lens. This arrangement, however, causes a loss in sensitivity.

To control the uniformity of the illumination of the slit in the present optical arrangement, the opening of the lens C_2 is shadowed with a piece of cardboard. If no sharp shadowing edge can be seen in the picture of the lens C_1 on the spectrograph slit when the cardboard is moved over the lens, but the picture merely grows uniformly dusky, and totally disappears when no more light passes through the lens C_2, the picture on the slit is uniformly illuminated through every point of the lens C_2. with subsequent uniform illumination of the slit.

---

[1] Anleitung für die Ausführung von spektrographischen quantitativen Bestimmungen an festen Legierungen mit Hilfe des Funkens. Mess 266/III, p. 8. 1938.

The positions of the lenses on the accessory bar can be found outside the bar by placing behind C_3 a screen at a distance equal to that of C_3, when mounted on the bar, from C_4. A small electric bulb is used as a light source, and its position, as well as those of C_1 and C_2, is changed until the right positions are found.

The mutual positions of the lenses were not found to exert any considerable effect upon the sharpness of the image on the photographic plate. The effect upon the intensity of the spectrum lines, on the other hand, is quite considerable. Care must be especially taken not to change the distance between the electrodes and the lens C_1 throughout the work.

ARCING TECHNIQUE

Specially purified carbon rods of 5 mm. diameter were used as electrodes. The cathode bore was 4 mm. deep and 1.5 mm. in diameter with an outside diameter of 3 mm., as given by Strock (1945, p. 4).

The igniting current, from a 110-volt supply, was at the start 4 amp. During the first 10 to 15 seconds of each exposure the current was slowly raised to 7—8 amp. to ensure that no loss of material could occur at the start.

The length of the slit was 22 mm. and the most suitable width of same was found to be 0.01 mm. By the use of a narrow slit the density of the background can be kept negligible. A broader slit, on the other hand, will allow of a more accurate determination of the end point of the lines. This is, however, not possible for the Nb line used, owing to the presence of the CN bands close by, at appr. 4 058.7 and 4 059.5 Å.

Throughout the work a constant speed of rotation of the sector, *viz.* 200 r. p. m., was maintained. The exposure times for the different series were 2′45″ for quartz and 4′ for titanium dioxide base, during which times all the material in the cathode bore was consumed. The distance of the electrodes during the exposure was kept at 10 mm., and continuously checked on the screen. The height of the rectangular opening on the screen was adjusted to correspond to $^1/_4$ of the length of the arc column, and the picture of the end of the cathode was kept 1.5 to 2 mm. over the upper edge of the opening on the screen. This was done in order to block out the bright continuous radiation of the cathode from the spectrograph, and, accordingly, to reduce the blackening of the background on the plate, a nuisance to the length measurement of the lines.

In the initial stages of the investigation much work was required for overcoming the serious defects involved in cathode layer methods and well-known to every analyst, *viz.* arc spitting, uneven consumption of the cathode, shooting away of the material, and the hissing arc phenomenon (»*Zischbogen*»), all of which influence the absolute blackening of the lines.

Spitting and shooting away in the arc were found especially annoying when arcing the Nb_2O_5-TiO_2 mixtures. These phenomena could be partly overcome with a cap of carbon powder at the top of the cathode filling, and by starting the exposure with a very low current. However, the best method to stabilize the arc was found to be the addition of carbon powder according to the instructions presented by Strock (1945, p. 3). Accordingly, every sample was diluted with 4 parts of pure carbon powder and one part of NaCl, and the mixtures, weighed out by an analytical balance, were thoroughly homogenized by grinding for 20 minutes in small agate mortars. Due to the high amount of carbon powder present the material acts as a conductor, and the arc burns very steadily, with only negligible current and light intensity fluctuations. The tests made by the present authors showed in addition that no appreciable loss in sensitivity is hereby effected. The addition of sodium chloride will prevent the intensity of the CN bands or the background from being enhanced by the large amount of carbon present in the samples.

MEASUREMENT OF THE LINE LENGTHS

The quality of the spectra obtained by the operating technique described above will be seen from Figs. 2 and 3 (on Plate I).

The measurement of the length of the spectrum lines was carried out under a microscope. The most convenient magnification was found to be appr. 50 times, by which the weak apex of the line could be distinguished, yet without any trouble arising from the grain of the photographic emulsion. The accuracy of the determination of the length of the lines is appr. 0.2 to 0.3 mm., less for short and weak lines, due to the blurring effect of the background.

The effect of the latter can be decidedly diminished by cutting with very dilute Farmer's reducer as described by Merton (1924, p. 381). To ensure the preservation of the full length of the lines the process should be allowed to proceed only until there still is a very weak trace of fog present. After cutting, the length can be measured with an accuracy of 0.1 mm.

In order to obtain an accurate zero line for the length measurement, a thin brass wire was soldered to the sector stand in a horizontal position to give a shadow on the slit just touching the shadow of the top of the wedge sector. The shadow of the wire, seen in the spectrum as a white line cutting the basal parts of the lines, was found very useful as a starting line for the length measurement. By this arrangement the small errors due to possible shifts in the position of the sector disc when removing and replacing it could be avoided. The basal part of strong lines was somewhat extended, due to diffraction caused on the surface of the wire. Accordingly, the basal point of some near-by weak line was chosen as zero point, seeing that the extension of the basal part of the lines is not due to the sector.

DETERMINATION OF NIOBIUM

TITANIUM DIOXIDE BASE

A series of mixtures of Nb_2O_5 in TiO_2 ranging from 0.01 to 5 per cent were prepared. The oxides, furnished by Messrs. Dr. Fraenkel and Dr. Landau in Berlin-Oberschöneweide, were of great and satisfactory purity. The various step mixtures were homogenized by grinding for 2^h in small agate mortars. To one part of each mixture were added 4 parts of pure carbon powder and 1 part of pure sodium chloride, as described by Strock (1945, p. 3), and the mixtures homogenized for 20′. The use of this com-

TABLE I

LENGTH OF ANALYSIS, SAFETY, AND CORRECTION LINES FOR THE DETERMINATION OF NIOBIUM

Nb_2O_5 %	Length of Nb I 4058.938 mm.		Length of Ti I 4027.485 mm.	Length of Ti II 4028.345 mm.	Length of Ti II 4053.837 mm.
	Measured	Corrected			
0.01	7.4	8.4	16.5	18.0	fogged
»	8.8	9.2	17.5	fogged	16.8
»	9.0	—	18.2	19.6	17.6
»	8.2	9.3	16.5	18.5	16.8
0.03	12.0	—	fogged	fogged	17.3
»	11.1	—	18.4	»	fogged
»	11.1	—	fogged	19.2	17.7
»	11.5	—	18.2	19.2	17.4
0.05	12.2	—	18.4	19.2	17.5
»	12.2	—	18.2	fogged	17.7
»	12.7	—	18.1	»	fogged
»	13.1	—	18.3	19.5	»
0.1	14.3	—	18.4	19.2	17.5
»	15.3	14.5	19.5	20.8	19.0
»	13.5	—	fogged	fogged	17.5
»	15.0	14.1	19.6	21.0	fogged
0.3	18.7	—	18.5	fogged	17.5
»	18.7	—	18.7	»	fogged
»	17.3	18.8	17.1	18.0	16.7
0.5	20.6	—	18.5	19.5	17.2
»	21.2	20.7	18.9	20.1	18.1
»	21.8	21.2	19.0	20.2	18.1
1.0	22.0	—	18.3	19.6	17.5
»	21.2	22.3	17.6	18.8	fogged
»	21.4	22.0	18.1	fogged	»
»	22.0	—	18.3	19.5	17.5
»	22.2	—	18.2	19.2	17.7
2.0	24.4	23.3	19.4	20.6	18.6
»	24.0	—	fogged	fogged	17.7
3.0	24.5	—	18.3	19.4	17.6
»	24.4	—	18.5	19.6	17.8
5.0	25[1]	—	—	—	—

---

[1] Full length obtained.

pound as well as the cathode dimensions given by Strock (*op. cit.*, p. 4) resulted in a very steady and stable discharge. Due to the presence of TiO_2 the volatilization of the sample was further levelled, and a current of 7 to 8 A was maintained to the end of each exposure. The time of the latter was 4′. Agfa Spektral Rot Extra Hart plates were used; they were developed for 2′ at 18°C in a maximum contrast hydroquinone - potassium hydroxide developer.

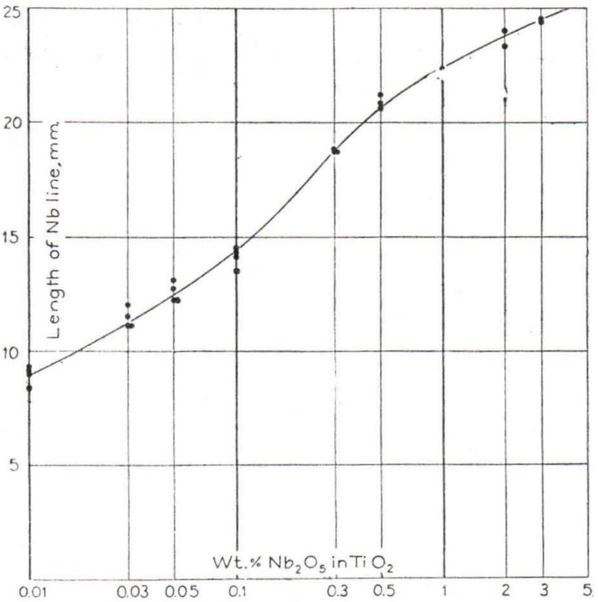


Fig. 4. Concentration calibration curve for Nb_2O_5 in TiO_2 (1 pt. standard mixture + 4 pts. C + 1 pt. NaCl).

When measuring up the lines, difficulties were encountered at the lower limit of the concentration series at 0.01 % Nb_2O_5, due to the intensity of the background. On the other hand, the Nb line could be quite easily followed up to 3 % Nb_2O_5. The line of the 5 per cent mixture had already the full length of 25 mm., which is probably obtained at appr. 4 % Nb_2O_5.

The results of the length measurements are given in Table I, and the calibration curve constructed on the basis of these values is presented in Fig. 4.

Some idea of the magnitude of the error involved in the determination of niobium may also be gained from the concentration calibration curve in Fig. 4. If the Nb_2O_5 percentages for the various points in Fig. 4 are calculated from the working curve, the results give for the various concentration steps mean errors ranging from 1 to 11 % of the absolute amounts as presented by the curve. The mean error from all points, m, as expressed by the well-known equation

$$m = \sqrt{\frac{a_1^2 + a_2^2 + \ldots + a_n^2}{n - 1}}$$

is found to be 14.5 %.

QUARTZ BASE

To construct the calibration curve a series of Nb_2O_5 - SiO_2 mixtures was photographed as described before, ranging from 0.001 to 0.1 % Nb_2O_5.

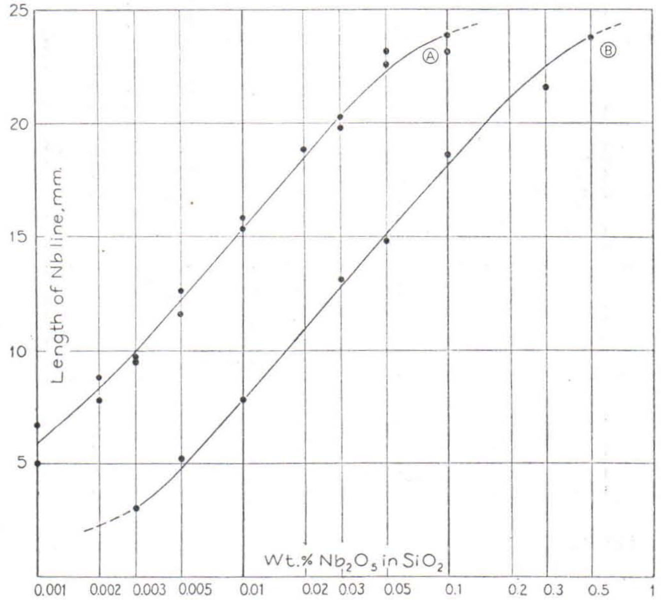


Fig. 5. Concentration calibration curves for Nb_2O_5 in SiO_2. Curve A: Standard mixture with 50 % Na_2CO_3. Curve B: 1 pt. standard mixture + 4 pts. C + 1 pt. NaCl.

50 per cent of sodium carbonate were added to each mixture as stabilizing diluent, and the mixtures homogenized. The time of exposure was 2′45″. The calibration curve (A) obtained from the above mixtures is presented in Fig. 5. Here the lower limit of sensitivity lies at 0.001 % Nb_2O_5. Spectra photographed from a 0.0003 % mixture no longer showed the Nb line investigated.

Seeing that the maintaining of constant arcing conditions was in these mixtures beset with difficulties arising from the fact that the samples were not diluted with carbon powder, a new concentration series in quartz base was prepared, each step being diluted with carbon powder and sodium chloride as described above. The length of exposure was, also this time, 2′45″. Agfa plates as mentioned above were used, the developing facts being similar to those given before. Compared with the exposures made in TiO_2 base, the burning properties of the arc were, however, now inferior, due to the absence of TiO_2 in the mixtures. Accordingly, the current showed a tendency to decrease to 4 A which resulted in the extinction of the arc, and the Nb lines did not obtain their proper lengths.

The calibration curve (B) obtained from the diluted mixtures is presented in Fig. 5. As is shown by this figure, the Nb lines in the diluted series are appr. 8 mm. shorter than in the first series, not diluted with carbon powder. A comparison with Fig. 4 will make evident that the SiO_2 series is somewhat more favorable than the TiO_2 series as regards the lower limit of sensitivity. This property, however, is counteracted by the enhanced stability of the burning arc in the latter instance. In any case, the determination of Nb_2O_5 in SiO_2 base is generally beset with no more difficulties than any of the other generally used quantitative spectrochemical methods in the carbon arc cathode layer.

THE USE OF SAFETY AND CORRECTION LINES

Any changes in the excitation conditions will affect the lengths of the spectrum lines photographed through the wedge sector. However, with not too large fluctuations the ratio of the lengths of two spectrum lines will remain stable. It accordingly lies quite close at hand to investigate whether this fact could be applied in connection with the present method as a safety measure.

In Table I length values for three titanium lines will be found inserted. This element is present in each sample in a concentration more than enough to produce lines of constant intensity in all spectra. Accordingly, the length of any weak Ti line in the neighborhood of the Nb line can be used as a safety line for judging the quality of the spectrum, the stability of the conditions of exposure and photographic procedure, and the reliability of the Nb value. For this purpose the lines Ti I 4 027.485, Ti II 4 028.345, and Ti II 4 053.837 Å have been used. Their standard lengths were found to be 18.5, 19.2, and 17.5 mm., respectively.

All plates showing a deviation of more than 2 mm. in the length of the safety line were discarded. This procedure was found to be an easy and effective way of retaining a high degree of reliability for the exposures.

Any suitable arc line used as a safety line can also be applied to correcting the length of the spectrum line, if the deviation from the normal length of the former is not too great. The line Ti I 4 027.485 has been used for the present purpose. If the deviation in the length of this line exceeded 0.4 mm., the ratio between its real and normal length was used as a correction factor, by which the length of the Nb line was multiplied in order to obtain the true length used in the determination of concentration. In the construction of the concentration calibration curve in Fig. 4 also the corrected values obtained by this method of calculation have been taken into account.

In some cases the base substance will not yield lines suitable for use as safety and correction lines and, accordingly, a small amount of a suitable comparison element must be added to the sample, most appropriately mixed with the carbon powder used as stabilizing diluent. The length of the reference line should be halfway between the maximum and minimum lengths of the analysis lines to be measured. The use of a line of the comparison element instead of one of the base substance allows of a sharper control of the analysis line, since the losses in material due to shooting away and arc spitting will affect both lines in a similar way.

CONCLUSIONS

The method described above would seem to be quite well applicable to purposes where ultimate accuracy is not called for. Accordingly, its adaptations will cover a quite large area of ordinary spectrochemical work. As another example of the uses of the present method, the determination of chromium in granites may be mentioned; the results of a series of such determinations, carried out in this laboratory, proved quite satisfactory [1].

As to the accuracy of the present method, the mean value of 14.5 % as presented above might be, to some extent, comparable with the values presented for the sector methods by some previous authors: 5 to 10 % by Twyman and Fitch (1930), and by Scheibe (1933, p. 138); usually within 10 % by Slavin (1933, p. 513). The accuracy of the method depends, as mentioned before, upon the accuracy in the length measurement of the lines. The latter may be increased in several ways, as presented by Slavin (1933, p. 511) and by Wilhelm (1937). By means of replicate exposures still more dependable results may be obtained, until a final limit is set by the properties of the photographic plate.

The advantages of the present method lie in its simplicity and speed. No addition of standard substances is necessary except for the study of safety and correction lines. The somewhat troublesome use of the spectrum line photometer is not called for.

GEOLOGICAL SURVEY OF FINLAND;
GEOCHEMICAL LABORATORY, THE MINERALOGICAL AND GEOLOGICAL INSTITUTE OF THE UNIVERSITY, HELSINKI, DECEMBER, 1945.

---

[1] The line Cr I 4254.346 Å was used and a calibration curve for Cr_2O_3 concentration range 0.0003—0.03 % in SiO_2 base was constructed, without any addition of NaCl or C. The cathode bore was 1 by 6 mm. Time of exposure was 2′30″ with 110 V and 7—8 A. The spectra were very clear and the effect of background in them negligible.

REFERENCES

KAISER, H., Über die verschiedenen Verfahren zur Auswertung der Spektren bei quantitativen spektrochemischen Analysen. Spectroch. Acta, Bd. 2, p. 1. 1941.

KIENLE, H., Photographische Photometrie. Naturwiss., 23. Jahrg., p. 759. 1935 (1935 a).

—»—, Über das Schwärzungsgesetz der photographischen Platte. Naturwiss., 23. Jahrg., p. 762. 1935 (1935 b).

MANNKOPFF, R. und PETERS, CL., Ueber quantitative Spektralanalyse mit Hilfe der negativen Glimmschicht im Lichtbogen. Z. Phys., Bd. 70, p. 444. 1931.

MERTON, T. R., On Ultra-Violet Spectro-Photometry. Proc. Roy. Soc. London, Ser. A., Vol. CVI, p. 378. 1924.

PREUSS, E., Beiträge zur spektralanalytischen Methodik. Die quantitative Spektralanalyse im Kohlebogen. Z. ang. Min., Bd. 1, p. 167. 1938.

ROLLWAGEN, WALTER, Die physikalischen Erscheinungen der Bogenentladung in ihrer Bedeutung für die spektralanalytischen Untersuchungsmethoden. Spectroch. Acta, Bd. 1, p. 66. 1939.

SAHAMA, TH. G., On the Chemistry of the East Fennoscandian Rapakivi Granites. C. R. Soc. géol. Finlande N:o XVIII; Bull. Comm. géol. Finlande N:o 136, p. 15. 1945.

SCHEIBE, G., Chemische Spektralanalyse. In: Physikalische Methoden der analytischen Chemie, Erster Teil. Leipzig 1933.

—»— und NEUHÄUSSER, A., Die Schnellbestimmung von Legierungsbestandteilen in Eisen durch quantitative Emissionsspektralanalyse. Z. ang. Chem., Bd. 41, p. 1218. 1928.

SCOTT, R. O., The Effect of Extraneous Elements on Spectral Line Intensity in the Cathode-Layer Arc. J. Soc. Chem. Ind., Vol. LXIV, p. 189. 1945.

SLAVIN, MORRIS, Analysis with Wedge Spectra. Its Recent Application to Zinc on a Quantitative Basis. Eng. Min. J., Vol. 134, p. 509. 1933.

STROCK, LESTER W., Zur Geochemie des Lithiums. Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl., Neue Folge, Bd. 1, p. 171. 1936 (1936 a).

—»—, Spectrum Analysis with the Carbon Arc Cathode Layer (»Glimmschicht»). London 1936 (1936 b).

—»—, Photographic Factors Influencing the Concentration-Calibration Curve in Quantitative Methods of Spectrochemical Analysis. II. Failure of the Reciprocity Law and Intensity-Retardation of Development Effect. Spectroch. Acta, Bd. 1, p. 123. 1939.

—»—, Quantitative Spectrographic Determination of Minor Elements in Zinc Sulphide Ores. A. I. M. E. Techn. Publ. N:o 1866, Metals Techn., April, 1945.

VAN TONGEREN, W., Contributions to the Knowledge of the Chemical Composition of the Earth's Crust in the East Indian Archipelago, I. The Spectrographic Determination of the Elements According to Arc Methods in the Range 3 600 —5 000 A. II. On the Occurrence of Rarer Elements in the Netherlands East Indies. Amsterdam 1938.

TWYMAN, F. and FITCH, A. A., Quantitative Analysis of Steels by Spectrum Analysis. J. Iron Steel Inst. London, Vol. 122, p. 289. 1930. — Ref. in C. A., Vol. 24, p. 5256. 1930.

TWYMAN, F. and HITCHEN, C. STANSFIELD, Estimation of Metals in Solution by Means of Their Spark Spectra. Proc. Roy. Soc. London, Ser. A, Vol. CXXXIII, p. 72. 1931.

—»— and SIMEON, F., The Logarithmic Wedge Sector and Its Use in Quantitative Spectrum Analysis. Trans. Opt. Soc. London, Vol. 31, p. 169. 1929—30. — Ref. in C. A., Vol. 25, p. 3928. 1931.

WILHELM, HARLEY A., Quantitative Spectrographic Analysis. Increased Accuracy in the Logarithmic Sector Method. Ind. Eng. Chem., Anal. Ed., Vol. 9, p. 170. 1937.

3

THE CALCULATION OF THE STRENGTH OF THE ANOMALY OF A MAGNETIC ORE AT A GIVEN DISTANCE ABOVE THE SURFACE OF THE EARTH

BY

MAUNU PURANEN

ABSTRACT

In the present paper are deduced the formulae, with the aid of which one can calculate the strength of the magnetic field associated with an ore body at points above the surface of the earth, when there is given a map of the vertical magnetic intensity at the surface.

Magnetic anomalies are often associated with ore bodies and for this reason it is possible to utilize magnetic measurements as an aid in ore prospecting. Ordinarily, one contents himself with measuring the vertical intensity of the earth's magnetic field, but in more exact investigations all components are measured, so that the magnetic field becomes completely known in the vicinity of the ore body. By eliminating the effect of the normal magnetic field of the earth we have left the magnetic field caused by the ore body, and on the basis of the size and nature of this field we make deductions as to the form and depth of the deposit. We use here the word »ore» only in an illustrative sense, meaning by it a geological object that gives rise to limited local magnetic disturbance areas.

There has been presented at times in literature a conception, that a magnetic disturbance area could be characterized more exactly by making measurements from the air also above the given area, and that, for example, the estimation of the depth of the deposit would in this way be made more reliable (Eve 1932, Sundberg 1937). In the present paper is shown that the magnetic field above the surface of the earth can be completely calculated on the basis of a map, giving the vertical magnetic intensity at the surface, and for this reason measurements from the air above the disturbance can give no new light as to the structure of the field. The formulae deduced below can be used in estimating the weakening effect of an overburden of varying thickness overlying the bed-rock on the strength of a magnetic anomaly. In addition they are necessary in estimating the feasibility of the so called aeromagnetic method of prospecting, because one of the central questions of this method concerns the rate at which the field of a magnetic anomaly weakens vertically.

Let us suppose in the following, that the area of the disturbance region is sufficiently small, so that the curvature of the earth need not be taken into consideration, and that the surface is fairly level, in which case the components of vertical intensity are perpendicular to the plane of observation. We consider the vertical component of the earth's normal magnetic field as eliminated from the observed results, the remainder representing the field due to the ore alone, and in speaking of the magnetic field this remainder is, for the sake of briefness, what we have in mind.

Already C. F. Gauss in his classical works on the theory of magnetism proposed that the external magnetic field of a body could be considered as being due to an apparent charge on its surface, without making any assumptions as to the state existing within the body itself. However, the calculation of the charge necessary is in general a difficult problem mathematically. In this case, the surface of observation being a plane, the surface charge necessary is easily determined. When the surface charge is given, it is unnecessary to know anything concerning the state of magnetism within the earth, as the field above the earth's surface can be calculated from the surface charge. By integrating, we obtain first an expression for the potential, and from this we obtain through derivation the components of the magnetic field.

Let the xy-plane of a rectangular system of coordinates coincide with the horizontal plane of observation, the z axis being directed vertically upwards (Fig. 1). Let the coordinates of the surface element, $d\omega$, be $x = \xi$ and $y = \eta$, and the vertical component of the magnetic anomaly at this point be $Z = Z(\xi, \eta)$. At the same point the surface density of the apparent surface charge necessary is according to the general statements of the potential theory (Kellog 1929, Jung 1937)

$$(1) \qquad \sigma = \sigma(\xi, \eta) = \frac{1}{2\pi} \cdot Z(\xi, \eta)$$

The surface charge is thus directly proportional to the vertical intensity at the same point. The charge of the surface element $d\omega$ is $dQ = \sigma \cdot d\omega$ and the value of the potential function $U(x, y, z)$ at a point, $A(x, y, z)$, above the observation surface is obtained by integrating.

$$(2) \quad dQ = \sigma \cdot d\omega$$

$$(3) \quad dU = \frac{dQ}{r} = \frac{\sigma\, d\omega}{r} = \frac{1}{2\pi} \cdot \frac{Z\, d\omega}{r}$$

$$(4) \quad U = \frac{1}{2\pi} \iint \frac{Z\, d\omega}{r}$$

$$(5) \quad U = U(x, y, z) = \frac{1}{2\pi} \iint \frac{Z(\xi, \eta)}{\sqrt{(x-\xi)^2 + (y-\eta)^2 + z^2}}\, d\xi\, d\eta$$

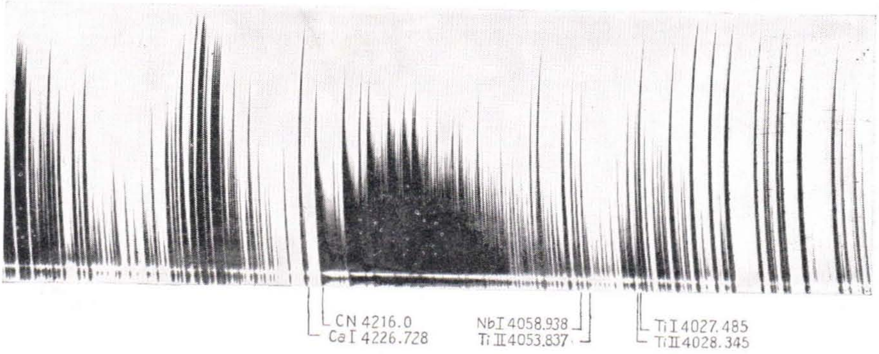


Fig. 2. General view of wedge spectrum of a mixture of 0.1 % Nb_2O_5 in TiO_2, diluted with 4 parts C powder and 1 part NaCl.

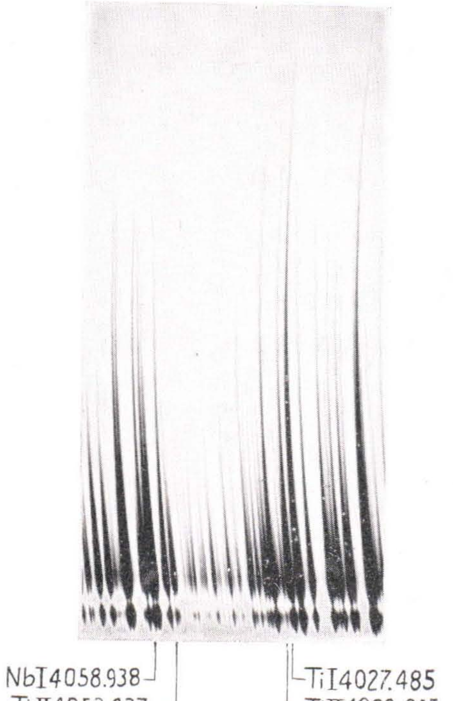


Fig. 3. Enlarged portion of wedge spectrum of 2 % Nb_2O_5 in TiO_2, diluted with 4 parts C and 1 part NaCl.

Kalervo Rankama and Oiva Joensuu: A Simplified Method of Quantitative Spectrochemical Analysis in the Carbon Arc Cathode Layer, Based on the Use of the Logarithmic Wedge Sector.

Integration of the surface integral (5), representing the potential function U (x, y, z), must be extended over the whole disturbance area. Theoretically, this disturbance extends infinitely, but its value approaches zero at such a rate on advancing to the side away from the disturbance area that its value soon is less than the observation error, so that the value of the surface integral taken beyond a certain boundary is insignificant (this holds especially for sources of disturbance close to the surface). In practice it is easy to estimate how far to the side the integration must be extended.

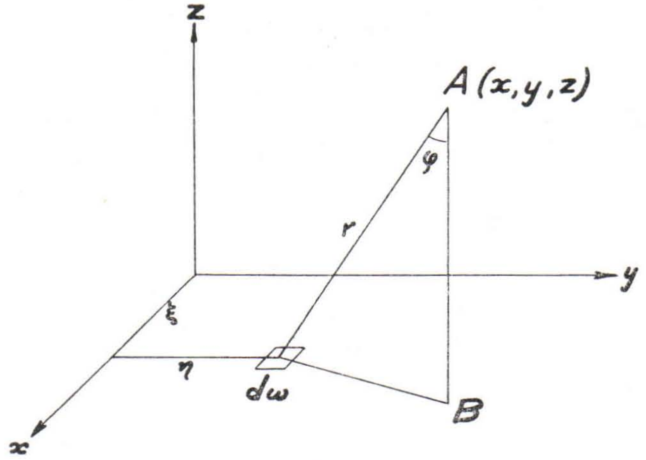


Fig. 1.

The components X, Y, and Z of the magnetic field at the point A (x, y, z,) are obtained by partially differentiating the expression (5) with respect to x, y, and z.

$$(6) \quad X = -\frac{\partial U}{\partial x} = \frac{1}{2\pi} \int\int \frac{(x-\xi) \cdot Z(\xi, \eta)}{[(x-\xi)^2 + (y-\eta)^2 + z^2]^{3/2}} \, d\xi \, d\eta$$

$$(7) \quad Y = -\frac{\partial U}{\partial y} = \frac{1}{2\pi} \int\int \frac{(y-\eta) \cdot Z(\xi, \eta)}{[(x-\xi)^2 + (y-\eta)^2 + z^2]^{3/2}} \, d\xi \, d\eta$$

$$(8) \quad Z = -\frac{\partial U}{\partial z} = \frac{1}{2\pi} \int\int \frac{z \cdot Z(\xi, \eta)}{[(x-\xi)^2 + (y-\eta)^2 + z^2]^{3/2}} \, d\xi \, d\eta$$

From a purely physical standpoint these formulae do not contain anything new, because they, as is apparent from their derivation, are based on the general statements of the potential theory. However, they have not as yet, to the author's knowledge, been applied to the problem treated in the present paper.

In performing numerical calculations using the above formulae, it is generally advantageous to transfer to polar coordinates. For example formula (8), for the vertical component, is then given by

$$(9) \quad Z = \frac{1}{2\pi} z^2 \int\int Z \cos^3 \varphi \, d\omega$$

Using formula (9) it is easy to perform an elementary integration by dividing the plane of observation into concentric circles with B, the projection of point A (x, y, z), as their center, and determining the average value of the vertical component Z along each circle. In this connection there is no cause for going into greater detail with respect to the technicalities of the calculations. Let it alone be mentioned, that also numerical calculations using the above given formulae can be performed in a relatively short time, so that if necessary, the magnetic field of an ore body above the surface of the earth can in practice actually be calculated. Experiments with a small scale model gave observation results which coincided well with those calculated according to formula (9). Unfortunately, it has not been possible to obtain sufficiently detailed results of measurements obtained over a real ore body for testing the applicability of the above formulae in practice.

As the magnetic field of an ore body above the surface of the earth can be calculated with such ease, there arises the question: »Would it not be possible to deduce, on the same basis, the structure of this field below the earth's surface as well?» Such a result, were it possible, would be considerably more valuable from the standpoint of practice, as it would then be easier to determine, on the basis of the paths of the lines of force, the form and location of the ore body from which the field arises. Unfortunately, the answer to the question is in the negative (Haalck 1927). The paths of the flux within the earth on the basis of the above assumptions are not uniquely determined, but, on the contrary, it is possible to construct an infinite number of differently shaped bodies, all of which will give the same field at the surface. It is possible that there will be opportunity later on for the treatment of this problem, as well as the question of practical application of the above formulae.

The performance of numerical calculations using the above formulae will consume so much time, that their application for the calculation of, *e. g.*, the horizontal components at the surface is impracticable, it being much easier to make the actual measurements. On the other hand measurements above the earth's surface are in such a degree difficult to execute (they have been made in America from wooden towers built on the mine area and in Sweden balloons have been used as an aid), that it is easier to calculate the field. Logically however, such determinations can throw no new light on the structure of the field, so that interpretation of a map of vertical intensity will give as reliable a picture of the size and location of the deposit as that including them.

I wish to express my most sincere thanks to professor W. Heiskanen, who has been kind enough to go through the above calculations, as well as to Mr. A. Kahma, M. A., in cooperation with whom the experiments on the model were performed.

GEOLOGICAL SURVEY OF FINLAND, HELSINKI, JANUARY, 1946.

REFERENCES

EVE, A. S., A Magnetic Method of Estimating the Height of Some Buried Magnetic Bodies. Trans. A. I. M. E., Geophysical Prospecting 1932, p. 200.

HAALCK, HANS, Die magnetischen Verfahren der angewandten Geophysik, p. 121. Berlin. 1927.

JUNG, KARL, Direkte Methoden zur Bestimmung von Störungsmassen aus Anomalien der Schwereintensität. Z. Geophys., Bd. 13, p. 45. 1937.

KELLOG, O. D., Foundations of Potential Theory. Berlin. 1929.

SUNDBERG, KARL, Moderna malmletningsmetoder. Jernk. Ann., Vol. 121, p. 521. 1937.

4

A STATISTICAL METHOD FOR THE QUANTITATIVE REFRACTIVE INDEX ANALYSIS OF MINERALS IN ROCKS

BY

AARNO KAHMA AND TOINI MIKKOLA

ABSTRACT

The present paper contains the principles of a statistical immersion method for the quantitative refractive index analysis of minerals in rocks, as well as a practical procedure for its performance. With the aid of this method it is possible to determine the indices of refraction of the minerals present in a rock sample, as well as their volume and weight ratios.

CONTENTS

INTRODUCTION

A problem familiar to every petrologist in the course of his work is the establishment of the positions occupied by the minerals of a rock in terms of isomorphic mixtures, as well as the determination of the relative volume and weight ratios of same. Seeing that the optical properties of minerals depend upon their composition, it is sufficient for the latter purpose to make certain optical determinations. As foremost exemples of the latter can be considered the determination of extinction angle, double refraction, optic angle, and index of refraction. With the exception of the last mentioned determinations the study of the optical properties of relatively small grains of rock is best carried out with the aid of a universal stage. However, such measurements can be made to advantage only with respect to mineral grains lying in a certain orientation; as the number of such grains in a thin section is generally small, these measurements can give information about the properties of only these individual grains. The indices of refraction of a mineral constituent of a rock are usually determined in the powdered sample of the rock in question by the immersion method. However, in order to obtain satisfactory results it is necessary that the mineral in question can be distinguished in the immersion media, in which case the results of measurements obtained by the use of different immersion liquids makes it possible to determine the indices of refraction of the mineral in question. If, on the other hand, the rock contains two or more minerals having similar indices of refraction, and if it is impossible to distinguish between them on the basis of their appearance, the ordinary immersion methods become useless. It is true that one can, by rinsing an individual grain free of the previous immersion liquid with the aid of a suitable solvent, determine the indices of refraction of the grain in question, regardless of whether the sample contains other mineral grains having like indices of refraction or not, but this time-absorbing process must be repeated for a number of mineral grains in order to obtain some picture of the mineral composition of the rock in the particular refractive index region. On the other hand, the quantitative estimation of the minerals contained in the rock is performed by separation of the minerals from one another with the aid of heavy liquids, or optically by the integration stage. For the former procedure it is necessary that the densities of the minerals under consideration differ from one another sufficiently, while for the integration stage method it is necessary to be able to identify the different minerals in the thin section from one another. This is quite possible if the studied minerals differ from one another considerably in their appearance, but speedy identification of, for example, different plagioclases in the same rock as well as differentiation between different feldspars and quartz in many fine-grained metamorphic rocks may meet with unsurmountable difficulties, especially as the integration stage cannot be turned into different positions. In the following there is presented a statistical immersion method for the quantitative refractive index analysis of rocks, giving the indices of refraction found in the rock as well as their volume ratios, regardless of whether it is possible to identify the given refraction index types under the microscope or not.

THE MAIN PRINCIPLES OF THE METHOD

The object of the statistical immersion method is to determine with the highest possible accuracy the curve, $k = k(n)$, (*cf.* Fig. 2, p. 35), which gives the percentage distribution of the indices of refraction in the mineral mixture studied as a function of the index of refraction. The ordinate of any point informs us as to how many vol. per cent, k, of the grains of the mineral mixture in question have an index of refraction greater than n, the abscissa corresponding to the given point. Thus it is possible to read from Fig. 2 that in this mixture 43 % of all mineral grains have an index of refraction greater than 1.492 and that none have an index of refraction less than 1.477.

The curve, k = k(n), can be obtained, for instance, optically in the following way. The mixture in question is ground to a fine powder and homogenized, using a suitable method, so that each different refraction index type is as evenly distributed throughout the mixture as possible. A small quantity of this homogeneous powder is then transferred to a glass plate, a drop of the immersion liquid is added and the whole covered with a cover glass. After this is determined, with the aid of the Becke line method and using a laterally adjustable stage, how many per cent of the grains passing before the field of the microscope have an index of refraction greater than that of the liquid used, so that one obtains the ordinate corresponding to the given value of n. The same procedure is renewed, using a different immersion liquid, and the values thus obtained are plotted to give the curve, k = k(n), representing the percentage distribution of the different refractive index intervals in the mixture, assuming that all minerals have been crushed during grinding in the same way. Each step of the curve thus represents a certain refractive index type, the percentage content of which is numerically identical with the difference between the two values of the ordinates on both sides of the drop in the curve, and whose index of refraction is the same as that of the immersion liquid corresponding to the steepest portion of the drop. However, with the aid of the method presented above it is possible to determine, using, *e. g.*, 300 to 600 mineral grains, points on the horizontal portions of the curve with an accuracy of 3 to 8 %. Deviations of the points from one another are due mainly to two reasons, *viz.* to chance, which determines in what degree the results obtained by counting grains of a certain size represent the total composition of the original mixture, and to differences in grain size, due to which the number of grains corresponding to a definite amount of given material varies on both sides of its average value. It is impossible to entirely remove the former factor, but its effect can be decreased to give any desired degree of accuracy by increasing the total number of grains used for obtaining the statistical data. If ν is the number of grains used in the determination, and k the percentage of grains having an index of refraction greater than that of the immersion liquid, the error of mean square (in per cent) due to the former factor can be calculated from the following formula:

$$\mu = \sqrt{\frac{k\,(100 - k)}{\nu}}$$

From this we see that μ reaches a maximum value when k is 50 %. In the following table there are given the values of μ for different values of ν when k is 50 %.

TABLE I

ν	μ
100	5 %
500	2.2
1 000	1.6
2 000	1.1
10 000	0.5

On the other hand, the factor due to differences in size between the different grains can be almost entirely eliminated by making the determinations from a homogenized mixtures, whose grains are of the same size. This can be accomplished by fractionally sieving a homogenized mineral mixture with a sieve shaker, and using a definite fraction for the determination. This of course holds good only in case that the fraction thus obtained actually represents in its composition the original mixture, or that each refractive index type is either enriched or impoverished in the given fraction in a definitely known way, so that it can be taken into account. As will be seen further on, the composition of the fraction obtained by sieving will for a certain rock remain constant with an accurary of about one per cent, independent of its previous treatment. Accordingly, the different minerals have every time been ground and sieved in the same way. To obtain a measure for the reliability of the present method, pure powdered samples of rock minerals are taken in the proportions present in the rock, the grain size being approximately the same as that of the rock. This mixture is crushed, homogenized, and sieved, and the control mixture thus obtained is subjected to a series of determinations of the k values on the horizontal terraces between the steps. By this method, also the corrections for the percentages of the different minerals will be found.

If the mixture in question contains any anisotropic mineral, its indices of refraction α', γ' having different values depending on the orientation of the grain, the determinations of the k values will be divided into two groups, *viz.*, those giving »terrace» points and those giving »drop» points (*i. e.*, points along the steep portion of the curve). For the »terrace» points, which are located on the horizontal portions of the curve outside of the intervals containing the indices of refraction of the minerals, the behaviour of only that index of refraction, which is most clearly visible in the immersion liquid in question, is observed for each grain without rotation of the microscope stage. In this way the process of counting can be performed with considerable speed, and with the aid of the horizontal portions of the curve thus obtained it is possible to calculate the volume ratios of those refractive index intervals, which differ sufficiently from one another. If, on the other hand, it is desired to determine in the mixture the indices of refraction of some anisotropic mineral, or if the zonal structure of, *e. g.*, plagioclase is in question, the drop points are also necessary. In the determinations of these points the behaviours of both indices of refraction in each grain on rotation of the stage are observed, and it is possible to determine, from the data thus obtained, the indices of refraction of the anisotropic mineral. In minerals with zonal structure even the volume ratios of the different refractive index types can be determined, assuming that the distribution curves of the homogeneous zonal components are known in the interval of index of refraction in question. As a matter of fact, if the mineral is homogeneous, the drop of the curve obtained is steep, but if a zonal structure is developed, the curve slopes gradually, the form of the curve representing the volume ratios of the zonal components. The mineral in question being anisotropic the corresponding drops of the curve are marked ω, α, β, or γ, depending on the main indexes of refraction represented by it.

PROCEDURE IN PRACTICE

When preparing a sample for the quantitative refraction index analysis the crushing and grinding of the sample can naturally be done in a number of ways, the only precaution necessary being, that crushing of the rock in question and control mixture, on the basis of which the corrections for the different minerals are made, is done in as much as possible the same way. It is safer to use the same initial amount of material for the control mixture as that taken for the analysis of the rock, as it has been found that for pure minerals small amounts give a larger percentage of material of relatively small dimensions for study. We have performed the operation of crushing in an Ellis mortar, using a sample weighing 20 g. After a certain period of crushing the powder was transferred to a sieve, after which the crushing of the coarser material was continued until all had passed through the larger mesh sieve.

For the speedy and thorough homogenization of the powder, it is practicable to subject it to violent mixing in water in some suitable mixer. After a thorough homogenization of 2 to 4 hours, the water and the finest grained material are decanted away, after which the residue is dried in a drying oven. If greater accuracy is not desired, or if a sieve shaker is not available, the immersion determination can be performed on the homogenized powder thus obtained which consists of grains of varying size. For more accurate measurements, however, it is necessary to separate a fraction of certain dimensions by sieving. This is best achieved with the aid of a sieve shaker, which is capable of separating the fraction, 0.088—0.100 mm., used by us, in about half an hour. Naturally, other fractions can also be used, provided that the grain size interval is sufficiently narrow.

The microscopic slide is prepared by first placing with the aid of a stirring rod a drop of the proper immersion liquid on a glass slide, over which is then scattered a small quantity of the powder to be examined, and a small cover glass is placed over the whole. As the composition and index of refraction of the immersion liquid are subject to variations on evaporation, the liquids being usually composed of two or more liquids of different vapour pressure, care must be taken to see that the liquid does not reach beyond the edge of the cover glass. If, on the other hand, the liquid remains within the boundaries of the cover glass, the index of refraction will remain constant, as has been established by experiments performed, using a crystal refractometer (the liquid had an index of refraction = 1.528), — with an accuracy of 0.001 (the accuracy of the instrument used) for a period of 85 min. which is quite sufficient for a single determination. In order to make a control determination of the actual index of refraction of the liquid used, it is to the purpose to place into the refractometer the same amount of liquid as was placed on the slide, and to close the refractometer only after the cover glass has been placed over the slide, possible changes in the index of refraction due to evaporation being thus in both cases very nearly identical.

The determination of a terrace point from a slide prepared in the above manner can be carried out in the following way. By moving the slide with the aid of some laterally adjustable stage there is determined, with the aid of the Becke line method, the percentage of all grains passing before the field of view, which distinctly have an index of refraction greater than that of the immersion liquid used. The data are speedily obtained, *e. g.*, in the following manner: for some definite position of the stage, the number of grains is counted, in which the Becke line on elevation of the microscope tube moves towards the centre of the grain, and subsequently also the number for which the Becke line moves away from the outer boundary. With the aid of the laterally adjustable stage the slide is then moved into another position, the grains are counted again, and the process continued until the desired number of grains is counted. To obtain a preliminary picture of the form of the curve, points, for which from 300 to 600 grains have been counted, are generally sufficient. For the horizontal terrace portions on the other hand, on the basis of which the volume ratios of the different refractive index types are calculated, 600 to 2 000 grains should be used, so that the path of the curve may be accurately determined. A conception of the accuracy of the method can be obtained by comparing, at the same time, *e. g.*, the separate groups of 500 grains, the total number being 2 000 grains. The magnification used depends of course on the size of grain and on the analyst. We have, for the fraction 0.088—0.100 mm., found the magnification of 170 times as most suitable. As the terrace points are located outside the intervals of index of refraction of the minerals contained in the sample, an ordinary illumination system can well be used.

The determination of points along the drop is carried out in a similar way, with the exception, however, that it is made in either monochromatic or ordinary light; and that for such grains as have an index of refraction close to that of the liquid, the class to which the values of γ' and α' of the grain belong is determined on rotating the stage and lifting the tube, the groups being $\gamma' > n$, $\gamma' \gtrsim n$ or $\gamma' < n$, $\alpha' > n$, $\alpha' \gtrsim n$ or $\alpha' < n$. Also these grains, whose boundaries vanish in the liquid in one of its positions of extinction, will be included in the data, as they will almost always be found with the aid of their other index of refraction, which differs from that of the immersion liquid. As it is probable that the grains vanish in the same way, regardless of the direction from which we approach the index of refraction of the grain, we can consider that one half of the class $\gamma' \gtrsim n$ belongs to the class $\gamma' > n$, and similarly, one half of the class $\alpha' \gtrsim n$ belongs to the class $\alpha' > n$. On the basis of this grouping the errors that arise in the data for a narrow zone in the vicinity of α and γ are sufficiently small and they need not be taken into consideration. Points along the drop determined in the way described above will thus, for anisotropic minerals, give two branches, $k(n_{\alpha'})$ and $k(n_{\gamma'})$, on the basis of which one can uniquely determine the curve, characterizing some main index of refraction of the mineral in question. However, for this purpose it is necessary to know the curves $k(\alpha')$ and $k(\gamma')$, which have been obtained for the homogeneous non-zonal mineral and which represent the probabilities of appearance of the indices of refraction corresponding to different positions of the grains. In the following are presented some points of view, with the aid of which it is possible in principle to calculate the curves $k(\alpha')$ and $k(\gamma')$, as soon as the indices of refraction, α, β, and γ, of the mineral are known. As the values of α' and γ' for each grain depend, besides on the main indices of refraction, α, β, and γ, of the mineral in question, only on the angles, made by the ray of light with its main directions of vibration, one can for each value of n in the three-axis refraction index ellipsoid determine that spacial angle (having its vertex at the centre of the ellipsoid) for which those values of γ', whose directions fall within the angle, are all greater than n. And the probability, that the observed value γ' for the grain is greater than n, is the ratio of this angle to that which is composed of those directions, corresponding to the index of refraction β. Similarly can be computed the probability of appearance of different values of α' in the grains. According to the principles explained above the probability for uniaxial crystals, that the value of ε' for the grain is greater than n, can easily be calculated by the following formula:

$$k = \frac{100\, F\varphi}{F\pi/_2} = \frac{100 \cdot 2\,\pi\, r^2 \int\limits_0^{\varphi} \sin\varphi\, d\,\varphi}{2\,\pi\, r^2 \int\limits_0^{\pi/_2} \sin\varphi\, d\,\varphi} = 100\,(1 - \cos\varphi\ ),$$

where φ is the angle, made by the direction of vibration of $\varepsilon'_\varphi = n$ with the main optical axis and $F\varphi$ that spacial angle within which $\varepsilon' > n$. The index of refraction corresponding to angle φ can on the other hand be calculated by the formula:

$$\varepsilon'\varphi = \omega \sqrt{\frac{tg^2\,\varphi + 1}{tg^2\,\varphi + \left(\frac{\omega}{\varepsilon}\right)^2}}$$

so that on the basis of what has been explained above, the curve $k = k\,(\varepsilon')$ can be constructed.

For optically biaxial minerals the curves $k = k\,(\alpha')$ and $k = k(\gamma')$ can in principle be determined in the same manner, but the mathematical treatment of the question is more complicated and will be presented, together with the results obtained by it, in other connection. It is true that by using drop points obtained experimentally it is possible to arrive at the same result, but the minerals necessary for such determinations must be as homogeneous and non-zonal as possible, and the finding of such minerals will be attended by great difficulty. Let us assume, that $1\alpha'$, and $1\gamma'$ in Fig. 1 represent the curves $k(\alpha')$ and $k(\gamma')$ for some zonal plagioclase. If $2\alpha'$, $3\alpha'$, $2\gamma'$ and $3\gamma'$ represent the curves $k(\alpha')$ and $k(\gamma')$ for the homogeneous, non-zonal plagioclase types, obtained either by calculation or experimentally, and between which are located those obtained for the zonal plagioclase in question we can now, by mixing intermediate plagioclase types in the proper proportions, construct curves $1\alpha'$ and $1\gamma'$, and thus arrive at the ratios of the different zonal components relative to one another. As the forms of the curves $2\alpha'$ and $2\gamma'$ will not change noticeably for plagioclases whose compositions approximate that studied, the curves obtained can be used for the study of other plagioclase types in a given vicinity by a translation in the direction of the n-axis.

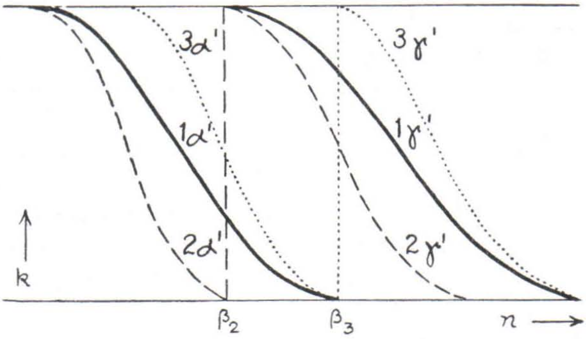


Fig. 1.

The terrace and drop points, obtained in the way described above, are then plotted to give the curve k(n), in which for anisotropic minerals there is made, next to the drop, a notation of that index of refraction α, β, γ, or ω it represents. Ordinarily, it is sufficient, for zonal minerals, to know only that interval in which it is zonal, as well as the percentage content of that particular mineral. The performance of a single refraction index analysis will take 1 to 4 workdays depending on what minerals the mixture contains and the interval of index of refraction in question. The determination of a single terrace point, obtained on the basis of 500 grains, will take 10 to 30 minutes for a person accustomed to the work. The determination of the points along the drop, however, will take 40 to 80 minutes, but unless one wishes to study some interval in greater detail, only a few such points are necessary for a single analysis.

DISCUSSION OF RESULTS

In the following a number of refraction index analyses of minerals in rocks and mixtures of minerals will be presented, performed according to the method set forth above. Fig. 2 represents a distribution curve which was obtained for a mixture consisting of 57 % sodalite and 43 % glass. As is seen from Fig. 2 there is a steep drop for both of the indices of refraction of the minerals composing the mixture, and the terrace divides the curve in the above mentioned ratio. These steps are not, however, as sharp as could be expected for isotropic substances, for they are slightly rounded at the corners. This is due to the fact that when the index of refraction of the immersion liquid is close to that of some grain type, a part of these grains remains unnoticed and thus affects the composition of the data. If by a we denote the number of grains whose index of refraction N is above that of the immersion liquid n, and by b, the number whose $N < n$ and by $\triangle$ the number of grains that remains unnoticed in the immersion, we then have the following equations:

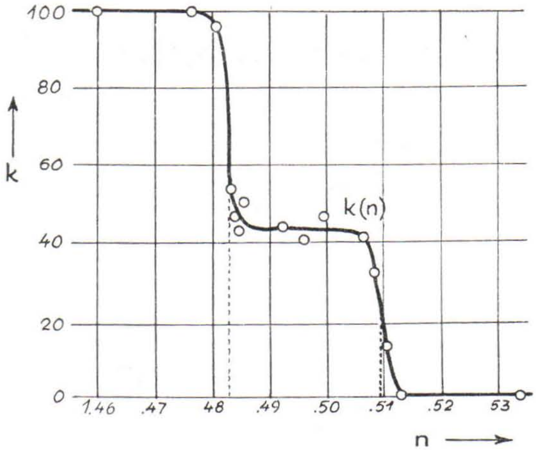


Fig. 2.

$$k = \frac{a}{a + b};\ k_1 = \frac{a - \triangle}{(a - \triangle) + b} < k;\ k_2 = \frac{a}{a + (b - \triangle)} > k$$

where k represents the actual ratio of the grains in the data, k_1 that ratio observed when N is approached along the curve from the side $n < N$, and k_2, on the other hand, the ratio observed when N is approached from the opposite side. This rounding off of the corners of the steps due to the »hiding of the grains» can never be completely eliminated, but for minerals, which ordinarily contain foreign inclusions, it is relatively small (expressed as refractive index 0.001—0.003), as the grains can then be

Fig. 3.

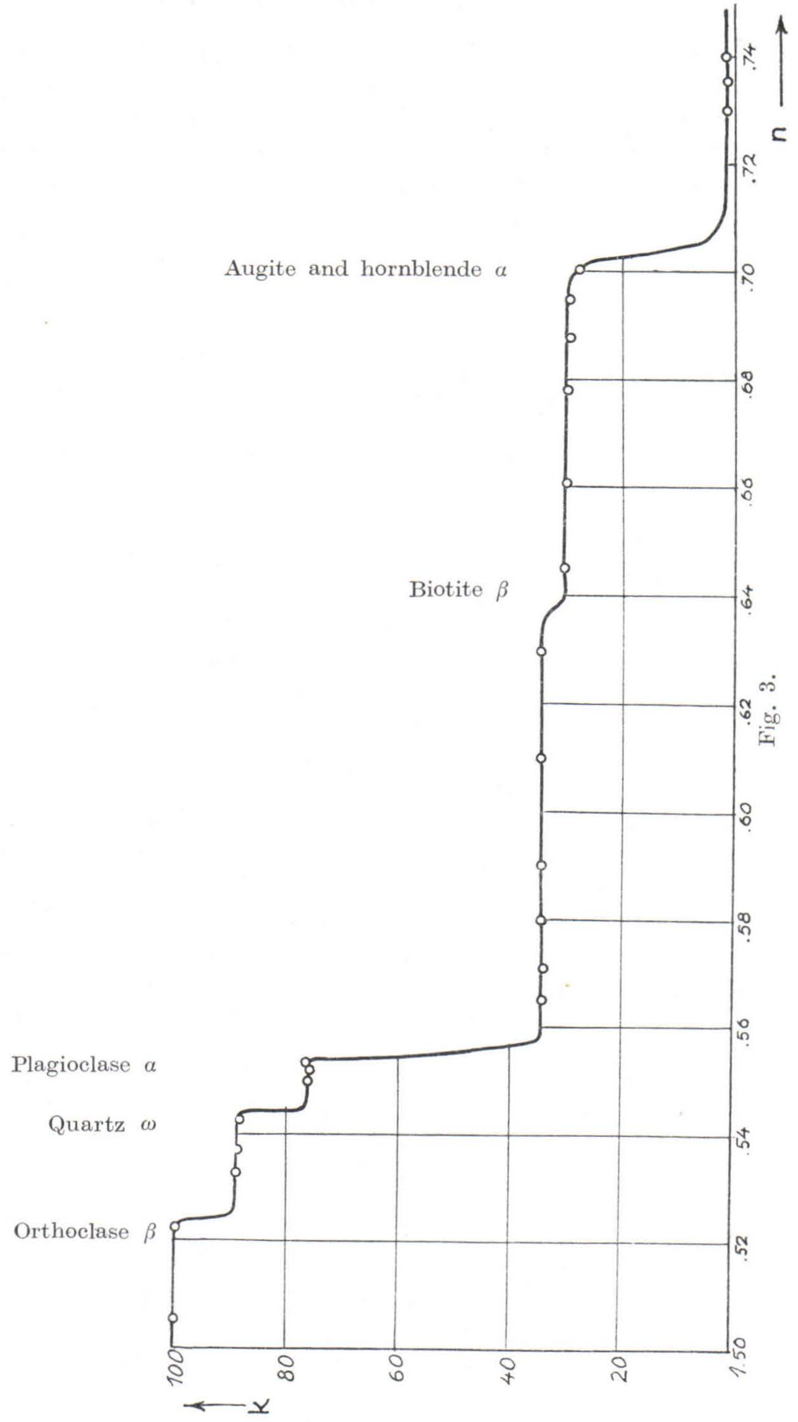


Diagram of the refractive index analysis of a hybrid rock.

identified on the basis of these inclusions, while, on the other hand, for optically pure glass it may be quite considerable.

Fig. 3 represents a refractive index analysis of a hybrid rock between diabase and rapakivi. Above each step there is the name of the mineral represented by it. We can ascertain, on the basis of this diagram, that the sieved fraction contains 11 % orthoclase, 12.5 % quartz, 42 % plagioclase, 3.5 % biotite, 29.5 % augite and hornblende, and 1.5 % magnetite. In order to obtain a conception of how crushing, homogenization and sieving affect the form of the distribution curve and relationships of the different refractive index types to one another, there were prepared, by subjection of the above mentioned hybrid rock to different modes of crushing, homogenization and sieving, four different samples, for which were determined the values of k in three different immersion liquids. The results obtained are given in Table II, where in the extreme left hand column are given the indices of refraction of the immersion liquids, and in the following columns the values of k in these liquids for samples 1, 2, 3, and 4 (each determination based on 500 grains), as well as on the extreme right, their average values. Deviations from the average values are in general less than 1 %, the error of mean square being 0.4 %.

TABLE II

VALUES OF k FOR A HYBRID ROCK ON SUBJECTION TO DIFFERENT PRELIMINARY TREATMENT

Index of refraction of immersion liquid	Sample				Average
	1	2	3	4	
1.5377	88.7	89.4	89.9	88.4	89.1
1.5546	63.9	63.0	63.4	62.7	63.4
1.5714	33.6	33.4	33.1	33.5	33.4

We thus notice that the mineral composition for the same rock remains constant in the sieved fraction (0.088 —0.100 mm.) with a sufficient degree of accuracy, regardless of the preliminary treatment when preparing the sample, but it is quite as important to know in what degree the composition of the sieved fraction obtained represents the actual composition of the rock. In order to shed some light on this question, a few determinations of terrace points were made for a mixture composed of the pure minerals in the same proportions as obtained in the analysis of the hybrid rock. Seeing that, as earlier observed, compositions of mixtures obtained from larger lumps of the minerals deviated in the resulting fraction considerably from one another, due to the fact that they were not crushed every time in the same way, the minerals were mixed from powders, with grain sizes approximating the original grain sizes in the rock, and the mixtures were then subjected to the ordinary treatment preliminary to analysis. In Table III will be presented the results obtained from three control mixtures by different preparation of sample. In column M_1 there are presented the volume ratios as obtained on the basis of the refractive index analysis of the hybrid rock. The corresponding amounts by weight were then mixed to give the control mixtures, columns 1, 2, and 3 giving the percentages by volume of the minerals as obtained on the basis of determinations of the terrace points in the mixtures, their averages being given in column M_2. The values obtained for the different mixtures thus deviate relatively little from their average values (the error of mean square is only 0.8 %), but, on the other hand, differences of as much as 7 % exist between M_1 and M_2. This may be due to two reasons, *viz.*, to differences in the densities of the minerals and to differences in the ways the different minerals were crushed. As the figures in column M_1 represent the proportions by weight of the minerals to one another, the volumes corresponding to these values, as well as the numbers of grains in the mixtures, are inversely proportional to the densities of the minerals. On the other hand, the way in which the minerals are crushed, being thus either enriched or impoverished in the fraction has a decisive effect on the percentages by volume obtained (M_2). Thus the relatively high percentage of, *e. g.*, biotite, is due to its well-developed cleavage, while the enrichment of microcline and quartz in the sieve fraction is due in part to their lower densities. Seeing that the percentages by volume as given in Tables II and III deviate relatively little from their average values, their correction coefficients, $C = M_1/M_2$ are given in column C for each mineral. With the aid of these, by multiplying them with the corresponding volume ratios obtained in an analysis of a mixture, whose composition approximates that represented in Table III, are obtained the values, representing the actual proportions by weight of the minerals contained in that mixture. If they are applied to the values in column M_1 in Table III, we obtain the values given in column M_3, which

TABLE III

	M_1	1	2	3	M_2	C	M_3	M_4
Orthoclase	11.0 %	13.1 %	11.9 %	11.1 %	12.0 %	0.92	9.5 %	11.4 %
Quartz	12.5 »	16.7 »	17.1 »	16.4 »	16.7 »	0.75	8.8 »	11.7 »
Plagioclase	42.0 »	36.6 »	38.8 »	40.1 »	38.5 »	1.11	43.7 »	42.4 »
Biotite	3.5 »	8.6 »	8.4 »	8.1 »	8.4 »	0.42	1.4 »	2.3 »
Augite	29.5 »	23.4 »	21.5 »	22.9 »	22.6 »	1.28	35.5 »	31.0 »
Magnetite	1.5 »	1.6 »	2.3 »	1.4 »	1.8 »	0.83	1.1 »	1.2 »
	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	—	100.0 %	100.0 %

then represent the actual percentages by weight of the minerals in the hybrid rock analyzed. As a control there was performed an analysis of index of refraction of a mixture that contained the pure minerals in the proportions given in column M_3. Comparison of the results obtained, column M_4, with the corresponding percentages by volume in column M_1 shows that they, with the exception of biotite, differ very little from one another. In columns 1 and 2 in Table IV we can see the results of analysis obtained from the mineral mixtures in column, W representing the weight ratios of rapakivi granite. The grain size in the initial mixture 1 varied from 0.15 to 1.00 mm. and in mixture 2 from 1.00 to 1.50 mm. Column V, on the other hand, represents the calculated volume percentages obtained from column W by the aid of the correction coefficients in column C, which, with the exception of more albitic plagioclase (C = 1.00), are the same as in Table III. According to the Tables presented above there is reason to believe that correction coefficients determined as described above for mixtures of different composition and even different grain size can successfully be applied in the interpretation of refractive index analyses of a variety of rock types.

TABLE IV

	W	C	V	1	2
Orthoclase	39.3 %	0.92	35.0 %	34.8 %	35.4 %
Plagioclase	18.3 »	1.00	15.0 »	15.1 »	14.6 »
Quartz	38.4 »	0.75	42.0 »	40.9 »	41.6 »
Biotite	4.1 »	0.42	8.0 »	9.2 »	8.4 »
	100.1		100.0	100.0	100.0

CONCLUSIONS

In the foregoing there has been presented a statistical immersion method for the quantitative refractive index analysis of rocks or other mineral mixtures, by the aid of which the indices of refraction of the different minerals contained therein as well as their volume and weight ratios can be determined with an accuracy of a few per cents. The method is especially adaptable to the examination of the composition and weight ratios of different feldspars, especially in rocks containing simultaneously different members of the plagioclase series. The performance of a single analysis by a person accustomed to the work takes 1 to 4 workdays and the necessary appliances, consisting of a petrographic microscope, a series of immersion liquids, a mixing apparatus, and a sieve shaker, can be found in any well-equipped geological laboratory.

We wish to express our sincere thanks to Mr. K. Westerlund for his assistance in the translation of the manuscript.

GEOLOGICAL SURVEY OF FINLAND, FEBRUARY, 1946.

5

ZWEI TONPROFILE AUS SÜD-POHJANMAA

VON

KARL MÖLDER

VORWORT

Im Sommer 1944 hatte ich die Möglichkeit, bei der Kartographierung in der Umgebung der Stadt Vaasa zwei Vertikalprofile aus den Tonsedimenten am Flussufer bei Tervajoki am Ufer des Flusses Kyröjoki und in Laihia, bei Hulmi, zu erbohren. Die Tonablagerungen sind in diesen Gegenden weit verbreitet und bilden fruchtbare Böden für den Ackerbau. Das Land ist in diesen Gegenden beinahe tafelförmig, und hier und da erheben sich kleine Moränenhügel über den flachen Tonboden.

Bei der Erbohrung dieser Vertikalprofile kam es darauf an festzustellen, wie dick diese Tonsedimentablagerungen sind, welchen Verlauf die ökologisch-geologische Entwicklungsgeschichte des Bottnischen Meerbusens in der Umgebung der Stadt Vaasa genommen hat. Die Untersuchung dieser Profile ist in der Geologischen Reichsanstalt (Geologinen tutkimuslaitos) durchgeführt worden. Die Baumpollen hat Mag. phil. Ester Uussaari untersucht, der ich an dieser Stelle meinen besten Dank zum Ausdruck bringen möchte.

Die Diatomeen sind ebenso quantitativ untersucht worden, wie es schon in meinen früheren Arbeiten geschehen ist (Mölder 1943).

Helsinki, Januar 1946.

Der Verfasser

INHALTSVERZEICHNIS

EINLEITUNG

Seit längerer Zeit haben die Quartärgeologen und Moorforscher in Finnland die Geologie von der Eiszeit bis zur Gegenwart an mehreren Stellen des Landes untersucht. Bei diesen Untersuchungen haben sie die in den Sedimenten vorkommenden Baumpollen und Diatomeen berücksichtigt. Mit der vorliegenden Arbeit im Zusammenhang stehen Backmans (1919) sowie Backmans und Cleve-Eulers (1922) Untersuchungen, die die Gebiete etwas weiter nördlich der Stadt Vaasa behandeln. Zu den obengenannten Arbeiten ist auch die von Backman und Cleve-Euler (1937) »Om litorinagränsen i Haapavesi och diatomacéfloran på Suomenselkä» zu rechnen.

Die ersten Untersuchungsergebnisse über dieses Gebiet, wo die obengenannten Vertikalprofile erbohrt worden sind, finden wir in Aarnios »Agrogeologisia karttoja n:o 5, Etelä-Pohjanmaa» Kartenblatterklärung, in der ein Querprofil durch die Niederung des Flusses Kyröjoki bei Tervajoki dargestellt ist (Aarnio 1927, S. 29). Das von Aarnio untersuchte Vertikalprofil ist ca. 1.5 km von der Stelle entfernt, an der ich das Vertikalprofil aus Tervajoki erbohrt habe. Die Diatomeen aus dem Vertikalprofil von Aarnio hat Dr. Astrid Cleve-Euler bestimmt, und wie man sieht, hat sie in den untersten Sedimentablagerungen aus 770 bis 800 cm Tiefe nur *Thalassiosira baltica* feststellen können. In den Sedimenten aus 670 bis 700 cm Tiefe kommen *Cymatopleura elliptica*, *Gyrosigma attenuatum*, *Melosira islandica* ssp. *helvetica* und *Pinnularia viridis* vor, die zu der Ancylusvegetation gehören sollen. In den Sedimenten aus 570 bis 600 cm Tiefe hat Dr. Cleve-Euler *Cyclotella comta v. radiosa*, *C. Kützingiana v. Schumannii*, *Cymatopleura elliptica*, *C. solea*, *Epithemia Hyndmannii*, *Eunotia*

Clevei, Gyrosigma attenuatum, Melosira arenaria, M. islandica ssp. helvetica, Stephanodiscus astraea und *Tabellariae* festgestellt und der Ancylusflora zugerechnet. In den Sedimenten von 470 bis 500 cm Tiefe treten *Caloneis latiuscula, Campylodiscus noricus* und *v. hibernica, Cymatopleura elliptica, C. solea, Cymbella sistula, Epithemia Hyndmannii, E. turgida, Eunotia Clevei, Gyrosigma attenuatum, Melosira islandica ssp. helvetica, Rhopalodia parallela* und *Stephanodiscus astraea* auf und machen die Ancylusflora in den seichteren Gewässern aus. In den Sedimenten aus 370 bis 400 cm Tiefe kommen schon Litorinadiatomeen vor, die eigentlich die Übergangsperiode vom Ancylus zum Litorina darstellen. In diesen Sedimenten hat Cleve-Euler folgenden Arten festgestellt: *Campylodiscus clypeus v. bicostata, C. echeneis, Epithemia turgida v. Westermannii, Melosira arenaria, M. moniliformis, Diploneis interrupta, D. Smithii v. rhombica* und *Synedra tabulata.* In 270 bis 300 cm Tiefe sind pelagische Formen anzutreffen, die zu der schwachen Litorinaflora gehören. Diese Arten sind: *Thalassiosira baltica, Coscinodiscus septentrionalis, Epithemia turgida v. Westermannii, Mastogloia Braunii, M. Smithii v. amphicephala, Melosira moniliformis* und *Synedra tabulata.* Es ist interessant zu bemerken, dass die von Dr. Cleve-Euler als pelagisch bezeichnete Diatomeenflora nur zwei pelagisch lebende Formen enthält, nämlich *Thalassiosira baltica* und *Coscinodiscus septentrionalis,* während alle anderen oben angeführten Arten zu den Benthosformen gehören. Die letzten Diatomeenanalysen über das Vertikalprofil sind aus den Sedimenten von 170 bis 200 cm Tiefe gemacht, und es wurden festgestellt *Coscinodiscus oculus-iridis, C. septentrionalis, Actinocyclus Ehrenbergii, Epithemia turgida v. Westermannii, Hyalodiscus scoticus, Melosira moniliformis, Rhabdonema arcuatum* und *Synedra tabulata,* die eine stärkere Litorinaflora darstellen sollen. Ausser den obengenannten Formen sind noch *Eunotia Clevei, Cymatopleura elliptica, Stephanodiscus astraea* und *Melosira arenaria* beobachtet worden, die aber aus den Ancylussedimenten ausgespült sein sollen.

Dieses oben angeführte Vertikalprofil aus Tervajoki soll nach Aarnio (1927) ca. 17 m ü. M. liegen, und in den untersten Sedimenten hätten wir es mit Eisseesedimenten zu tun, die recht dünn wären. Auf diesen Ablagerungen liegen Ancylussedimente, und die obersten sind während der Litorinazeit abgesetzt worden. Die oberste sehr schwache Ablagerung ist nach Aarnio Rhabdonemaablagerung, wahrscheinlich deshalb, dass in diesen Schichten *Rhabdonema arcuatum* sehr reichlich vorkommt.

Aarnio hat ferner ein Vertikalprofil aus Nurmo untersucht, und dessen Diatomeen hat auch Dr. Astrid Cleve-Euler bestimmt. Die Tiefe des Profils beträgt 1 180 cm, wo der Ton zo zähe geworden ist, dass man mit Hillers Moorbohrer nicht tiefer eindringen kann. Nach Dr. Cleve-Eulers Untersuchungen enthalten die Sedimente in 1 140 bis 1 170 cm Tiefe reine Ancylusdiatomeen wie z. B. *Amphora ovalis, Caloneis latiuscula, Campylodiscus noricus v. hibernica, Cyclotella bodanica, C. comta v. radiosa, C.*

Kützingiana, v. Schumannii usw. In den Sedimenten aus 1 070 bis 1 100 cm Tiefe kommen noch Ancylusformen vor. In einer Tiefe von 970 bis 1 000 cm kommen schon schwache Brackwasserdiatomeen vor, während die Ancylusformen zurücktreten. Ein Meter höher kommen schon reine Litorinaformen vor, und Süsswasserdiatomeen fehlen vollkommen. In den Sedimenten aus 770 bis 800 cm Tiefe treffen wir wieder reine Ancylusseediatomeen, und 1 m höher, in 670 bis 700 cm Tiefe, gehen sie in schwach brackige Formen über. Eine Übergangsdiatomeenflora vom Ancylus zum Litorina finden wir noch in den Sedimenten in 570 bis 600 cm Tiefe, wo aber die Ancylusformen noch herrschende Arten sind. In den Sedimenten aus 470 bis 500 cm Tiefe treten reine Litorinadiatomeen auf, von denen *Thalassiosira baltica, Coscinodiscus septentrionalis, Diploneis didyma, D. interrupta, D. Smithii v. rhombica, Epithemia turgida v. Westermannii, Rhopalodia gibba, Grammatophora oceanica, Melosira moniliformis, M. Juergensi, Navicula humerosa, Surirella striatula* usw. zu nennen sind. Von 500 cm an aufwärts bis zu den obersten Sedimentschichten sind nur Litorinaformen anzutreffen, und in den Ablagerungen aus 220 bis 250 cm Tiefe tritt *Rhabdonema arcuatum* reichlicher hervor, weshalb Aarnio diese Ablagerungen *Rhabdonema*-Gyttja genannt hat.

Über das Vertikalprofil von Nurmo schreibt Aario (1932, S. 127) folgendes: »Das Pollendiagramm zeigt, dass die Sedimentation in einer birkenreichen Zeit begonnen hat. Im Verlaufe der Schichtablagerungen wurde die Kiefer die dominierende Holzart, um dann in den obersten Schichten wieder ganz zurückzutreten. Das Diagramm lässt sich leicht mit dem Generaldiagramm für N-Satakunta (S. 165) konnektieren. Dabei ergibt sich, dass die obersten Teilen der Serie kurz vor der Ankunft der Fichte entstanden sind, zu einer Zeit, wo die edlen Laubbäume ihre grösste Ausdehnung erreichten und die Birke der vorherrschende Baum war. Das Meeresufer befand sich damals in N-Satakunta in Gegenden, die heute 50—60 m hoch liegen. Das letzte Salzwasserstadium wiederum begann kurz vor dem letzten Maximum der Birke, zu einer Zeit, wo der Meeresspiegel in 90 m Höhe lag. Wie später gezeigt werden soll, treten auf dem Boden der Moore Litorina-Diatomeen von diesem Niveau nach unten auf. Die obere Salzwasserschicht in dem Profil von Nurmo entspricht also der Litorina-Zeit. Da die untere Salzwasserschicht in diesem Profil älter sein muss, liegt die Vermutung nahe, dass sie in die Yoldia-Zeit fällt [1].

[1]. Die untere Süsswasserschicht wäre am einfachsten als Ablagerung zu erklären, die verhältnismässig nahe am Eisrand entstanden ist, wo das Wasser infolge reichlicher Schmelzwasserzufuhr ausgesüsst war.»

Auf Grund der Diatomeenfunde kommt Aarnio (1927, S. 33) zu den Schlussfolgerungen, dass in Pohjanmaa die spätglazialen Yoldia-Ablagerungen nur in einigen Stellen sehr dünne Schichten bilden, sonst aber in den grösseren Gebieten fehlen.

In meiner Untersuchung (Mölder 1944 b) konnte ich feststellen, dass das Karelische Eismeer sogar bis nach Nurmo gereicht hat und die älteren Sedimente, in denen die Süsswasserdiatomeen vorkommen, während der Zeit abgesetzt worden sind, als das Karelische Eismeer diese Gegende überflutet hat. Es ist möglich, dass das Landeis damals, als das Karelische Eismeer bis nach Nurmo gereicht, alle höher gelegenen Gebiete südlich davon bedeckt hat, weshalb die Sedimente an diesen Stellen auch nicht vorkommen.

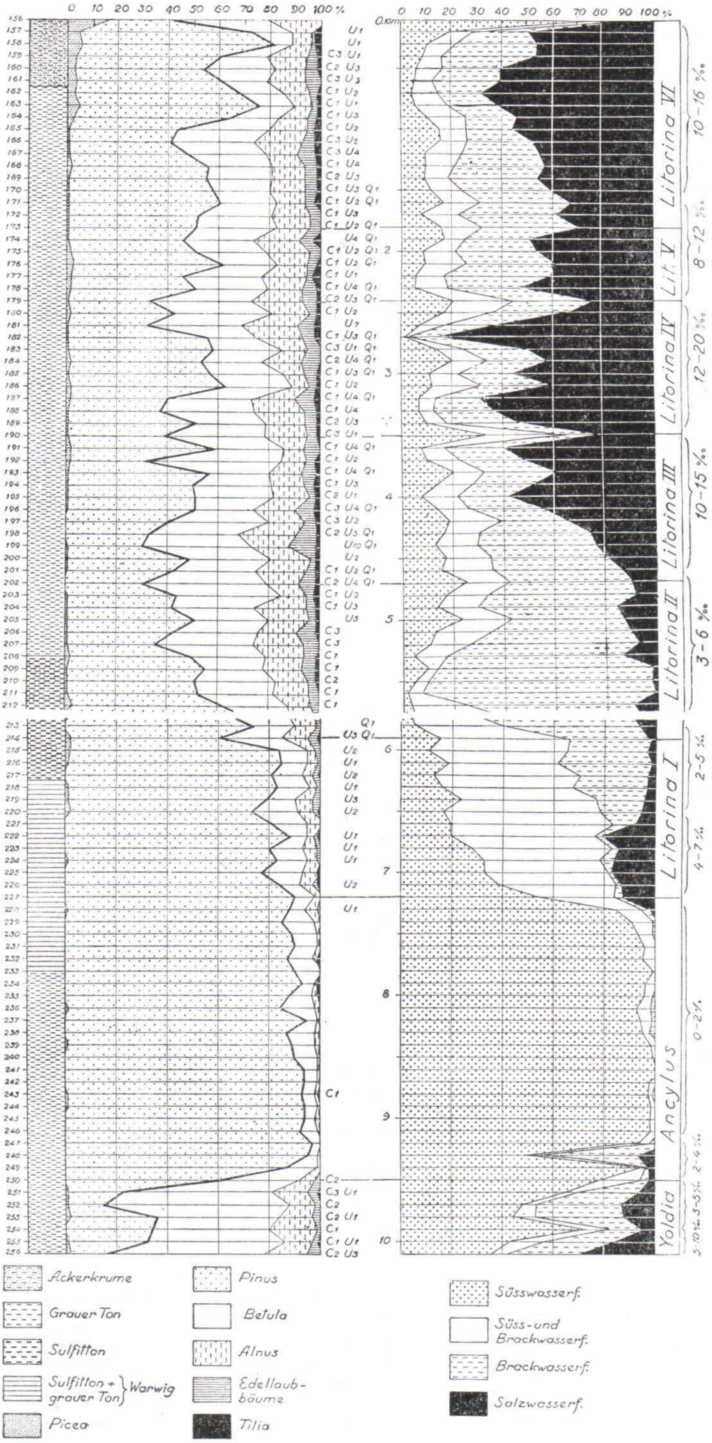
DAS VERTIKALPROFIL AUS TERVAJOKI

Das Vertikalprofil aus Tervajoki wurde am Südufer des Flusses Kyröjoki ca 300 m unterhalb des Elektrizitätswerks Vähäkyrö und des Wasserfalles Hiirikoski entnommen. Das Ufer an dieser Stelle, wo das Profil erbohrt wurde, liegt 13 m und 80 cm ü. M. und, wie man sieht, ca 3 m niedriger, als das von Aarnio (1927) erbohrte Vertikalprofil. Die obersten Schichten dieser Profilstelle enthielt 75 cm dicke Ackerkrume (Diagr. 1). Die Ackerkrume wird nach der Tiefe zu langsam tonhaltiger, und in 75 cm Tiefe kommt schon grauer Ton entgegen. Diese graue Tonschichten gehen bis eine Tiefe von 540 cm oder bis dahin, wo die Tonschichten unter das Flusswasser tauchen und die Sedimente nicht mehr mit der Luft in Berührung kommen. Von 540 cm an abwärts begegnet man einer 95 cm dicken Sulfidtonschicht, bei der schwarze Farbe in die Augen fällt. Von 635 cm abwärts kommen Sulfidton und grauer Ton schichtenweise vor, dünne Warven bildend. Diese Warvige Tonschicht ist hier 155 cm dick und geht in 790 cm Tiefe in grauen Ton über. Wie man sieht, sind die Tonablagerungen an dieser Stelle über 10 m dick und reichen noch tiefer, sind aber so fest, dass der Moorbohrer nicht einzudringen vermag.

Aus dem Profil sind Baumpollen und Diatomeen untersucht worden, und aus Diagr. 1 gehen die Resultate dieser Untersuchung übersichtlich hervor. Betrachtet man das Vorkommen des *Picea*-Pollens, so ist zu ersehen, dass er von Probe 220 an aufwärts mehr oder weniger regelmässig, beinahe in allen Schichten sehr spärlich auftritt. Nur in den obersten Sedimenten tritt er etwas reichlicher hervor, in der Probe 156 sein Maximum erreichend. Von Probe 220 an abwärts findet man *Picea*-Pollen sehr selten, nur in einigen Proben. Etwas häufiger tritt er erst von Probe 251 an abwärts auf, erreicht aber keine grösseren Zahlen.

Der in der folgenden Kolumne dargestellte *Pinus*-Pollen tritt von oben bis zu Probe 212 beinahe gleichmässig in allen Proben auf, ausgenommen die zwei obersten, in denen der *Pinus*-Pollen deutlich zurückgegangen ist. In den Sedimenten aus 580 bis 590 cm Tiefe erreicht *Pinus* ihr Maximum, und von 960 cm abwärts geht die Pollenzahl sehr schnell zurück (Diagr. 1).

Betrachtet man das Vorkommen von *Betula*, so ist zu erkennen, dass *Betula* ihr Maximum in den untersten Sedimentschichten, von 960 cm



Diagr. 1. Vertikalprofil aus Tervajoki.

an abwärts, gefunden hat. In diesen Sedimentproben, wo *Pinus* ihr Maximum erreicht, kommt *Betula* sehr spärlich vor, und erst von Probe 212 an auswärts findet man *Betula*-Pollen reichlicher in den Tonsedimenten. Beinahe ähnlich wie *Betula* tritt auch *Alnus* im Profil auf. In den Sedimenten von 960 cm an abwärts und von 600 cm an aufwärts erreicht sie über 10 % von allen Baumpollen, während in den Sedimenten aus 610 bis 950 cm Tiefe die *Betula*-Pollen so zurückgehen, dass sie in einigen Proben sogar vollständig fehlen und in den anderen nur einige Prozent ausmachen (Diagr. 1).

Besonders interessant ist es zu sehen, wie die edlen Laubbäume im Vertikalprofil vorkommen. Von 950 cm an abwärts sind sie in allen Proben anzutreffen. Besonders findet man *Corylus* in allen Sedimenten, während *Ulmus* nur in 4 und *Tilia* in 2 Proben beobachtet worden sind. Von 950 cm Sedimenttiefe an aufwärts bis zu 660 cm Sedimenttiefe findet man Pollen edler Laubbäumen in den Proben sehr selten. Es ist charakteristisch für diese Sedimente, dass *Corylus*, die in den untersten Sedimenten in allen Proben vorkommt, in diesem Abschnitt nur ein einziges Mal gefunden worden ist. Von 720 cm Sedimenttiefe an aufwärts findet man beinahe regelmässig in allen Proben *Ulmus*-Pollen und auch häufiger *Tilia*-Pollen.

Von 620 cm Sedimenttiefe an bis zu der obersten Probe kommt Pollen edler Laubbäume recht häufig und in grösserer Anzahl vor, ausgenommen die Proben 155 und 156, in denen er überhaupt nicht mehr vorhanden ist. Wie aus Diagramm 1 zu ersehen, gesellt sich zu den schon oben genannten Edellaubbäumen noch *Quercus*. *Quercus*-Pollen findet sich in den Sedimenten aus 160 bis 480 cm Tiefe, wo er recht regelmässig in den Proben auftritt.

Sehr wichtig ist es hier festzustellen, dass die Sedimente aus 900 bis 950 cm Tiefe sehr wenig Baumpollen enthielten. Ebenso enthielten die Sedimente aus 690 bis 730 cm Tiefe weniger Baumpollen als die übrigen Sedimentschichten, aber hier kamen die Pollen doch häufiger vor als in 900—950 cm Tiefe. Weiter unten werden wir näher betrachten, warum gerade in diesen Sedimenten die Baumpollen viel weniger vorkommen als in den anderen Sedimenten dieses Profils.

Die in dem Vertikalprofil vorkommenden Diatomeen sind in die Süss-, die Süss- und Brack-, die Brack- und die Salzwassergruppe eingeteilt und für jede Gruppe die Prozentzahlen der in jeder Probe festgestellten Diatomeen errechnet worden. Die Prozentsätze dieser Diatomeengruppen sind graphisch dargestellt in Diagramm 1, aus dem auch die Sedimenttiefen zu ersehen sind.

Bei näherer Betrachtung der Diatomeenflora in der obersten Probe ist sogleich zu erkennen, dass sie deutlich von den Diatomeenfloren in den darunter liegenden Proben stark abweicht. So machen die Süsswasserformen allein schon 82.5 % aller in dieser Probe vorkommenden Diatomeen aus (Diagr. 1). Nur in dieser Sedimentprobe finden sich *Eunotia monodon, E. pectinalis v. ventralis, E. sudetica, E. valida, Gomphonema acuminatum, G. acuminatum v. trigonocephala, G. gracile, G. parvulum, Meridion circulare* und die Varietät *constricta, Pinnularia borealis v. brevicostata, P. gibba v. linearis* und *v. subundulata, P. maior, P. nobilis* und *P. stomatophora* von den Süsswasserdiatomeen. Aus anderen ökologischen Gruppen sieht man keine Diatomeen, die nur in der obersten Sedimentprobe vorhanden wären.

Diese 16 Süsswasserdiatomeen zeigen ohne Zweifel, dass die Probenahmestelle damals, als sich diese Sedimente abgesetz haben, von einem kleinen und flachen Gewässer mit sogar saurem bedeckt gewesen ist, denn beinahe alle oben aufgezählten Diatomeen gedeihen heute in den kleinen und sauren Gewässern Finnlands. Aus diesen Tatsachen kann man schliessen, dass Tervajoki damals vom Meere abgeschnürt gewesen ist und sich die letzten Sedimente beinahe in ganz versüsstem Wasser abgesetzt haben.

In den Sedimentschichten von 20 bis 710 cm Tiefe treten die Süsswasserdiatomeen beinahe in allen Proben mehr oder weniger individuenarm hervor (Diagr. 1). Kleinere Schwankungen kann man sehen in 240, 350 und 640 cm Tiefe, wo die Süsswasserformen grössere Prozentsätze annehmen. Dagegen gehen sie in 270 und 560 cm Sedimenttiefe so in ihrem Individuen- wie auch Artenreichtum zurück, dass sie beinahe völlig verschwinden. Allein schon die Süsswasserdiatomeengruppe zeigt, dass die Salzkonzentration im Wasser im Laufe der Jahrtausende stark geschwankt hat.

Von 700 cm Sedimenttiefe an abwärts nehmen die Süsswasserdiatomeen schnell im Arten- und Individuenreichtum zu und machen in der Probe aus 780 cm Tiefe sogar 100 % aus (Diagr. 1). In den Sedimenten aus 730 bis 920 cm Tiefe kommen beinahe nur Süsswasserformen vor, und das Wasser sollte während dieser Zeit, als diese Sedimente sich abgesetzt haben, süss gewesen sein.

Von 920 cm Sedimenttiefe an abwärts nehmen die Süsswasserdiatomeen langsam ab, machen aber grössere oder kleinere Sprünge hin und her, bis sie in der untersten Probe nur 36 % ausmachen. Diese Sprünge in der Diatomeenflora zeigen, dass wir es mit den Sedimenten einer Übergangsperiode vom Yoldiameer zum Ancylussee zu tun haben, wo Salz- wie auch Süsswasser sprungweise in das Becken Finnlands eingedrungen ist.

Jetzt ist es interessant zu betrachten, wie die Süss- und Brackwasserdiatomeen im Vertikalprofil vorkommen. Den Süss- und Brackwasserdiatomeen habe ich auch die früherer als selbständige Gruppe dargestellten Süss- und Salzwasserdiatomeen angeschlossen, da die Unterscheidung dieser Diatomeen nach den bisher mangelhaften ökologischen Tatsachen sehr erschwert ist (Mölder 1943 und 1944 a). Wie man aus Diagr. 1 ersieht, kommen die Süss- und Brackwasserdiatomeen von der obersten

Probe an bis in 580 cm Sedimenttiefe mehr oder weniger gleichmässig in den Proben vor. Eine Ausnahme bilden die Sedimente in 270 und 350 cm Tiefe. Im ersten Fall gehen sie so zurück, dass sie beinahe verschwinden, und im zweiten Fall nimmt die Individuenzahl so reichlich zu, dass diese Gruppe sogar 32 % aller Diatomeen ausmacht. Diese jähen Schwankungen in der Diatomeenflora sind von den plötzlichen ökologischen Veränderungen des Wassers abhängig. Es ist eine Aufgabe dieser Untersuchung die Gründe dieser plötzlichen Veränderungen festzustellen.

In den Sedimenten aus 580 bis 720 cm Tiefe kommen die Süss- und Brackwasserdiatomeen viel individuenreicher vor und in diesen Schichten tritt *Epithemia turgida* viel reichlicher hervor als in den darüber und darunter liegenden. Auch findet man in diesen Schichten häufiger *Epithemia zebra, Rhoicosphenia curvata, Rhopalodia gibba* und *Synedra pulchella,* von denen die letztgenannte beinahe nur in dieser Tiefe verbreitet ist.

Von 720 cm Tiefe an abwärts bis zum Grunde treten zu der Süss- und Brackwassergruppe gehörende Diatomeen sehr individuenarm auf. Sie bilden keine Schwankungen in der Diatomeenflora oder, mit anderen Worten, reagieren sehr schlecht auf die Veränderungen in den ökologischen Wachstumsbedingungen (Diagr. 1).

Die dritte Kolumne bilden die Brackwasserdiatomeen, und aus Diagr. 1 geht sehr gut hervor, dass die Brackwasserdiatomeen in ihrem Reichtum in den Sedimenten beträchtliche Grössenschwankungen durchmachen. In der obersten Sedimentprobe machen sie nur 6 % der Diatomeen aus, nehmen aber tiefer gehend schnell zu. Dieses reichlichere Auftreten setzt sich bis in 260 cm Sedimenttiefe fort und von da an abwärts gehen sie zurück, in den Tiefen 270 und 350 cm ihren minimalen Individuenreichtum erreichend.

Von 360 cm Sedimenttiefe an abwärts nehmen die Brackwasserdiatomeen wieder schnell zu und erreichen ihre maximalen Individuenzahlen in 560 cm Tiefe, wo sie allein 92.5 % aller Diatomeen ausmachen (Diagr. 1). So kommen sie bis 650 cm Sedimenttiefe vor, von dieser Tiefe an abwärts nehmen sie schnell ab und bis 920 cm Sedimenttiefe kommen sie in vielen Proben überhaupt nicht vor. Von der letztgenannten Tiefe an abwärts nehmen die Brackwasserdiatomeen wieder zu, erreichen aber nicht mehr so grosse Individuenzahlen, wie wir das schon in 560 cm Tiefe gesehen haben.

Die letzte oder vierte Kolumne bilden die Salzwasserdiatomeen, die im einer von den früher betrachteten Diatomeengruppen ganz abweichenden Weise im Profil vorkommen (Diagr. 1). Diese Gruppe tritt ebenso in der obersten Probe sehr individuenarm auf, wie die Süss- und Brackwasser- sowie Brackwassergruppen. Von der obersten Probe an abwärts nehmen die Salzwasserdiatomeen in der Arten- und der Individuenzahl schnell zu und erreicht ihr erstes Maximum in 70 cm Sedimenttiefe, wo sie allein 68 % aller in der Probe vorkommenden Diatomeen ausmachen.

Weiter abwärts gehen sie wieder im Reichtum zurück, und in 180 cm Tiefe machen sie nur 29.5 % der Diatomeen aus.

Von diesem Minimum abwärts gehend, nehmen die Salzwasserformen wieder zu, erreichen aber nicht mehr so grosse Prozentzahlen wie in 80 cm Sedimenttiefe. Dieses kleine Maximum reicht bis in 240 cm Tiefe, wo sie wieder so zurückgegangen sind, dass man nur 23.5 % der Salzwasserformen feststellen konnte (Diagr. 1). Dieses Minimum ist sogar 6 % kleiner als das oben festgestellte.

Von der letztgenannten Tiefe an abwärts nehmen die Salzwasserdiatomeen wieder zu und erreichen ihren maximalen Individuenreichtum in dem Vertikalprofil in 270 cm Sedimenttiefe, wo sie allein 85 % aller in der Probe festgestellten Formen ausmachen. Es ist in diatomeenökologischer Hinsicht besonders interessant festzustellen, dass in dieser Probe *Thalassionema nitzschioides* eine Massenproduktion erreicht hat und sich allein auf 61.5 % der in der Probe vorkommenden Diatomeen beläuft. Warum diese Diatomeen in Sedimentschichten einen so grossen Individuenreichtum erreicht hat, lässt sich nicht zu erklären.

Von dieser Stelle an abwärts, wo die Salzwasserdiatomeen ihr Maximum erreicht haben, nehmen sie wieder in ihrem Individuenreichtum langsam ab und verschwinden in 740 cm Sedimenttiefe vollständig. Erst in 930 cm Tiefe erscheinen sie wieder, und in der untersten Probe machen sie schon 28 % aller in dieser Probe vorkommenden Diatomeen aus (Diagr. 1).

Ich habe dieses Vertikalprofil aus Tervajoki deshalb so genau beschrieben, weil ich zeigen wollte, dass die Sedimentierung an der betreffenden Stelle regelmässig ohne Unterbrechungen vor sich gegangen ist. Man sieht im Baumpollen- und ebenso im Diatomeenprofil keine Stellen, wo die geologische Entwicklung unterbrochen wäre. Diese Tatsache ist grundlegend bei den Schlussfolgerungen und beim Vergleich mit den an anderen Stellen erbohrten Vertikalprofilen. Alle Schwankungen, die in diesem Vertikalprofil vorkommen, sind von den Veränderungen der ökologischen Wachstumsbedingungen und den geologischen Zeitperioden abhängig sowie mit diesen aufs engste zusammenhängend.

ÜBER DIE GEOLOGIE UND ÖKOLOGIE DES VERTIKALPROFILS BEI TERVAJOKI

Bei der geologischen Zeiteinteilung werde ich die im Vertikalprofil vorkommende Diatomeen als Grundlage verwenden, denn die geologischen Zeitperioden sind in den Untersuchungen nach den Meeres- und Seestadien durchgeführt worden, wie z. B. Litorinameer, Ancylussee, Yoldiameer und Litorinazeit, Ancyluszeit sowie Yoldiazeit. Die Diatomeen werde ich deshalb als Grundlage verwenden, weil sie gerade die obengenannten Meeres- und Seestadien in den Sedimentablagerungen richtig wiederspiegeln.

Die untersten Sedimente von 950 bis 1 010 cm Tiefe sind nach meiner Ansicht während der letzten Stadien des Yoldiameeres oder nach Hyyppä (1943) während der letzten Stadien des Bottnischen Meeres abgesetzt worden. In diesen Sedimenten kommen die Salzwasserdiatomeen *Rhabdonema arcuatum, Grammatophora oceanica, Thalassionema nitzschioides, Hyalodiscus scoticus* und *Cocconeis scutellum* reichlich vor. Von einer Tiefe vom 950 cm an aufwärts verschwinden diese Salzwasserdiatomeen, und in der Probe aus 930 cm Tiefe findet man beinahe von den Salzwasserdiatomeen nur *Coscinodiscus plicatulus* allein.

Fast ähnlich kommen in diesen Sedimenten die Brackwasserdiatomeen vor. Die Brackwasserdiatomeen *Coscinodiscus lacustris* und die Varietät *septentrionalis, Synedra tabulata* und *Thalassiosira baltica* erreichen recht grosse Individuenzahlen. Von einer Tiefe von 950 cm an aufwärts verschwinden die obengenannten Arten und beinahe alle Brackwasserdiatomeen. Die Süsswasserdiatomeen dagegen nehmen in den Sedimenten von unten nach oben in gleicher weise zu, wie die Salz- und Brackwasserdiatomeen abnehmen.

Die Diatomeenflora zeigt uns ohne Zweifel, dass das Wasser im Yoldiameer während der Endstadien langsam süsser geworden ist und eine grössere Veränderung in den ökologischen Wachstumsbedingungen der Diatomeen eingetreten ist, als sich die Sedimente in 950 cm Sedimenttiefe abgesetzt haben. Diese Sedimente sind ohne Zweifel während der Rhabdonemaperiode entstanden, weshalb wir auch sehr viel *Rhabdonema arcuatum* in den Sedimenten gefunden haben.

Aus dem Baumpollenprofil sehen wir, dass sich die Baumpollen ebenso in 950 cm Sedimenttiefe ändern, vonwo die Probe 250 entnommen ist (Diagr. 1). Man sieht, dass beinahe in allen Proben *Picea*-Pollen anzutreffen ist. *Pinus*-Pollen kommt auch in allen Sedimentschichten vor, erreicht aber nicht so grosse Prozentzahlen, wie aus der Tiefe von 950 cm an aufwärts. Charakteristisch ist *Betula*, die sehr reichlich vorkommt. Ähnlich wie *Betula* kommen *Alnus* und Edellaubbäume vor.

Die Salzkonzentration des Wassers war am Ende der Yoldiazeit im Yoldiameer bei Tervajoki recht klein. Nach den Berechnungen enthielt das Wasser während der Zeit, als sich die Sedimente von 990 bis 1 010 cm Tiefe abgesetzt haben, ca. 5—10 $^0/_{00}$ Salz. Diese Meinung bestätigen die Salzwasserdiatomeen *Thalassionema nitzschioides, Rhabdonema arcuatum, Hyalodiscus scoticus, Grammatophora oceanica* und *Cocconeis scutellum*, die alle recht individuenreich in den Sedimenten vorkommen. Alle obengenannten Salzwasserdiatomeen kommen an einigen Stellen des Finnischen Meerbusens bei der Südgrenze Finnlands recht selten rezent vor. Diese Arten gehen aber nirgends in ein Wasser, das weniger als 5 $^0/_{00}$ Salz enthält. Mann kann einzelne Exemplare zufällig wohl an Stellen finden, wo weniger als 5 $^0/_{00}$ Salz im Wasser enthalten ist, aber wie ich feststellen konnte, enthielten diese Zellen kein Chlorophyll mehr.

Von 990 cm Tiefe an aufwärts nehmen die Salzwasserdiatomeen ab, und das Wasser sollte in der Zeit, als sich die Sedimente von 950 bis 990 cm Tiefe abgesetzt haben, 3—5 $^0/_{00}$ Salz enthalten haben. Von den obengenannten Salzwasserdiatomeen findet man in den Proben nur einzelne Individuen. Dagegen tritt *Navicula peregrina* reichlicher hervor, und wie aus den Untersuchungen in der Pojo-Bucht hervorgegangen ist, kann sie erst dann gut gedeihen, wenn im Wasser 5 bis 6 $^0/_{00}$ Salz enthalten ist (Mölder 1943, S. 69). In dem Baumpollenprofil lassen sich während jener Zeit, als in dem Meereswasser Salzkonzentrationsveränderungen vor sich gehen, gar keine Veränderungen feststellen (Diagr. 1).

Von 950 cm Sedimenttiefe an aufwärts ist das Wasser im grossen ganzen süss, denn die Salzwasserdiatomeen verschwinden beinahe vollständig, und in 930 cm Sedimenttiefe kann man eine plötzliche Veränderung in der Diatomeenflora feststellen. Nach meiner Ansicht haben wir es in jener Zeit mit der Ancylustransgression zu tun, als der Aufstieg des Wasserspiegels reichlich Brackwasserdiatomeen mitgebracht hat. Damals konnte das Wasser ca. 2—4 $^0/_{00}$ Salz enthalten (Diagr. 1). In dem Baumpollenprofil tritt dagegen in der betreffenden Zeit eine recht grosse Änderung in die Erscheinung. *Pinus* hat so zugenommen, dass sie allein über 90 % aller Baumpollen ausmacht, weil die Edellaubbäume vollständig verschwinden und ebenso *Alnus* zurückgeht.

Während dieser Zeit, als die Sedimente zwischen 720 und 920 cm Tiefe sich abgesetzt haben, enthielte das Wasser überhaupt nicht mehr Salz oder, mit anderen Worten, 0 bis 2 $^0/_{00}$ Salz, wie heutzutage die Süsswasserseen. In jener Zeit flutete in der betreffenden Gegend der Ancylussee, denn man findet in den Sedimenten 90 bis 100 % Süsswasserdiatomeen, die Salz- und Brackwasserdiatomeen verschwinden vollständig, und die Süss- und Brackwasserdiatomeen treten noch sehr spärlich auf (Diagr. 1). Von den häufiger vorkommenden Süsswasserformen sind zu nennen *Cyclotella comta, C. Kützingiana, Epithemia Hyndmanni, Melosira ambigua, M. distans, M. islandica ssp. helvetica, Stephanodiscus astraea* zusammen mit der Varietät *minutula* und *Tabellaria fenestrata* oder insgesamt 9 Planktondiatomeen. Es ist sehr interessant festzustellen, dass *Melosira arenaria,* die von den Quartärgeologen als Charakterart für die Ancylusseesedimente gehalten worden ist, nur in den obersten Ancylusseesedimenten vorkommt. Aus Diagramm 1 geht ohne Zweifel hervor, dass die Ancylusseesedimente in 720 bis 950 cm Sedimenttiefe vorkommen und dass das Seewasser damals, als diese Sedimente sich abgesetzt haben, bei Tervajoki süss gewesen ist.

Von 720 cm Sedimenttiefe an aufwärts finden wir schon Salz- und Brachwasserdiatomeen reichlicher, und wie man aus Diagramm 1 ersieht, ist eine deutliche Veränderung in den ökologischen Wachstumsbedingungen eingetreten, oder Salzwasser ist in den Ancylussee eingedrungen. Von den Salzwasserformen findet man recht individuenreich *Campylodiscus echeneis, Diploneis interrupta, D. Smithii* sowie seltener *Grammatophora oceanica* und *Rhabdonema arcuatum*. Von den Brackwasserformen findet man häufiger nur *Synedra tabulata*, während *Mastogloia Smithii* zusammen mit der Varietät *amphicephala* und *Nitzschia tryblionella* zusammen mit der Varietät *victoriae* sehr selten vorkommen. Dass gerade die Salzwasserdiatomeen in diesen Sedimentschichten so reichlich auftreten, zeigt seinerseits ohne Zweifel, dass das Salzwasser diese Formen mitgebracht hat und sie deshalb so individuenreich erscheinen und die Brackwasserformen dagegen beinahe fehlen. Diese Übergangsperiode hat bis in das Niveau gedauert, in dem die Probe 214 entnommen worden ist, oder bis in 590 cm Sedimenttiefe. Diese Periode entspricht Litorina I, und nach den Diatomeen sollte das Wasser bei Tervajoki damals am Anfang des Litorinameeres 4—7 $^0/_{00}$ Salz enthalten haben. In den Proben 214—219 sind die Salzwasserformen nicht mehr so individuenreich vorhanden, und das Wasser hat 2—5 $^0/_{00}$ Salz enthalten. Es ist auch möglich, dass das Wasser in dieser Zeit 4—7 $^0/_{00}$ Salz enthalten hat und die Salzwasserdiatomeen, die zusammen mit dem Salzwasser in das Baltischen Becken eingedrungen, im Brackwasser ausgestorben sind.

Beobachten wir im Diagramm 1 das neben den Diatomeen dargestellte Baumpollenprofil, dann sehen wir, dass unter den Baumpollen keine solche Veränderung stattgefunden hat wie unter den Diatomeen. Man sieht, dass *Alnus* und edle Laubbäume etwas reichlicher vorkommen, *Pinus* aber ebenso, wie während des Ancylusseestadiums hervortritt. Eine deutlichere Veränderung sehen wir bei den Baumpollen erst in den Proben 210 und 211 oder in 550—560 cm Sedimenttiefe. Von dieser Tiefe an aufwärts nehmen die Pollen der edlen Laubbäume so sehr zu, dass wir nach dem Profil die Litorinazeit vorfinden.

Aus dem Obigen get deutlich hervor, dass man nach den Diatomeen in den Sedimenten die Grenze zwischen Ancylus- und Litorinasedimenten viel sicherer feststellen kann als nach den Baumpollen. Es ist wohl möglich, dass man auch nach den Baumpollen die Grenze in 720 cm Sedimenttiefe gezogen hätte, aber so sicher ist man doch nicht.

Von Probe 214 oder 590 cm Tiefe an aufwärts ändert sich die Diatomeenflora völlig. Die Salzwasserformen *Campylodiscus echeneis, Diploneis interrupta* und *D. Smithii* verschwinden, und statt dessen treten *Coscinodiscus plicatulus* und *Grammatophora oceanica* individuenreich hervor. In der Probe 205 gesellt sich zu diesen *Cocconeis scutellum, Hyalodiscus scoticus* und *Thalassiosira decipiens*, die aber nicht besonders grosse Individuenzahlen erreichen. Wie man aus Diagramm 1 ersieht, erreichen die Brackwasserdiatomeen in diesen Sedimentschichten grosse Individuenzahlen, weshalb auch die Prozentsätze sehr hoch steigen. Trotzdem die Brackwasserdiatomeen sehr reichlich vorkommen, gibt es nur *Coscino-*

discus lacustris nebst der Varietät *septentrionalis, Synedra tabulata* und *Thalassiosira baltica* oder insgesamt 3 Arten und 1 Varietät, die so hohe Hundertsätze ausmachen. Interessanterweise treten *Mastogloia Smithii* und die Varietät *amphicephala* nicht mehr in den obersten Sedimentablagerungen auf, was bestätigt, dass das Seewasser für diese Diatomeen viel Salz enthalten hat. Diese Periode, wo die Brackwasserdiatomeen gute Wachstumsbedingungen gefunden haben, dauert von 590 cm Sedimenttiefe bis zu Probe 202 oder bis 470 cm Sedimenttiefe, und diese Periode habe ich Litorina II genannt. Während dieser Zeit enthielte das Seewasser 3—6 $^0/_{00}$ Salz, und wir haben es mit einer ruhigeren Periode zu tun, wo im Wasser keine grösseren Veränderungen stattgefunden haben. Während Litorina II treten die Pollen der edlen Laubbäume sowie von *Alnus* viel reichlicher hervor, als wir das während Litorina I gesehen haben. Auch geht *Pinus* im Reichtum zurück, und *Betula* nimmt zu.

Von 470 cm Tiefe an aufwärts steigt die Prozentzahl der Salzwasserformen deutlich und erreicht schon in Proben 195 58 % aller in dieser Probe vorkommenden Diatomeen. Es gibt eigentlich sehr wenig neue Formen, die hier und da in den Proben vorkommen, aber dagegen haben die letztgenannten Salzwasserformen im Individuenreichtum stark zugenommen. Von den neuen Arten sind zu nennen *Achnanthes brevipes, Actinocyclus Ehrenbergi, Coscinodiscus asteromphalus, C. radiatus, C. oculus iridis, Diploneis notabilis* und *Thalassionema nitzschioides,* von denen die letztgenannte in einigen Proben recht grosse Individuenzahlen erreicht.

Die Brackwasserdiatomeen sind in den Sedimenten zwischen 350—470 cm Tiefe im Individuenreichtum zurückgegangen, aber interessanterweise findet man als neue Formen *Achnanthes taeniata* und *Amphora coffeaeformis,* die aber keine grossen Individuenzahlen erreichen. Erst in Probe 190 gehen die Salz- sowie Brackwasserdiatomeen in ihrem Reichtum plötzlich stark zurück, was zeigt, dass eine Veränderung in den ökologischen Wachstumsbedingungen stattgefunden hat, die von den äusseren Faktoren abhängig war. Die obengenannte Sedimentschicht in 350 bis 470 cm Tiefe ist Litorina III genannt, und die Salzkonzentration des Wassers in dieser Zeit, als die obengenannten Sedimente sich abgesetzt haben, betrug zwischen 10 und 15 $^0/_{00}$, am Anfang weniger und am Ende etwas mehr.

Von 350 cm Tiefe an aufwärts erreichen die Salzwasserdiatomeen ihren maximalen Individuenreichtum und machen in Probe 182 sogar allein 85 % aller in der Probe vorkommenden Formen aus. Wie man aus Diagramm 1 ersieht, gehen die Salzwasserdiatomeen in den Sedimenten aus 240 cm Tiefe wieder deutlich zurück, und wir haben es wieder mit einer ökologischen Periode zu tun, die so lange gedauert hat, bis sich die Sedimente von 240 bis 350 cm Tiefe abgesetzt haben.

Von den Salzwasserdiatomeen findet man in den Sedimenten dieser Periode eigentlich als neue Arten *Stephanopyxis turris,* die reichlicher in den Proben vorkommt. Ganz eigenartig tritt *Thalassionema nitzschioides* in den Sedimenten auf. Sie erreicht in der Probe 182 eine Massenproduktion und macht allein 61.5 % aller in dieser Probe vorkommenden Diatomeen aus. In dieser Probe können wir ruhig von einer *Thalassionema nitzschioides*-Flora sprechen, denn im Präparat sieht man beinahe nur diese Diatomee. Unter den Brackwasserformen kann man keine Änderung feststellen, denn die oben aufgezählten Arten treten mehr oder weniger individuenarm hervor. Auf Grund der Diatomeenflora habe ich diese Periode Litorina IV genannt, und die Salzkonzentration des Wassers erreicht ihr Maximum oder schwankt zwischen 12—20 $^0/_{00}$ (Diagr. 1).

Von 240 cm Tiefe an aufwärts kommen die Salzwasserdiatomeen nicht mehr so reichlich in den Sedimentschichten vor, aber die Brackwasserformen haben in diesen Proben im Individuenreichtum zugenommen, und als neue Art ist *Melosira Juergensi* zu nennen. Eine Änderung können wir erst in einer Tiefe von 180 cm feststellen, wo die Salzwasserdiatomeen zurückgehen und in den Wachstumsbedingungen grössere Schwankungen stattgefunden haben (Diagr. 1). Diese Periode ist als Litorina V bezeichnet, und die Salzkonzentration des Seewassers hat damals 8—12 $^0/_{00}$ betragen.

Von 180 cm Tiefe an aufwärts nehmen die Salzwasserdiatomeen wieder in der Individuenzahl deutlich zu und erreichen ihr Maximum in Probe 162 in 70 cm Sedimenttiefe, wo sie 68 % aller in dieser Probe festgestellten Formen ausmachen. Von diesem maximalen Vorkommen an aufwärts treten die Salzwasserformen in allen Sedimentschichten reichlich hervor, und erst in der obersten Probe gehen sie so zurück, dass sie sich auf nur 7.5 % belaufen. Als neue Formen in diesen Sedimenten sind zu nennen *Diploneis notabilis, Grammatophora arcuata, G. marina,* die häufig vorkommt, *Navicula digitoradiata, N. humerosa, N. peregrina, Nitzschia granulata, Pyxidicula minuta* und *Rhabdonema minutum,* die alle als sehr selten in einzelnen Proben festgestellt worden sind. Bei den Brackwasserdiatomeen lässt sich keine Veränderung feststellen, aber bei den Süsswasserformen liegt in Probe 156 aus 10 cm Sedimenttiefe eine deutliche Wandlung, und sie machen schon 82.5 % der Diatomeen dieser Probe aus, während sie in den darunter liegenden Proben nur einige Prozent betragen.

Es ist sehr interessant näher zu beobachten, welche Formen nur in der obersten Probe vorhanden waren. Nur in Probe 156 fanden sich *Eunotia diodon, E. exigua, E. faba, E. lunaris, E. monodon, E. pectinalis* nebst den Varietäten *minor* und *ventralis, E. praerupta, E. robusta v. tetraodon, E. sudetica, E. valida, E. veneris, Fragilaria virescens, Comphonema acuminatum, G. gracile, G. parvulum, Melosira distans v. lirata, Meridion circulare* nebst der Varietät *constricta, Navicula radiosa, Pinnularia borealis, P. borealis v. brevicostata, P. gibba, P. gibba v. linearis, P. gibba f. subundulata, P. maior, P. nobilis, P. stomatophora, Surirella robusta, Synedra ulna* und *Tetracyclus lacustris* oder insgesamt 32 Arten und Varietäten. Diese obengenannten Diatomeen bestätigen, dass das Wasser damals, als sie gediehen sind, süss und zugleich sehr klein gewesen ist, denn rezent kommen diese Formen in Finnland nur in kleineren Gewässern häufig vor. Tervajoki war damals schon vom Meer abgeschnürt, und an Ort und Stelle war ein Süsswasserbecken vorhanden.

Nach den Diatomeen gehört dieses Stadium, als sich die Sedimente von 20 bis 180 cm Tiefe abgesetzt haben, zu Litorina VI, und die oberste Probe diesen Sedimenten entnommen, die sich schon nach der Abschnürung abgesetzt haben. Während Litorina VI enthielte das Wasser bei Tervajoki 10 bis 16 $^0/_{00}$ Salz, und das Maximum hatte es an dieser Stelle, wo die Probe 162 entnommen worden ist, oder in 70 cm Sedimenttiefe (Diagr. 1).

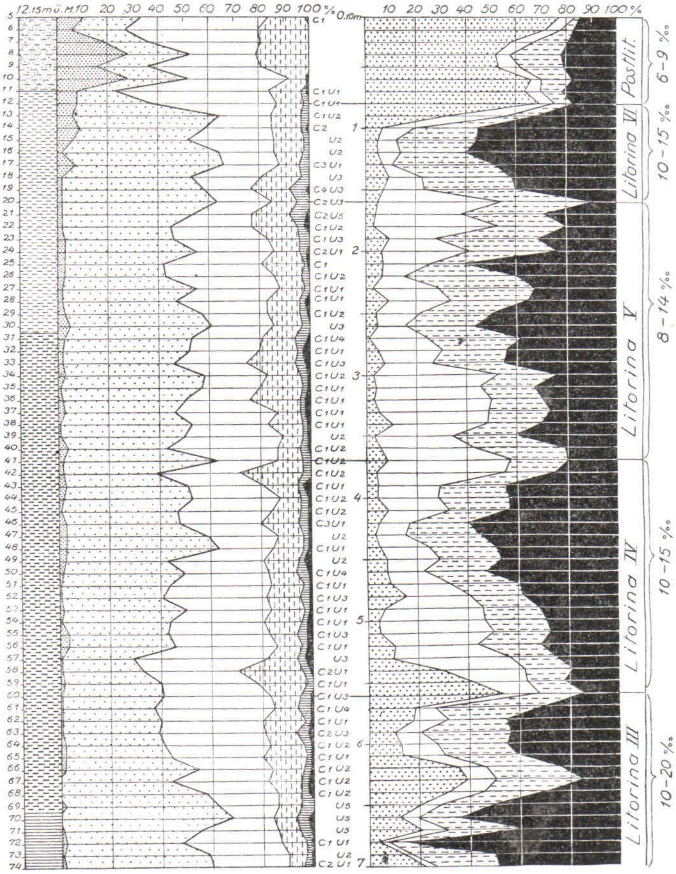
Betrachten wir das nebenstehende Baumpollenprofil in Diagramm 1, dann sehen wir, dass die Baumpollen in der Litorinazeit keine solchen Schwankungen durchmachen, wie wir das bei den Diatomeen gesehen haben. *Picea* tritt in allen Proben sehr selten auf und erst von Probe 163 an aufwärts nimmt sie etwas zu. Die Edellaubbäume treten in allen Sedimentschichten häufig hervor, und erst in der obersten Probe fehlen sie vollständig.

Diese nebeneinanderstehenden Baumpollen- und Diatomeenprofile zeigen uns deutlich, dass die Diatomeen die geologischen Zeitperioden und ebenso die ökologischen Bedingungen an Ort und Stelle viel besser wiedergeben als die Baumpollen, die durch den Wind über weite Strecken transportiert werden können.

DAS VERTIKALPROFIL AUS HULMI IN LAIHIA

Es ist möglich, dass bei Tervajoki die Diatomeen in den Sedimenten so vorkommen und wir an anderen Stellen diese Veränderungen nicht mehr erkennen können. Um festzustellen, dass die Diatomeen auch an anderen Stellen, wo die Sedimente genügend dick sind, ebenso vorkommen, habe ich ein Vertikalprofil in Hulmi, Laihia, am Ufer des Flusses Laihiajoki erbohrt. Diese Stelle liegt 12 m ü. M. und es wurde insgesamt 14 m tief erbohrt. Tonsedimente setzten sich noch tiefer for, aber sie wurden so fest, dass Hillers Moorbohrer nicht tiefer ging.

Auch hier kommt oben Ackerkrume vor, die 70 cm dick ist, wie wir das auch bei Tervajoki gesehen haben (Diagr. 1 und 2). Unter der Ackerkrume kommt eine ca. 2 m dicke graue Tonschicht vor, die in 260 cm Tiefe in Sulfidton übergeht. Der Sulfidton ist bei Hulmi 390 cm dick und geht in 650 cm Tiefe in warvigen Sulfid- und graue Tonsedimente über, in denen die Warven einige mm bis 1 cm dick waren. Diese warvigen Tonsedimente reichen 980 cm tiefe und gehen dann wieder in schwarzen

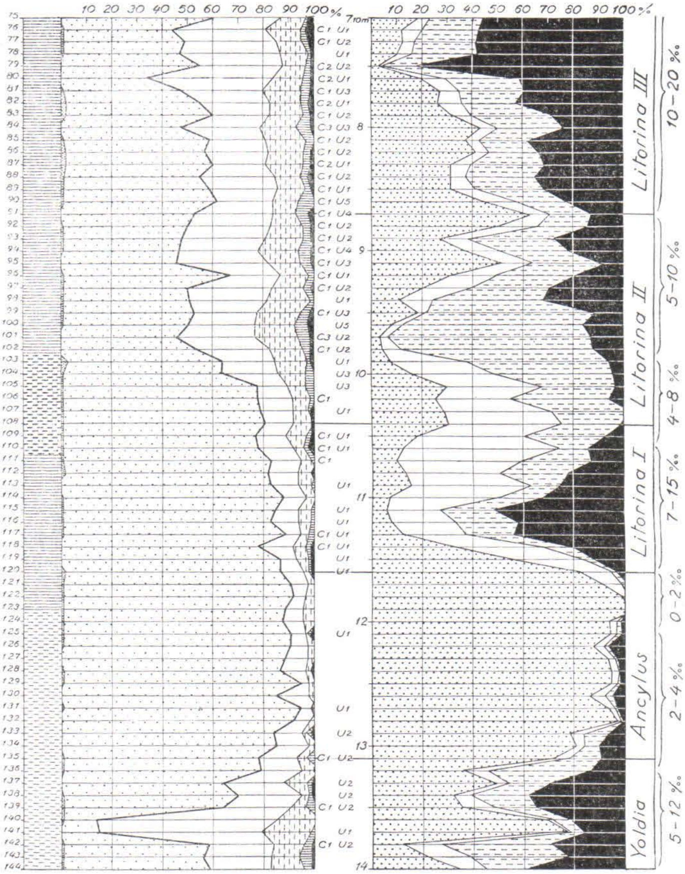


Diagr. 2. Vertikalprofil aus Hulmi.

Sulfidton über, der ca. 80 cm dick ist. In 1 070 cm Sedimenttiefe geht der Sulfidton wieder in warvigen Sulfid- und grauen Ton über. Diese warvigen Tone reichen bis 1 190 cm Tiefe und werden dann tiefer grau bis in 1 400 cm Sedimenttiefe. Vergleicht man die Tonablagerungen aus Tervajoki mit denen bei Hulmi, dann sieht man, dass an beiden Stellen die Ablagerungen beinahe ähnlich vorkommen und das in der Sedimentierung bei Hulmi auch keine Störungen auftreten.

Beim Vergleichen von Diagramm 1 mit 2 sieht man, dass die Diatomeen und ebenso die Baumpollen an beiden Stellen in den Sedimenten fast ähnlich auftreten. So kommen die Salzwasserdiatomeen in den Sedimenten des Ancylussees bei Hulmi etwas reichlicher vor, desgleichen die Edellaubbäume etwas reichlicher in den Proben aus Ancylussedimenten. Eine Abweichung finden wir erst bei den obersten Sedimenten von Probe 11 an aufwärts, welche Sedimente bei Tervajoki nicht vorkommen.

Forts.



Diagr. 2. Vertikalprofil aus Hulmi.

ÜBER GEOLOGIE UND ÖKOLOGIE DES VERTIKALPROFILS AUS HULMI IN LAIHIA

Bei der geologischen Zeiteinteilung werde ich ebenso wie bei Tervajoki auch bei Hulmi die im Vertikalprofil vorkommenden fossilen Diatomeen als Grundlage anwenden, denn diese spiegeln die einzelnen Perioden viel genauer wieder als die Baumpollen, wie wir das schon bei dem ersten Vertikalprofil gesehen haben.

Aus Diagramm 2 ist ersichtlich, dass in den Tonablagerungen von 1 320 cm Tiefe an abwärts bis 14 m die Salzwasserdiatomeen recht individuenreich vorkommen und ihr Prozentsatz sogar in einigen Proben auf 38 % steigt.

Von den Salzwasserformen finden sich in den Sedimenten *Achnanthes brevipes, Campylodiscus echeneis, Cocconeis scutellum, Coscinodiscus radia-*

tus, Diploneis interrupta, D. Smithii, D. Stroemi, Grammatophora oceanica, Hyalodiscus scoticus, Melosira Westii, Pyxidicula minuta, Rhabdonema arcuatum, Thalassiosira decipiens und *Thalassionema nitzschioides* oder insgesamt 14 Arten. Diese Salzwasserdiatomeen kommen ganz gewöhnlich in den Litorina- und Yoldiaablagerungen oder nach Hyyppä in den Sedimenten des Bottnischen Meeres vor. Trotztdem in diesen Sedimenten insgesamt 14 Arten festgestellt worden sind, kommen folgende Arten eigentlich so reichlich vor, dass nur sie tonangebend sind, und zwar *Grammatophora oceanica, Hyalodiscus scoticus, Melosira Westii, Rhabdonema arcuatum* und *Thalassionema nitzschioides* oder nur 5 Salzwasserdiatomeen.

An Brackwasserdiatomeen finden sich in den obengenannten Sedimenten *Achnanthes taeniata, Coscinodiscus lacustris, C. lacustris v. septentrionalis, Synedra tabulata* und *Thalassiosira baltica* oder insgesamt nur 5 Arten und Varietäten, die in der Probe 142 ihr Maximum mit 43.5 % erreichen. Diese Diatomeenflora reicht bis zu der Probe 135, von den an aufwärts treten mehr die zufälligen Arten hervor und die obengenannten häufig vorkommenden Arten verschwinden. Die Sedimente von 1 310 cm an abwärts bis 14 m Tiefe sind während des Yoldiameerstadiums oder nach Hyyppä während des Bottnischen Meerstadiums abgesetzt worden. Nach den Diatomeen enthielte das Meerwasser in jener Zeit 5 bis 12 $^0/_{00}$ Salz (Diagr. 2). Damals waren die Wachstumsbedingungen für die Diatomeen nicht die ganze Zeit gleich gut. Es kamen grössere Veränderungen vor, wie wir in Probe 141 beobachten können.

Betrachten wir nebenstehendes Baumpollenprofil, dann sehen wir, dass in diesen Sedimenten Edellaubbäume reichlich vorkommen und erst in den obersten Ablagerungen, aus denen die Proben 134 und 135 entnommen worden sind, zurückgehen. Auch die Baumpollen bestätigen, dass wir es mit den Yoldiasedimenten zu tun haben.

Von 1 310 cm Sedimenttiefe an aufwärts kommt in den Sedimentproben eine ganz neue und von der früheren abweichende Diatomeenflora vor, die unter ganz anderen ökologischen Bedingungen gediehen ist. An Salzwasserformen finden sich in den untersten Schichten zufällig nur einzelne Individuen *Cocconeis scutellum, Grammatophora oceanica, Hyalodiscus scoticus, Nitzschia apiculata, N. sigma, Rhabdonema arcuatum* und *Thalassionema nitzschioides,* die alle Überbleibsel aus der Yoldiazeit sind. Wie man aus Diagramm 2 ersieht, machen sie nur einige Prozent aller in diesen Proben vorkommenden Diatomeen aus.

Interessanterweise gehen die Brackwasserdiatomeen in diesen Sedimenten noch mehr zurück als die Salzwasserdiatomeen. Man findet sehr selten *Synedra tabulata* und *Thalassiosira baltica,* während alle anderen Arten verschwinden sind. Beinahe ähnlich kommen die Süss- und Brackwasserformen vor, von denen nur *Epithemia turgida, Gyrosigma attenuatum* und *Rhoicosphenia curvata* selten in den Proben enthalten sind.

Von den Süsswasserdiatomeen findet man in den Sedimenten *Cyclotella* *comta, C. Kützingiana, Cymatopleura elliptica, C. solea, Melosira ambigua, M. arenaria, M. distans, M. granulata, M. islandica ssp. helvetica, Stephanodiscus astraea, S. astraea v. minutula* und *Tabellaria fenestrata* oder insgesamt nur 12 Arten und Varietäten. Alle obengenannten Diatomeen kommen rezent in den Binnenseen Finnlands vor, und ebenso hat man diese Formen in den Ancylusseesedimenten gefunden. Die obengenannten Süsswasserdiatomeen einerseits und das Zurückgehen der Salz- und Brackwasserdiatomeen andererseits bestätigen, dass diese Sedimente von 1 160 bis 1 310 cm Sedimenttiefe während der Ancylusperiode abgelagert worden sind. In den obersten Schichten fehlen die Salz- und Brackwasserdiatomeen vollständig und die Süsswasserformen machen 100 % aller in den Proben vorkommenden Diatomeen aus (Diagr. 2). Die Salzkonzentration des Wassers konnte während dieser Zeit zwischen 0 und 4 ‰ schwanken, am Anfang mehr und am Ende weniger.

Betrachtet man das Vorkommen der Baumpollen, dann sieht man, dass *Alnus* sowie die Edellaubbäume in diesen Sedimenten sehr selten auftreten, wie überhaupt in den Ancylussedimenten. *Pinus*-Pollen dagegen kommt sehr reichlich in den Proben vor, und wie man aus Diagramm 2 ersieht, treten sie noch in den darauf liegenden Sedimenten ebenso reichlich hervor. Auch haben in den obersten Sedimenten, die auf den Ancylusseesedimenten liegen, die Edellaubbäume nicht besonders zugenommen, so dass wir auch hier dieselbe Erscheinung sehen, die wir schon bei Tervajoki gesehen haben, dass die Bäume sich nicht so schnell verändern und nicht so gut reagieren, wie das die Diatomeen getan haben.

Von Probe 120 an aufwärts kommen die Salzwasser- sowie Brackwasserdiatomeen in den Sedimenten wieder vor. Man findet von den Salzwasserformen *Campylodiscus clypeus, C. echeneis, Cocconeis scutellum, Coscinodiscus radiatus, Diploneis didyma, D. interrupta, D. Smithii, Grammatophora oceanica, Hyalodiscus scoticus, Rhabdonema arcuatum* und *Thalassionema nitzschioides* oder insgesamt 11 Arten. Vergleichen wir diese Diatomeen mit den im Vertikalprofil bei Tervajoki in den untersten Litorinasedimenten vorkommenden Formen, dann sehen wir, dass in beiden Profilen fast dieselben Salzwasserformen vorhanden sind.

Unter der Brackwasserdiatomeen findet man *Achnanthes taeniata, Coscinodiscus lacustris, Epithemia turgida v. Westermanni, Mastogloia Smithii, M. Smithii v. amphicephala, Synedra tabulata* und *Thalassiosira baltica*, die beinahe alle auch bei Tervajoki im Litorina I vorhanden waren.

Die Süsswasserdiatomeen gehen in den Proben so zurück, dass sie in nur vereinzelnen Individuen anzutreffen sind. Als neue Formen finden sich *Achnanthes linearis, Diploneis elliptica, D. puella, Eunotia alpina, Pinnularia borealis* und *Synedra acus*, die alle selten festgestellt worden sind.

Auf Grund der Diatomeenflora haben sich Sedimente von 1 040 bis 1 160 cm Tiefe während Litorina I abgesetzt, denn wie aus Diagramm 2 gut ersichtlich, haben wir es mit einer ökologischen Entwicklungsperiode zu tun, in der das Wasser langsam salzhaltiger und wieder süsser geworden ist. Diese Veränderungen könnten nur durch äussere Bedingungen hervorgerufen sein, denn es ist undenkbar dass in einem Wasser mit gleicher Salzkonzentration die Salzwasserdiatomeen von selbst verschwanden, wie wir das in den Sedimenten sehen, in denen die Grenze zwischen Litorina I und II im Diagramm 2 gezogen worden ist. Bei Hulmi haben die Diatomeen eine beinahe ähnliche Entwicklung durchgemacht, wie wir das bei Tervajoki früher schon gesehen haben (vergl. Diagr. 1 und 2).

Bei den Baumpollen in Diagramm 2 können wir keine so scharfe Veränderung feststellen wie bei den Diatomeen. Wohl steigt der Prozentsatz der Edellaubbäume und der Erle etwas, aber der Unterschied ist eigentlich sehr klein. Ebenso geht *Pinus* nicht zurück, wie man erwarten kann, trotztdem wir es mit Litorina I zu tun haben.

Von 1 040 cm Tiefe an aufwärts steigt der Anteil der Brackwasserdiatomeen, und in Probe 101 machen sie schon 80.5 % aus. Ebenso nehmen die Salzwasserdiatomeen zu, erreichen aber grössere Individuenzahlen etwas später als die Brackwasserdiatomeen (Diagr. 2). Unter diesen tritt *Coscinodiscus lacustris v. septentrionalis* sehr individuenreich hervor, erreicht in der Probe sogar 38 % aller Diatomeen, was eigentlich sehr gross ist. Unter den Salzwasserdiatomeen kann man keine grössere Veränderung feststellen, und die obengenannten Formen kommen mehr oder weniger häufig vor. Diese Periode, die wir Brackwasserperiode nennen können, dauert so lange, bis sich die Sedimente in 870 cm Tiefe abgesetzt haben. Diese Periode ist als Litorina II bezeichnet worden, denn sie weicht ökologisch von den älteren sowie jüngeren Perioden ganz bedeutend ab.

Am Anfang von Litorina II treten auch Edellaubbäume sowie *Alnus* bedeutend reichlicher auf, als wir das in den älteren Sedimenten gesehen haben, ausser in den Yoldiasedimenten. Ebenso geht der Prozentsatz des *Pinus*-Pollens in dieser Periode sehr zurück und bleibt während der Litorinazeit mehr oder weniger gleich gross.

Von 870 cm Sedimenttiefe an aufwärts nehmen die Salzwasserdiatomeen langsam zu und die Brackwasserdiatomeen ab, an einigen Stellen kleinere Schwankungen aufweisend. Die Salzwasserformen erreichen ihren maximalen Individuenreichtum in den Proben 72 und 79, wo sie allein 84.5 und 82 % aller in diesen Proben vorkommenden Diatomeen ausmachen. Eigenartig in diesen beiden Proben kommt *Thalassionema nitzschioides* vor oder, richtiger gesagt, bildet hier eine *Thalassionema*-Flora. So macht sie in der ersten 67 und in der zweiten Probe 54.5 % aus. Warum gerade diese Diatomee in den genannten Zeiträumen so gut gediehen ist, lässt sich unmöglich sagen. An Brackwasserformen findet man in den Proben nur *Achnanthes taeniata*, *Synedra tabulata* und *Thalassiosira baltica*, die grössere oder kleinere Individuenzahlen erreichen. Der Anteil der Salzwasserformen dagegen ist viel grösser, und man findet viele neue

Arten, die in Litorina I und II fehlen. Von diesen Arten sind zu nennen *Achnanthes brevipes, Actinocyclus Ehrenbergi, Coscinodiscus excentricus, C. oculus iridis, Diploneis Stroemi, Navicula peregrina, Nitzschia apiculata, Pyxidicula minuta, Rhabdonema minutum, Stephanopyxis turris* und *Thalassiosira decipiens* oder insgesamt 11 Arten, die in den Sedimenten recht selten verbreitet sind.

Diese einförmige Diatomeenflora dauerte bis in 560 cm Tiefe, aus der die Probe 60 erbohrt ist. Erst an dieser Stelle treten die Süsswasserdiatomeen plötzlich sehr reichlich hervor, und wie man sicher nach den Diatomeen schliessen kann, ist das durch eine äusserliche Veränderung hervorgerufen worden. Diese einförmige Diatomeenflora aus den Sedimenten von 560 bis 870 cm Tiefe ist als Litorina III bezeichnet worden, und das Seewasser in dem damaligen Litorinasee sollte 10 bis 20 $^0/_{00}$ Salz enthalten haben, oder ist ungefähr ebenso salzhaltig gewesen wie bei Tervajoki während dieser Zeit.

Von 560 cm Tiefe an aufwärts bis zu 370 cm Tiefe machen die Diatomeen wieder eine Entwicklungsperiode durch. In den untersten Ablagerungen treten die Salzwasserdiatomeen recht individuenarm hervor, nehmen aber langsam zu und erreichen ihren maximalen Individuenreichtum in Probe 46 in 420 cm Sedimenttiefe, wo sie sogar 59.5 % aller in dieser Probe gefundenen Diatomeen ausmachen (Diagr. 2). Von dieser Probe an aufwärts nehmen die Salzwasserformen wieder langsam ab, bis sie in der Probe 41 aus 370 cm Tiefe auf 19.5 % sinken. Bei den Brackwasserformen sieht man keine Veränderungen im Vorkommen, dagegen bei den Süsswasserdiatomeen sinkt ihr Prozentsatz einigermassen und bleibt die ganze Zeit derselbe.

Unter den Salzwasserformen finden sich sehr selten in einigen Proben als neue Arten *Diploneis Smithii, Melosira moniliformis, Navicula digitoradiata, N. humerosa, N. palpebralis v. angulosa, Nitzschia apiculata, N. granulata, Stephanopyxis turris v. arctica* und *Tropidoneis lepidoptera* oder insgesamt 9 Formen. Sonst kommen die anderen schon früher genannten Salzwasserdiatomeen mehr oder weniger reichlich in den Sedimenten in dieser Tiefe vor. Diese Periode, während welcher Zeit sich die Sedimente von 370 bis 560 cm Sedimenttiefe abgesetzt haben, ist als Litorina IV bezeichnet worden, und die Salzkonzentration schwankte damals im Wasser zwischen 10 und 15 $^0/_{00}$ oder war etwas kleiner als in der Zeit, als die Salzwasserformen im Litorina III ihren maximalen Individuenreichtum hatten. Wie man aus Diagramm 2 im Baumpollenprofil ersieht, reagieren die Baumpollen überhaupt nicht, daher können wir die einzelnen Litorinaperioden nicht unterscheiden.

Von 370 cm Tiefe an aufwärts finden wir wieder eine Entwicklungsperiode, in der die Salzwasserdiatomeen grössere und kleinere Schwankungen durchmachen. Diese Periode dauert bis dahin, wo Probe 20 aus 160 cm Tiefe erbohrt worden ist, und diese Periode habe ich Litorina V genannt. Von den Salzwasserformen in diesen Sedimentablagerungen sind zu nennen *Actinocyclus Ehrenbergi*, *Campylodiscus echeneis*, *Grammatophora marina* und *Rhabdonema minutum*, die hier etwas häufiger verbreitet sind. Unter den Brackwasserdiatomeen finden sich sehr selten *Achnanthes Hauckiana*, *Mastogloia Smithii* und *Nitzschia tryblionella v. levidensis*, die man auch sonst sehr selten angetroffen hat.

Von Probe 20 an aufwärts finden wir noch eine Entwicklungsperiode unter den Diatomeen, in der die Salzwasserdiatomeen in 120 cm Tiefe ihren maximalen Individuenreichtum erreichen. Neue Formen findet man unter den Salzwasserformen nicht, aber wie man aus Diagramm 2 ersieht, machen die Diatomeen zwischen 80 und 160 cm Tiefe eine ökologische Periode durch. Diese Periode ist als Litorina VI bezeichnet worden und das Meereswasser enthielt in jener Zeit 10 bis 15 $^0/_{00}$ Salz.

Wenn man das Profil der Baumpollen betrachtet, ist zu erkennen, dass die Baumpollen in 80 cm Tiefe oder an der Stelle, wo das Litorina endet, eine grössere Veränderung durchmachen. Die Edellaubbäume verschwinden, und *Picea* nimmt dagegen recht viel zu. Ebenso geht *Pinus*, die zu dieser Zeit im Litorina noch recht häufig vorgekommen ist, so sehr zurück, dass sie etwas über 10 % aller Baumpollen ausmacht.

Von 80 cm Sedimenttiefe an aufwärts bis zu der Oberfläche kommt in den Sedimenten eine ganz andere Diatomeenflora vor. Unter den Salzwasserformen sieht man sehr selten *Campylodiscus echeneis*, *Cocconeis scutellum*, *Dimerogramma fulvum*, *Diploneis Smithii* und *Navicula peregrina*, und häufig findet man *Grammatophora marina*, *G. oceanica* und *Rhabdonema arcuatum*, die aber nicht so grosse Individuenzahlen erreichen wie in den Litorinasedimenten.

An Brackwasserdiatomeen finden sich in diesen obengenannten Sedimentablagerungen *Achnanthes taeniata*, *Bacillaria paradoxa*, *Nitzschia tryblionella*, *Synedra tabulata* und *Thalassiosira baltica*, die ebenso sehr selten vorkommen, wie wir das schon bei den Salzwasserdiatomeen gesehen haben.

Bei den Süsswasserdiatomeen finden wir eine recht grosse Veränderung. Unter diesen sieht man *Achnanthes Biasolettiana*, *Asterionella formosa*, *Cymatopleura elliptica*, *C. solea*, *Cymbella naviculiformis*, *Diploneis domblittensis v. subconstricta*, *D. elliptica*, *Eunotia alpina*, *E. Clevei*, *E. diodon*, *E. exigua*, *E. faba*, *E. formica*, *E. lunaris*, *E. lunaris v. subarcuata*, *E. pectinalis*, *E. pectinalis v. minor* und *v. ventralis*, *E. praerupta*, *E. robusta v. tetraodon*, *E. triodon*, *E. veneris*, *Fragilaria virescens*, *Frustulia rhomboides*, *Gomphonema acuminatum*, *G. constrictum*, *G. gracile*, *G. parvulum*, *Hantzschia amphioxys*, *Navicula pupula*, *Neidium bisulcatum*, *Pinnularia borealis*, *P. esox*, *P. gentilis*, *P. gibba*, *P. interrupta*, *P. leptosoma*, *P. mesolepta f. angusta*, *P. polyonca*, *P. stomatophora*, *P. subcapitata*, *P. viridis*, *Synedra ulna* und *Tabellaria flocculosa* oder alle solche Arten und Varietäten, die heutzutage in Finnland in kleinen Gewässern sehr verbreitet sind. Auf Grund dieser Diatomeenflora lässt sich ohne Zweifel sagen dass Hulmi, wo die Proben erbohrt worden sind, damals vom Meere abgeschnürt worden ist, als sich die Sedimente in 80 cm Tiefe abgesetz haben.

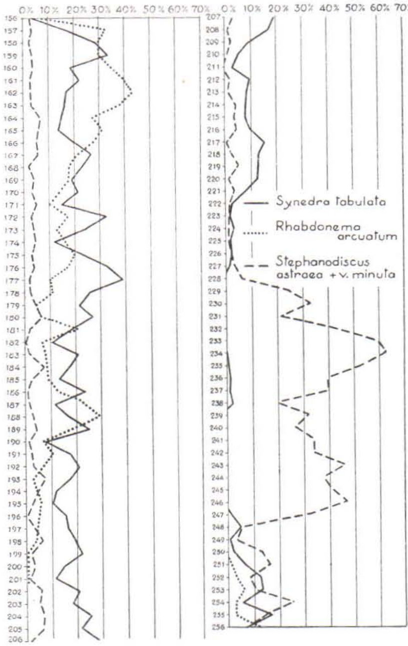
Diese Abschnürungszeit können wir auf Grund der Diatomeen nicht feststellen, denn in allen abgeschnürten Wasserbecken fangen die obengenannten Süsswasserformen an zu gedeihen. Diese Abschnürung können wir aber auf Grund der Baumpollen in Diagramm 2 feststellen. Nach ihnen können wir sicher sagen, dass die Abschnürung bei Hulmi am Ende der Litorinazeit vor sich gegangen ist, denn das Postlitorina fängt dann an, wenn die Edellaubbäume nicht mehr vorkommen (Sauramo 1940). Ebenso tritt *Picea* während der Postlitorinazeit viel reichlicher hervor als in den Litorinasedimenten, was seinerseits die Abschnürungszeit bestätigt.

Bei gegenseitigem Vergleich der Profile aus Tervajoki und Hulmi ist zu ersehen, dass sie recht ähnlich sind. Bei Hulmi ist das Postlitorina vorhanden, was bestätigt, dass am Ort und Stelle während dieser Zeit noch Wasser und bei Tervajoki trockenes Land vorhanden waren. Diese beiden Vertikalprofile zeigen uns, dass man auf Grund der Diatomeen, die in den Sedimenten vorkommen, über die Ökologie der Vorzeiten gute Resultate erhalten kann, wenn die Sedimentation an der betreffenden Stelle ununterbrochen vor sich gegangen ist. Je dicker die Ablagerungen sind, desto genauer kann man die ökologischen Bedingungen der Vorzeiten feststellen, denn dann lassen sich die kleineren Schwankungen genauer verfolgen, wie wir das bei Tervajoki und Hulmi gesehen haben (Diagr. 1 und 2).

DAS VORKOMMEN DER EINZELNEN DIATOMEEN IN DEN VERTIKALPROFILEN AUS TERVAJOKI UND HULMI

Im obigen haben wir betrachtet, wie die Salzwasser-, Brackwasser-, Süss- und Brackwasser sowie Süsswasserdiatomeengruppen in den Vertikalprofilen aus Tervajoki und Hulmi vorkamen. Es ist noch interessanter zu verfolgen, wie die einzelnen Diatomeenarten in ihnen gedeihen konnten. Schwierigkeiten macht nur die Tatsache, dass es sehr wenig Arten gibt, die so grosse Individuenzahlen erreichten und in allen Proben vorkommen, dass man eine Übersicht über die Verhältnisse und die Ökologie erhalten kann.

Obschon die Süsswasserdiatomeen in allen Sedimentproben in den Vertikalprofilen vorkommen, treten die einzelne Arten ganz eigenartig hervor. Beobachten wir zuerst das Vorkommen von *Stephanodiscus astraea und v. minutula,* die graphisch in Diagramm 3 wiedergegeben sind. Diese in den Ancylusseesedimenten in Finnland sehr verbreitete Süsswasserdiatomee tritt im Vertikalprofil bei Tervajoki fast in allen Sedimentschichten sehr selten hervor, erreicht aber ihren maximalen Individuenreichtum in den Sedimenten, denen die Proben 230—246 entnommen worden sind. Wie wir früher gesehen haben, sind gerade diese Sedimente während der Ancylusperiode abgesetzt worden. Auch das Vorkommen dieser Süsswasserdiatomee in den betreffenden Sedimenten bestätigt seinerseits, dass diese Sedimente ganz sicher im Ancylussee sedimentiert worden sind.



Diagr. 3.

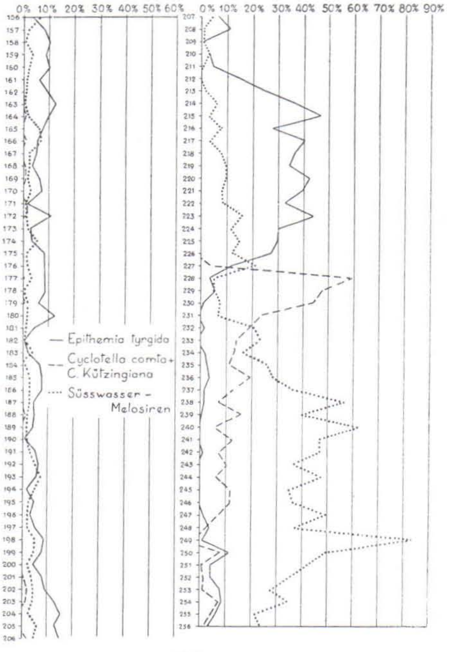
Betrachten wir jetzt das Vorkommen der Süsswasser-Melosiren in Diagramm 4, dann sehen wir, dass auch sie beinahe ähnlich, wie *Stephanodiscus astraea* in dem Vertikalprofil aus Tervajoki vorkommen. Ein Unterschied liegt nur darin, dass die Melosiren ihr Maximum etwas früher erreichen oder in Probe 249, wenn *Stephanodiscus* noch sehr spärlich vorhanden ist.

Ganz anders als die oben beschriebenen Formen kommen *Cyclotella comta und C. Kützingiana* vor (Diagr. 4). Man findet diese Diatomeen vom Yoldia bis zum Ende des Ancylus, danach aber verschwinden sie in den Litorinasedimenten vollständig. Ihre maximale Entwicklung erreichen sie erst dann, wenn Melosiren und *Stephanodiscus* kulminiert haben oder erst am Ende der Ancyluszeit.

Jetzt betrachten wir, wie die in Finnland überall in den Yoldia- sowie Litorinasedimenten und auch rezent an den Meeresküsten verbreitete Salzwasserdiatomee *Rhabdonema arcuatum* in dem Vertikalprofil aus Tervajoki vorkommt. Wie aus Diagramm 3 ersichtlich, tritt diese Diatomee individuenreich in den obersten Litorinameersedimenten auf, erreicht aber ihr Maximum erst in der Probe 162 in 70 cm Tiefe. Man findet sie noch in den Yoldiasedimenten, wo sie aber nicht so grosse Individuenzahlen aufweist. Ähnlich wie die obengenannte Diatomee kommen die Salzwasserdiatomeen *Cocconeis scutellum, Grammatophora oceanica, Hyalodiscus scoticus* und *Thalassionema nitzschioides* vor, erreichen aber nicht so grosse Individuenzahlen. Ganz eigenartig kommt *Grammatophora marina* vor. Sie erscheint erst in den Sedimenten von Litorina VI, findet aber keine besonders guten Entwicklungsbedingungen im Seewasser.

Ganz anders als die Salzwasserdiatomeen treten die Brackwasserdiatomeen im Vertikalprofil auf. So kommt *Synedra tabulata* fast ähnlich in allen Sedimentschichten während der Litorina- und Yoldiazeit vor, grössere oder kleinere Schwankungen durchmachend (Diagr. 3). Sie kommt schon in den ältesten Litorinasedimenten vor, während die obengenannten Salzwasserformen in diesen nicht vorhanden sind. Ähnlich wie *Synedra tabulata* finden sich die Brackwasserdiatomeen *Coscinodiscus lacustris v. septentrionalis* und *Thalassiosira baltica* im Vertikalprofil, erreichen aber nicht so grosse Individuenzahlen wie die erstgenannte Diatomee.

Wenngleich die Süss- und Brackwasserdiatomeen in dem Vertikalprofil in allen Proben mehr oder weniger gleichmässig vorkommen, treten die einzelnen zu dieser Gruppe gehörenden Arten ganz eigenartig auf. So sieht man in Diagramm 4 *Epithemia turgida*, die während Litorina I ihre maximalen Individuenzahlen erreicht und bei den anderen Sedimenten von Litorina und Yoldia recht selten in den Proben anzutreffen ist. Wie man sieht, tritt sie in den Ancylussedimenten beinahe überhaupt nicht hervor. In Litorina I sind auch die zu dieser Gruppe gehörenden Arten *Amphora ovalis*, *Epithemia zebra*, *Rhoicosphenia curvata*, *Rhopalodia gibba* und *Synedra pulchella* reichlich anzutreffen, aber auch in den anderen Teilen des Vertikalprofils nicht fehlend.

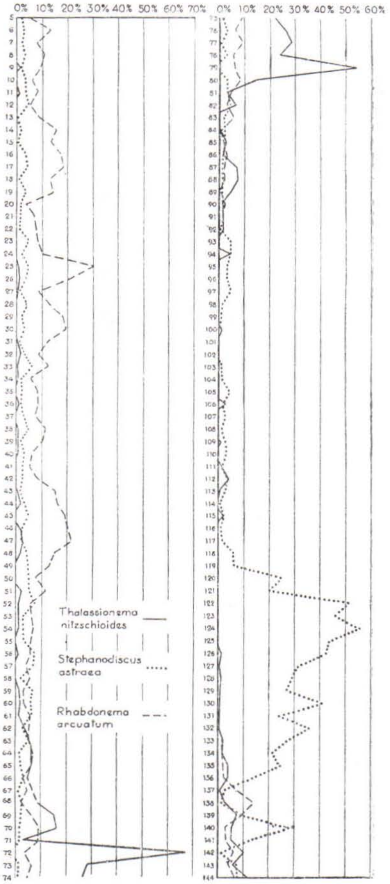


Diagr. 4.

Jetzt ist es interessant, näher zu betrachten, wie die einzelnen Diatomeenarten im Vertikalprofil bei Hulmi vorkommen, da die beiden Profile sehr ähnlich sedimentiert sind und ähnliche Diatomeenfloren enthalten, wie wir das schon oben gesehen haben. Zuerst betrachten wir die Süsswasserdiatomee *Stephanodiscus astraea*, die in Diagramm 5 graphisch dargestellt ist. Wie man sieht, kommt sie fast in allen Sedimentschichten sehr selten vor, erreicht aber ihre besten Entwicklungsbedingungen erst in den Sedimenten, denen die Proben 120—135 entnommen worden sind. Vergleichen wir jetzt Diagr. 5 mit Diagr. 2, dann sehen wir, dass diese Proben, in denen *Stephanodiscus astraea* das Maximum erreicht, aus den Ancylussedimenten erbohrt sind. In Diagr. 3 haben wir schon festgestellt, dass diese charakteristische Ancylusseediatomee auch bei Tervajoki in den Ancylusseesedimenten ebenso wie auch bei Hulmi ihre maximale Entwicklung erreicht hat.

Cyclotella comta und *C. Kützingiana* kommen nur in den Sedimenten vor, denen die Proben 118—137 entnommen worden sind und die zu den Ancylusseesedimenten gehören. Ihr Maximum erreichen sie auch hier ebenso wie bei Tervajoki am Ende der Ancyluszeit oder in Probe 120, an Stelle, wo die Grenze zwischen Ancylus und Litorina I gezogen ist (Diagr. 2, 4 und 6).

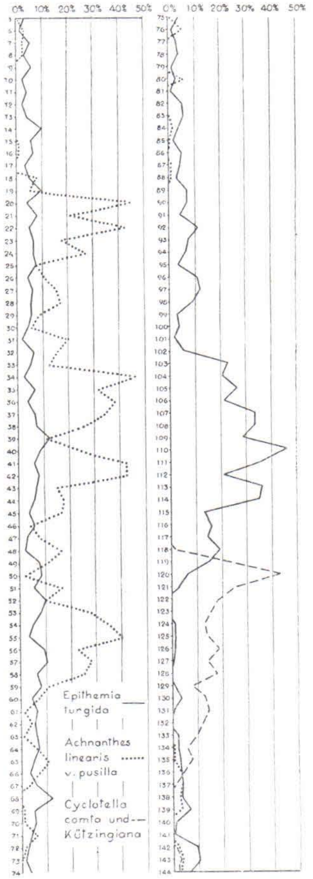
Ausser den obengenannten Süsswasserdiatomeen finden sich in den Ancylusseesedimenten häufig *Cymatopleura elliptica, C. solea, Diploneis domplittensis, Melosira arenaria* und *Tabellaria fenestrata,* die in den anderen Sedimentschichten beinahe nicht oder sehr vereinzelt erscheinen. Alle diese Süsswasserdiatomeen bestätigen ihrerseits, dass wir es in 1 160 bis 1 310 cm Sedimenttiefe mit den Ancylusseesedimenten zu tun haben.



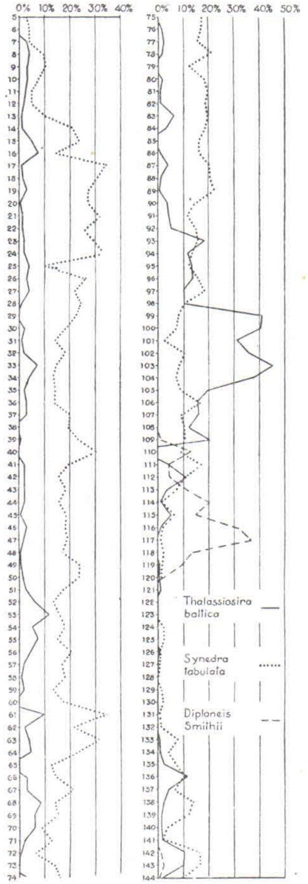
Diagr. 5.

Die Salzwasserdiatomee *Rhabdonema arcuatum* kommt im Vertikalprofil in den Yoldiasedimenten und in den obersten Schichten der Litorinasedimente reichlich vor, fehlt aber in den Ablagerungen von Litorina I und II, wie wir das schon bei Tervajoki gesehen haben (Diagr. 5). Ganz anders kommt die Salzwasserdiatomee *Diploneis Smithii* in den Sedimenten vor. Sie tritt nur in Litorina I auf und fehlt in allen anderen Sedimenten ausser Yoldia, wo sie in den Proben 142—144 sehr selten gefunden worden ist (Diagr. 7). Ebenso eigenartig zeigt sich *Thalassionema nitzschioides* im Vertikalprofil. Sie erreicht ihre maximalen Individuenzahlen in den Proben 72 und 79, die beide zu den Sedimenten von Litorina III gehören (Diagr. 2 und 5). In den anderen Sedimentschichten erscheint diese Diatomee ebenfalls, erreicht aber nicht so grosse Individuenzahlen wie in diesen beiden obengenannten Proben. Ökologisch ist es unerklärbar, warum diese Diatomee plötzlich so gute Entwicklungsbedingungen gefunden hat, dass sie so individuenreich vorkommen kann. Heutzutage sind ähnliche Erscheinungen von den Küsten Finnlands nicht bekannt.

Die rezent im Plankton des Finnischen und Bottnischen Meerbusens häufig anzutreffende Brackwasserdiatomee *Thalassiosira baltica* kommt fast in allen Sedimentschichten des Litorina- und Yoldiameeres vor, erreicht aber gute Wachstumsbedingungen in Litorina II, wo sie ihr Maximum in 990 cm Sedimenttiefe erreicht (Diagr. 7). *Synedra tabulata,* die auch zu den Brackwasserformen gehört, kommt wieder in ganz anderer Weise im Vertikalprofil vor als *Thalassiosira baltica*. Man findet sie beinahe in allen Sedimentschichten, abgesehen von einem recht dünnen Teil der Ancylusseesedimente, in dem sie überhaupt nicht gefunden worden ist. Wie aus Diagramm 7 zu entnehmen, reagiert diese Diatomee auf die ökologischen Veränderungen nicht so gut wie die oben beschriebenen Arte, die an einigen Stellen grosse Individuenzahlen aufweisen. Es ist aber auch möglich, dass *Synedra tabulata* keine guten Wachstumsbedingungen gefunden hat und deshalb so regelmässig vorkommt.



Diagr. 6.



Diagr. 7.

Im Vertikalprofil bei Hulmi kommt *Epithemia turgida* fast ähnlich vor, wie wir das schon bei Tervajoki gesehen haben (Diagr. 4 und 6). Den maximalen Individuenreichtum erreicht sie in Litorina I, und er setzt sich noch bis in das Litorina II weiter, von wo an aufwärts diese Art schnell abnimmt und dann bis zu den obersten Proben recht selten vorkommt.

Ebenso findet man sie recht selten in den Yoldiasedimenten, und in den Ancylusseesedimenten verschwindet sie völlig in einigen Proben.

Ganz eigenartig tritt *Achnanthes linearis v. pusilla* hervor (Diagr. 6). Man findet sie häufig in den Sedimenten von Litorina IV und V, wo sie manchmal beträchtliche Individuenmengen erreicht. Von Litorina IV an abwärts kommt sie sehr selten vor und in Litorina I und II fehlt sie ganz. Sehr selten sieht man diese Diatomee noch in den Yoldia sedimenten, aber wie man aus den ermittelten Zahlen schliessen kann, hat sie im Yoldiameer keine guten Wachstumsbedingungen gefunden.

Zusammenfassend kann man sagen, das Vorkommen der einzelnen Diatomeenarten in den Vertikalprofilen bei Tervajoki und Hulmi haben sehr übersichtlich gezeigt, dass die ökologischen Wachstumsbedingungen während der verschiedenen geologischen Perioden (Litorina I—VI) ganz voneinander abweichend gewesen sind und dass die einzelnen Arten uns bei den geologischen Einteilungen der Sedimente in den Vertikalprofilen starkunt erstützen. Auch zeigen sie durch das Vorkommen, wann die Sedimentierung an Ort und Stelle ununterbrochen vor sich gegangen ist und wann Unterbrechungen eingetreten sind.

VERGLEICH DER RESULTATE MIT DEN ERGEBNISSEN ANDERER FORSCHER·

Wie schon in der Einleitung angeführt, hat Aarnio ein Profil in Tervajoki erbohrt und Astrid Cleve-Euler die Diatomeen der Sedimente bestimmt. Wenn wir die beiden Profile aus Tervajoki miteinander vergleichen, ist ersichtlich, dass sie in den grossen Zügen übereinstimmen. Cleve-Euler hat in den untersten Sedimenten aus 770—800 cm Tiefe nur *Thalassiosira baltica* gefunden, die auch in dem von mir erbohrten Vertikalprofil in den untersten Sedimentschichten vorkommt, aber etwas häufiger, als Cleve-Euler ermittelt hat. Nach meiner Ansicht gehört diese Periode, in der die im Vertikalprofil dargestellten untersten Sedimentschichten sich abgesetzt haben, zum Yoldia oder, genauer gesagt, zur Rhabdonemazeit. Auch in dem von Aarnio erbohrten Vertikalprofil gehören diese untersten Sedimente, in denen *Thalassiosira baltica* vorkommt, zur Yoldiazeit.

Auf diese Sedimente folgen Schichten, in denen Cleve-Euler Ancylusseediatomeen festgestellt hat, die auch in meinem Profil in den Ancylusseesedimenten häufig vorkommen. Bei Betrachtung der beiden Artenlisten, ist zu erkennen, dass fast 95 % der in beiden Profilen vorkommenden Ancylusseesedimentdiatomeen beiden gemeinsam sind.

Nach Cleve-Euler verändert sich die Diatomeenflora in 270—300 cm Tiefe langsam, und wir haben es mit einer Litorinameerdiatomeenflora zu tun. Ebenso ist die Diatomeenflora in meinem Profil aus Ancylus- in Litorinaflora langsam übergangen, und alle von Cleve-Euler gefundene Formen sind von mir festgestellt worden, zu denen sich aber noch viele gesellen, die sie nicht gefunden hat. Aus dem Obigen geht deutlich hervor, dass die Untersuchungsergebnisse über beide Vertikalprofile bei Tervajoki gut miteinander übereinstimmen und dass sich die untersten Sedimente während der Yoldiazeit im Yoldiameer abgesetzt haben. Hier ist nicht zu vergessen, dass der Ton an dieser Stelle, wo ich mein Vertikalprofil erbohrt habe, noch tiefer reicht, so dass an Ort und Stelle noch ältere Sedimente vorhanden sind als diejenigen, die in Diagramm 1 dargestellt sind.

Sehr interessant ist ein Vergleich meiner Ergebnisse mit dem Vertikalprofil aus Nurmo, dessen Diatomeen Cleve-Euler untersucht hat (Aarnio 1927, S. 25). In den Sedimenten aus 1 140—1 170 cm Tiefe soll nach Cleve-Euler reine Ancylusseeflora vorkommen. In diesen sowie 1 m höher liegenden Sedimenten treten wohl reine Süsswasserdiatomeen auf, die in 970—1 000 cm Tiefe langsam in Brackwasserdiatomeen übergehen, wo Süss-, Brack- und Salzwasserformen zusammen vorkommen. Etwa 1 m höher oder in 870—900 cm Tiefe ist nach Cleve-Euler reine Litorinaflora anzutreffen, in der Süsswasserdiatomeen überhaupt nicht mehr vertreten sind. So hat Cleve-Euler festgestellt, dass in diesen Schichten *Coscinodiscus septentrionalis, Grammatophora oceanica, Hyalodiscus scoticus, Melosira moniliformis, M. Juergensi, Synedra tabulata, Diploneis interrupta, Mastogloia Smithii v. amphicephala* usw. enthalten sind, die beinahe alle in den Profilen aus Tervajoki und Hulmi in den Yoldiasedimenten sowie in den Litorinasedimenten mehr oder weniger häufig vorkommen.

Diese obengenannte von Cleve-Euler bestimmte Diatomeenflora aus 870—900 cm Tiefe in Nurmo erinnert an die von mir in den oben dargestellten Vertikalprofilen aus den Yoldiasedimenten bestimmte Diatomeenflora, so dass wir es nach meiner Ansicht in 870—900 cm Sedimenttiefe bei Nurmo mit Yoldiasedimenten zu tun haben, aber nicht mit Litorinaflora, wie Cleve-Euler geäussert hat. Die in 1 140—1 170 cm Tiefe festgestellte Süsswasserdiatomeenflora ist älter als die Yoldiadiatomeenflora und gehört sicher, nach Hyyppäs (1943) Benennung, zu der Baltischen Eismeerflora. Da nach Aarnio der Moorbohrer nicht bis zum Grund durchzugehen vermochte und die Tonsedimente sich gleicherweise fortgesetzt haben, wie ich es bei Tervajoki und Hulmi gesehen habe, sind diese Tonsedimente noch älter als die Süsswasserdiatomeen, die Cleve-Euler aus den untersten Proben bestimmt hat.

Im Vertikalprofil bei Nurmo geht die Diatomeenflora nach Cleve-Euler in 770—800 cm Tiefe wieder in reine Ancylusseeflora über, in der *Cymatopleura elliptica, C. solea, Campylodiscus noricus v. hibernica, Caloneis latius-*

cula, Diploneis domplittensis, Melosira arenaria, Stephanodiscus astraea, S. astraea v. minutula, Eunotia Clevei, Epithemia Hyndmanni, E. turgida und andere Arten festgestellt worden sind. Diese Diatomeen habe ich auch in den beiden oben beschriebenen Vertikalprofilen in den Ancylusseesedimenten gefunden, und nach meiner Ansicht haben wir es auch bei Nurmo in 770—800 cm Tiefe mit Ancylusseesedimenten zu tun, die auf Yoldiasedimenten liegen.

Von 670 cm Tiefe an aufwärts hat Cleve-Euler eine Litorinadiatomeenflora gefunden, die sich in den verschiedenen Sedimenttiefen recht stark verändert oder an einigen Stellen mehr und an anderen weniger Süsswasser- sowie Salzwasserformen enthält. Bei Betrachtung der Diatomeenlisten dieser Schichten ist sogleich zu ersehen, dass in diesen grösstenteils dieselben Arten vorkommen, die ich in den Litorinasedimenten von Tervajoki und Hulmi gefunden habe. Sicher haben wir es bei Nurmo in diesen Tiefen mit Litorinasedimenten zu tun, in denen dieselben Schwankungen wie in den von mir oben beschriebenen Profilen vor sich gehen.

In den Sedimenten aus 220—250 cm Tiefe hat Cleve-Euler reichlich *Rhabdonema arcuatum* gefunden, und Aarnio hat diese Sedimente demgemäss als Rhabdonemagyttja bezeichnet (Aarnio 1927, S. 28). Auch bei Tervajoki und Hulmi kommt diese Salzwasserdiatomeen in den obersten Sedimentschichten des Litorinameeres sehr individuenreich vor, so dass damals dieselben ökologischen Wachstumsbedingungen in weiten Gebieten geherrscht haben als *Rhabdonema arcuatum* gut gediehen hat.

Wie schon in der Einleitung angeführt, hat Aario (1932, S. 125) auch die Baumpollen aus dem Vertikalprofil bei Nurmo untersucht, und die Ergebnisse sind in seiner Veröffentlichung in Figur 9 b graphisch wiedergegeben. Auf Grund der Baumpollen kommt er zu den Resultaten, dass die untere Salzwasserschicht in diesem Profil älter sein muss als die oberste und dass sie in die Yoldiazeit fällt. Selbstverständlich sind diese Sedimente, die unter den untersten Salzwasserdiatomeen liegen, noch älter und gehören nach Hyyppäs neueren Benennung in das Baltische Eismeerstadium, denn nach Hyyppä befanden sich damals in Finnland das Baltische Eismeer und nicht einzelne Baltische Eisseen, wie Sauramo glaubt.

Jetzt ist es interessant zu vergleichen, wie die Salzkonzentrationen von Tervajoki und Hulmi mit denen anderer Stellen übereinstimmen. Für einen Vergleich passt hier sehr gut die Untersuchung von Salmi (1944), der die Salzkonzentrationen aus einem Vertikalprofil bei Ruukki untersucht hat. Bei diesem Vergleich ist nicht zu vergessen, dass Ruukki ca. 25 km südlich der Stadt Oulu liegt sowie viel nördlicher als Tervajoki und Hulmi und dass das Wasser damals bei Ruukki ebenfalls weniger Salz enthalten hat, als es heutzutage im Bottnischen Meerbusen der Fall ist. Nach Salmi sollte das Wasser im Litorinameer von 5 bis 8 $^0/_{00}$ Salz enthalten haben, während meine Salzkonzentrationen zwischen 4 und

20 $^0/_{00}$ schwanken. Diese Resultate stimmen recht gut miteinander überein, denn bei Ruukki sind die Sedimentschichten viel dünner, so dass die Schwankungen überhaupt nicht so gut in die Erscheinung treten. Auch ist das Salzwasser von Süden bis nach Ruukki vorgedrungen, wo früher Süsswasser vorhanden war, weshalb die Salzmengen in den nördlichen Teilen selbstverständlich viel geringer gewesen sind und Salzwasserdiatomeen nicht in so grossen Mengen vorkommen können.

Vergleichen wir die Profile aus Tervajoki und Hulmi mit dem Vertikalprofil aus der Bucht Pieni Huopalahti in der Stadt Helsinki, dann ist zu ersehen, dass die Sedimente des Bottnischen Meeres bei Helsinki viele gleiche Diatomeen enthalten, wie z. B.: *Cocconeis scutellum, Coscinodiscus radiatus, Grammatophora oceanica, Rhabdonema arcuatum, Synedra tabulata, Thalassiosira baltica* u. a. Ebenso finden sich dieselben Formen in den Ancylus- und Litorinasedimenten. Der Unterschied liegt zum grössten Teil darin, dass die Salzkonzentration bei der Stadt Helsinki im Litorina- und Baltischen Eismeerstadium etwas grösser gewesen ist als bei Tervajoki und Hulmi (Mölder 1944, Diagr. 1). Dieselbe Erscheinung können wir in der Pojo-Bucht bei der Stadt Tammisaari sehen, wo Verfasser Vertikalprofile erbohrt hat (Mölder 1943, Diagr. 10). Aus dem Obigen geht hervor, dass das Meerwasser im Baltischen Eismeer, Yoldiameer und Litorinameer in Südfinnland mehr Salz enthalten hat und die Salzmenge nach Norden allmählich immer geringer wird. Da diese Stellen, wo die Vertikalprofile bei Tervajoki und Hulmi erbohrt worden sind, heutzutage nur 12 bis 14 m ü. M. liegen, waren sie in der Yoldia- und Litorinazeit recht tiefe Meeresbecken, wo das Wasser gewöhnlich viel mehr Salz enthielt als die in Ufernähe liegenden seichten Stellen; so kommen die Salzwasserdiatomeen auch in den Vertikalprofilen reichlicher vor, als in ufernahen seichten Wassersedimenten.

Aus dem Obigen lässt sich die Auffassung gewinnen, dass die Resultate nur auf Grund der Diatomeen überein stimmen und dass die Baumpollenprofile ganz andere Resultate geben können. Um dieser Frage weiter nachzugehen, werde ich hier die Baumpollenprofile aus Tervajoki und Hulmi mit dem Gesamtbaumpollenprofil aus dem Lehrbuch Sauramos (1940) vergleichen. Bei einem Vergleich der Yoldiazeitbaumpollen ist zu ersehen, dass die beiden von mir dargestellten Baumpollenprofile sehr gut mit Sauramos Gesamtbaumpollenprofil Übereinstimmen und dass die untersten Sedimente in meinen Profilen sicher zu den Yoldiasedimenten gehören. In den Ancylusseesedimenten kommt *Pinus* sehr reichlich, ihre maximalen Zahlen erreichend, während die Edellaubbäume fehlen. Derselben Erscheinung begegnen wir auch bei Tervajoki und Hulmi, wo *Pinus* in den Ancylussedimenten ihr Maximum hat und die Edellaubbäume so zurückgehen, dass sie im grossen ganzen verschwunden sind. Die Baumpollenprofile stimmen auch in den Ancyluszeiten sehr gut überein, und die geologische Zeiteinteilung ist von mir richtig durchgeführt worden.

In den Litorinasedimenten geht der *Pinus*-Pollen sehr weit zurück, und die Edellaubbäume sowie *Alnus* haben zugenommen oder, richtiger gesagt, erscheinen wieder. Dasselbe können wir auch in meinen obengenannten beiden Vertikalprofilen sehen, so dass ebenfalls die Litorinazeit von mir richtig festgestellt worden ist.

Vergleichen wir jetzt die Baumpollenprofile mit dem aus dem Moor Alasenjärvensuo im Gebiet Sotkamo, das von Kilpi (1937) untersucht und veröffentlicht worden ist. Im Baumpollenprofil des Alasenjärvensuo kommen ganz unten Yoldiasedimente vor, in denen *Betula* grössere Pollenzahlen hat und *Pinus* recht selten vertreten ist. In diesen Sedimenten tritt *Alnus* häufig hervor, und in einer Probe hat man sogar *Ulmus*-Pollen gefunden. Bei Tervajoki und Hulmi kommen die Baumpollen in den Vertikalprofilen gleicherweise vor, so dass die Yoldiasedimente mit der von Kilpi durchgeführten Einteilungen übereinstimmen. Ebenso stehen die Bestimmungen der Ancylus- und der Litorinasedimente miteinander im Einklang, so dass wir sagen können, dass die geologische Zeitbestimmung nach den Baumpollen richtig durchgeführt worden ist und so die Ergebnisse unterstützt, die man mittels der Diatomeen dieser Stellen erhalten hat. Dasselbe können wir feststellen, wenn wir die Baumpollenprofile mit dem aus dem Leppäsenneva im Kirchspiel Kihniö vergleichen, das von Aario (1932) untersucht und veröffentlicht worden ist. In Leppäsenneva kommen unter den untersten Sedimenten untersuchten Sedimenten noch dicke Schichten vor, die nach Aario Tonablagerungen sein sollen und so zu älteren Sedimenten gehören als diejenigen, die im Vertikalprofil dargestellt sind.

Ferner ist es interessant zu vergleichen, wie die obengenannten Ergebnisse über Süd-Pohjanmaa mit den Resultaten über Südfinnland übereinstimmen. Zum Vergleich sind die Baumpollenprofile der Moore Pienjärvi und Kämärä herangezogen worden, die Profile, die Hyyppä (1937, S. 15) erbohrt und veröffentlicht hat. Die Ergebnisse stimmen sehr gut miteinander überein und bestärken die Resultate, dass die in Süd-Pohjanmaa (Nurmo, Tervajoki, Laihia, Kihniö) erhaltenen Untersuchungsergebnisse gut mit den Ergebnissen aus Südfinnland im Einklang stehen und dass in Süd-Pohjanmaa alte Sedimente vorkommen, die sogar älter als die Yoldiasedimente sind.

Bis zu dieser Zeit haben wir die Untersuchungsresultate verglichen und gefunden, dass die Ergebnisse sehr gut übereinstimmen. Bei Betrachtung der von Sauramo 1934 veröffentlichten Karte des Yoldiameeres ist zu erkennen, dass das Landeis in der Yoldiazeit die von mir untersuchte Gegende bedeckt und weiter süd- und ostwärts gereicht hat, so dass nach Sauramo in Süd-Pohjanmaa keine Yoldiasedimente haben entstehen können. Zu denselben Resultaten kommt er auch in der 1936 erschienenen Darstellung in »Suomen maantieteen käsikirja».

Im Jahre 1940 veröffentlichte Sauramo ein Lehrbuch über die Quartärgeologie Finnlands, in dem er auf Seite 120 eine Karte von B V darstellt. Aus dieser Karte ist ersichtlich, dass das Landeis im Baltischen Eisseestadium V bis zum Salpausselkä II reichte und ganz Süd-Pohjanmaa bedeckte, so dass sich in diesem Gebiet keine Sedimente haben absetzen können. In demselben Lehrbuch findet sich auf Seite 124 eine Karte über Yoldia I, auf der das Landeis weite Strecken Finnlands bedeckt und die Stellen, wo die beiden Vertikalprofile von mir erbohrt worden sind, sowie Nurmo und Leppäsenneva unter dem Eise sehr weit vom dessen Rande entfernt liegen.

Nach den Untersuchungsergebnissen, die ich sowie andere Forscher über Süd-Pohjanmaa erhalten haben, war das Landeis an diesen Stellen im Yoldiazeit wie auch in den Baltischen Eisseestadien oder nach Hyyppä Baltischen Eismeerstadium verschwunden. Seine eigenartige Auffassung konnte Sauramo wahrscheinlich dadurch erhalten, dass er in diesen Gegenden keine Untersuchungen durchgeführt hat und die Warventone keine richtige Vorstellung von dem Rückzug des Landeises geben können, da die Konnektierung der einzelnen Warven verschiedener Stellen sehr unsicher ist, wie aus Sauramos Untersuchung »Geochronologische Studien über die spätglaziale Zeit in Südfinnland» hervorgeht. Will man an Ort und Stelle feststellen, wann die Gegend vom Landeis befreit worden ist, so sind die betreffenden Sedimente gründlich zu untersuchen, und erst auf Grund der Baumpollen- und Diatomeenprofile lässt sich aussagen, welche geologische Perioden an diesen Stellen vertreten sind.

Schon in meiner Untersuchung »Das Karelische Eismeer im Lichte der fossilen Diatomeenfunde» habe ich geschrieben, dass das Karelische Eismeer über den Oulunjärvi bis zum Bottnischen Meerbusen gereicht hat und dass diese Gebiete, aus denen die obengenannten Vertikalprofile stammen, viel früher vom Landeis befreit gewesen sind, als Sauramos Untersuchungen ergeben haben.

LITERATURVERZEICHNIS

AARIO, L., 1932, Pflanzentopographische und paläogeographische Mooruntersuchungen in N-Satakunta. Fennia 55, N:o 1. — Communic. Inst. Forest. Fenniae, 17, 1. S. 1.

AARNIO, B., 1927, Agrogeologisia karttoja N:o 5. Etelä-Pohjanmaa. Karttalehtiselostus. Valtion maatutkimuslaitos. S. 1.

BACKMAN, A. L., 1919, Torvmarksundersökningar i mellersta Österbotten. Acta Forestalia Fennica. 12.

—»— und CLEVE-EULER, ASTRID, 1922, Die fossile Diatomeenflora in Österbotten. Ibid., 22. S. 1.

—»— —»—, 1937, Om litorinagränsen i Haapavesi och diatomacéefloran på Suomenselkä. Acta Soc. Fauna et Flora Fenn., 60. S. 209.

FLORIN, MAJ-BRITT, 1944, En sensubarktisk transgression i trakten av södra Kilsbergen enligt diatomacésuccession i områdets högre belägna fornsjölagerföljder. Geol. Fören. Förhandl. Bd. 66, H. 3. S. 417.

FROMM, E., 1938, Geochronologisch datierte Pollendiagramme und Diatoméenanalysen aus Ångermanland. Ibid., Bd. 60, H. 3, S. 365.

HALDEN, B. E., 1929, Kvartärgeologiska diatomacéstudier belysande den postglaciala transgressionen å svenska västkusten. Ibid., Bd. 51, H. 3. S. 311.

—»—, 1936, Isavsmältning och strandförskjutningar i Siljansdalen. Ibid., Bd. 58, H. 1. S. 19.

HYYPPÄ, E., 1936, Über die spätquartäre Entwicklung Nord-Finnlands mit Ergänzungen zur Kenntnis des spätglazialen Klimas. Bull. Comm. géol. Finlande. 115, S. 401.

—»—, 1937, Post-Glacial Changes of Shore-Line in South Finland. Ibid., 120.

—»—, 1943, Itämeren historia uusimpien Itä-Karjalassa suoritettujen tutkimusten valossa. Terra. N:o 3—4, S. 122.

KILPI, S., 1937, Das Sotkamo-Gebiet in spätglazialer Zeit. Bull. Comm. géol. Finlande. 117.

LUNDQVIST, G., 1927, Bodenablagerungen und Entwicklungstypen der Seen. Die Binnengewässer. 2.

—»—, 1940, Zur Mikroskopie der Binnenseesedimente. Verh. Intern. Ver. theor. u. angew. Limnologie. 9. S. 111.

MÖLDER, K., 1937, Die rezente Eunotienflora Finnlands. Ann. Bot. Soc. Zool. — Bot. Fenn. Vanamo. 8, N:o 7. S. 8.

—»—, 1943, Studien über die Ökologie und Geologie der Bodendiatomeen in der Pojo-Bucht. Ibid., 18, N:o 2.

—»—, 1944 a, Die postglaziale Klimaentwicklung im Lichte der fossilen Diatomeenfunde in Südfinnland. Bull. Comm. géol. Finlande. N:o 132. S. 15.

—»—, 1944 b, Das Karelische Eismeer im Lichte der fossilen Diatomeenfunde. Ibid., N:o 132. S. 55.

SALMI, M., 1944, Ein Seehundfund aus Ruukki und die Salzwasserkonzentrationsschwankungen des Wassers in dieser Gegend während der Postglazialzeit auf Grund der fossilen Diatomeenflora. Ibid., N:o 132. S. 165.

SAURAMO, M., 1918, Geochronologische Studien über die spätglaziale Zeit in Südfinnland. Ibid. N:o 50. S. 1.

—»—, 1934, Zur spätquartären Geschichte der Ostsee. Ibid., N:o 104. S. 1.

—»—, 1936, Suomen maantieteen käsikirja. S. 1—18. Helsinki.

—»—, 1940, Suomen luonnon kehitys jääkaudesta nykyaikaan. Porvoo—Helsinki.

6

ON A MANGANESE GARNET ENCLOSED IN SPHALERITE FROM KIMITO IN S. W. FINLAND

BY

OLEG v. KNORRING

CONTENTS

INTRODUCTION

For more than 200 years the occurrences of pegmatite on the island of Kimito (Kemiö) have aroused the interest of scientists, especially mineralogists, and their many unique minerals have contributed to more than one collection.

Pegmatite dikes occur in several localities within the Sveco-Fennian Leptite Belt in South Finland and are enriched principally near the contact of the microcline granite complex. According to the classical monograph »On the Petrology of the Orijärvi Region in Southwestern Finland», published by Eskola in 1914, which contains a detailed account of the geology of these regions, the pegmatites originate from residual solutions of microcline granite. Considering the notable amount of accessory minerals present in the complex pegmatites on the island Kimito, one is entitled to believe that those residual solutions have been quite rich in trace elements and mineralizing agents. — In his excellent paper »Die Granitpegmatite von Kimito (S. W.-Finnland) und ihre Minerale» Pehrman (1945) gives a detailed description of all minerals found on the island up to the present.

Manganese minerals are in these pegmatites principally represented by several manganese phosphates and their alteration products, whereas manganese silicates are very rare. Eskola (1914) describes a manganese muscovite found in the pegmatite quarry near Mattkärr. During my visit to Rosendal, S. E. of Lemnästräsk, in the summer of 1945, the quarry foreman, Mr. Nordell, handed me a specimen of sphalerite, which on closer inspection proved to enclose a considerable amount of garnet. It was the unusual intergrowth of these two minerals which at that time arrested my attention. — The garnet proper, which afterwards was identified as spessartite, interested me mostly because it could be expected to have a composition which differed from the ordinary, and possibly to contain some Zn.

Upon Professor Pentti Eskola's advice a closer examination of the mineral was carried out. For the interest shown in my work and for the invaluable help given to me in the course of my investigation I desire to express my grateful thanks to Professor Eskola, Professor Th. G. Sahama, Preparator H. Nyberg, Mr. T. Borg, M. A. and Mr. Oiva Joensuu, M. A.

STRUCTURE AND ISOMORPHISM OF THE GARNETS

The garnets are cubic crystals with the chemical composition $R_3^{2+} R_2^{3+} Si_3 O_{12}$. R^{2+} and R^{3+} can be replaced by the following bi- and trivalent elements:

$$R^{2+} = Mg,\ Ca,\ Mn^{2+},\ Fe^{2+};$$
$$R^{3+} = Al,\ Ti^{3+},\ Cr^{3+}, Mn^{3+},\ Fe^{3+}.$$

The SiO_4 groups are independent of each other. The R^{3+} atoms are in the center of the group of six oxygen atoms and the R^{2+} atoms in the center of a group of eight or four oxygen atoms. Si is partly replaced by Ti, but within the garnet lattice also SiO_4 groups can be replaced by groups of PO_4, as is also the case in some spessartite garnets from Western Australia (*cf.* Mason and Berggren 1941). Menzer (1929) has shown that the unit cell of the garnets consists of 8 molecules, which corresponds to the above formula. According to him, the lattice constant or the edge length of the unit cell *e. g.*, for spessartite, is 11.603 ± 0.003 Å.

Boeke (1914), Eitel (1921), and Ford (1915) were the first to give a schematic representation of the complicated chemical composition of the garnets with the help of triangle diagrams. These investigations clearly showed the isomorphous miscibility of the garnets, so that Ford arrived at the conclusion that of all the garnets examined about 85 % were binary or ternary, and only 15 % polynary compounds.

v. Philipsborn (1928) believed that even very small amounts, such as 2—3 mol. per cent of a fourth constituent could perceptibly alter either specific gravity or refringence, or both. In opposition to the above mentioned investigators, v. Philipsborn based his representation on a tetrahedral diagram which made it possible to represent also quaternary or even higher systems.

The miscibility of the various garnet constituents is summarily presented in the following table:

	Limited miscibility			
Unlimited miscibility	Grossularite	$Ca_3Al_2\ (SiO_4)_3$	Pyrope	$Mg_3Al_2\ (SiO_4)_3$
	Andradite	$Ca_3Fe_2\ (SiO_4)_3$	Almandite	$Fe_3\ Al_2\ (SiO_4)_3$
	Uvarovite	$Ca_3Cr_2\ (SiO_4)_3$	Spessartite	$Mn_3Al_2\ (SiO_4)_3$

SPESSARTITE GARNETS

The chemical formula deduced for pure spessartite is $Mn_3Al_2Si_3O_{12}$. However, garnets with a composition exactly like this are seldom found in Nature. Ordinarily one understands by spessartite a manganese garnet whose principal components are spessartite and almandite in varying proportions, with smaller quantities of pyrope, andradite, and grossularite thrown in. Other combinations (*cf.* Fermor 1909; Mason and Berggren 1941) are more rare. The varieties which are richest in manganese have been found in Central India, at Tsilaisina (Madagascar), Amelia (Virginia) and Wodgina (Western Australia).

Spessartite and isomorphous mixtures with it mostly occur in connection with granites, pegmatites and metamorphic schists. — Lacroix (*cf.* Rosenbusch und Mügge, 1925, p. 52) states that on Madagascar pure spessartite is a characteristic ingredient of Na-Li pegmatites; its mixture series with almandite occur in K pegmatites. — In pneumatolytic formations, spessartite in close association with topaz and bixbyite is recorded from Simpson in Utah. — Another locality is reported from the Wetz schists in the Ardennes, containing large amount of spessartite, which is often found to be perfectly pure.

Spessartites often occur in intimate association with various deposits of manganese ore, especially those found in the provinces of Central India. Fermor (1909) reports from these localities mixtures of Mn and Ca garnets to which he gave the names spandite and grandite.

OCCURRENCES OF SPESSARTITE IN FINLAND

In Finland, spessartite belongs to the more uncommon minerals. It was identified for the first time in 1925 by Saksela at Vittinki, where the garnet occurs sparsely along with other manganese-rich minerals such as knebelite, rhodonite, manganapatite, and rhodocrosite. No chemical analyses or mineralogical data are available.

In 1936, Hietanen described a spessartite from Simsiö which occurs in quartzite together with manganese-rich minerals, mostly rhodonite, forming crystals of a brownish-red shade (diam. about 0.5—0.9 cm.), with faces (110) and (211) well developed.

Erämetsä (1945) mentions a spessartite from Hunttila in Impilahti.

In 1945, Eskola identified an almandite-spessartite at Ylöjärvi which contained 13.04 % MnO and 18.52 % FeO (oral communication).

In the pegmatite quarries of Kimito garnets occur in many places, though not in large quantities. Most of them are cherry-red and to all appearance almandite garnets.

Pehrman (1945, p. 47) describes an almandite garnet from the same pegmatite quarry at Rosendal, but does not mention any spessartite in this connection.

THE LOCALITY AT ROSENDAL

According to Pehrman (1945, p. 8), the pegmatite quarry No. 12 at Rosendal lies about 1 km. S. E. of Lemnästräsk and was in the summer of 1945 the only one being worked.

The pegmatite dike mainly consists of microcline, albite, and quartz in hornblende gabbro; along with these pegmatites also a fine-grained aplite is to be found. Eskola (1914, p. 39) who examined the occurrence in 1910 writes, *i. a.*: »As an excellent example of perfect differentiation by successive separation of crystals in a definite order is the pegmatite dike near Rosendal in Kimito. The middle part of the dike consists as usual of pure quartz, but otherwise the dike is unsymmetrically formed. Each mineral occurs in an almost pure form. The ixionolite is found most abundantly in the muscovitic and albitic zones. At the boundary between the latter and the quartz zone, beryl occurs in groups of short prisms, sometimes more than 100 kg. in weight».

Several accessory minerals such as tantalite, tapiolite, ixionolite, microlite, and gahnite have been found in the quarry. The last mentioned mineral, a zinc spinel, occurs according to Pehrman (1945, p. 21) together with muscovite in sphalerite, which in turn is found in cavities of the quartz. The sample of sphalerite given to the author evidently had been taken from such a cavity. — Manganese minerals have not previously been found in this quarry.

EXAMINATION OF THE MATERIAL

The specimen of sphalerite-garnet weighed nearly 1.6 kg. The zinc blende was quite massive, coarse-grained, greyish-black with brown streak.

The polished section proved that the sphalerite contained numerous inclusions of chalcopyrite. High magnification (540 x) revealed small ovoids and irregular grains of chalcopyrite. The ovoids were partly orientated and might be considered as unmixings from the sphalerite. No galena could be detected. — In thin section the colour of the sphalerite is a pronounced reddish-brown, and the dodecahedral cleavage can be clearly seen; the mineral is isotropic.

The density of the sphalerite measured by suspension in Clerici solution was 3.946 ± 0.002.

The following elements were chemically determined in sphalerite:

Zn	54.20 %
Fe	9.70
Mn	0.53
Cu	0.03

A spectrographic analysis was carried out by Mr. Oiva Joensuu, M. A., and gave the following results:

Cd	0.17 %
In	0.025
Sn	0.008
Pb	0.003
Bi	0.05
Co	0.02

The Fe content in the sphalerites varies considerably, according to investigations made by López de Azcona and Fraile Alcarraz (1942), and by Gabrielson (1945) from 0—20 %. A high Fe content often indicates a high formation temperature.

Many observations are presented in literature, stating that there also is a distinct relation between the Mn content and the formation temperature which thus can be conjectured to favour the adsorption of Mn into the sphalerite lattice. In this special case I was particularly interested in the Mn content on account of the numerous occurrences of manganese-bearing garnets in sphalerite. The analysis, however, showed a comparatively low Mn content, which agrees well with the above-mentioned investigations, taking into consideration that we are dealing with a pegmatite mineral. The other elements whose presence could be proved occur as trace elements and their distribution in sphalerite varies over a wide range.

Bismuth is one of the more uncommon elements. The polished section revealed no Bi minerals or native Bi. According to López de Azcona and Fraile Alcarraz (1942) the presence of this element could be proved only in 12 specimens of sphalerite out of the 133 which were examined.

The specimen contained numerous garnet crystals which were mostly clear, with a diameter of 0.5—3 mm., but it was also possible to identify some bigger crystals up to 6 mm. of diameter. The colour of the garnet varies from pale red to brown, the faces (110) and (211) of the individual crystals are well-developed, but no pronounced crystal form could be observed in the garnet which formed bigger masses. In polished sections the lustre of the garnet is intense.

Under the microscope it can be seen from the thin section that on the whole the garnets are nearly unaltered. Only a very narrow reaction zone, just the beginning of an alteration, denotes the contact with sphalerite. Some individuals clearly show intergranular alteration at different stages, usually most advanced in the smallest grains. The alteration products are difficult to interpret but probably consist for the most part of a chloritic substance. Bigger cracks usually contain sphalerite and quartz. In other respects the garnet is nearly free of inclusions, colourless and perfectly isotropic.

The quartz forms irregular masses in which some grains are undulatory. The sequence of crystallization seems to be the following: spessartite, sphalerite, and quartz, the latter having been formed at different stages.

For the chemical analysis the purest garnet crystals were picked out, crushed to a grain size of 0.1—0.5 mm. and treated with Clerici solution.

The garnet was separated and again crushed to a very fine powder. This was treated with diluted HNO_3 (1:1) on a water-bath. After this the material was washed and dried at 110° C.

The chemical analysis gave the following results:

%		Mol. prop.	
SiO_2	37.05	6170	6182
TiO_2	0.10	12	
Al_2O_3	20.24	1985	2119
Fe_2O_3	2.14	134	
FeO	12.44	1732	5623
MnO	27.21	3840	
MgO	trace	—	
CaO	0.24	43	
Na_2O	0.05	8	
K_2O	trace		
H_2O+	0.35		$RO : R_2O_3 : SiO_2$
H_2O-	0.04		$= 2.65 : 1 : 2.92$
Total	99.86 %		

For the determination of manganese the bismuthate method was applied (*cf.* Hillebrand and Lundell, 1929, p. 343) the average of three determinations being used. The manganese occurs as bivalent; Mn_2O_3 was determined by the method described by Otto (1936, p. 93), but the result was negative. The CaO precipitate was tested qualitatively for Sr and Ba with positive results. Determination of Zn was made chemically but with negative results. FeO was determined by the Washington, and H_2O+ by the Penfield method. The ratio $RO : R_2O_3 : SiO_2 = 2.65 : 1 : 2.92$ is not in agreement with the theoretical ratio which ought to be 3 : 1 : 3. RO differs perceptibly from the theoretical value 3. Fleischer (1937, p. 752) and v. Philipsborn (1928, p. 33) have pointed out that such differences often occur as a consequence of partial oxidation of Fe^{2+} during the FeO determination. The author carried out several analyses of the material and noticed that the maximum FeO value was reached only after decomposition of 2 1/2 hours. The material was then completely decomposed, but partial oxidation may very well have taken place, as under favourable conditions the decomposition does not require more than 30—40 minutes.

The clear colour of the garnet, varying megascopically from reddish-brown to light red, and its colourless aspect in the thin section denote the presence of an insignificant amount of Fe^{3+}. If, on the basis of this observation, the whole amount of Fe is computed as FeO, the ratio may be expressed as follows:

$$RO : R_2O_3 : SiO_2 = 2.96 : 1 : 3.10,$$

which lies very near the theoretical ratio.

The mixture ratio of the different garnet components is as follows:

Spessartite	65.3 %
Almandite	34.0
Grossularite	0.7
	100.0

The specific gravity of the garnet was measured by suspension in Clerici solution. The average of three determinations at 18° C was

$$G = 4.171 \pm 0.002.$$

The index of refraction was determined by the prism method and found to be

$$n_{Na} = 1.808.$$

This garnet thus consists for the main part of spessartite and almandite at the nearly exact ratio of 2 : 1.

COMPARISONS AND DISCUSSION

SPHALERITE

Gabrielson (1945, p. 43) mentions a sphalerite from the pegmatite quarry at Skuleboda in Sweden which along with the common pegmatite minerals contains yttrotantalite and native bismuth. Nothing is known about the possible occurrence of Mn garnets at the locality. For comparison I give the following analytical data for the Skuleboda sphalerite according to Gabrielson (1945, p. 16):

Zn	58.0 %
Fe	6.0
Mn	0.45
Cu	1.0
Cd	0.16
Ga	0.001
In	$<$ 0.003
Pb	0.2
Co	0.01
Ni	$<$ 0.001

We have in this case approximately the same element combination as in the sphalerite from Rosendal and, moreover, the Mn and Cd contents in both are nearly identical. Bismuth occurs here in native form which apparently is the case also in the Rosendal sphalerite. It is possible that due to its low degree of hardness this mineral has been carried away during the making of the polished section and thus could not be noticed under the microscope.

I further want to mention a couple of zinc ore localities of considerable extent in which sphalerite is associated with manganese minerals, amongst them spessartite. These localities are Broken Hill in S. E. Australia and the Sullivan Mine in British Columbia, Western Canada.

SPESSARTITE

When comparing the analysis of the spessartite from Rosendal with analyses made of other spessartites, one's attention is drawn in the first place to the low CaO and MgO content. Even pure spessartites rich in MnO usually contain some CaO: 0.30—2 %. The content of MgO is usually under 1 %. Another type of spessartite contains about 30 % MnO and 2—5 % CaO. Such garnets are often found in skarn in association with manganese ore occurrences. In spessartites with high percentage of almandite the CaO content may be several per cent.

Manganese silicates in general rarely occur in Nature; spessartite probably is one of the most common. Clarke and Washington (1924, p. 20) assume the Mn/Fe ratio in Nature to be 1 : 50. Where manganese is enriched in minerals to exceed this ratio, changes occur mainly in the optical properties of the minerals, such as refringence, colour, and pleochroism. The manganese mostly replaces iron, due to the position of these elements in the periodical system and to their ionic radii:

$$\mathrm{Fe}^{2+} = 0.83\ \text{Å} \qquad \mathrm{Fe}^{3+} = 0.67\ \text{Å}$$
$$\mathrm{Mn}^{2+} = 0.91\ \text{Å} \qquad \mathrm{Mn}^{3+} = 0.70\ \text{Å}.$$

An increase of the Mn content in the Mn-Fe system of manganese minerals is accompanied by a decrease in the index of refraction. For the spessartite this is illustrated by Table I, which shows, in addition, how

TABLE I

COMPARISON BETWEEN THE CHEMICAL COMPOSITION, SPECIFIC GRAVITY, AND REFRINGENCE OF SOME SPESSARTITES

No.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	H_2O	Total	G	n_{Na}
1	36.06	0.28	20.38	0.54	0.69	40.88	0.21	1.88	n.d.	n.d.	n.d.	100.92	4.152	1.799
2	35.65	n.d.	20.93	n.d.	5.67	37.21	n.d.	0.48	»	»	»	99.94	4.169	1.806
3	36.61	0.13	20.41	0.28	7.54	33.90	0.56	1.38	»	»	0.04	100.25	4.181	1.805
4	37.82	n.d.	22.00	0.23	6.09	30.62	0.53	3.44	»	»	n.d.	100.73	—	1.801
5	36.83	0.12	20.70	0.78	12.41	29.06	0.14	0.27	»	»	0.02	100.33	4.211	1.813
6	37.05	0.10	20.24	2.14	12.44	27.21	tr.	0.24	0.05	tr.	$\begin{cases}+0.35\\-0.04\end{cases}$	99.86	4.171	1.808
7	36.59	tr.	21.07	2.83	13.07	25.75	0.84	0.48	n.d.	n.d.	n.d.	100.63	4.219	1.816
8	35.72	n.d.	19.66	2.68	15.62	24.36	tr.	1.84	»	»	0.48	100.36	4.229	1.812
9	36.85	tr.	21.14	2.45	16.66	22.78	0.30	0.28	»	»	0.01	100.47	4.232	1.814
10	36.43	0.08	21.17	1.01	23.78	16.20	0.74	0.71	»	»	0.06	100.18	4.240	1.815

1. Tsilaisina, Madagascar, Pegmatite, (Menzer 1929, p. 374).
2. Connecticut, U. S. A., Pegmatite, (Otto 1936, p. 99).
3. Budislav, Czecho-Slovakia, Pegmatite, (Novaček 1940, p. 2).
4. Simsiö, Finland, Quartzite, (Hietanen 1936, p. 398).
5. Publice, Moravia, Pegmatite (Novaček *loc. cit.*).
6. Kimito, Finland, Pegmatite, (v. Knorring 1946).
7. Marsikow, Czecho-Slovakia, Pegmatite, (Novaček *loc. cit.*).
8. Drahonina, Moravia, Pegmatite, (Novaček *loc. cit.*).
9. Sobotin, Czecho-Slovakia, Pegmatite, (Novaček *loc. cit.*).
10. Hoslau, Czecho-Slovakia, Pegmatite, (» » »).

the specific gravity is changed in the same direction. Naturally, variations always occur, mostly depending on the degree of purity of the sample on which the analyses are made and on divergences in the methods of determination. Otto (1936, p. 121) reports the following data resulting from chemical and optical investigations of different manganese minerals:

Ionic radius, Å	Miscibility	Divergences between ionic radii	15 % of the shorter radius
Mn (0.91) — Fe (0.83)	Complete	0.08	0.125
Mn (0.91) — Mg (0.78)	Partial	0.13	0.117
Mn (0.91) — Ca (1.06)	Partial	0.15	0.137
MnMn (1.82) — LiAl (1.35)	Low	0.47	0.203
Mn (0.91) — Zn (0.83)	Low	0.08	0.125
Mn^{3+} (0.70) — Fe^{3+} (0.67)		0.03	0.101
Mn^{3+} (0.70) — Al^{3+} (0.57)		0.13	0.086

The Mn-Zn system forms an exception, the Zn-Mn minerals having a different crystal structure in comparison to the Fe-Mn minerals, possibly due to chemical divergences in the atomic structure of the elements Fe, Mn, and Zn.

As I could expect to find Zn in the spessartite from Rosendal, also a spectrographic investigation of the garnet was carried out by Mr. Oiva

Joensuu, M. A., to determine the content. Two determinations were made on different samples, but in both cases the Zn content was found to be very low, *viz.* < 0.01 % ZnO. This agrees well with Otto's investigations of the Mn-Zn system.

Erämetsä (1945) made spectrographic investigations of the Zn content of several minerals, among them 41 garnets, coming from different parts of Finland. The tests showed that the ZnO content in most cases was insignificant, 0.003 % or less. Only in some cases did the minerals contain 0.1 to 0.3 % ZnO, all of these being skarn minerals connected with zinc ores from Pitkäranta and Orijärvi Mining Fields. Among these garnets there was also a unique grossularite from Lupikko in Pitkäranta, whose ZnO content was chemically determined to be 0.49 % (Erämetsä 1945, p. 5). Unfortunately, no exact data on the character of the material are available. In addition, the collection comprised a spessartite from Munttila at Impilahti with a ZnO content of 0.003 %.

The present investigation is a further proof of the correctness of the assumption that Zn only with difficulty can enter into the garnet lattice, especially as far as spessartite is concerned.

THE MINERALOGICAL AND GEOLOGICAL INSTITUTE OF THE UNIVERSITY, HELSINGFORS, MAY 1946.

REFERENCES

BOEKE, H. E., Die Granatgruppe. Z. Krist., Bd. 53, p. 149, 1914.

CLARKE, F. W. and WASHINGTON, HENRY STEPHENS, The Composition of the Earth's Crust. U. S. G. S., Prof. Paper 127, 1924.

DOELTER, C., Handbuch der Mineralchemie, Bd. II, 3. p. 356. Dresden und Leipzig 1921.

EITEL, W., Ueber die polynäre Mischbarkeit der Granatmineralien. Z. Krist., Bd. 56. p. 526, 1921.

ERÄMETSÄ, OLAVI, Zinkgehalte finnischer Minerale mit nichtmetallischem Charakter. Ann. Acad. Sci. Fennic., Ser. A, II. 14, 1945.

ESKOLA, PENTTI, On the Petrology of the Orijärvi Region in Southwestern Finland. Bull. Comm. géol. Finlande, N:o 40, 1914.

—»— Kiteet ja kivet, Porvoo ja Helsinki 1939. (Finnish).

FERMOR, L. L., The Manganese Ore Deposits of India. Mem. Geol. Survey of India Vol. XXXVII, 1909.

FLEISCHER, M., The Relations between Chemical Composition and Physical Properties of the Garnet Group. Amer. Min., Vol. 22, p. 751, 1937.

FORD, W. E., A Study of Relations Existing between the Chemical, Optical and Other Physical Properties of the Members of the Garnet Group. Amer. J. Sci., Vol. 40, p. 33, 1915.

GABRIELSON, OLOF, Studier över elementfördelningen i zinkbländen från svenska fyndorter. S. G. U. Ser. C. No. 468, 1945.

HIETANEN, ANNA, Ueber den Rhodonit und andere Manganminerale von Simsiö, Pohjanmaa. C. R. Soc. géol. Finlande N:o IX; Bull. Comm. géol. Finlande N:o 115, p. 387, 1936.

HILLEBRAND, W. F. and LUNDELL, G. E. F., Applied Inorganic Analysis. New York 1929.

LÓPEZ DE AZCONA, J. M. y FRAILE ALCARRAZ, C., Estudio espectroquímico de las blendas de la Peninsula Iberica. Las Ciencias, Año VIII, No. 3, 1942.

MASON, BRIAN and BERGGREN, THELMA, A Phosphate-bearing Spessartite Garnet from Wodgina, W. Australia. Geol. För. Förh., Bd. 63, p. 413, 1941.

MENZER, G., Die Kristallstruktur der Granate. Z. Krist., Bd. 69, p. 300, 1929.

NOVAČEK, R., Ueber Granate der Pegmatite aus der Tschechoslowakei. Fortschr. Min., Bd. 24, p. 2, 1940.

OTTO, HELMUT, Die Rolle des Mangans in den Mineralien. Min. Petr. Mitt., Bd. 47, p. 89, 1936.

PEHRMAN, GUNNAR, Die Granitpegmatite von Kimito (S. W.-Finnland) und ihre Minerale. Acta Acad. Aboensis, Math. et phys., XV. 2, 1945.

v. PHILIPSBORN, H., Beziehungen zwischen Lichtbrechung, Dichte und chemischer Zusammensetzung in der Granatgruppe. Abh. Sächs. Akad. Wiss., math.-phys. Kl. Nr. III, 1928.

ROSENBUSCH, H. und MÜGGE, O., Mikroskopische Physiographie. 5. Aufl. p. 52, Stuttgart 1925.

SAXÉN (SAKSELA), MARTTI, Om manganjärnmalmfyndigheten i Vittinki. Fennia 45, N:o 11, 1925.

7

ON THE CHEMISTRY OF THE MINERAL TITANITE

BY

TH. G. SAHAMA

ABSTRACT

Based upon the crystal structure analysis of titanite given by Zachariassen, the assumption to which he has drawn attention is made that the titanite lattice in practice contains water (hydroxyl) and fluorine in remarkable amounts. Some new complete analyses of titanite minerals with additional optical *etc.* data are presented and compared with those found in literature. The general chemical composition and especially the water and fluorine content of the mineral are discussed. A scheme of a general mineralogical classification of the titanite group is proposed.

CONTENTS

INTRODUCTION

With regard to its mode of occurence in minerals, titanium occupies a transitional position between those elements which never form specific mineral species in ordinary igneous rocks, but are always camouflaged in the lattices of common rock constituents (rubidium, strontium, barium, *etc.*) and those elements which show a very marked tendency to build up special minerals in which they play the rôle of one of the principal cations (zirconium in zircon, fluorine in fluorite, phosphorus in apatite, *etc.*). Of the petrologically important titanium minerals ilmenite, titanite, and rutile are the most abundant. In addition, almost all dark constituents of rocks contain more or less titanium.

Now, let us consider the distribution of the titanium amount available in the lithosphere between various titaniferous minerals and mineral groups. According to some well-known calculations the average titanium content of the lithosphere is as follows:

British igneous rocks (A. Harker)	0.52 % TiO_2
Igneous rocks of the U. S. (A. Knopf)	0.73
Igneous rocks (F. W. Clarke and H. S. Washington)	1.05
Plutonic rocks (J. H. L. Vogt)	0.60
Finnish rock ground (J. J. Sederholm)	0.41
Norwegian glacial clays (V. M. Goldschmidt)	0.79

These figures show considerable fluctuations. Which of them is considered to lie nearest the truth, is a question which would lead us outside the scope of this work. At any rate, the values given show the order of magnitude of the average titanium content which is to be taken into account for the present purpose.

Besides the titanium minerals mentioned above, the igneous rocks contain according to Clarke (1924) 3.8 % biotite and 16.8 % pyroxenes and amphiboles. These two mineral groups are quantitatively the most important titanium-bearing constituents of the igneous rocks in average without being titanium minerals proper. In order to obtain an approximate picture of the average titanium contents of these mineral groups the mean figures put forward by Tschirwinsky (1928) may be used. According to his review, the granite biotite contains 1.25 % TiO_2 and the ordinary pyroxenes and amphiboles about 0.5 % TiO_2, the latter figure being rather too high than too low. Of course, these figures are by no means to be regarded as exact. However, if they were twice as high, it would not affect the result of the present discussion in any noteworthy degree. According to the figures presented the biotite of the igneous rocks would contain about 0.05 % TiO_2 and the amount of pyroxenes and amphiboles about 0.08 % TiO_2 of the bulk. As will be seen, these amounts represent only a small part of the whole titanium content of igneous rocks given above. It is thus evident that the greatest part of titanium is contained in the titanium minerals proper.

Which one of the three mentioned titanium minerals quantitatively bears the major part of the element, is a question which cannot be answered exactly. v. Hevesy, Alexander and Würstlin (1920) have made an attempt in the matter. On the basis of the titanium-niobium ratio in the titanium minerals under consideration and, on the other hand, in the igneous rocks in average they arrive at the conclusion that ilmenite obviously represents the most important titanium carrier of the lithosphere. The abundance relation between titanite and rutile can hardly be estimated with any considerable reliability. Independent of this, however, the statement can be made that our element preferably is bound to oxidic minerals.

This latter statement has a certain value when discussing the entering of titanium into mineral lattices. A very characteristic feature of the chemical behavior of titanium is represented by the fact that the two simple silicates, the metasilicate $TiSi_2O_6$ as well as the orthosilicate $TiSiO_4$, are not known as crystallized compounds. The cause of the lack of a simple orthosilicate of titanium can easily be seen on purely geometrical grounds. The quadrivalent titanium ion of an ionic radius of 0.64 Å shows a coordination number 6 against oxygen in mineral lattices. In a simple orthosilicate of a quadrivalent cation, in which no additional anions are present and which accordingly is not to be classified among the »subsilicates» as defined by Berman (1937), the oxygen ion belonging to a SiO_4 tetrahedron is wholly satisfied if $n \cdot Q/CN = 1$ where Q is the charge of the cation, CN its coordination number against oxygen, and n the number of cations around an oxygen ion. Here $Q = 4$, and in the case of titanium $CN = 6$. Hence n should be $1\ ^1/_2$. In zircon lattice $CN = 8$, and $n = 2$. In that case one oxygen is linked to two zirconium ions and electrostatic neutrality is reached. In titanium orthosilicate every oxygen ion should be surrounded by $1\ ^1/_2$ titanium ions. This demand would lead to a defect lattice, where one oxygen ion would be linked to one titanium ion and the next oxygen ion to two titanium ions. Such a defectness obviously being very strong, this atomic arrangement does not seem to be at all stable, even if geometrically possible. Those cases where the deviation from Pauling's demand for electrostatic neutrality throughout the lattice is as strong as it would be in $TiSiO_4$, are not realized in general among the petrologically more important minerals. Reasons similar to those which make the titanium orthosilicate impossible or at least improbable are obviously in action also in respect of titanium metasilicate.

Thus, the only way for titanium to build up a comparatively simple silicate mineral is to form a complex compound with some other cation of a different coordination number. Of these only calcium, sodium, and potassium are present in rocks in sufficient amounts. The corresponding calcium compounds showing in general greater heats of formation, it can be understood that titanium preferably will be bound with calcium to a complex calcium titanium silicate and form titanite.

However, the chemical composition as well as the crystal structure of titanite shows some peculiarities which are of interest. Although titanite is very common in all kinds of silicate rocks, one can find in literature but very few analyses which can be regarded as wholly complete. Therefore I shall in the following present some new analyses with additional optical *etc.* data. On the basis of these and earlier data I shall discuss some features very beautifully represented in the chemistry of the minerals classified under the heading »titanite group». The publication of these thoughts may further be justified by the circumstance that the peculiarities which can be traced in titanite minerals are perhaps of a more general importance when trying to learn to understand the chemistry of other minerals also, such as they really are to be found in Nature. The »chemical formulas» of minerals given in handbooks are mostly more or less idealized from the true composition and just the actual deviations from these idealized formulas and the reasons thereof are of very great importance in the matter.

ACKNOWLEDGMENTS

For the present investigation I have obtained samples from various collections. The specimen No. 6 has been put at my disposal by Professor Pentti Eskola, specimen No. 3 by Dr. Olavi Erämetsä and Mr. N. Lounamaa, and specimen No. 2 by Mr. Erkki Viluksela. To all these gentlemen I express my sincere thanks.

In the analytical work I have been assisted by Mr. Oleg v. Knorring, M. A., and Mr. Oiva Joensuu, M. A. In addition, Mr. M. Härme, M. A., and Mr. Juhani Seitsaari, M. A., have made some determinations. The chemical and spectrographical determinations were carried out by the following persons:

All determinations by means of optical spectrography, *viz.* Nb, V, Cr, Zr, Sr, Ba	Joensuu
Rare earths, Ta	Sahama
H_2O+	v. Knorring and Seitsaari
All determinations of F and Cl	v. Knorring
The rest of Anal. 1, 2, 4, 5 and 6	v. Knorring
The rest of Anal. 3	Härme and v. Knorring

The optical spectrograms needed were photographed by Mr. J. Vuojela. All determinations of the optical constants were made by Mrs. Toini Mikkola, M. A., and of the specific gravities by the author. Mrs. Mikkola and Mr. Vuojela have also helped in the separation of the minerals analyzed.

To the co-workers mentioned above I acknowledge my great indebtedness.

NEW ANALYSES OF TITANITE MINERALS

METHODICS

The valuation of the six new analyses given below being closely connected with a knowledge of the methods used, some notes may be added concerning the determination of the various constituents. Some of the determinations were made chemically, others by means of optical or X ray spectrography.

The determination of SiO_2, TiO_2,Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, MnO, Cl, and H_2O— was effected in the way generally used in mineral analyses. They need no further explanation.

For the determination of niobium and tantalum the ammonia precipitate was prepared. Niobium was determined from this precipitate by means of optical spectrography according to the method recently described by Rankama and Joensuu (1946). Only a small part of the corresponding precipitate having been used for this determination, the chemical pre-enrichment for tantalum was continued with the rest of the available precipitate. This was fused with potassium carbonate, and the melt boiled with salicylic acid according to the instructions given by Rankama (1944). A determination of the final enrichment product was made by means of X ray spectrography with a visual estimation through comparison with standard comparison spectra. The figures obtained were subtracted from those of titania found chemically.

The determination of vanadium, chromium, zirconium, and strontium was effected by means of optical spectrography in analogy with the principles put forward by Rankama and Joensuu (*op. cit.*) when determining niobium. As a safety and correction line Mn 4257.659 was used. In the mixture to be photographed the content of manganese amounted to 1.0 per cent MnO. Because of the fact that the manganese oxide available was found to contain minute traces of barium, the determination of this element was carried out without any addition of manganese. As safety and correction lines those of vanadium, chromium, strontium or zirconium were used. These elements having been determined previously, they served as comparison elements instead of manganese. The content of the constituents in question was taken into account when writing the figures of lime, alumina, and titania. However, a correction of these figures due to the respective vanadium content was not made. The degree of oxidation of the small vanadium amounts found not being separately determined and, accordingly, the influence of the vanadium amount upon the figures of alumina as well as ferric and ferrous iron not being estimable, the figures of V_2O_5 were not included in the analysis sums given in Table I.

The presence of the rare earths was checked by means of optical spectrography. If they were present in sufficient amounts, the mineral was decomposed by hydrofluoric acid and evaporated to dryness a couple of times. After digestion with cold water containing a little hydrofluoric acid the solution was filtered, the residue brought into solution with as little sulphuric acid as possible and the rare earths precipitated with oxalic acid as described by Schoeller and Powell (1940, p. 77). The precipitate being usually contaminated with calcium, the ignited oxides were brought into solution and reprecipitated with ammonia. This final precipitate was analyzed X ray spectrographically as described by Minami (1935) and Sahama and Vähätalo (1939). The amount of the rare earths found was taken into account when writing the figure for alumina.

The total amount of water expellable at temperatures above appr. 110 degrees centigrade was determined as follows: The very finely powdered sample was mixed thoroughly with at least a six-fold amount of sodium tungstate from which all crystal water had been removed through heating it gently at a temperature well below the melting point of the salt. In the lack of a suitable platinum boat the mixture was placed in one of silver and pushed into a tube of a highly refractory Jena »Supremax» glass. A current of dried air was sucked through this tube to a collector consisting of a calcium chloride tube. The whole apparatus was built up according to the instructions given by A. W. Groves in his »Silicate Analysis» [1]. The glass tube was heated with gas and the mixture held in a well-fused condition about 40 minutes. The increase in weight of the calcium chloride tube indicates directly the amount of water present in the mineral. Blanks made with corresponding amounts of sodium tungstate alone showed practically no increase of the weight of the calcium chloride tube. Before each determination the sample was kept a couple of hours at a temperature of 110—120 degrees centigrade in order to remove all secondary hygroscopic moisture. Accordingly, in the figures of H_2O+ given below only that water is included which will be given off above this temperature. Some of the titanite samples containing appreciable amounts of fluorine, experiments were made in order to prove whether fluorine also would be set free in the sodium tungstate flux and enter into the calcium chloride tube. It was found, however, that even from a mixture of calcium fluoride and quartz in the procedure explained above no fluorine entered into the absorption tube. Calcium always being in a strong excess over fluorine in the mineral titanite the fluorine apparently will be bound as calcium fluoride practically quantitatively and is not expelled away from the flux. — The results obtained were controlled with the ordinary Penfield method using, however, not the mineral powder as such, but a mixture of the mineral with lead oxide and minium. The two oxides of lead were taken in a weight ratio of about 1: 1 and served as fluxing material. Also for this method experiments were made as to the behavior of fluorine. When heating calcium fluoride with lead oxide mixture in the Penfield tube no attacking of the tube was observed. Fluorine is apparently retained in the flux as lead fluoride.

The determination of fluorine was effected by means of the standard thorium nitrate method, as described by Cumming and Kay (1939, p. 178). In order to ensure a complete solution of fluorine when digesting the cake after the sodium carbonate fusion in water, very finely powdered quartz

---

[1] London 1937, p. 87--93.

was added to the titanite powder to be analyzed before making the soda fusion. Blanks of known material and parallel determinations of titanites showed the applicability of the method for the present purpose.

A few words may be added concerning the determination of the optical properties of the titanites investigated. The axial angles as well as the extinction angles on (010) were determined by means of the universal stage. The indices of refraction being too high for ordinary immersion liquids, the determinations were carried out with immersion melts prepared according to the principles given by Larsen and Berman (1934). All results of optical measurements are given for sodium light.

The specific gravities were determined with Clerici solution.

ANALYSIS RESULTS

The results of the analyses carried out on the six titanite specimens mentioned above are represented in Table I. As mentioned before, the figures for V_2O_5 are not included in the corresponding analysis sums. The molecular numbers are given in Table II, the figures for the separate rare earths in Table III.

TABLE I. NEW ANALYSES OF TITANITE MINERALS

Anal. No.	1	2	3	4	5	6
Locality	Miask	Ylöjärvi	Parainen	Kola	Kola	Kola
SiO_2	29.50	30.37	30.32	30.44	30.48	29.86
TiO_2	40.89	38.57	33.70	39.66	38.00	39.84
Nb_2O_5	0.030	0.041	0.69	0.34	1.52	1.10
Ta_2O_5	[1] 0	[2] 0	0.03	0.01	0.02	0.03
V_2O_5	0.016	0.11	0.09	0.10	0.005	0.015
Al_2O_3	0.00	1.24	4.44	0.00	0.05	0.00
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00
Cr_2O_3	0.00	0.01	0.02	0.00	0.00	0.00
FeO	0.17	0.29	0.20	0.14	0.10	0.20
MgO	0.00	0.16	0.16	0.00	0.00	0.00
ZrO_2	0.06	0.06	0.06	0.11	0.05	0.06
CaO	28.78	27.42	28.40	27.20	27.32	26.56
SrO	0.004	0.007	0.005	0.32	0.29	0.44
BaO	0.005	0.005	0.003	0.005	0.006	0.005
Na_2O	n. d.	0.00	0.16	0.37	1.05	0.81
K_2O	n. d.	0.00	0.00	0.00	0.00	0.00
Rare Earths	[3] tr.	0.47	0.30	0.37	0.26	[3] tr.
MnO	0.00	0.03	0.01	0.05	0.08	0.032
F	0.10	0.19	1.40	0.61	0.68	0.53
Cl	0.10	0.00	0.00	0.00	0.00	0.00
H_2O+	0.71	1.13	0.54	0.56	0.61	0.49
H_2O	0.14	0.31	0.18	0.08	0.12	0.24
O	0.06	0.08	0.59	0.26	0.29	0.22
Sum	100.42	100.21	100.02	100.00	100.34	99.97

---

[1] If present, not more than about 0.01 per cent.

[2] If present, not more than about 0.01–0.02 per cent.

[3] Detected by means of optical spectrography. The corresponding spectrum lines were found to be very weak and, accordingly, a chemical determination was not effected.

TABLE II. MOLECULAR NUMBERS OF THE ANALYSES OF TABLE I

Anal. No.	1	2	3	4	5	6
Locality	Miask	Ylöjärvi	Parainen	Kola	Kola	Kola
Si	489	504	503	505	506	495
Ti	510	482	421	495	474	497
Nb	—	—	5	3	11	8
Al	—	24	87	—	1	—
Fe	2	4	3	2	1	3
Mg	—	4	4	—	—	—
Ca	513	489	507	485	487	473
Sr	—	—	—	3	3	4
Na	—	—	5	12	34	26
Rare Earths	—	3	2	2	2	—
Mn	—	—	—	1	1	—
F	5	10	74	32	36	28
Cl	3	—	—	—	—	—
OH	79	125	59	62	68	54
Si	489	504	503	505	506	495
Ti+Nb+Al+Fe+Mg	512	514	520	500	487	508
Ca+Sr+Na+RE+Mn	513	492	514	503	527	503
OH+F(+Cl)	87	135	133	94	104	82

TABLE III. THE RARE EARTH CONTENT OF THE TITANITE MINERALS OF TABLE I

Anal. No.	2	3	4	5
La_2O_3	0.05	0.02	0.04	0.03
Ce_2O_3	0.11	0.06	0.12	0.10
Pr_2O_3	0.02	0.01	0.02	0.01
Nd_2O_3	0.09	0.07	0.08	0.06
Sm_2O_3	0.03	0.02	0.02	0.01
Gd_2O_3	0.03	0.02	0.02	0.01
Dy_2O_3	0.02	0.02	<0.01	<0.01
Er_2O_3	<0.01	<0.01	<0.01	<0.01
Yb_2O_3	<0.01	<0.01	—	—
Y_2O_3	0.10	0.06	0.05	0.02
Sum	0.47	0.30	0.37	0.26
Yttrium Earths	57	67	32	24
Cerium Earths	100	100	100	100

TITANITE FROM MIASK, URAL

The titanite from Miask was taken from the collections of the Institute of Geology of the University of Helsinki (Collection Number 2848). It was composed of a few separate crystals with well developed faces weighing a couple of grams in average. They were almost clear and transparent with a very light yellowish color. No inclusions or other impurities were observable. Optical properties:

$$\left.\begin{aligned}\alpha &= 1.901\\ \gamma &= 2.093\end{aligned}\right\}\text{(Oriented prism)}$$
$$2V = ca.\ 23^\circ$$

Sp. gr. = 3.54.

As is seen from Table I (Anal. No. 1), the composition is almost ideal for a titanite, only a very slight deficiency of silica being observable. In spite of this, water is present in considerable amount. The content of fluorine is very small, that of chlorine, however, being higher than in any one of the other titanite minerals given in the Table.

TITANITE FROM YLÖJÄRVI, FINLAND

The mineral occurs in a very coarse-grained gabbro on a small island named Varissaari in the Gulf of Kohmalanlahti, Lake Näsijärvi, Parish of Ylöjärvi in the neighborhood of the town Tampere (Anal. No. 2). It shows typical wedge-shaped crystals of a deep brown color. The sizes of the crystals amounted to only a few millimeters. The constituents of the gabbro are as follows: Plagioclase, hornblende, biotite, apatite, titanite, ore, zircon.

From the rock about 70 kg. was crushed with a suitable machine. The separation was effected first with a shaking table and an electric magnet, and the sample was finally purified with Clerici solution. In the analyzed titanite fraction the impurities consisted mainly of hornblende and only traces of feldspar. Some few inclusions of ore were visible. The total amount of impurities was estimated to be less than 1.5 per cent and most probably even less than 0.5 per cent.

The optical properties are as follows:

$$\begin{aligned}\alpha &= 1.94\\ \gamma &= 2.10\\ 2V\gamma &= 34^\circ\text{—}36^\circ\\ c\wedge\gamma &= 51^\circ\end{aligned}$$

Sp. gr. 3.52.

According to Anal. 2 in Table I the mineral is a comparatively pure titanite containing, however, a considerable amount of alumina. The water content is noticeably high.

When separating the comparatively large amount of titanite (the pure fraction weighed about 200 grams) a small fraction of zircon was obtained, amounting to ab. 10 grams. This zircon fraction contained no other impurities than possibly minute traces of titanite. If no crystal faces are visible, these two minerals are not always easy to distinguish from each other under a binocular microscope. Those cases where both titanite and zircon have been analyzed from the same ordinary basic igneous rock are very rare, if at all existent. Therefore, I asked Mr. v. Knorring to make an analysis also of this zircon. In order to compare the deviations of the compositions of the two minerals from the ideal ones I add the zircon analysis in question.

Zircon from gabbro, Ylöjärvi

SiO_2	31.24	518	
TiO_2	0.15	2	
ZrO_2	66.44	542	
Al_2O_3	0.61	6	
Fe_2O_3	0.71	4	(Total iron)
MnO	0.00	—	
MgO	0.00	—	
CaO	0.36	6	
H_2O+	0.70	39	
H_2O-	0.10	—	
	100.31		

According to the determination made by Mr. Joensuu by means of optical spectrography the mineral contained 0.000 per cent Nb_2O_5. By means of X ray spectrography carried out by me the hafnium content was found to be about 2 per cent. The indices of refraction of the zircon in question were as follows:

$$\omega = 1.875$$
$$\varepsilon = 1.91$$

After crushing, and before the separation with the shaking table, an average sample was taken of the rock. From this sample the following spectrographical determinations were made by Mr. Joensuu (the determination of titania was effected chemically by Mr. Härme):

Gabbro, Ylöjärvi

TiO_2	2.44
V_2O_5	0.07
Cr_2O_3	0.02
ZrO_2	0
Nb_2O_5	0.010
SrO	0.09
BaO	0.11

When comparing these figures with the average of gabbroic rocks given in literature it is to be noted that the strontia and baria content is higher than the content set up by Noll (1934) and v. Engelhardt (1936) respectively. The figure for niobium is also higher than that given by Goldschmidt (1937) for gabbros in average.

In order to get a view of the enrichment or impoverishment of the above-mentioned elements in relation to calcium or titanium respectively the concentration ratios of these elements may be calculated in titanite and in the whole gabbro. The lime and titania were taken as 100 and the other constituents corrected correspondingly. The lime content on the gabbro not having been determined, the respective figure was taken as 10 per cent. The inaccuracy of this figure apparently has no influence upon the conclusions drawn in the matter.

	Titanite	Whole gabbro
CaO	100	100
SrO	0.03	0.9
BaO	0.02	1.1
TiO_2	100	100
Cr_2O_3	0.03	0.8
V_2O_5	0.3	2.9
Nb_2O_5	0.106	0.4

As seen from the figures presented, strontium and barium are both very greatly impoverished in titanite in relation to calcium. In analogy therewith, chromium, vanadium, and niobium are impoverished in relation to titanium in titanite. This fact is very interesting as regards strontium and niobium, both these elements being known in some other titanites in very remarkable amounts. As to niobium, the statement may further be stressed that it does not enter into the zircon of the rock at all. It seems most likely that the unusually high niobium content of the rock is due to biotite.

GROTHITE FROM PARAINEN, FINLAND

This titanite variety occurs as typical wedge-shaped crystals of deep brown color in the limestone of Parainen (Anal. No. 3). Other constituents in the limestone are: Plagioclase, pyroxene and amphibole, apatite, very minute amounts of ore.

Of the rock about 20 kg. was taken. The material was crushed and separated as explained in the case of the titanite from Ylöjärvi. The analyzed fraction was found to be very pure. The total amount of impurities is in any case smaller than in the foregoing titanite. Optical properties:

$$\alpha = 1.84$$
$$\gamma = 1.975$$
$$2V\gamma = 38^\circ$$
$$c \wedge \gamma = 50^\circ$$

Sp. gr. = 3.52.

As seen from the analysis, the mineral shows a composition considerably deviating from the ideal titanite. The content of alumina being exceedingly high and, on the other hand, that of the rare earths very low, the mineral affords a beautiful representation of a titanite variety called grothite. However, when comparing the analysis of the Parainen grothite with the general grothite composition summarized, *e. g.*, by C. Doelter in his »Handbuch der Mineralchemie», Bd. III, Part I, p. 61, and more recently by Kunitz (1936), the statement can be made that the Parainen mineral is remarkably devoid of iron. Taking the mode of occurrence of the mineral into account, the high content of niobium is to be noticed. The most striking feature in the composition of the mineral in the present connection is, however, the exceedingly high figure for fluorine. So far as I know, a titanite mineral has never been found where fluorine in such an amount is enclosed in the lattice. Simultaneously the water content is low. The remarkably low values of α and γ obviously are connected with the high fluorine content.

TITANITES FROM THE KOLA PENINSULA

The titanites from the Kola Peninsula, represented by the analyses No. 4—6 in Table I, are all from the well-known nephelite syenite *massif* of that region. The specimens of which the analyses 4 and 5 were made bore no closer information as to the locality. The sample of Anal. 6 was collected by Prof. Eskola from Kukisvumchorr in the Khibina *massif* (Collection Number 4719).

The properties of the titanites under consideration are as follows:

Titanite of Anal. 4 in Table I.

The mineral occurs as long prismatic crystals of a light brown color with a tendency to a reddish tone. The rock consists mainly of titanite (so called »titanitite»). The separation was effected with Clerici solution. The analyzed material was almost free from impurities. Optical properties are as follows:

$$\alpha = 1.94$$
$$\gamma = 2.095$$
$$2V\gamma = 23^\circ$$
$$c \wedge \gamma = 53^\circ$$

Sp. gr. = 3.54.

Titanite of Anal. 5 in Table I.

The mineral apparently occurs in a miarolitic cavity. The whole specimen was composed mainly of titanite forming long acicular crystals in spherulitic aggregates. The color is honey yellow. The separation was effected with

Clerici solution and the analyzed fraction was practically free from impurities. The optical properties are as follows:

$$\alpha = 1.93$$
$$\gamma = 2.11$$
$$2V\gamma = 25^\circ$$
$$c \wedge \gamma = 51^\circ—52^\circ$$

Sp. gr. = 3.51.

Titanite of Anal. 6 in Table I.

The mineral occurs as acicular crystals forming veins or clumps in the rock. These are composed mainly of titanite. Color light violet. The separation was effected with Clerici solution and the analyzed fraction was practically free from any impurities. The optical properties are as follows:

$$\alpha = 1.92$$
$$\gamma = 2.08$$
$$2V\gamma = 37^\circ$$
$$c \wedge \gamma = 53^\circ$$

Sp. gr. = 3.54.

The analyses of the three titanites mentioned above may be compared with the analyses of the Kola Peninsula titanites analyzed by Egorov and Vlodavez, and summarized by Bohnstedt in the description of the Kola Peninsula minerals edited by Fersman (1937). The accordance of the Russian analyses and those given in the present paper is very good. The minerals are poor in rare earths, and, on the other hand, exceedingly rich in niobium and strontium. The content of sodium is also comparatively high. However, the figures for fluorine in the present analyses are considerably higher than those given by the Russian analysts. The same can be said of the water content. In the Russian analyses only »loss on ignition» has been given, and the values thus obtained are lower than my figures for H_2O+.

THE TITANITE LATTICE

For the present purpose it is very instructive to follow the reasoning put forward by Zachariassen (1930) about the crystal structure of titanite. According to this author, the titanite lattice contains independent silicon oxygen tetrahedra with groups of $[CaO_7]$, $[TiO_6]$ and $[SiO_4]$. The twenty oxygen atoms of the unit cell are in positions of three different kinds (O_I, O_{II}, O_{III}) and one of them (O_I) is not bound in any of the $[SiO_4]$ groups. The oxygen atoms are linked to cations with the corresponding bonds as follows:

4 O atoms (O_I)	to: 1Ca + 2Ti	with a total bond of 1.62 of a unit.
8 O atoms (O_{II})	to: 2Ca + 1Ti + 1Si	2.24
8 O atoms (O_{III})	to: 1Ca + 1Ti + 1Si	1.96

These values of the bonds of the different oxygen atoms in titanite lattice reported by Zachariassen show no ideal agreement with the rule of electrostatic neutrality set up by Pauling. This is especially the case for O_I. In his paper Zachariassen emphasizes that »the less satisfactory agreement in the case of O_I may be explained by the fact that in titanite O_I is partly replaced by OH, so the resulting valency of O_I is between 1 and 2» (*op. cit.*, p. 15). In addition, he mentions that »titanite might as well contain small amounts of fluorine, replacing O_I» (*l.c.*).

Taking as a basis the interpretation of the coordination of the titanite structure put forward by Zachariassen, the sum of deviations from neutrality for all the bonds between atoms of the unit cell can be calculated. If divalent calcium and quadrivalent titanium be substituted by cations of the same coordination, and a different charge, the values of the respective bonds will be different from that calculated by Zachariassen. Calcium can be replaced by monovalent sodium or by trivalent yttrium (lanthanides); titanium by pentavalent niobium or trivalent aluminium (ferric iron). Under the assumption that in all the »end members» thus obtained the coordination of the different ions against each other is the same as in the ideal titanite structure referred to above, the bonds of the three kinds of oxygen atoms are as follows:

	Total bond for:		
Compound:	O_I	O_{II}	O_{III}
NaNb [O $\mid$ SiO$_4$]	1.90	2.11	1.97
YAl [O $\mid$ SiO$_4$]	1.43	2.36	1.93
CaAl [OH $\mid$ SiO$_4$]	1.28	2.06	1.78
NaTi [OH $\mid$ SiO$_4$]	1.48	1.95	1.81

In this review the symbols under »Compound» indicate only the valency of the corresponding ion. Taking into account that, according to Zachariassen, four »molecules» are enclosed in the unit cell, the whole deviation from neutrality of the unit cell is as follows:

Compound:	Total sum of the deviations of bonds of the unit cell from neutrality:
CaTi [O $\mid$ SiO$_4$]	3.68
NaNb [O $\mid$ SiO$_4$]	1.92
YAl [O $\mid$ SiO$_4$]	5.72
CaAl [OH $\mid$ SiO$_4$]	3.52
NaTi [OH $\mid$ SiO$_4$]	3.84

When calculating the deviations tabulated above, no attention has been paid to the sign of the separate deviations.

These figures, calculated on the basis of the structure analysis given by Zachariassen, are very illustrative. They show that a replacement of Ti-O through Al-OH is connected with a better agreement with the Pauling rule. In the replacement of Ca-Ti through Na-Nb the agreement is best. On the other hand, the replacement of Ca-Ti through Y-Al is absolutely worst from the present point of view.

THE WATER AND FLUORINE CONTENT

The citations after Zachariassen (*l. c.*) given above express the conviction of the said author that fluorine to a certain amount enters into the lattice of titanite, replacing O_I. In addition, Strunz (1937, p. 11) when comparing the titanite structure with that of tilasite says: »Von Titanit kennt man übrigens auch Kristalle, in denen ein Teil des nicht an Si gebundenen Sauerstoffs durch Fluor ersetzt ist». In fact, in the analyses of titanite minerals available in literature, I know previously only those from the Kola Peninsula occurrences where quantitative determinations of fluorine have been presented. The analyses referred to by Bohnstedt, in Fersman (1937), contain fluorine as well as chlorine determinations. However, the figures obtained by the respective analysts are very low, in many cases showing no presence of these elements at all. Only in one case has a considerable content of chlorine, *viz.* 0.29 % Cl, been detected. As to chlorine, the present determinations carried out by v. Knorring (Table I) failed to show the element in the titanite minerals investigated, except as regards the mineral from Miask. Contrary to the data obtained by various Russian analysts reported by Bohnstedt in his summary of the Kola Peninsula titanites, the titanites of the same nephelite syenite region analyzed in our Institute all contain fluorine in amounts considerably exceeding the figures presented by Bohnstedt. The two Finnish titanite minerals, *viz.* the titanite from a gabbro in Ylöjärvi and the grothite from limestone in Parainen, also showed fluorine, the latter being unusually rich therein. I have specially investigated the analyzed samples under the microscope in order to find traces of fluorite in same, the result of this search being, however, in all cases negative. Therefore, I cannot explain the fluorine content found in any other way than as being due to a real content thereof in the titanite itself.

As to the water (H_2O+) content, the matter is not so simple. In almost all modern titanite analyses presented in literature the figures for water have been given without, however, any closer account regarding the method of determination used. I have paid special attention to the fact that the determination of water in titanite is connected with certain difficulties. As stressed by many prominent mineral analysts in their respective handbooks, the ordinary Penfield method succesfully used when analyzing rocks of various kinds is not suitable for a number of water-containing minerals. The »water» occurring as hydroxyl ions with fixed positions in the lattice of the mineral, is by far not always expelled away by a simple heating in the Penfield tube at the temperature reached with those tubes without melting of the glass. Many minerals give off the whole amount of their water, but this only at comparatively high temperatures, where a Penfield tube can no longer be used. Smethurst (1935) has given a very striking example of such behavior in the case of epidote.

For the reasons pointed out above, the water determinations on the titanite minerals investigated in this paper were carried out by completely breaking down the titanite lattice. This was effected by means of fluxes of sodium tungstate or lead oxide mixture as explained above (p. 93). In order to illustrate the firmness with which water is bound to the titanite minerals, the water determinations were carried out also with the ordinary Penfield method without using any flux. The respective figures are as follows (Table IV):

TABLE IV

H_2O+ with	Anal. No. (in Table I):					
	1	2	3	4	5	6
The ordinary Penfield method	0.62	0.33	0.38	0.12	0.24	0.16
Flux of sodium tungstate or lead oxide mixture	0.71	1.13	0.53	0.56	0.61	0.49

As will be seen from the review just given, the figures obtained with the ordinary Penfield method are in many cases considerably lower than those obtained by means of breaking down the lattice with fluxes. This is especially characteristic of the Ylöjärvi titanite as well as of the Kola Peninsula minerals.

The significance of the customary »loss on ignition» in judging of the true water content of titanite may be illustrated by the following figures (Table V):

TABLE V

	Anal. No. (in Table I):					
	1	2	3	4	5	6
Loss on ignition	1.12	1.11	1.61	0.52	0.76	0.96
Sum of H_2O+ and H_2O-	0.85	1.44	0.71	0.64	0.73	0.73
Sum of F(Cl), H_2O+ and H_2O-	1.05	1.54	2.11	1.25	1.41	1.26

The figures for »loss on ignition» are, as is seen, in some cases higher and in others lower than the total water including the hygroscopic moisture. However, if the fluorine (chlorine) content be added to the total water, this figure will almost always be higher than the »loss on ignition». This will mean that, when igniting the mineral without breaking down the lattice through melting, a part of the fluorine content will be expelled away, this part being, however, very variable.

The results of the water determinations given above clearly show that the water content obtained with the customary Penfield method is by no means representative of the true water content of the mineral. This circumstance affords an indication that the figures for water in titanite previously given by various authors in literature might be too low if determined only with the Penfield method. The most extended modern analysis series so far published of titanites has been given by Kunitz (1936). Because of the fact that no account has been given by him as to the method used in the respective water determinations, the corresponding figures cannot be used in the present discussion. As mentioned above, this is a circumstance characteristic of most of the titanite analyses available in literature. As shown by the analyses of the present paper, all titanite analyses where water and fluorine have not been determined according to the principles presented above cannot be regarded as complete. In accordance with the predictions by Zachariassen (*l. c.*) and Strunz (*l. c.*) it seems that titanite, contrary to the classical opinion of its composition, represents a mineral in which water and fluorine play a noticeable rôle in the lattice.

When sifting this rôle the fact may first be noticed that the analytical evidences available so far are very scarce. It is obvious that a more extended analysis material of the water and fluorine content of titanite minerals is needed before drawing any definite conclusions. At any rate, the data presented in Table I in connection with the interpretation of the titanite structure given by Zachariassen seem to afford support to the prediction stressed by him. The amount of »water», being often very firmly bound in the titanite lattice, seems most likely to be due to hydroxyl ions having defined positions in the network. Together with fluorine they seem to substitute oxygen. It is, of course, not possible to prove this assumption solely on the basis of analytical data and to abandon the other alternative in the present case, according to which water could be thought to form independent molecules outside the titanite lattice proper. The fact, however, that fluorine to a very considerable part is present seems to indicate that hydroxyl and fluorine play similar rôles in the lattice.

If a replacement of oxygen through hydroxyl and fluorine is assumed, two different alternatives will still remain. The OH and F ions may either occupy positions of O_I or, on the other hand, they may build up a $[OH, F]_4$ group in place of a silicon oxygen tetrahedron $[SiO_4]$. In the latter case the place of Si would be vacant in the same way as is the case, *e. g.* in the minerals recently called garnetoids. Taking into account the comparatively small amount of such $[OH, F]_4$ groups in the lattice indicated by the molecular numbers in Table II, the decreasing of the density of the mineral would be practically insignificant. As can be shown through calculations based upon the dimensions of the unit cell of titanite reported by Zachariassen, the variations of the density of titanite demanded by the replacement in question are considerably smaller than the actual variations of specific gravity of natural titanite minerals. If the whole amount of hydroxyl and fluorine is assumed to occur as $[OH, F]_4$ groups and the molecular numbers of Table II are calculated according to such an assumption, the combined number of $[SiO_4]$ and $[OH, F]_4$ groups would in general be higher than the molecular numbers of (Ti+Nb+Al+Fe+Mg) and (Ca+Na+RE+Sr+Mn). Only in the Miask titanite would the agreement be better, the mineral showing a slight deficiency in silica. The assumption made by Zachariassen, according to which OH and F replace O_I, thus seems to explain the water and fluorine content more satisfactorily.

Looking on the figures presented in Table II, the fact may be stressed that the molecular numbers of OH and F are by no means dependent on each other. True, the grothite from Parainen is especially rich in fluorine and simultaneously remarkably poor in water, the opposite case being most beautifully represented by the titanite from Ylöjärvi. However, the relation between the content of these two constituents is not regular. The same can be said of the sum of water and fluorine. The molecular numbers of Si, (Ti+Nb+Al+Fe+Mg), and (Ca+Na+RE+Sr+Mn) in Table II show in general a very good agreement with the theoretical titanite formula, the numbers of (OH+F+Cl), however, varying within comparatively wide limits. If the whole amount of water and fluorine is considered to replace O_I, the resulting valency for the ion $(O, OH, F)_I$ would in the analyzed titanites of Table I be as follows (Table VI).

TABLE VI

	Anal. No. (in Table I)					
	1	2	3	4	5	6
Resulting valency of $(O, OH, F)_I$	1.83	1.73	1.74	1.81	1.80	1.84

The calculated values of the resulting valency of $(O, OH, F)_I$ clearly show that the incorporation of hydroxyl and fluorine in place of O_I has not led to the complete electrostatic neutrality, *viz.* 1.62, demanded by the titanite structure. However, through this replacement the deviation for $(O, OH, F)_I$ is no longer greater than for O_{II}.

According to all reasoning given above it seems justified to write the ideal titanite formula

$$CaTi\ [(O, OH, F) \mid SiO_4] \text{ or } CaTiSiO_4\ (O, OH, F),$$

instead of the conventional

$$CaTi\ [O \mid SiO_4] \text{ or } CaTiSiO_5.$$

Of course, the replacement of O_I through $(OH, F)_I$ brings about a certain defectness in the structure, the total neutrality of the lattice being slightly disturbed. As seen from the analyses presented above, the amount of water and fluorine is independent of the substitution of Ca and Ti through cations of other valency. It would be very interesting to know whether hydroxyl and fluorine play a similar rôle also in other minerals. This would be of a certain importance as regards for the general mode of occurrence of these two constituents in minerals in Nature. Recently, Jakob (1937, 1940, 1941) has shown that the minerals andalusite and kyanite also contain remarkable amounts of water. He suggests that this water content is not due to accessory contaminations in the lattice, but belongs to it as an essential constituent. It would be of considerable interest to check whether these minerals also contain fluorine. This has not been done so far.

CLASSIFICATION OF THE TITANITE GROUP

The whole conception of the titanite species was explored for the first time by Pictet in 1787. The mineral has since been found in a great number of varieties differing from one another through their general habit, dominant crystal faces, color, optical properties and chemical composition. Accordingly, a number of variety names has been given, most of them, however, being no longer to the purpose in modern mineralogical nomenclature. The designation titanite (sphene) is to day usually reserved for types comparatively closely corresponding to the ideal composition $CaTiSiO_5$ or simply to »titanites» in general, if not chemically analyzed. In any case, some varieties show deviations from this ideal composition so characteristic that the use of special names for them seems to be justified.

Starting from the structure formula of titanite, as set up by Struntz (1941) in his general classification of natural minerals, based upon known crystal structural features, *viz.*

$$CaTi\ [O \mid SiO_4],$$

the theoretical possibilities of variations in the titanite composition may be viewed. According to general mineralogical experience, the titanite lattice seems to be very capable of incorporating other ions in place of its ideal constituents.

In the ordinary titanite formula calcium, titanium, and oxygen can be substituted by other ions of a similar coordination. The following replacements are in practice to be taken into account:

Calcium: Na, Rare Earths, Mn, Sr, (Ba).
Titanium: Al, Fe (ferric and ferrous), Mg, Nb, (Ta), V, (Cr).
Oxygen: OH, F, (Cl?).

In addition, phosphorus may be thought to replace silicon. In some silicates, even in those containing separated [SiO_4] tetrahedra, such a replacement has in fact been observed. As an example zircon may be mentioned, its traceable content of phosphorus as well as its isotypic relation to xenotime being well-known. Recently, Mason and Berggren (1941) have shown that even garnet (spessartite) occasionally seems to be able to take up a considerable amount of phosphorus in its lattice. In titanite, however, phosphorus has so far not been met with in amounts causing a special search for and detection of it in the course of an analysis.

The ability of the afore-mentioned elements to build up a crystal lattice closely related to titanite may be judged in the following way: If these elements are readily capable of entering into a complex coordination corresponding to that of a titanite lattice, they will also be found in that mineral. One or other of the elements under consideration being enriched in titanite in average as compared with calcium or titanium respectively, this circumstance obviously affords an indication that the affinity to titanite lattice structure of the element is greater than the corresponding affinity of calcium or titanium. If, on the other hand, titanites in general are exceedingly devoid of a certain element, it can be deduced that such an element must show a reluctance towards the titanite lattice in conditions prevailing in rocks.

The replacement of calcium through sodium is actually realized in the mineral ramsayite found in the nephelite syenites of the Kola Peninsula. A summary of this very interesting mineral species is given by Kostyleva in the general description of the Khibina and Lovozero minerals edited by Fersman (1937). According to X ray data given by Kraus and Mussgnug (1941) the unit cell of ramsayite shows a perfect orthorhombic symmetry with dimensions deviating from those of titanite found by Zachariassen (1930). Whether the type of coordination of the cations of ramsayite really shows any resemblance to that of titanite is not known at present, the formula, according to the analyses, being $Na_2Ti_2[O \mid (SiO_4)_2]$ or $Na_2Ti_2Si_2O_9$. The deviation of the external symmetry of the mineral from that of titanite obviously is connected with certain displacements in crystal structure, this assumption being supported by the fact that the ordinary titanites, even in sodium-rich nephelite syenites, show only a comparatively low content of sodium, while, on the other hand, ramsayite is very devoid of calcium. Accordingly, there seems to exist only a very limited miscibility between titanite and ramsayite. At any rate, until the ramsayite structure is shown to be of an entirely different type to that of titanite, both minerals have to be grouped together as related species.

The mode of occurrence of ramsayite being limited only to the very sodic nephelite syenites and even there mostly to pegmatitic dykes and segregations, the question may be raised, whether a formation of it is possible in connection with the spilite reaction. In spilitized basic rocks only plagioclase has been metasomatically changed from a calcium compound to a corresponding sodium one. The optical properties of titanite and ramsayite being practically alike, a distinguishing between these two minerals does not always seem to be possible in a thin section, especially if the grains are small. Therefore, it is easily understandable that attention has never been paid to the matter. According to the summary given by Kostyleva (Fersman 1937), ramsayite also occurs as a secondary alteration product from lamprophyllite.

Were the rare earths, manganese, strontium, and barium to be present in titanite in the same abundance relation as compared with calcium as in the igneous rocks in average, the mean content of these elements in the mineral would be as follows (when taking CaO = 28 % for titanite):

Rare Earth oxides	0.1 % approx.
MnO	0.7
SrO	0.1
BaO	0.1—0.2

It is a well-known fact that titanites in general show rare earth oxides, according to modern analyses, in amounts mostly exceeding the percentage figure stated above. This is the case already in the titanites of ordinary igneous and metamorphic rocks, as pointed out in principle by Goldschmidt and Thomassen (1924), and as shown quantitatively by the beautiful analysis series published by Kunitz (1936) and Bohnstedt (in Fersman 1937). In addition, special titanite types, showing a very high content of the rare earths, occur in pegmatites of granitic as well as of nephelite syenitic origin. For those rare earth titanites the designation keilhauite has been given by Erdmann in 1844 and this name has been accepted by mineralogists also in the modern nomenclature of minerals. If one accepts the principle of giving a special name to a distinct chemical variety of a mineral species, the designation keilhauite must be considered as wholly justified. However, it should be kept in mind that keilhauite is not a separate species, but only a variety name. The analyses of keilhauite found in literature, even those most rich in rare earths, always show a comparatively high content of calcium. and a pure rare earth titanite is not known so far. On the contrary, a sifting of the matter leads to the opinion that the compound (YCe. .) (AlFe) [O | SiO_4] where calcium has been totally replaced by yttrium, cerium, *etc.* and titanium completely by aluminium, ferric iron and the like is at least to be considered as comparatively unstable.

This last-named opinion is supported by the occurrence of the mineral chevkinite, mineralogically defined and described for the first time by Rose in 1839. The whole conception of chevkinite being still not quite exact it seems, however, very probable that this mineral is to be classified together with titanite and keilhauite. According to the descriptions given by various authors, also chevkinite is, like many other rare earth pegmatite minerals, mostly decomposed in its crystal lattice. Therefore, the structure of the mineral is unknown so far.

In its whole appearance chevkinite affords a certain analogy with the structurally decomposed zircons. The question of the decomposition of the zircon lattice, causing a strong decrease of the specific gravity of the mineral down to about 3.9, has been stressed especially by the staff of the Mineralogical and Petrological Institute of the University of Bonn. Of the contributions published by the scientists of this Institute I will mention only the paper by Bauer (1939) and the account of the highly interesting experiment by v. Stackelberg and Rottenbach (1940). Especially the last-named paper seems to indicate that the decomposition of the zircon lattice really is caused by radioactive radiation. As pointed out by Bauer, the facts known about the decomposition of the zircon lattice obviously provide justification for the general statement that the crystallized compound $ZrSiO_4$ is »bei weitem nicht so stabil, als man meist anzunehmen geneigt ist» (1939, p. 202). The reasons why the zircon lattice can be broken down comparatively easily are so far not explored in detail. It may well be that they are entirely different in principle from that to which the disorder of the chevkinite structure is due. In spite of this the external analogy of chevkinite with the more or less decomposed zircon varieties containing rare earths, called cyrtolite, alvite, malacon, *etc.*, seems to be worth noting in this connection. As pointed out by Machatschki (1941) in connection with the decomposition of the zircon lattice, a contamination of radioactive elements, say, of thorium, is not in itseld sufficient to break down the lattice in question, as many minerals, *e. g.* monazite, practically always show a comparatively high content of it without, however, being decomposed. In order to become decomposed the lattice must, an addition, show a certain »instability» in its structure. In zircon this instability is due to the high coordination number of the comparatively small quadrivalent zirconium ion. In chevkinite, if structurally resembling titanite, the corresponding instability may be thought to be due to the considerable deviation of the unit cell from neutrality.

Thus, according to the reasoning presented above, the existence of a pure rare earth titanite is so far not to be regarded as certain. When classifying the titanite group I have therefore indicated the rare earth »end member» in the series only with the respective chemical formula and have given the mineral name chewkinite in parenthesis (*cf.* Fig. 1).

A manganese-rich variety called greenovite by Dufrenoy, obtained from a small manganese mine in St. Marcel, Piedmont, has been analyzed by Delasse and de Marignac. According to their old analyses reprinted, *e. g.*, in Doelter's »Handbuch der Mineralchemie», manganese really seems to replace calcium as it does in pegmatitic manganese apatites and some other calcium minerals. One seems justified in assuming that manganese in greenovite is present in the divalent state. Owing to this, the replacement of calcium through manganese does not affect the electrostatic neutrality of the lattice.

Of the two earth alkali metals, strontium and barium, but few determinations in titanites have been carried out. Due to the comparatively great ionic size, barium apparently shows no marked tendency to enter into the titanite lattice. Strontium, on the other hand, has been detected in some titanite types of the Kola Peninsula in considerable amounts. In accordance with these respective analyses made by Vlodavez and referred to by Bohnstedt (Fersman 1937), the analyses of the Kola titanites given in Table I also show very high figures for SrO. Many other rare minerals very rich in strontium (calcioancylite, lamprophyllite, rinkolite, lovchorrite, calcium rinkite, vudyavrite, yuksporite, apatite) occurring in the nephelite syenites of the Kola Peninsula (*cf.* Fersman 1937), the occasional contamination of strontium in the titanite lattice is perhaps merely due to the richness of the respective rock in strontium rather than to a special affinity of strontium to the titanite lattice. The relative impoverishment of strontium in regard to calcium in the Ylöjärvi titanite stressed above (p. 98), as compared with the whole rock, is to be noted in the present connection.

On the other hand, turning to the possible replacements of titanium through the elements mentioned above, the fact may first be recalled that aluminium and ferric iron (ferrous iron, magnesium) show a very striking impoverishment in relation to titanium in titanite lattice. Being a natural consequence of the circumstance that titanite on the whole represents a titanium mineral, this statement is, however, of very great importance when building up a general classification of the titanite mineral group. As is seen from the reasoning presented above in connection with the titanite lattice structure analyzed by Zachariassen (1930), there seem to exist no purely structural grounds making a complex silicate of calcium and aluminium or ferric iron of a titanite lattice type less stable than the corresponding calcium titanium silicate. The idealized formula of such a compound would be $CaAl[OH \mid SiO_4]$ where Al could be replaced by ferric iron. However, a mineral of this composition and lattice structure is not known. The reason for the non-existence of that mineral is considered to lie in the circumstance that calcium and aluminium (ferric iron) are able to form other lattices apparently more stable than the above assumed compound. In spite of this, it may be stressed that some titanite varieties show remarkable amounts of Al_2O_3 and Fe_2O_3. These titanite varieties J. D. Dana has designated as grothite, named after P. Groth, who first detected and analyzed the variety in question. The designation grothite being as well justified as that of keilhauite, I have used this name in the classification given below. Grothite is, thus, a variety name, not a species like ramsayite.

If the abundance relation of titanium to niobium, tantalum, vanadium, and chromium in titanite lattice were the same as in the igneous rocks in average, the mineral titanite would contain these elements in the following amounts (taking the mean TiO_2 content of titanite as 40 %):

Nb_2O_5	0.16 % approx.
Ta_2O_5	0.01
V_2O_5	1.4
Cr_2O_3	1.6

Vanadium and chromium have been determined in titanite only in a few cases, the analyses summarized by Bohnstedt (Fersman 1937) as well as those given in this paper representing the only examples in the matter known to me. In spite of the small number of determinations it seems, however, exceedingly likely that both the mentioned elements are not in general present in titanites in amounts corresponding to the figures mentioned above. For vanadium this statement is especially noteworthy the element in many respects showing a certain geochemical relationship to titanium. Thus it seems that in the titanite lattice vanadium does not feel itself quite at home. On the other hand, one must reckon with the possibility that, in a mineral paragenesis extremely rich in vanadium, also titanite may be found to contain high amounts thereof. So far this has not been found to occur.

As to niobium and tantalum in titanite minerals, quantitative determinations have been carried out previously by v. Hevesy, Alexander, and Würstlin (1926), Borowsky and Blochin (1937), and Burova (in Fersman 1937). In addition, Rankama (1944) has given the tantalum content in a series of titanite. The niobium content of the same minerals being under preparation by him, the combined niobium and tantalum content of his titanite series is not yet available. The highest niobium and tantalum content of a titanite mineral known so far is found by Burova (*op. cit.*) in a titanite from the Kola Peninsula, *viz.* 1.87 % $Nb_2O_5 + Ta_2O_5$. In accordance with this result the analyses No. 5 and 6 of Table I of this paper show considerable amounts of the earth acids.

When looking over the determinations of niobium and tantalum in titanite minerals available in literature, the general impression will be obtained that both these earth acids are well able to enter into the titanite lattice in amounts exceeding the mean value demanded above, *viz.* 0.16 % Nb_2O_5 and 0.01 % Ta_2O_5. In fact, this is also to be expected beforehand. As regards the general geochemistry of these two elements it is known that they are mostly camouflaged or, more correctly speaking, captured in titaniferous minerals in place of titanium. However, it is in this connection especially to be stressed that niobium and tantalum are not able to form a titanite lattice alone. As pointed out above (p. 98), in the titanite from Ylöjärvi, niobium really is impoverished in relation to titanium when compared with the bulk rock. If titanium be replaced by niobium or tantalum, calcium must simultaneously be replaced by sodium. The replacement CaTi through NaNb (NaTa) already suggested by Bohnstedt (Fersman 1937) seems really to play some rôle in titanite when crystallizing in surroundings very rich in niobium and tantalum. In accordance with the corresponding suggestion by Bohnstedt, the titanite minerals of Table I in fact show higher figures for sodium if niobium is present in high degree. As seen from Table II, however, sodium is in most cases in excess over the atomic ratio Na : Nb = 1 : 1 and the molecular amount of the hypothetical compound $NaNb[O \mid SiO_4]$ is only very small. Like a pure calcium aluminium (ferric iron) »titanite», a pure sodium niobium (tantalum) »titanite» seems not to be stable at all. In pegmatites, where the content of niobium and tantalum would be high enough for the purpose, compounds of the titanite lattice type of a composition nearly $NaNb[O \mid SiO_4]$ have never been met with. In these rocks niobium and tantalum show a very strong tendency to crystallize out as oxidic minerals, like members of the pyrochlore group, as oxides with rutile structure, *etc.* As in the case of a pure calcium aluminium »titanite», with regard to the pure sodium niobium »titanite» there do not seem to be any serious structural reasons which would make the respective atomic arrangement unstable. Thus, also here one has simply to rest content with the fact that such a compound does not occur as a mineral in Nature, without our being able to give any true explanation of the matter.

As a result of the whole reasoning given above, the mineralogical classification of the »titanite group» may be set up as is seen from Fig. 1. The »end members» and isomorphic series not being represented in Nature are indicated in the said Fig. by dotted lines; the questionable yttrium aluminium compound with the corresponding series by a dashed one. With Y all rare earths containing the lanthanides and yttrium are meant, and with Al aluminium as well as ferric and ferrous iron and magnesium. Ca means calcium, in lesser amounts manganese and strontium. Nb means niobium and tantalum. The minerals and mineral varieties actually met with in Nature, with the isomorphic mixtures combining them together, are indicated by straight lines. Of course, in practice the titanite minerals found in Nature are not binary mixtures of two compounds only, but contain all the compounds mentioned in proportions varying within the limits qualitatively pointed out in Fig. 1. Because of the fact that the analytical evidences put forward about the water and fluorine content of titanite minerals by no means are to be regarded as absolutely binding for a replacement of O_I through OH and F, I have not used the structure formulas proposed by Strunz in the figure.

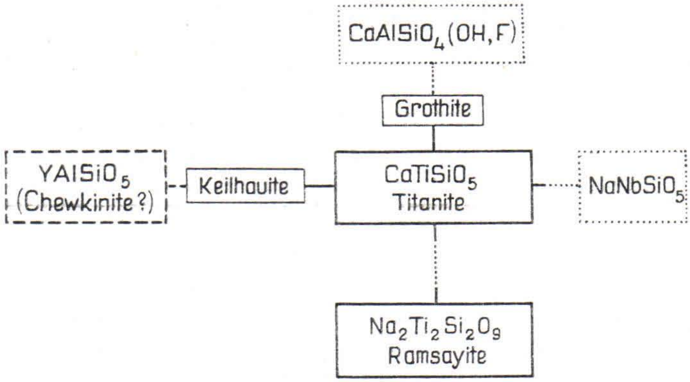


Fig. 1. Mineralogical classification of the titanite group.

Besides the titanite types mentioned above, Ramdohr (1936) has reported a titanite very rich in tin (10 per cent Sn). So far as I know, a complete analysis has not, however, been made of this mineral. Therefore, I have not included the variety in question in the general classification just proposed.

In addition, a few words may be added concerning the relative proportions of the rare earths and the niobium tantalum ratio in titanite.

As to the rare earths, their relative proportions in the titanite minerals of Table I are given in Table III. All the six analyzed titanite minerals being no representatives of a rare earth titanite proper, but containing only small amounts of these elements, the odd lanthanides from europium up to lutecium have not been estimated quantitatively. From the Table it will be seen that the cerium earths are dominant. As shown already by Goldschmidt and Thomassen (1924) in their very important paper on the subject, titanite on the whole represents a mineral where the abundance curve of the rare earths does not always show a fixed form like that of orthite, xenotime, *etc.* On the contrary, in respect to the lanthanide content, both yttrium and cerium titanite are known. As stressed above in connection with the strontium content of titanite, it seems that the titanite lattice serves as a certain indicator of the bulk composition of the rock. Goldschmidt has pointed out in various papers that, of the rare earths, the yttrium ones are especially characteristic of granitic rocks, whereas the cerium earths usually are comparatively strongly enriched in nephelite syenites. This is also to be seen in the rare earth content of the titanite minerals given in Table III. The analyses 4 and 5 representing nephelite syenite titanites of the Kola Peninsula, the cerium earths play in their rare earth content a very dominant rôle this being less pronounced in the analyses 2 and 3. It is true, in the Norwegian granite pegmatites, of the mineral content of which Bjørlykke (1939) has given a general review, the yttrium titanite has often been found in connection with orthite, apparently showing a dominance of the cerium earths. Thus, as will be easily understandable on the basis of the ionic radii of the rare earths, the yttrium earths obviously enter more easily into the titanite lattice than do the cerium earths. However, the fact that also cerium earth titanite proper is known in Nature seems to justify the designation keilhauite for all rare earth titanites, independent of their relative rare earth proportions. As stressed in »Gmelins Handbuch der anorganischen Chemie, 8. Auflage, System-Nummer 39, Seltene Erden» on p. 85, the name yttrotitanite is better used as a special designation for those keilhauites which, in contrast to »cerium titanite», contain more yttrium earths than cerium earths. Therefore, I have not used the term yttrotitanite in the classification given above.

In analogy with the rare earth content, also the niobium tantalum ratio in titanite shows no definite value. All the minerals given in Table I happen to contain much more niobium than tantalum. Because of a greater general abundance of niobium in relation to tantalum this is quite natural. However, as shown by v. Hevesy, Alexander, and Würstlin (1926), also such titanites are met with in which tantalum is more abundant than niobium. The general abundance relation of niobium and tantalum being under preparation by Rankama, the matter cannot be sifted any closer in the present connection. It is very probable that also the relation between these two earth acids will afford an indication of the corresponding relation in the bulk rock.

SUMMARY

Seeing that the analysis material available in literature so far is very scarce in regard to the water and fluorine content of titanite, six new complete analyses of titanites from different localities are presented. In order to make them usable in judging of the influence of the chemistry upon the optics of the mineral, some optical data are given. When analyzing the specimens special attention was paid to the determination of fluorine and water. It was found that the water content is bound very firmly into the lattice. In order to obtain the total amount of this firmly bound

water, the respective determinations were carried out by breaking down the whole titanite lattice. This was found to be the only way to make sure that water was quantitatively expelled away from the mineral.

Contrary to the major part of the titanite analyses available in literature and, on the other hand, in full accordance with the prediction put forward by Zachariassen, the titanites investigated were found to contain fluorine and/or water in remarkable amounts. This seems to be a circumstance most probably common to all titanite minerals.

Based upon the crystal structure analysis of titanite given by Zachariassen, it was suggested that water is present in titanite as hydroxyl, being partly replaced by fluorine. Both are supposed to be present in the lattice in exactly defined positions, replacing O_I. Thus, when writing the titanite formula it is better to use the form

$$CaTi[(O, OH, F) \mid SiO_4] \quad \text{or} \quad CaTiSiO_4(O, OH, F).$$

The replacement of O_I through $(OH, F)_I$ results in a better agreement of O_I with the rule of electrostatic neutrality demanded by Pauling. The mineral titanite affords one of the most beautiful examples of those crystal lattices which, though of very wide distribution in Nature, show a marked defectness in their crystal structure. This defectness is to a certain extent corrected through the replacement pointed out above.

Taking into account all practically important possibilities of diadochic replacements of the cations of the titanite formula, a general mineralogical classification of the titanite froup is presented in Fig. 1. The following replacements are of a more general theoretical importance:

1. Ca-Ti — Na-Nb
2. Ti-O — Al-OH
3. Ca-Ti — Y-Al
4. Ca-O — Na-$O_{\frac{1}{2}}$

The first of these cases is realized only to a very limited extent, the pure sodium niobium compound not having been met with in Nature.

The second possibility is also realized to a comparatively limited extent. The respective isomorphic mixtures are met with as grothite.

The third replacement is very common. The corresponding isomorphic mixture is generally designated keilhauite. The mineral chevkinite not being defined sufficiently exactly, a pure »end member» is to be considered as unknown so far.

The fourth of the replacements is realized in the mineral species ramsayite. The isomorphism between titanite and ramsayite seems to be exceedingly limited.

APPENDIX

ON THE TITANITE FROM NUOLAINNIEMI, IMPILAHTI

To the data and general discussion given above, a short description of an interesting titanite from Nuolainniemi in Impilahti may be added. The mineral is very rarely met with in the pegmatite dykes of that locality, well-known for their content of wiikite, only a couple of samples of titanite having been found so far. This titanite has been previously mentioned by Borgström (1910), who measured a crystal and determined its specific gravity to be unusually high for a titanite, *viz.* 3.591. Later on, a sample measuring about 10—15 cm. in diameter was found and has been placed in the collections of the Technical High School at Helsinki (Collection Number 4807). Professor Heikki Väyrynen, chief of the respective Institute, very kindly put this sample at my disposal.

The titanite sample, representing a single crystal individuum, shows a marked zoned structure where a dark brown kernel is surrounded by alternating dark and light zones in regular arrangement. The light zones are very soft and can easily be scraped away with a knife. In its marginal parts the whole crystal seems to be altered, this decomposed outer zone cutting abruptly through the zoned kernel of the crystal. The structure of the crystal may be presented schematically in Fig. 2.

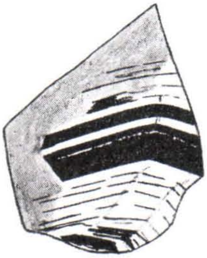


Fig. 2.

A microscopic investigation of the mineral showed that the brown kernel of the crystal contained numerous almost opaque inclusions. It is very possible that these inclusions are wiikite, this mineral not, however, occurring as separate grains in the sample. Because of the fact that wiikite, according to a powder photograph, showed no undecomposed crystal structure, an identification of the nature of these inclusions was not possible. At any rate, when judging the analysis given below, the possibility that the analyzed material might have been contaminated with this mineral has to be taken into account. In the zoned outer parts of the crystal the dark zones were often almost opaque too, showing a deep brown color. It is obvious that the original titanite in these zones has been altered. The light zones are also isotropic without any external traces of crystalline matter. The marginal parts of the crystal were altered to an undeterminable isotropic matter with relict remainders of crystalline titanite. A small number of quartz inclusions are also visible.

A chemical and spectrographical analysis was made of the unaltered brown kernel with inclusions, as well as of the light zones. The results are presented in Table VII.

TABLE VII. ZONED TITANITE, NUOLAINNIEMI, IMPILAHTI

	Brown crystalline kernel	Light-colored zone
SiO_2	27.80	19.2
TiO_2	35.71	45.0
Nb_2O_5	1.60	3.3
Ta_2O_5	1.75	2.9
V_2O_5	0.05	0.04
Al_2O_3	1.96*	0.0
Fe_2O_3	1.91	0.0
FeO	0.69	0.0
ZrO_2	0.06	0.05
CaO	24.18	11.2
SrO	0.01	n. d.
BaO	0.01	n. d.
Sc_2O_3	0.03	0.03
Y_2O_3	0.96	0.02
La_2O_3	0.01	0.01
Ce_2O_3	0.19	0.07
Loss on ign.	3.40	10.6
Sum	100.32	92.4
H_2O-	0.02	1.0

*Including the lanthanide oxides from Pr_2O_3 to Lu_2O_3.

The material for the second analysis in Table VII, *viz.* the light-colored zone, was obtained through boring off a number of those zones by means of a small dentist's drill driven by an electric motor. However, the material obtained was very scanty, amounting only to about 50—60 mg. Therefore, the corresponding analysis could be carried out only very roughly and incompletely. As to the methods used for both analyses in Table VII, they were the same as earlier given in a separate chapter. Due to the scantiness of the material in both analyses of Table VII the rare earths were not chemically enriched. Accordingly, in the first analysis of the brown crystalline kernel, the figure of Al_2O_3 includes also the rare earth oxides from Pr_2O_3 to Lu_2O_3. Taking into account the considerable content of Y_2O_3 in this analyzed material, it seems most probable that the greatest part, if not all, of the alumina given actually is rare earths.

When looking at the analyses presented in Table VII the fact may be emphasized that, already in the brown crystalline kernel, a slight deficiency of lime (and its substitutes) as well as of silica is to be observed as compared with titania (and its substitutes). This deficiency is, however, exceedingly characteristic of the light-colored zone of the titanite. The loss on ignition is very great in both analyses, especially in the second one. In addition, in the light-colored zone, lime shows a marked deficiency also in respect of silica.

The deficiency mentioned above in the crystalline kernel obviously is due to the inclusions of the supposed wiikite. According to microscopical investigation these inclusions are, however, lacking in the light-colored zones. In order to prove whether these light zones are crystalline at all or not, powder photographs were taken from the materials of both analyses in Table VII as well as of the marginal part of the crystal. For the sake of comparison a powder photograph was taken also of the chemically almost ideal titanite from Miask, the composition of which has been given in Table I.

The powder photographs mentioned above clearly show that the brown crystalline kernel does not contain any crystalline matter other than titanite. However, both the light-colored zones and the marginal parts of the crystal contain quartz, besides titanite. A very remarkable feature in the respective photographs is the fact that lines of the TiO_2 modification in the form of anatase are visible. In these parts of the crystal an alteration of titanite to a mixture of anatase and relict titanite has taken place. Thus the peculiarities of the second analysis of Table VII will be understandable.

The data shortly reported above of the zoned structure of the titanite under consideration are very interesting. However, because of the fact that only one single crystal of this kind has been found so far in Nuolainniemi, I will not in this connection touch more closely upon the problem of the sequence of crystallization of the mineral. Two alternatives seem to be possible in the matter. According to the first, the crystallization has been rhythmic and the strong alteration of the light zones is due to some reason or other in the composition or to the conditions prevailing during the crystallization. According to the second, the alteration of the light zones has taken place in the mineral after complete crystallization. The leaching out of lime and silica seems to be evident, and the mechanism as well as the reasons thereof cannot yet be entirely solved. I have only used the opportunity to report my observations in the matter in order to call attention to the phenomenon under consideration. It seems very possible that a thorough solving of the present problem will furnish us with a more complete knowledge of the stability relations of the titanite lattice. Whether similar zoned structures are common also in other titanites is a matter unknown to me.

Finally, I desire to add some words of gratitude to Professor Heikki Väyrynen for his kind permission to use the rare specimen of titanite from Nuolainniemi in the present investigation. I am also indebted to Dr. Frans E. Wickman of the Mineralogical Institute, Stockholms Högskola, Sweden, for helping me in the interpretation of the powder photographs.

GEOCHEMICAL LABORATORY, INSTITUTE OF GEOLOGY,
UNIVERSITY OF HELSINKI, JUNE 1946.

REFERENCES

BAUER, ANTON, Untersuchungen zur Kenntnis der spezifisch leichten Zirkone. Neues Jahrb. Min. *etc.*, B.-Bd. 75, Abt. A, p. 159, 1939.

BERMAN, HARRY, Constitution and Classification of the Natural Silicates. Am. Min., Vol. 22, p. 342, 1937.

BJØRLYKKE, HARALD, Feltspat, V. De sjeldne Mineraler på de Norske Granittiske Pegmatittganger. Norges Geol. Undersökelse, Nr. 154, 1939.

BOLDYREW, A. K., Bull. de l'Acad. des Sc. de Russie, 1924. (Russian). Cited according to the Summary: Kristallographische Untersuchung des Tscheffkinits. Neues Jahrb. Min. etc., Abt. A, I Bd., p. 247, Jahrg. 1926.

BORGSTRÖM, L. H., Mineralogiska notiser 7—10. Geol. För. Stockholm Förh., Bd. 32, p. 1525, 1910.

BOROWSKY, I. B. and BLOCHIN, M. A., The Analysis of Minerals by the X-Ray Spectroscopical Method. Bull. l'Acad. Sci. l'URSS, Cl. Math. Nat., Ser. Géol., No. 5, 1937. (Russian with English Summary.)

CLARKE, F. W., The Data of Geochemistry. U. S. Geol. Surv., Bull. 770, 1924.

CUMMING, A. CH. and KAY, S. A., A Text-Book of Quantitative Chemical Analysis. Edinburg, 1939.

v. ENGELHARDT, W., Die Geochemie des Barium. Chem. d. Erde, Bd. 10, p. 187, 1936.

FERSMAN, A. E., Minerals of the Khibina and Lovozero Tundras. Lomonossov Institute of the Academy of Sciences of USSR, Moscow and Leningrad, 1937.

GOLDSCHMIDT, V. M. und THOMASSEN, L., Geochemische Verteilungsgesetze der Elemente, III. Röntgenspektrographische Untersuchungen über die Verteilung der seltenen Erdmetalle in Mineralen. Skr. Norske Vid. Akad. Oslo, I, Matem.-Naturv. Kl., No. 5, 1924.

GOLDSCHMIDT, V. M., The Principles of Distribution of Chemical Elements in Minerals and Rocks. Journ. Chem. Soc. London, p. 655, 1937.

v. HEVESY, G., ALEXANDER, E. und WÜRSTLIN, K., Über das Häufigkeitsverhältnis Niob-Tantal in Titanmineralien. Zeitschr. anorg. allg. Chem., Bd. 181, p. 95, 1926.

v. HEVESY, G., ALEXANDER, E. und WÜRSTLIN, K., Die Häufigkeit der Elemente der Vanadiumgruppe in Eruptivgesteinen. Zeitschr. anorg. allg. Chem., Bd. 194, p. 316, 1930.

JAKOB, J., Über den Alkaligehalt der Disthene. Schweiz. Min. Petr. Mitt., Bd. XVII, p. 214, 1937.

—»— Über den Chemismus des Andalusits. Schweiz. Min. Petr. Mitt., Bd. XX, p. 8, 1940.

—»— Chemische und strukturelle Untersuchungen am Disthen. Schweiz. Min. Petr. Mitt., Bd. XXI, p. 131, 1941.

KRAUS, O. und MUSSGNUG, F., Identität von Lorenzenit und Ramsayit. Naturwissenschaften, Jahrg. 29, p. 182, 1941.

KUNITZ, WILHELM, Beitrag zur Kenntnis der magmatischen Assoziationen III. Die Rolle des Titans und Zirkoniums in den gesteinsbildenden Silikaten. Neues Jahrb. Min. *etc.*, B.-Bd. 70, Abt. A, p. 385, 1936.

LACROIX, A., Minéralogie de Madagascar. Paris, Tome 1, 1922.

LARSEN, ESPER S. and BERMAN, HARRY, The Microscopic Determination of the Nonopaque Minerals. U. S. Geol. Surv., Bull. No. 848, 1934. (Second Edition).

MACHATSCHKI, F., Zur Frage der Stabilität des Zirkongitters. Zentralbl. Min. *etc.*, Abt. A, Jahrg. 1941, p. 38, 1941.

MASON, BRIAN and BERGGREN, THELMA, A Phosphate-bearing Spessartite Garnet from Wodgina, Western Australia. Geol. För. Stockholm Förh., Bd. 63, p. 413, 1941.

MINAMI, E., Gehalte an seltenen Erden in europäischen und japanischen Tonschiefern. Nachr. Ges. Wiss. Göttingen, Fachgruppe IV, Neue Folge, Bd. 1, p. 155, 1935.

NOLL, W., Geochemie des Strontiums. Chem. d. Erde, Bd. 8, p. 507, 1934.

RAMDOHR, PAUL, Ein Zinnvorkommen im Marmor bei Arandis, Deutsch-Südwestafrika. Neues Jahrb. Min., Abt. A, B.-Bd. 70, p. 1, 1936.

RANKAMA, KALERVO, On the Geochemistry of Tantalum. Bull. Comm. géol. Finlande, N:o 133, 1944.

RANKAMA, KALERVO and JOENSUU, OIVA, A Simplified Method of Quantitative Spectrochemical Analysis in the Carbon Arc Cathode Layer, Based on the Use of the Logarithmic Wedge Sector. C. R. Soc. géol. Finlande, N:o XIX; Bull. Comm. géol. Finlande, N:o 138, p. 8, 1946.

SAHAMA, TH. G. and VÄHÄTALO, VEIKKO, The Rare Earth Content of Wiikite. C. R. Soc. géol. Finlande, N:o XIII; Bull. Comm. géol. Finlande, N:o 125, p. 97, 1939.

SCHOELLER, W. R. and POWELL, A. R., The Analysis of Minerals & Ores of the Rarer Elements. London, 1940.

SMETHURST, A. F., Anomalies in the Analytical Determination of Water in Epidote. Min. Mag., Vol. XXIV, p. 173, 1935.

v. STACKELBERG, M. und ROTTENBACH, E., Dichte und Struktur des Zirkons. IV Die Ursache der Isotropisierung des Zirkons. Zeitschr. Krist., Abt. A, Bd. 102, p. 207, 1940.

STRUNZ, HUGO, Titanit und Tilasit. Zeitschr. Krist., Abt. A, Bd. 96, p. 7, 1937.

—»— Mineralogische Tabellen. Leipzig, 1941.

TSCHIRWINSKY, P., Durchschnittliche chemische Zusammensetzung der wichtigsten Mineralien der Eruptivgesteine und der Meteorite. Memoires de l'Institut Polytechnique du Don, 11. (Cited according to the Summary: Neues Jahrb. Min. etc., II, p. 160, 1931).

ZACHARIASSEN, W., The Crystal Structure of Titanite. Zeitschr. Krist., Abt. A, Bd. 73, p. 7, 1930.

Uusia jäseniä Suomen Geologiseen Seuraan valitaan kahden jäsenen ehdotuksesta.

Seuran julkaisut ilmestyvät sarjassa *Bulletin de la Commission géologique de Finlande* ja jaetaan

1. kaikille jäsenille,
2. niille, jotka saavat mainitun sarjan,
3. laitoksille ja yhdistyksille, jotka haluavat julkaisujen vaihtoa.

Suomen Geologisen Seuran osoite on Bulevardi 29, Helsinki.

Medlemmar i Geologiska Sällskapet i Finland inväljas på förslag av två av Sällskapets medlemmar.

Sällskapets publikationer utgivas i serien *Bulletin de la Commission géologique de Finlande* och utdelas till

1. Sällskapets medlemmar,
2. personer, som fått mottaga nämnda serie,
3. institutioner och sammanslutningar, vilka önska träda i skriftutbyte med Sällskapet.

Geologiska Sällskapets i Finland adress är Bulevarden 29, Helsingfors.

Pour devenir membre de la Société géologique de Finlande on doit être présenté par deux membres.

Les publications de la Société seront éditées dans la série *Bulletin de la Commission géologique de Finlande* et seront distribuées

1. aux membres de la Société,
2. aux personnes ayant reçues la présente série,
3. aux institutions et aux associations désirant entrer en échange des publications.

S'adresser à la Société géologique: Bulevardi 29, Helsinki.