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Applications of lithogeochemistry in the search for Proterozoic porphyry-type molybdenum, copper and gold deposits, southern Finland

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APPLICATIONS OF LITHOGEOCHEMISTRY IN THE SEARCH FOR PROTEROZOIC PORPHYRY-TYPE MOLYBDENUM, COPPER AND GOLD DEPOSITS, SOUTHERN FINLAND

by

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with 14 figures, 2 tables and one appendix

Extensive primary halos are associated with the porphyry-type occurrences in southern Finland. The halo patterns are variable in shape, size and associated elements in and around each occurrence, depending on local conditions, but the halos exhibit a general zoning towards the core: $Zn(\pm Pb)$ — $Au(\pm Sb \pm As)$ — $Cu(\pm S \pm Ag)$ — $K_2O(\pm Rb \pm Rb/Sr \pm Ba \pm SiO_2)$ — Mo. The major ore metals, Cu and Mo, exhibit high anomaly contrasts and are most suitable for explorational purposes. Elements forming the broadest halos have low anomaly contrasts but are useful pathfinders for slightly eroded or sub-surface deposits. Variables associated with wall-rock alteration, K_2O, Rb and SiO_2, are of limited value because they exhibit only confined halos in the root and central zones of mineralization with low anomaly contrasts. A few tens of samples/km² seem to be adequate in local exploration in delineating the halo pattern and the most promising parts of a mineralization.

The porphyry-type occurrences were formed by extensive hydrothermal processes, which produced scattered anomalies over large areas. The host rocks of Cu-bearing porphyry-type occurrences are characterized by an abnormally high variation in Cu contents, although the median contents of Cu are higher in phases with more mafic composition. Regional Cu anomalies are concentrated in and around mineralized areas and are often associated with more confined anomalies of other variables related to mineralization such as Mo, As, K_2O and Rb/Sr. The low and constant background contents of ore metals in granitoids makes it possible to study small changes in element concentrations and to use low density sampling; one to five samples/km² is adequate for regional investigations.

Outside mineralized areas the host granitoids exhibit no geochemical specialization and cannot be distinguished from barren granitoids either in bulk geochemistry or average contents or ore metals.

The target surveys are based on about 700 samples collected from the plutonic host rocks in and around five occurrences, and a reconnaissance study conducted on about 1.000 samples collected from 49 granitoid phases of 21 areas in southern Finland; 11 of the granitoids are considered productive for Mo, Cu and Au mineralization. All the samples were analysed for over 30 elements with INAA, XRF and AAS.

Key words: geochemical prospecting, geochemistry, mineral potential, primary halos, cluster analysis, porphyry deposits, granitoids, host rocks, molybdenum, copper, gold, Proterozoic, Finland.

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PREFACE

This work stems from the Porphyry Project that was carried out at the Department of Geology, University of Helsinki, from 1980 to 1983. The Project was initiated to study the potential of the Svecokarelian granitoids for the occurrence of porphyry-type Mo, Cu and Au deposits. The main aims of the research were: 1) to give the geological and petrographical characteristics of the Mo, Cu and Au occurrences associated with the granitoids; 2) to investigate the geology, petrography and geochemistry of the host granitoids; and 3) to study the applicability of lithogeochemistry to regional and local exploration.

Altogether 49 granitoid phases were studied in 21 areas (Fig. 1) in which 10 targets contain Mo and/or Cu occurrences, some of which are Au-bearing. The results have been summarized by Nurmi et al. (1984). Five areas were chosen for more detailed lithogeochemical investigation: the Mo-Cu-Au occurrence of Susineva, Kalajoki (No. 3 in Fig. 1); the Mo-Cu occurrence of Luukkolansaari, Puumala (No. 1); the Cu occurrence of Tienpää, Halsua (No. 4); the Mo occurrence of Lahnanen, Viitasaari (No. 2); and the Cu-Au occurrence of Kopsa, Haapajärvi (No. 14). Regional studies were done over the Rautio batholith enclosing the Susineva occur-rence and over the Käkövesi batholith enclosing the Luukkolansaari occurrence in addition to local surveys conducted in and around the occurrences. About 700 samples were collected from the plutonic host rocks and analysed for over 30 elements.

Results of the lithogeochemical surveys have been published from the Luukkolansaari area and Käkövesi batholith, and from Tienpää, Lahnanen and Kopsa by Nurmi (1984), and from the Susineva area and Rautio batholith by Nurmi and Isohanni (1984). In the latter the results are compared on a regional scale with those of till and stream-sediment geochemistry and on a local scale with those of till geochemistry. Moreover, the history of the crystallization of the Rautio batholith has been outlined by Nurmi (1983), utilizing trace element geochemistry.

The present paper aims to summarize the applicability of lithogeochemistry to the search for Proterozoic porphyry-type deposits with special reference to the character and sequence of primary halos. Furthermore, the possibility of applying lithogeochemistry at the reconnaissance stage is discussed. In this context, the analytical results of about 1.000 samples from 49 granitoid phases in 21 areas are included.

PREVIOUS STUDIES

Phanerozoic porphyry ores are nowadays important suppliers of the world's Cu and Mo and include significant by-product metals such as Au, Ag, Re, U, W and Sn, of which the last two may be the principal metals in deposits (Sutherland Brown and Cathro, 1976). The number of comprehensive papers published recently shows how much progress has been
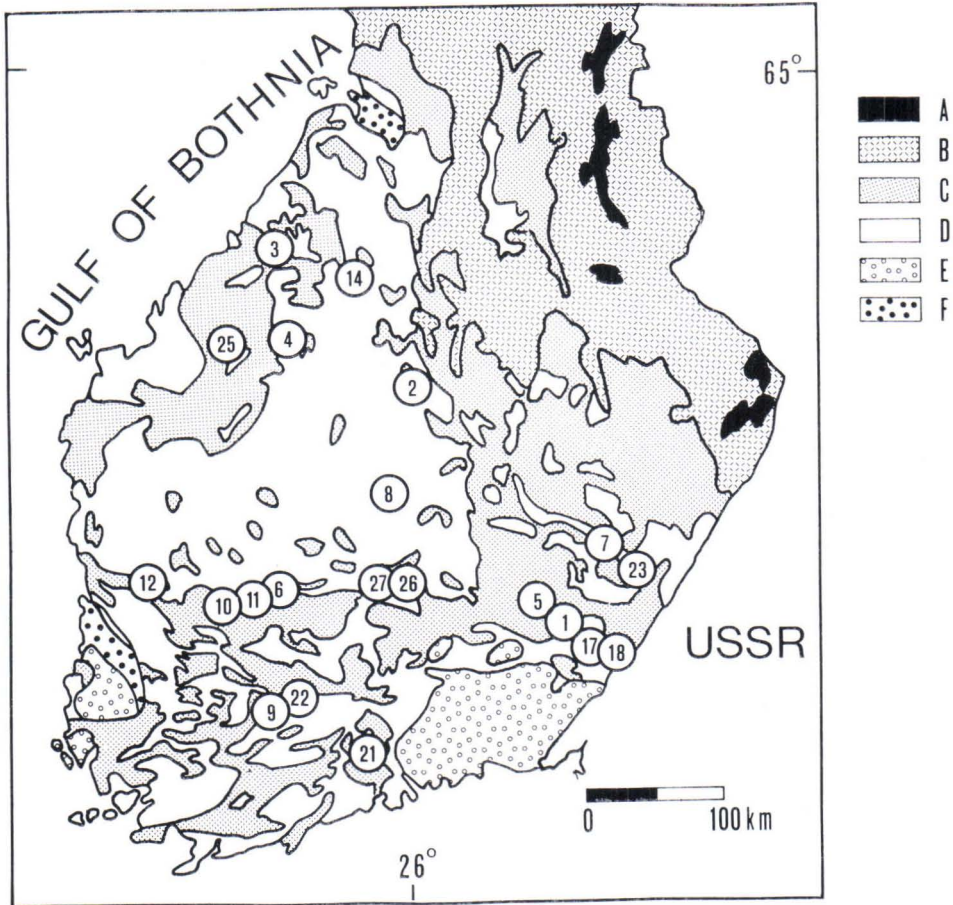
Fig. 1. Location of study areas and associated occurrences on a geological map of southern Finland (simplified from Simonen, 1980). *Study areas:* 1 = Käkövesi, Puumala (Mo-Cu occurrence of Luuk-kolansaari); 2 = Lahnanen, Viitasaari (Mo occurrence of Lahnanen and Cu-As showing of Kotanen); 3 = Rautio, Kalajoki (Mo-Cu-Au occurrence of Susineva); 4 = Tienpää, Halsua (Cu occurrence); 5 = Luonteri (Hirvensalo), Anttola; 6 = Kutemajärvi, Orivesi; 7 = Varparanta, Enonkoski (Mo occurrence); 8 = Palokka, Jyväskylä (Cu-As/Pb-Zn/Cu-Fe showings); 9 = Renkajärvi, Renko; 10 = Hämeenkyrö (Cu-W mine of Ylöjärvi); 11 = Värmälä, Tampere; 12 = Majajärvi, Kankaanpää (Mo showing); 14 = Kopsa, Haapajärvi (Cu-Au occurrence); 17 = Äitsaari, Ruokolahti; 18 = Salosaari, Ruokolahti; 21 = Mäntsälä; 22 = Aulanko, Hämeenlinna; 23 = Silvola, Savonlinna; 25 = Kalliokangas, Evijärvi; 26 = Sydänmaa, Luhanka; 27 = Hernemäki, Luhanka. *Bedrock units:* A = Archean greenstone belts; B = Presvecokarelian granitoids; C = Svecokarelian supracrustal rocks; D = Svecokarelian plutonic rocks (predominantly granitoids); E = rapakivi granites; F = Jotnian sediments.

made in understanding the genesis and characteristics of porphyry deposits (e.g., Laznicka, 1976; Sutherland Brown, 1976; Sillitoe, 1979; Beane and Titley, 1981; Titley and Beane, 1981; Westra and Keith, 1981; White *et al.*, 1981; Titley, 1982). Lithogeochemical studies of porphyry deposits are much fewer (see Govett, 1983) even though the large size and characteristic alteration zones of the deposits make them very suitable targets for such survey.

In recent years, Precambrian analogies for the Phanerozoic porphyry deposits have been described from the Baltic Shield (Gaál and Isohanni, 1979; Gaál *et al.*, 1981; Walser and Einarsson, 1982; Nironen and Csongrádi, 1984; Nurmi *et al.*, 1984) and from other shield areas (Blecha, 1974; Kirkham, 1974; Wolfe, 1974; Chute and Ayres, 1977; Findley and Ayres, 1977; Davies and Luhta, 1978; Wakefield, 1978; Colvine and Sutherland, 1979; Goldie *et al.*, 1979; Sinclair, 1979; Ayres and Černý, 1982; Barley, 1982; Sinclair, 1982). The studies indicate that porphyry mineralization represents

a potential new ore type, in the Precambrian, too, although most of the occurrences found so far are subeconomic. Possible exceptions are the exhausted Ylöjärvi mine in Finland (Himmi *et al.*, 1979), the Aitik mine in Sweden (Zweifel, 1976) and a few deposits in Canada (Ayres and Černý, 1982, p. 480; Sinclair, 1982). Lithogeo-chemical studies of the Precambrian porphyry-type occurrences, however, are still scarce and based on only a limited number of elements and samples (Wolfe, 1974; Friske *et al.*, 1979; Gaál and Isohanni, 1979; Davies, 1980; Sinclair, 1982).

Characteristics of porphyry mineralization

One of the most typical features of Phanerozoic porphyry deposits is their extensive wall-rock alteration and metallization, usually accompanied by pronounced zoning. The deposits have an exceedingly complex pattern, and by no means all of them fit the general models proposed by Lowell and Guilbert (1970) and Rose (1970). Considered broadly, however, the central parts of porphyry deposits exhibit

potassic alteration (K-feldspar, biotite and muscovite) succeeded by sericitic (sericite and quartz), argillic (clay minerals and quartz) and propylitic (chlorite, epidote group, albite, quartz and carbonates) zones (Fig. 2). A complete series of alteration is only rarely present, the zones often being diffuse and overlapping or telescoped (Boyle, 1982a). Furthermore, one or more of the zones may be lacking (Sillitoe *et*
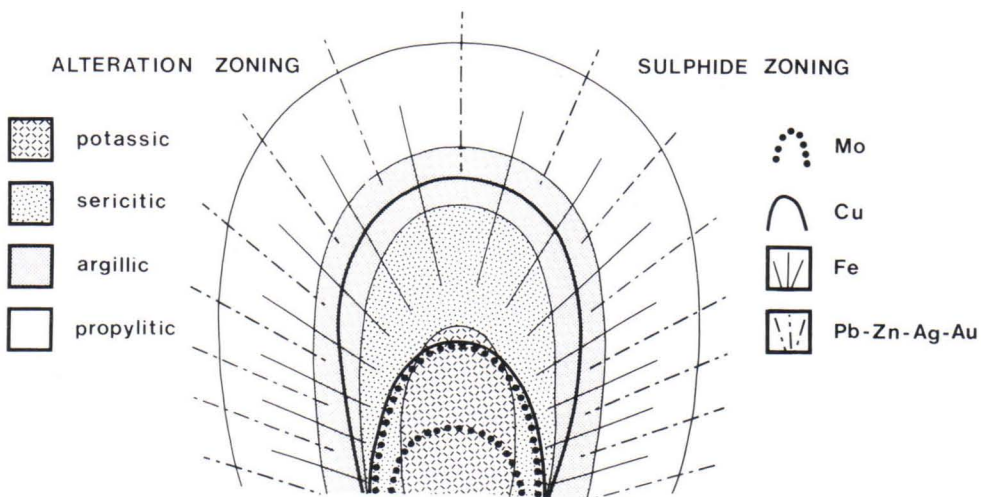

Fig. 2. Generalized model for sulphide and alteration zoning in Phanerozoic disseminated and stockwork porphyry copper and molybdenum deposits (modified from Boyle, 1982a).

al., 1982), the argillic alteration may be due to supergene processes (Beane, 1982; Boyle, 1982a), and in some deposits propylitization is difficult to distinguish from low-grade metamorphism (Drummond *et al.,* 1976; Boyle, 1982a).

Alteration and metallization are mainly controlled by temperature, acidity, and oxygen and sulphur activity of the hydrothermal fluids (Beane and Titley, 1981). Potassic alteration is caused by high salinity (on the order of 30 to 60 wt % NaCl equiv.) and temperature magmatic-hydrothermal solutions, which have a high K^+/H^+ activity ratio (Beane, 1982). The solutions affect K exchange for the Na and Ca that were originally present in the igneous plagioclase of granitoids, and result in K-feldspar addition. In high-Mg environments, K additions lead to biotitization.

In the outer zones, the solutions are at lower temperature and salinity ($<$ 15 wt % NaCl equiv.) and contain a marked proportion of meteoric water; K^+/H^+ activity ratio is lower and acidity is higher (Beane, 1982). Chemical changes in the alteration depend on the composition of the original rock types. In sericitic zones typical components added are K, H_2O, B, F, Cl and Si; extracted ones may include Na, Ca, Mg and Si (Boyle, 1982a). Argillic zones are characterized by removal of Ca, Mg, Mn, Na and Si, and by addition of H_2O, CO_2 and B. Propylitic alteration causes only minor chemical changes. Water and CO_2 are introduced, and weak extraction or redistribution of Si may occur.

Metallization includes disseminations, fracture fillings and quartz veinlets. Zoning of sulphide minerals varies not only between different types of porphyry deposit, but also between individual deposits (Boyle, 1982a). Figure 2 exhibits the typified zonal pattern of copper and molybdenum deposits. The deepest part is composed of a weakly mineralized or barren core around which Mo is concentrated. In porphyry molybdenite deposits, molybdenite occurs prin-

cipally in stockworks of quartz-molybdenite-fluorite veins associated with source intrusions originally enriched in H_2O, F and Mo (Woodcock and Hollister, 1978; White *et al.,* 1981).

Economic mineralization of Cu is invariably restricted to the highly sericitized and argillized zones. Chalcopyrite mainly deposits late in the evolution of potassic alteration or during the transitional stage between potassic and sericitic alteration (Beane, 1982). The deposition may proceed according to various mechanisms: 1) cooling of hydrothermal solutions decreasing the solubility of sulphides and the stability of Cu-Cl complexes, 2) diffusion of Fe from wall rocks and combining Cu and S in vein solutions, 3) dilution of concentrated solutions resulting in dissociation of Cu-Cl complexes, 4) mixing of fluids transporting individual components, 5) neutralization of acid solutions leading to dissociation of H-S complexes, and 6) oxidation-reduction (Beane and Titley, 1981; Beane, 1982).

The chalcopyrite zone is surrounded by a broad pyrite halo, and base metal veins with Au, Ag, Zn and Pb are found in the periphery of the pyrite halo. The zonal pattern of ore and associated metals is broadly the same as in epigenetic ore deposits in general (Beus and Grigorian, 1977) and suggests that deposition is principally controlled by a progressive decrease in the stability of the compounds in which the metals are transported by ore-forming solutions, although Beane (1982) expresses the importance of compositional changes in the evolution of mineralizing solutions.

The vast majority of fluid inclusions from porphyry copper deposits have homogenization temperatures in the range of optimal heat and mass transfer in a convecting hydrothermal system, ca. 300° to 450°C (Beane and Titley, 1981), but values over 700°C have been reported (e.g., Roedder, 1971). Formation temperatures of alteration zones exhibit high variations even within a particular deposit and temperatures of different zones are largely

overlapping. Beane and Titley (1981) give approximate temperature ranges from 300° to over 400°C for potassic zones; from 250° to 350°C for phyllic zones; and from 150° to 300°C for propylitic zones in the porphyry copper deposits of southwestern North America. Pressure varies from 150 to 1.500 bars and there is good evidence of pressure fluctuations in individual deposits possible as a result of repeated episodes of fracturing.

In porphyry copper and molybdenum deposits of Central Asia temperatures of 400° to 730°C and pressure of about 1.400 bars are given for potassic alteration; temperatures of 320° to 430° are reported for argillic and sericitic alteration (Berzina and Sotnikov, 1977). Silicification takes place in a wide temperature range between 200° and 800°C, and the principal ore deposition at 200° to 400°C in specific areas where phase transformation occurs in the solutions. Mineralizing solutions were invariably enriched in Cl, F and CO_2 in individual occurrences.

Principal deposition of Mo in Climax-type porphyry molybdenum deposits took place at corrected temperatures of ca. 500° to 550°C (White et al., 1981). Overpressures greater than lithostatic pressure by 150 to 250 bars probably caused the stockwork fracturing.

Primary halos in and around porphyry deposits

Considering their great economic importance, relatively few detailed lithogeochemical studies have been published of porphyry deposits. However, the contributions by Davis and Guilbert (1973), Theodore and Nash (1973), Jambor (1974), Gunton and Nichol (1975), Olade and Fletcher (1975), Oyarzun (1975), Olade and Fletcher (1976a and 1976b), Chaffee (1976a and 1976b), Armbrust et al. (1977), Olade (1977), Govett and Nichol (1979), Boyle (1982a and 1982b), Chaffee (1982), and Govett (1983) show that primary halos of porphyry deposits are broader and even more intense than mineralogical alteration zones. Chemical analysis provides a simple tool for quantifying the changes in the composition of wall rocks by mineralization.

Major elements or element ratios have been applied in only a few studies to delineate alteration envelopes and their proximity to mineralization. In the porphyry copper deposits associated with the Guichon Creek batholith K values and K/Na ratios generally increase from the periphery of the property to the inner zones of intense alteration and metallization (Olade, 1977). A significant positive correlation exists between K and Cu. In contrast, abundances of Na, Ca, Mg and Fe decrease inwards. The increase of the K/Na ratio towards the core of deposits is related to potassic alteration. In some deposits, however, albitization predominates over K-feldspathization and a marked Na enrichment is found (Gunton and Nichol, 1975). Other major components of potential use include Si/total volatiles, which decrease with the approach to mineralization, and Al/Ca and Fe^{2+}/Fe^{3+} ratios, which generally increase towards the core (Boyle, 1982a).

Several case histories have been reported on the application of Rb and Sr, and of Rb/Sr and K/Rb ratios (e.g., Olade and Fletcher, 1975; Oyarzun, 1975; Armbrust et al., 1977; Davies, 1980). The variation in alkali elements and the Rb/Sr ratio reflects differentiation and alteration in granitoids (Nockolds and Allen, 1953; Taylor, 1965; Lawrence, 1975). Rubidium is generally increased and Sr depleted in potassic alteration zones (Armbrust et al., 1977; Olade and Fletcher, 1975). Leached Sr has been redeposited at the periphery of some deposits in association with carbonates and other propylitic minerals (Olade and Fletcher, 1976a). In

deposits connected with the Guichon Creek batholith Rb and Sr do not produce larger halos than K and Ca, and Rb/Sr and K/Rb ratios give comparable information on individual elements (Olade and Fletcher, 1975; Olade, 1977). On the other hand, the halos of K/Rb and Rb/Sr are larger than those of individual elements in Chilean porphyry copper deposits (Armbrust *et al.*, 1977). However, data on elements related to alteration should be treated with caution because they are only indicative of mineralization and not of ore bodies.

Many chalcophile trace elements have been described to produce halos extending far beyond alteration zones. Sulphur has been demonstrated to be one of the most useful elements in the exploration for porphyry deposits (e.g., Jambor, 1974; Olade and Flet-cher, 1976a). Copper gives broad and highly contrasted halos around most porphyry copper deposits, whereas Mo exhibits halos of limited size (e.g., Olade and Fletcher, 1976a; Wood-cock and Hollister, 1978).

Relatively few studies have been published of elements other than the major ore elements and those associated with alteration. In certain deposits, Ba, As, Sb, Ag, Pb, Zn, Au, Bi, Te, Se and Mn have been described to display broad halos around deposits (e.g., Beus and Grigorian, 1977; McCarthy and Gott, 1978; Chaffee, 1982). These elements are usually not homogeneously diffused in wall rocks but produce scattered leakage halos along shear zones and fractures. The general applicability and sequence of zoning of the pathfinder elements are to be established in further studies.

METHODS

Sampling

Target surveys

Samples were principally taken from outcrops. At each site several unaltered samples collected from an area of about 16 m² were combined to make up a composite sample weighing 1.5 to 2.5 kg. In addition, 24 duplicate samples were taken at random sites to study the reproducibility of the methods. The samples were collected from the same 16-m² areas with methods similar to those used in the study proper.

Chip samples were collected from around the Tienpää occurrence and during the regional study of the Käkövesi batholith. Powder samples were taken with percussion drilling from Luukkolansaari and Lahnanen and during the regional study of the Rautio batholith.

Detailed mapping was carried out in the sample areas, and reference samples were collected in the course of sampling. Thin or polished sections were made from about one third of the samples and studied under the microscope.

From around the Susineva occurrence the majority of samples were collected from drill cores. Five-centimetre samples were taken every metre from the upper five metres of the cores. The sample net was completed with a few outcrop samples and with 30-cm drill powder samples taken through the overburden with a pneumatic drill mounted in a tractor (for the method see Kokkola, 1976).

Sulphides generally occur very heterogeneously in fractures and veinlets and as disseminations in granitoids. The purpose of this study was to investigate large-scale geochemical trends

in the host granitoids caused by mineralization and crystallization. Hence, megascopically mineralized or strongly hydrothermally altered rocks were excluded.

At Kopsa samples were selected from a larger set collected earlier by Outokumpu Oy Exploration (Gaál and Isohanni, 1979). The samples were taken with a tractor-mounted pneumatic drill or with conventional diamond drilling. A more detailed study was done in and around the Susineva occurrence with a pneumatic drill as well (Nurmi and Isohanni, 1984). The uppermost two metres of the cores at Kopsa and the 30-cm samples at Susineva were analysed. Mineralized samples were included in both cases.

The average sample densities around the occurrences are $42/km^2$ at Susineva, $16/km^2$ at Luukkolansaari, $7/km^2$ at Tienpää, $68/km^2$ at Lahnanen and $170/km^2$ at Kopsa. The regional studies of the prevailing granodiorites of the

Rautio and Käkövesi batholites comprise 1 sample/2 km^2 and the detailed study at Susineva 500 samples/km^2. Attempts were made to collect the samples on as even spaced a grid as possible at each locality. However, in most targets the sample nets are more or less irregular owing to the presence of covered and undrilled areas.

Reconnaissance survey

In the other areas chip samples were collected or sampling was done with percussion drilling as in the target surveys. The total number of samples is about 1.000 with a few to dozens of samples from each area (Appendix). At least three samples from each granitoid phase were submitted for chemical analysis and modal calculations.[1]

Analytical techniques

Chip samples were first passed through a jaw crusher. Representative fractions of crushed rock and of powder samples of percussion or pneumatic drilling were then pulverized in a steel disc mill.

All samples were analysed for over 30 elements (Fig. 3), excluding the samples of the detailed study at Susineva, from which only Mo and Cu were analysed (Nurmi and Isohanni, 1984). Three different methods were employed. The major elements and certain trace elements (Fig. 3) were analysed from most targets on powder discs with an automatic Philips PW 1400 X-ray fluorescence spectrometer. The samples from Käkövesi, Rautio, Tienpää, Kutemajärvi, Varparanta, Hämeenkyrö, Värmälä, Majajärvi, Kopsa, Äitsaari, Salosaari,

Mäntsälä and Aulanko were analysed at the Geological Laboratory of Outokumpu Oy, and those from Lahnanen, Luonteri, Renkajärvi, Sydänmaa and Hernemäki at the Research Laboratory of Rautaruukki Oy. The samples from Palokka, Silvola and Kalliokangas were analysed by X-ray fluorescence spectrometry after fusing with lithium tetraborate at the Geochemistry Department of the Geological Survey. Strontium was analysed from these samples with AAS after total digestion at the same laboratory.

Most of the trace elements (Fig. 3) were analysed with the instrumental epithermal neutron activation method at the Reactor Laboratory of the Technical Research Centre of Finland. Details of the analytical method are given by Rosenberg et al. (1982).

Cobalt, Ni, Cu, Zn and Pb (and Ag from samples of Kopsa) were analysed with a Perkin

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[1] Throughout this paper plutonic rocks are named according to the recommendation of the IUGS subcommission (Streckeisen, 1974).

Fig. 3. Elements analysed and detection limits (in ppm) for elements often with contents below the limits. Analytical methods: XRF = X-ray fluorescence spectrometry, INAA = epithermal instrumental neutron activation analysis, and AAS = atomic absorption spectrophotometry.

Elmer 403 atomic absorption spectrometer at the Department of Geology, University of Helsinki. Samples weighing 3 g were digested on a boiling water bath in 5 ml of aqua regia for one hour; before centrifugation and analysis the samples were diluted to 30 ml. Low absorbances were measured with a recorder.

Data processing

Target surveys

Analytical results and field data were stored on magnetic tape for computer processing. In the statistical investigations the individual elements and several element ratios (K/Na, K/D.I., Si/D.I., Al/Ca, K/Rb, Rb/Sr, Ba/Sr and U/Th) and the differentiation index (D.I.) calculated from Barth mesonorms (Barth, 1959 and 1962) were utilized. Statistics for the Rautio and Käkövesi batholiths were done by rock type.

Percentiles of the distributions of the variables, estimates for the coefficients of deviation and skewness and interelement correlation coefficients were calculated with the programs of the Porphyry Project. Elemental associations from the data of Kopsa were studied by factor analysis utilizing programs in the IMSL (1982) package.

The distribution patterns of the elements that were generally above analytical detection limits and their respective elemental ratios were first studied on symbol maps drawn at the Geologi-

cal Survey with programs of the Geochemistry Department. After visual interpretation of the maps, variables showing anomaly patterns compatible with mineralization and variables indicating crystallization of the host rocks were selected.

The distribution patterns of these variables were recalculated at the Geological Survey with programs in the UNIRAS (1982) package, and redrawn with an ink jet colour plotter at the Technical Research Centre of Finland. The programs first change the preliminary, irregularly spaced data to an evenly spaced grid using a combination of linear, quadratic and weighted average techniques. Data on variables showing high positive skewness were logarithmically transformed to reduce the tendency of the programs to overestimate high single values. A specific search radius was selected for each target so that interpolation for grid points in larger unsampled areas was avoided. In order to obtain quadratic grid one hundred grid points were calculated for the longer side of each map, and fewer points for the shorter side, in proportion to the lengths of the sides.

In the second stage the programs contoured the gridded data. The percentile class limits of the original data, 90, 75, 50 and 25, were used for the contours. The two lowest classes were combined for variables with contents below analytical detection limits in 25 to 50 % of the samples. A relatively low percentage (90) was selected as the limit for the highest class, because the search was for broad trends rather than a few erratic samples and because the number of samples was comparatively small at all targets. Combinations of the halo patterns simplified from the colour surface maps are presented in this paper.

Reconnaissance survey

Percentiles, coefficients of deviation and skewness of the variables and interelement correlation coefficients were calculated for each of the 49 granitoid phases as in the target surveys. Moreover cluster analysis was employed to find out whether the granitoids with associated mineralization could be distinguished from barren granitoids on the basis of bulk geochemistry. Median contents of SiO_2, TiO_2, Al_2O_3, FeO, MgO, CaO, Na_2O, K_2O, P_2O_5, Rb, Sr, Ba, Cs, Sc, Cu, Zn, Pb, La, Sm, U and Th were calculated for each granitoid phase (Appendix). The 21 variables are those that were analysed from all phases and of which at least half of the values were above respective analytical detection limits. The data on each variable were first normalized to have a mean of 0 and a variance of 1. The cluster analysis included in the IMSL (1982) package was then employed. Grouping was done with the complete linkage method, the Euclidean distance being used as the similarity measure.

Contamination of samples

The effects of the hard metal drill bits of percussion drills on the chemical composition of samples were studied by taking a series of samples from a homogeneous, fine-grained granite boulder with the drilling equipment used and with a hammer. The samples were analysed for the same elements as in the study proper. Notable contamination was detected only in W contents (25 to 100 ppm) of the powder samples compared with chip samples. Hence, W is not considered in this study except at Kopsa, where samples were collected with a pneumatic drill causing a minimum contamination compared with the total variation in W contents. Slight contamination was also encountered in Cu (1 to 5 ppm), Co (1 to 3 ppm) and Au (2 to 5 ppb), but these values are insignificant compared with total variations and contents. Most of the

samples were collected with the same method from each target.

Both types of disc mill used to grind the samples were tested for possible contamination while pulverizing crushed pure quartz for dif-ferent times. The C-steel mill did not cause significant contamination, whereas the Cr-steel mill produced a considerable increase in Cr values. Therefore, Cr is not considered in this study.

Reproducibility of results

The reliability of geochemical results depends on the random errors of sampling and analysis and on possible analytical bias or contamination. Precision is more important than accuracy in geochemical exploration, when results are compared among themselves.

To estimate the reproducibility of the results the 24 duplicate samples collected were analysed with the methods used in the study proper. The reproducibility is in general good (Nurmi, 1984, Table 1, Fig. 2). Elements with contents far above analytical detection limits exhibit low and constant relative errors over their concentration range, for example, SiO_2 under 4 %, TiO_2 under 14 %, Al_2O_3 under 6 %, Ba under 15 % and Sr under 13 % at 90 % confidence level. On the other hand, increasing errors in the lower concentration levels of, for example, Pb, As, Sb and Sc are due to increasing analytical variability near the detection limits.

The high errors in Cu (60 to 80 %, depending on concentration) and K_2O (22 to 43 %) are due to their random presence in mineralized or altered granitoids. Many trace elements associated with mineralization obviously have similar or higher errors, although the reproducibility of Mo, Au and S could not be studied owing to their low contents in the sample set.

CHARACTERISTICS OF PORPHYRY-TYPE OCCURRENCES IN FINLAND

Most of the known Proterozoic Mo and Cu predominant occurrences associated with grani-toids in southern Finland are considered to be of the porphyry type (Nurmi et al., 1984). The occurrences are genetically connected with late-stage and often porphyritic phases of grano-diorite batholiths (e.g., Susineva and Luukko-lansaari), and of tonalite or trondhjemite stocks (e.g., Tienpää and Kopsa). Tectonic control is common to all mineralization, but the mode of occurrence of ore minerals is dissimilar not only between different types of mineralization but also within a particular occurrence. In stock-work-type occurrences mineralization is con-trolled by shear fractures (e.g., Kopsa; Gaál and Isohanni, 1979) or by extensional fractures (e.g., Tienpää; Nironen and Csongrádi, 1984) with minor disseminations. Fracture density varies from breccia to a few fissures. Mineralized frac-tures are either filled with or devoid of quartz. Molybdenum-predominant mineralization is concentrated in a granodiorite-porphyry stock at Susineva and in granite dykes at Luukkolan-saari. Chalcopyrite and associated ore minerals are spread over large areas in fractures and as disseminations in both areas.

The porphyry-type occurrences can be divided into Mo, Mo-Cu, Cu, Cu-Au and Cu-W miner-alization on the basis of the prevailing ore metals. The ore mineralogy of the occurrences

is fairly simple (Nurmi *et al.,* 1984, Table 6). The major ore minerals are usually molybdenite and chalcopyrite, but magnetite, arsenopyrite, pyrrhotite or scheelite are present as major constituents in certain occurrences. The number of accessory ore minerals is generally greater in Cu than in Mo-predominant mineralization.

Wall-rock alteration is usually exhibited as vein-veinlet alteration and selective alteration of certain minerals. Pervasive and relatively extensive alteration is only present at Kopsa. Propylitization is the most common and widespread of the alteration types, forming envelopes several hundreds of metres broad, for example, around the occurrences of Susineva (Nurmi and Isohanni, 1984) and Tienpää (Nironen and Csongrádi, 1984). The intensity of propylitization is variable, but the total abundance of secondary minerals (epidote, carbonate and chlorite) may reach several percentages. Other extensive alterations are muscovitization and biotitization at Tienpää, biotitization at Susineva, and potassic alteration at Kopsa. Potassic alteration, silicification and sericitization are usually restricted to the immediate vicinity of fractures and veinlets. The Cu-Au mineraliza-

tion at Susineva contains exceptionally discrete albititization. Tourmalinization, and casual prehnite and fluorite occur in some occurrences.

The occurrence of Lahnanen differs from the others in many respects (Oivanen and Eskola, 1972; Nurmi, 1984). Nevertheless, it may be considered a high temperature-pressure analogue of the porphyry-type mineralization.

The most pronounced difference between the Proterozoic porphyry-type occurrences studied and the Phanerozoic porphyry deposits is the considerably smaller size of the former. The grade of the porphyry-type occurrences can reach similar levels to the porphyry deposits, for example, Au in the Cu-Au mineralization of Kopsa and Susineva, and Mo at Susineva. The only deposit of economic importance, so far, is the exhausted Cu-W deposit of Ylöjärvi (Himmi *et al.,* 1979). Furthermore, wall-rock alteration is much weaker than in Phanerozoic porphyry deposits and strong pyrite halos and argillic zones are lacking. These features seem to be shared with many porphyry-type occurrences described from other shield areas (see Ayres and Černý, 1982).

Geology of the host granitoids

All the occurrences are associated with granitoids of the synorogenic age group having zircon U-Pb ages of 1850 to 1900 Ma and being roughly coeval with the Svecokarelian mafic plutonic rocks and metavolcanic rocks (Simonen, 1980; Neuvonen *et al.,* 1981).

The wall rocks of the granitoids are exceedingly variable in composition and metamorphic grade (Nurmi *et al.,* 1984, Table 5) but without clear signs of contact metamorphism. The granitoids were crystallized after the main stage of regional deformation and metamorphism. They have sharp and locally crosscutting contacts with supra-crustal rocks and are largely isotropic, although their margins may show

concordant foliation with the contacts (e.g., Käkövesi batholith). The Svecokarelian supracrustal belts on the other hand have undergone polyphase deformation (Gaál, 1982). The local shear zones that control mineralization in granitoids are signs of younger regional deformations (e.g., Kopsa; Gaál and Isohanni, 1979) or of local stress fields generated by the emplacement of voluminous and highly viscous granitoid magmas (e.g., Käkövesi batholith; Nurmi *et al.,* 1984, Fig. 15). Multiple deformation is only met with in the host granodiorite of the occurrence at Lahnanen.

The granitoids exhibit no or only weak signs of any alteration regardless of the metamorphic

grade of the surrounding supracrustal rocks. The weak alteration in some granitoids is related to postmagmatic autometasomatic processes or mineralization.

The host-rock batholiths are composite intrusions exhibiting concentric arrangements of intrusive phases (e.g., the Rautio and Käkövesi batholiths; Nurmi and Isohanni, 1984; Nurmi, 1984). Their margins are composed of dioritoids or tonalites and their centres of the prevailing granodiorites. The Tienpää mineralization occurs in a tonalite complex consisting of several intrusive phases, whereas the host stocks of the occurrences at Lahnanen and Kopsa are evidently single phase intrusions (Nurmi, 1984).

The mineral composition of the granitoids is simple (Nurmi et al., 1984, Table 2); plagioclase (oligoclase to andesine), K-feldspar, quartz, biotite and hornblende, and, exceptionally, hypersthene at Lahnanen occur in variable abundances as major constituents. The most common accessory minerals are sphene, apatite, zircon and magnetite. The host rocks of the occurrences or at least one phase adjacent to mineralization generally exhibit porphyritic texture.

Sharp contacts, breccia structures and fine-grained porphyritic intrusive phases refer, excluding Lahnanen, to the epizonal-mesozonal character of the granitoids.

Geochemistry of the host granitoids

According to the classification of calc-alkaline granitoids by Chappell and White (1974) the granitoids have I-type characteristics (Table 1):

1) They are generally calc-alkaline, although tonalites have calcic and some batholiths alkaline affinities (Nurmi et al., 1984, Fig. 6).

2) They have high compositional variations.

3) $^{87}Sr/^{86}Sr$ initial ratios in the Uusikaupunki — Kalanti gabbro — trondhjemite suite (Arth et al., 1978), Sottunga granodiorite (Welin et al., 1983), Hämeenkyrö batholith (Aro, 1983) and in the same group of granitoids in Sweden (Wilson, 1980) are all distinctly under 0.706.

4) Mol. $Al_2O_3/(CaO + Na_2O + K_2O)$ are mostly less than 1.1 (Nurmi et al., 1984, Fig. 12), but particularly tonalites and trondhjemites exhibit higher values. However, granitoids with overlapping I-type and S-type ratios have been noted in many areas (e.g., Takahashi et al., 1980; Wilson, 1980; Griffiths and Godwin, 1983; White and Chappell, 1983) and the classification of the granitoid

types should not be based on just one criterion.

5) Na_2O/K_2O ratios fall clearly in the field of the I-type granitoids of southeastern Australia (White and Chappell, 1983).

6) Sphene, hornblende and magnetite are commonly present (Nurmi et al., 1984, Table 2).

7) Some of the granitoids contain porphyry-type mineralization.

Table 1. Characteristics of I-type and S-type granitoids (Chappell and White, 1974; Beckinsale, 1979; Pitcher, 1979).

	I-type	S-type
Variation in composition	large	small
$^{87}Sr/^{86}Sr$	<0.706	>0.706
$\delta^{18}O$	6—10	>10
Mol $Al_2O_3/K_2O + Na_2O + CaO$	<1.1	>1.1
Na_2O/K_2O	high	low
$f(O_2)$ in magma	high	low
Fe^{3+}/Fe^{2+}	high	low
Typical minerals	magnetite, sphene, hornblende	ilmenite muscovite monazite
Typical ores	Cu, Mo, Au	Sn, W

The I-type character of the granitoids and the similarity of their age to that of gabbros and dioritoids and of metavolcanic rocks support the concept of an Andinotype plate tectonic model for the generation of the Svecokarelian crust (Hietanen, 1975; Wilson, 1980; Barker *et al.*, 1981; Gaál, 1982; Wilson, 1982; Nurmi, 1983). Furthermore, the initial Hf isotope ratios of Svecokarelian mafic plutonic rocks suggest that the rocks derive from the mantle (Patchett *et al.*, 1982). The genesis of Svecokarelian metavolcanic rocks and associated ore deposits has also been related to an island arc environment (Rickard and Zweifel, 1975; Rickard, 1978; Lundberg, 1980; Mäkelä, 1980).

The batholiths exhibit a complex genetic and crystallization history. The marginal dioritoid or tonalite phases are evidently cogenetic with the prevailing granodiorites but the gaps between the compositions of the rocks in the Rautio batholith (Nurmi, 1983, Fig. 3; Nurmi and Isohanni, 1984, Fig. 3) and in the Käkövesi batholith (Nurmi, 1984, Fig. 4) indicate multiple intrusions of the magmas.

Trace element variations in the Rautio batholith suggest that the intrusive phases are not comagmatic but the formation of the batholith includes the generation of magmas at various depths with continuous fractionation and multiple intrusions (Nurmi, 1983). The diorites have similar geochemical characteristics to high-K andesites in the Cordillerian chain, which may indicate the formation of the dioritic magma at mantle depths near an ancient subduction zone. Quartz monzodiorites were formed mainly by crystal fractionation of the dioritic magmas pooled in the lower crust. In contrast, the principal source of the voluminous granodiorite magma was evidently the earlier Svecokarelian magmatic rocks in the lower crust, the partial remelting of which was initiated by the mantle magmas. Furthermore, the batholith comprises two magmatic suites, both consisting of rocks from diorites to granodiorites, with slightly different trace element contents. This indicates that originally there must have been two separate magmas with different initial composition or with different crystallization conditions.
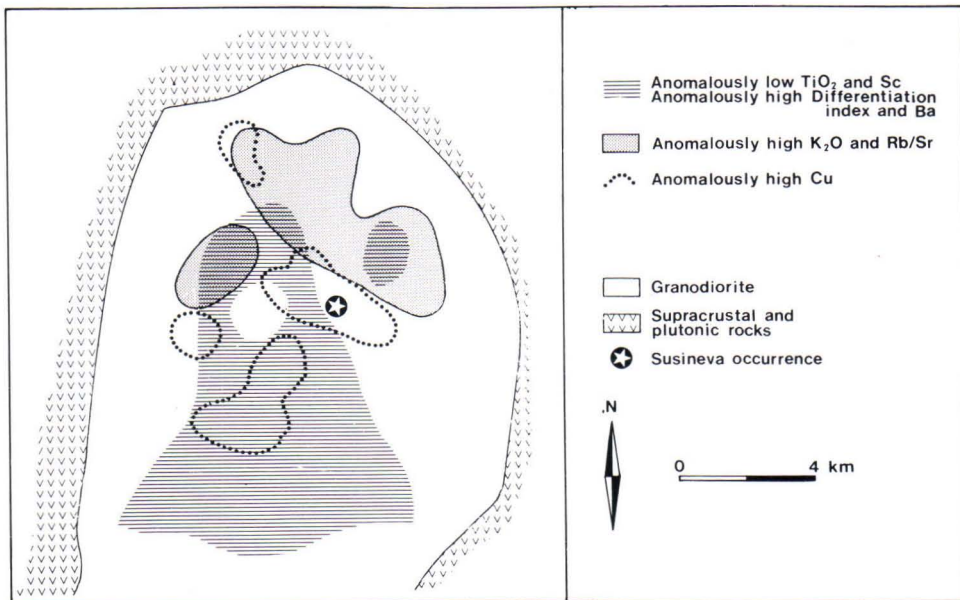

Fig. 4. Geochemical zoning in the granodiorite of the Rautio batholith (simplified from Nurmi and Isohanni, 1984) Based on analyses of 120 samples.

The prevailing granodiorites of the batholiths are petrographically homogeneous, exhibiting no broad trends in modal mineral abundances or alteration. Variations of most element contents are also small (Nurmi and Isohanni, 1984, Table 1; Nurmi, 1984, Table 2). Even so, many elements show systematic distribution patterns on geochemical maps (Nurmi, 1983, Fig. 5; Nurmi and Isohanni, 1984, Fig. 4; Nurmi, 1984, Fig. 5) reflecting the history of crystallization of the granodiorites. The bulk of the granodiorite of the Rautio batholith was emplaced as a single magma that crystallized from the margins inwards. The Hämeenkyrö batholith exhibits similar geochemical zoning (Gaál *et al.,* 1981). The extensive Rb/Sr and K$_2$O anomalies in the Rautio batholith, which are located NE of the most evolved granodiorite (Fig. 4), indicate autometasomatic potassic alteration associated with the crystallization of the voluminous granodiorite magma. The granodiorite porphyry

stocks represent residual magma that intruded into the already solidified granodiorite (Nurmi, 1983).

The geochemistry of the granodiorite in the Käkövesi batholith is more complicated. Evolved granodiorite occurs as three separate larger units in the central parts of the longish batholith (Nurmi, 1984, Fig. 5). The mode of occurrence of the units, their variable trace element contents and some sharp interphase contacts suggest that the granodiorite was formed by multiple intrusions. Rubidium shows a negative and Sr a positive correlation with D.I. values in the granodiorite (Nurmi, 1984), the exact opposite to normal differentiation (Nockolds and Allen, 1953; Taylor, 1965), indicating that the phases are obviously not comagmatic.

The granitoids in smaller intrusions are either slightly differentiated (e.g., Kopsa; Nurmi, 1984) or homogeneous (e.g., Lahnanen; Nurmi, 1984, Fig. 11 and Table 4).

LITHOGEOCHEMICAL EXPLORATION

Reconnaissance survey

Bulk geochemistry

The median contents of different variables were plotted on a great number of scatter diagrams to find out whether the productive granitoids could be discriminated from the barren granitoids on the basis of the contents of certain elements or elemental combinations. Unfortunately, not one of the diagrams was able to reveal the intrusive phases with which Mo or Cu mineralization is considered to be associated either genetically or spatially. This is well documented in the contents of the principal ore metals. The median contents of Cu vary from a few to over 30 ppm in the granitoids

studied, and from 4 to 24 ppm in the host phases (Fig. 5). The tonalite of Kopsa (No. 141) and the granite dykes of the Käkövesi batholith (No. 13) are omitted, because unmineralized samples were not available. The median contents of Mo and Au were below analytical detection limits (0.8 to 1.2 ppm and 3 to 7 ppb, respectively) in all granitoids except the penetratively mineralized phases (Nos. 13 and 141). Elsewhere, too, anomalous ore-metal contents have been noted to be restricted to mineralized areas in Precambrian porphyry-type occurrences (Wolfe, 1974; Friske *et al.,* 1979; Sinclair, 1982) and in Phanerozoic deposits (Brabec and White, 1971; Sheraton
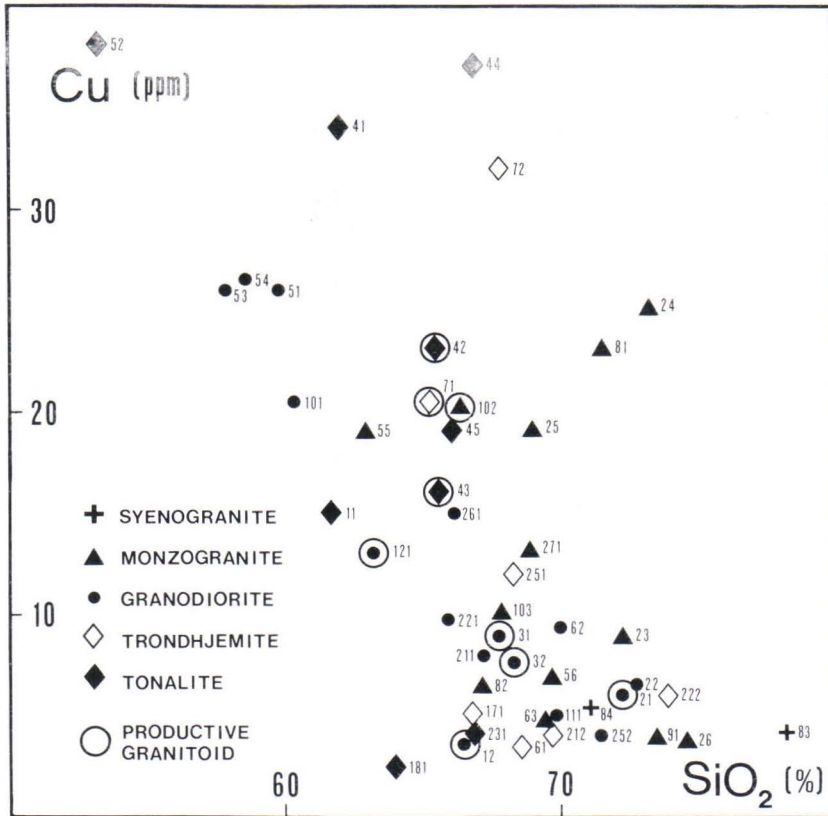
Fig. 5. Copper-SiO₂ diagram showing the median contents of granitoid phases studied. Numbers refer to the localities shown in Figs. 1 and 6.

and Black, 1973; Tilling *et al.,* 1973; Olade and Fletcher, 1976a), the host phases of which exhibit normal contents outside the occurrences.

Cluster analysis was employed as a multivariate approach to the study of the bulk geochemistry of the granitoids. It makes the grouping of similar samples possible using several variables simultaneously (Hesp and Rigby, 1973; Rickwood, 1983); thus, in this case, the host rocks of the porphyry-type mineralization could be identified if they exhibited geochemical specialization of a particular type.

The geochemical similarity is greatest between spatially related granitoids as at Tienpää, Varparanta, Lahnanen, Kutemajärvi and Rautio (Fig. 6). Granitoids from different areas

start to cluster with higher Euclidean distance values. A majority of the tonalites and trondhjemites form uniform groups, whereas granodiorites and granites are distributed among several families. The tonalites of Kopsa and Luonteri are the only outliers of the tonalite group. The former is affected by strong potassic alteration and mineralization (Nurmi, 1984); the latter belongs to the postorogenic granitoids and differs distinctly from those in the synorogenic age group (Appendix; Nurmi *et al.,* 1984). The granodiorite of Majajärvi, which is grouped together with tonalites, contains marked tonalitic portions. The difference in clustering between K-poor and K-rich granitoids is attributed to a more homogeneous source for the
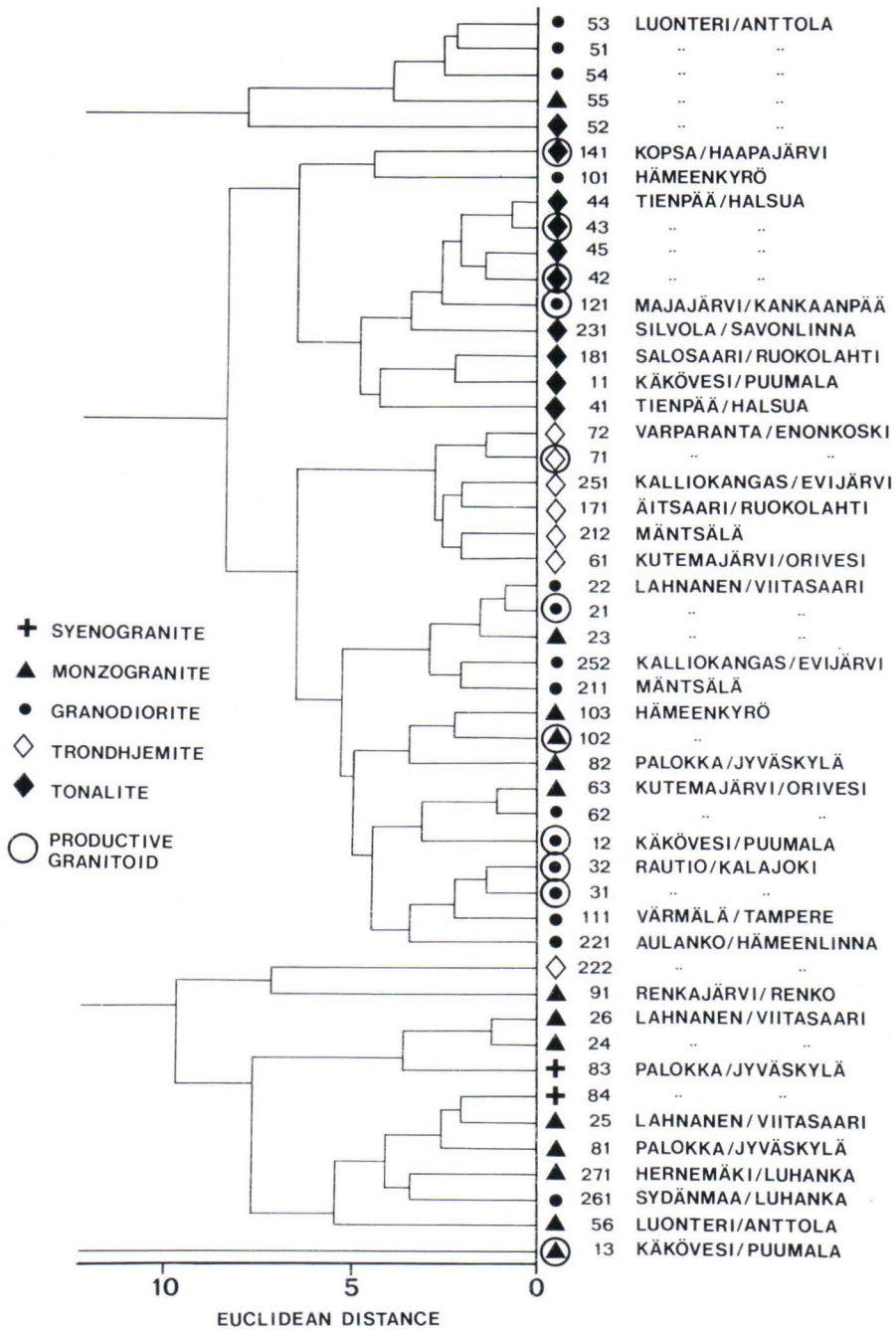
Fig. 6. Dendrogram showing interrelations and groupings between granitoid phases studied. Based on the median contents of 21 elements for each phase (Appendix). Localities of study areas shown in Fig. 1.

K-poor magmas. Tonalites and trondhjemites probably originate from a basaltic source by partial melting or by fractional crystallization as proposed for the Proterozoic tonalites in New Mexico (Condie and McCrink, 1982), whereas granodiorites and granites are formed by partial melting of a heterogeneous crust with possible hybridization with mantle magmas (Halliday *et al.,* 1980; Condie and McCrink, 1982; Nurmi, 1983).

Except spatially related phases the host granitoids of the Mo and Cu occurrences do not show any distinct clustering. Cluster analyses were also performed separately on the major and trace elements but with no better success. This indicates that the host rocks are not geochemically specialized to be reflected in bulk geochemistry. If some kind of specialization related to mineralization exists, it is effectively masked by geochemistry governed by genesis and crystallization of magma.

The lack of geochemical specialization in the host rocks of porphyry mineralization is the exact opposite of tin and other rare element mineralization associated with granitoids. The host rocks of the latter usually exhibit marked geochemical specialization, which is indicated by anomalously high contents of ore metals and many associated elements, even though, rather than being uniform, the element contents exhibit great variation (e.g., Sheraton and Black, 1973; Tischendorf, 1977; Haapala, 1978, Drake, 1981; Chatterjee *et al.,* 1983).

The difference in the specialization of the host granitoids of Sn and porphyry mineralization could be attributed to the difference in their genesis. Tin mineralization is related to S-type granitoids formed by partial melting of a sedimentary source rock (Chappell and White, 1974; White and Chappell, 1977; Beckinsale, 1979; Ruitenberg and Fyffe, 1982) that may be enriched in Sn (Barsukov and Durasova, 1966) and other rare element minerals or contain previous Sn deposits (Plimer, 1980; Ishihara, 1981). The mineralization process involves con-

tinuous fractional crystallization of the magmas and separation of mineralizing fluid from the magmas at a very late stage of solidification (Groves and McCarthy, 1978). This process leads to highly differentiated and anomalous host rocks.

In contrast, porphyry deposits are associated with I-type granitoids, which originate from igneous rocks (Chappell and White, 1974; White and Chappell, 1977; Beckinsale, 1979; Griffiths and Godwin, 1983) that were probably the major source of ore metals, S and Cl, although some of the S and Cl may originate from meteoric water (Ishihara, 1981). Mineralization is due to hydrothermal solutions that concentrated during the crystallization of magmas and then escaped into already solidified wall rocks through crackle zones generated by the initial wave of escaping solutions (McMillan and Panteleyev, 1980; White *et al.,* 1981). During this process ore elements are enriched in the mineralizing solutions from the host magma.

The different oxygen fugacities ($f(O_2)$) of I-type and S-type magmas may partly explain their different mineral potentials. In S-type magmas $f(O_2)$ is relatively low, reflecting the presence of reducing agents such as graphitic shales or carbonaceous metasediments (Beckinsale, 1979) in the source, which will adjust the $f(O_2)$ of the melt near the equilibrium curve of the reaction $CH_4 + 2O_2 = CO_2 + 2H_2O$ (Ohmoto and Kerrick, 1977) below the quartz-magnetite-fayalite buffer. The fugacity ratio of SO_2/H_2S is consequently low (Burnham and Ohmoto, 1980). Because the distribution coefficient of H_2S between the fluid phase and the magma is much lower than that of SO_2, it is evident that S concentrates in the residual solutions of high $f(O_2)$ I-type magmas rather than in those of low $f(O_2)$ S-type magmas. In this respect, I-type granitoids have a higher potential for sulphide mineralization.

In low $f(O_2)$ magmas Sn is present as Sn^{2+} which can concentrate in the residual

magma, whereas Sn^{4+} substitutes for Ti^{4+} and Fe^{3+} in rock-forming minerals in high $f(O_2)$ magmas (Ishihara, 1977 and 1978). This fact may explain the rarity of Sn mineralization in I-type granitoids.

On the other hand, Mo^{6+} is able to form volatile complexes (Candela and Holland, 1984), but Mo^{4+} preferably enters in Fe and Ti-bearing minerals (Uzkut, 1974). Although the behaviour of Au is poorly known in magmatic processes, the high magnetite contents of Au-bearing porphyry deposits indicate that the enrichment of Au in residual solutions

is favoured by abnormally high $f(O_2)$ and $f(O_2)/f(S)_2$ (Sillitoe, 1979). Generally, Au tends to become depleted in the residual melt in differentiating calc-alkaline magmas (Tilling *et al.*, 1973). The chemical properties of Mo and Au may explain the lack of large deposits of these metals in S-type granitoids.

Variation in ore metal contents

Although the host granitoids of the porphyry-type occurrences studied could not be identified from their average chemical composition, some
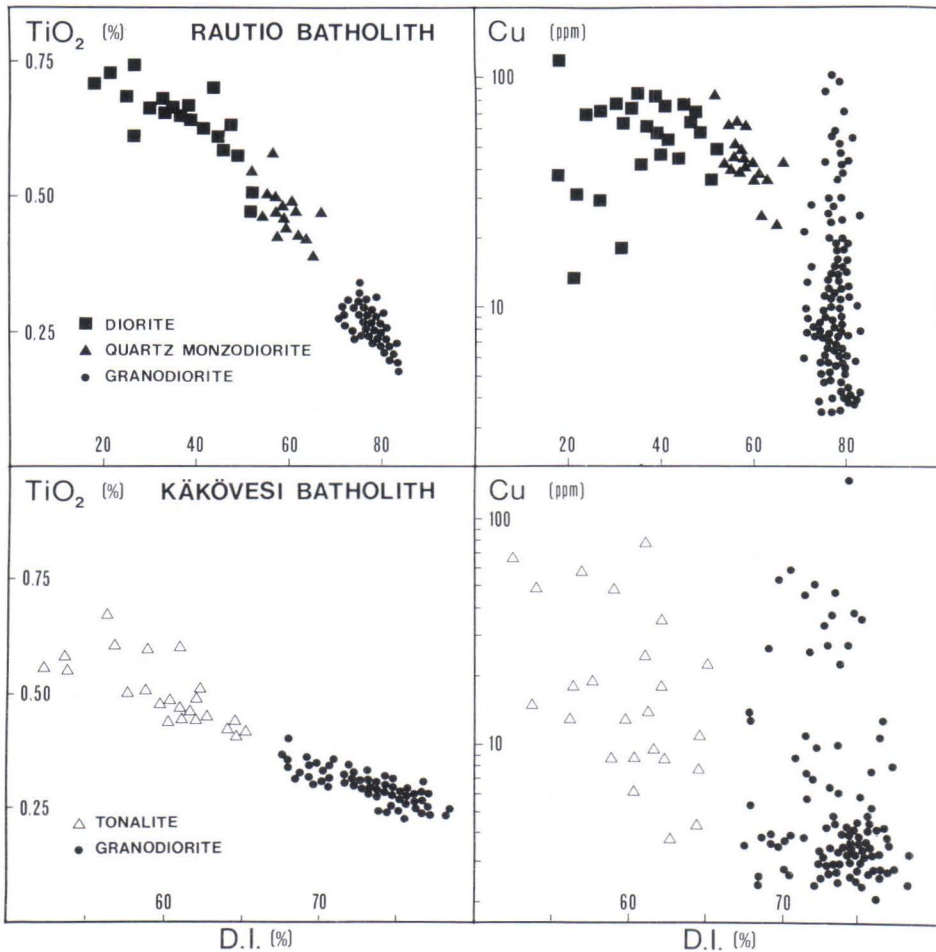

Fig. 7. Variation in TiO_2 and Cu contents with differentiation index (D.I.) in the Rautio and Käkövesi batholiths.

of them exhibit anomalous patterns in the variations of ore metals. For example, the mineral potential of the granodiorites in the Rautio and Käkövesi batholiths shows up in the variation of Cu contents (Fig. 7) as well as in the variation of As content in the Rautio batholith (Nurmi and Isohanni, 1984, Fig. 3). The median content of Cu decreases by rock type with increasing D.I. as does the median content of TiO_2 in both batholiths. However, the variables behave in a different way in the granodiorites: TiO_2 exhibits a limited variation in relation to D.I., whereas Cu contents fluctuate markedly. In the Rautio batholith, the variation of Cu contents is distinctly higher in the granodiorites than in the quartz monzodiorites and diorites. The tonalites and granodiorites of the Käkövesi batholith show equal total variation but in the tonalites the contents decrease with increasing D.I. whereas the granodiorites exhibit an anomalous population. The distribution of Cu demonstrates that contents in the granodiorites are governed by mineralization as well as magmatic crystallization and that at least Cu-bearing porphyry-type occurrences could be traced in a batholith with relatively low-density sampling.

The high deviation and skewness in the distributions of ore metals and the association of ore deposits in granitoids have been shown in many other areas as well (Beus, 1969; Brabec and White, 1971; Carrett, 1973; Tauson and Kozlov, 1973).

Regional exploration within mineralized batholiths

Copper seems to be the only element that forms anomalies of considerable regional extent around the porphyry-type occurrences. Scattered Cu anomalies are concentrated in the central parts of the Rautio batholith (Fig. 4), and the Susineva occurrence is situated in the middle of the most extensive anomaly. The western end of the Käkövesi batholith, which includes the Luukkolansaari occurrence, is likewise high in Cu (Nurmi, 1984, Fig. 5).

Anomalies of other ore elements are considerably more restricted and hence their presence or absence in regional data is more accidental. This is well demonstrated by Mo, which is the major ore metal in the Susineva and Luukkolansaari occurrences. The Mo content is largely under respective analytical detection limit (1 to 1.2 ppm) in the Rautio batholith, and not a single sample with a detectable value has been recorded from around the Susineva occurrence; the Luukkolansaari occurrence, however, shows up as a few-point Mo anomaly (Nurmi, 1984, Fig. 5). The tendency of Mo to exhibit only restricted anomalies indicates that exploration for Cu-deficient porphyry-type Mo deposits should be based on higher sample densities than exploration for Mo-Cu deposits.

Arsenic gives only a weak anomaly near the Susineva occurrence. On the other hand, As has proved to be the best regional indicator element for mineralized tourmaline breccias associated with the Hämeenkyrö batholith (Gaál et al., 1981), but then arsenopyrite is a prevailing ore mineral in this mineralization (Himmi et al., 1979).

Although relatively homogeneous, the granodiorites of the Rautio (Fig. 4) and Käkövesi (Nurmi, 1984, Fig. 5) batholiths exhibit geochemical zoning related to crystallization. The occurrences associated with small, late-stage stocks are, however, spatially unrelated to the large-scale trends on geochemical maps, in other words, they do not occur in the area of the most evolved granodiorite.

Many granitoids also exhibit regional geochemical features attributed to post-magmatic processes, which show up as an overprint on the element distribution by magmatic stage (Putman, 1972; Hesp and Rigby, 1973; Drake, 1981).

However, traces of postmagmatic processes do not necessarily mean that ore deposition also took place. This is demonstrated in the Rautio batholith where overlapping K_2O and Rb/Sr anomalies (Fig. 4), indicate regional potassic alteration. The anomalously low Cu contents in these areas have been interpreted as an indication that sulphide deposition was not connected to the alteration, at least not at present erosion level, and that lithologically associated Cu was leached by the alteration. No regional indica-

tions of potassic alteration were found from around the Susineva occurrence.

Scattered K_2O anomalies indicate potassic alteration in the Käkövesi batholith, as well (Nurmi, 1984, Fig. 5), but they are associated with elevated Cu and Mo contents only in a small area besides the area of the Luukkolansaari occurrence. These examples show that regional geochemical data should be interpreted with care, preferably utilizing multi-element data.

Local surveys

Pattern and sequence of primary halos

Regardless of their modest size, the porphyry-type occurrences studied exhibit primary halos of considerable extent, which can be traced with 10 to 40 samples per km². The halo pattern is not consistent in the various occurrences but depends on local geological and geochemical conditions, such as the extent of ore-forming processes, the primary composition of mineralizing solutions, the genetic relationship of the mineralization to its wall rocks,

the composition and structure of the wall rocks, temperature and pressure, the present level of erosion, and postdepositional tectonics. The elements in halos vary from one occurrence to another, but the sequence of halos is much the same in different mineralizations. Lahnanen, however, is a type of its own and is dealt with later.

Molybdenum is concentrated in the core of the occurrences, around the ore showings at Susineva (Fig. 8) and at Luukkolansaari (Fig.
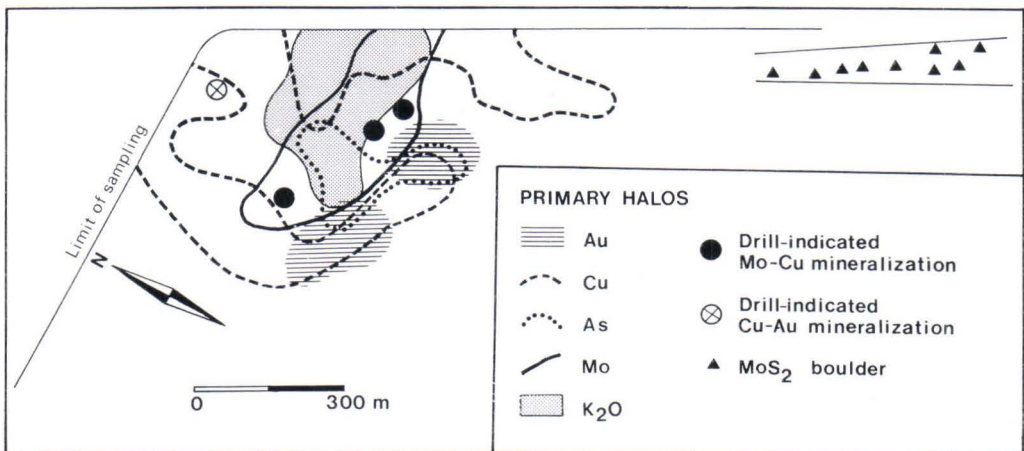

Fig. 8. Characteristic primary halos in and around the Mo-Cu occurrence of Susineva (simplified from Nurmi and Isohanni, 1984). Molybdenum and Cu halos based on the analyses of about 400 granodiorite samples and others on those of about 50 granodiorite samples.
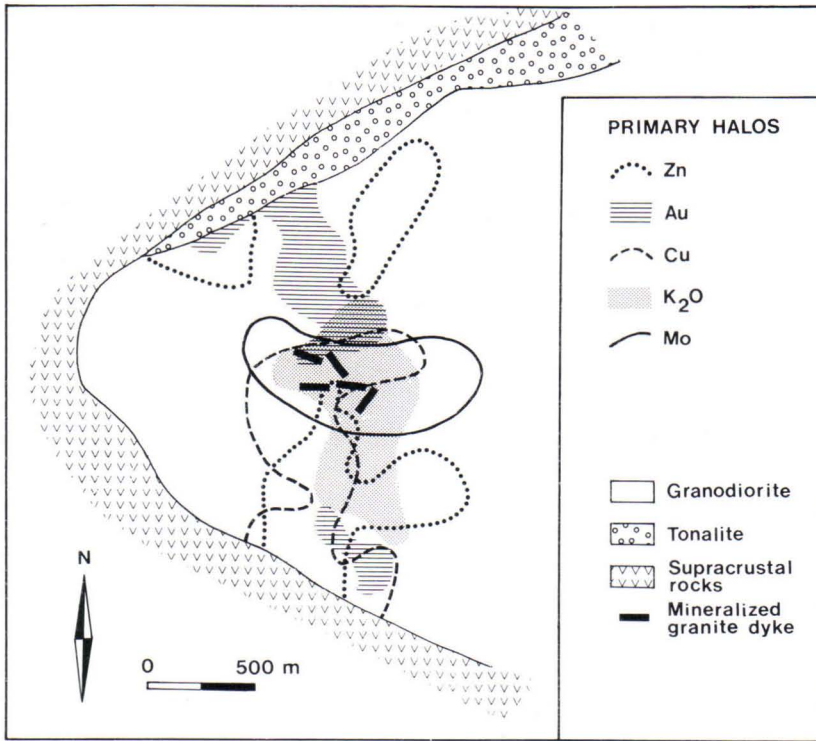
Fig. 9.   Characteristic primary halos in and around the Mo-Cu occurrence of Luukkolan-
saari (simplified from Nurmi, 1984). Based on analyses of 117 granodiorite samples.

9), in which it is the major ore metal. In the latter, Mo exhibits a more limited halo than does K₂O, especially in the NS direction. At Susineva the halos of Mo and K₂O overlap better, although comparison is difficult in this area owing to the very different number of analyses of Mo (and Cu) and other elements. At Tienpää and at Kopsa Mo is a minor component controlled by fortuitous quartz veins; the anomaly patterns are scattered and the Mo contents are mainly low.

Copper forms relatively broad and well-defined anomalies in all occurrences (Figs. 8—11). It shows distinctly larger halos than Mo in the Mo-Cu mineralizations of Susineva and Luukkolansaari. In the former Cu forms a circular halo around the Mo anomaly and in the latter the halos partly overlap at the core but the Cu halo extends distinctly beyond the Mo halo to

the south. At Kopsa Cu has a significant positive correlation with Ag and S. The distribution pattern of the scores of the Cu-Ag-S factor (Nurmi, 1984, Table 6) marks the major ore zone in the NE part of the stock. In the Tienpää area the Cu halos reveal best the occurrence of the stockwork ore zone.

Sulphur halos are very weak compared with those around Phanerozoic porphyry deposits in which the modal pyrite abundance reaches several percentages. At Luukkolansaari S halos are largely confined within the Cu halo. At Susineva and Tienpää S does not form consistent halos, and most of the samples have contents below the respective analytical detection limit (50 ppm). In contrast, S is anomalous in the whole stock at Kopsa. The anomaly of the scores of the Cu-Ag-S factor in the SW part of the intrusion is mainly due to high S contents.
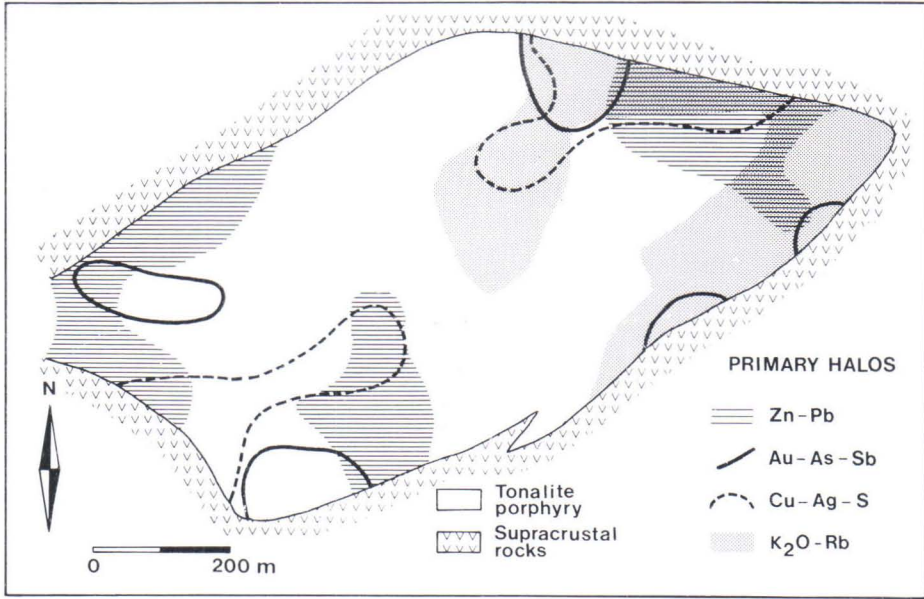
Fig. 10. Characteristic primary halos in the tonalite porphyry stock enclosing the Cu-Au occurrence of Kopsa (simplified from Nurmi, 1984). Based on analyses of 104 samples.
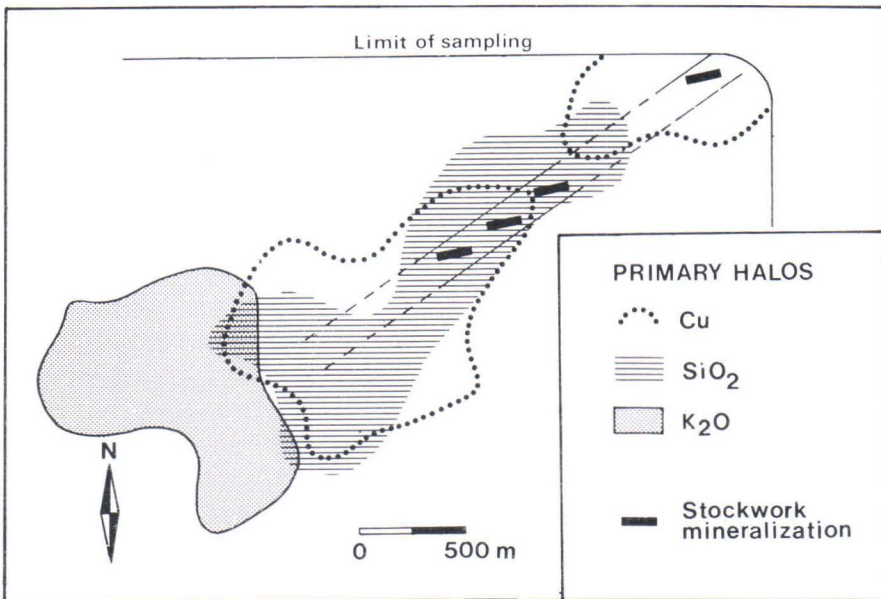

Fig. 11. Characteristic primary halos in and around the Cu occurrence of Tienpää (simplified from Nurmi, 1984). Based on analyses of 72 tonalite samples.

This area probably represents the barren Fe sulphide roof zone of the ore layer.

Broad Au halos are present at Susineva, Luukkolansaari and Kopsa. In the latter, Au is closely associated with As and Sb (Nurmi, 1984, Table 6). These elements form scattered anomalies in the stock, especially near the margins. In the Susineva area Au more or less follows Cu and exhibits discontinuous anomalies around the Mo halo (Fig. 8); it also overlaps Cu halos around the separate Cu-Au occurrence near the western margin of the study area (Nurmi and Isohanni, 1984, Fig. 6). Antimony, too, correlates partly with Au. Arsenic forms more confined halos than Au in the local study at Susineva. However, on a regional scale the As halos are broad enough to show up as a three-point anomaly. In the Luukkolansaari area, the Au halos are located distinctly farther from the centre of the mineralization than the Cu halos, but As and Sb are without any consistent pattern.

Zinc exhibits the broadest halos at Luukkolansaari and Kopsa, in which Zn and Pb show a close relationship (Nurmi, 1984, Table 6). Anomalous scores of the Zn-Pb factor overlap the major ore zone in the NE part of the stock, but the anomalies in the western part are unrelated to Cu, Ag, S or potassic alteration, and may indicate an ore zone at depth. On the other hand, the variation in Zn contents is very low in the samples from Susineva and Tienpää. Other elements typical of the upper parts of porphyry mineralization and present in other targets are lacking at Tienpää, which may indicate deep erosion of the occurrence.

Potassic alteration shows up in all occurrences in the distributions of one or more of the variables K_2O, K/Na, Al/Ca, Rb, Rb/Sr and Ba. Molybdenum halos are confined within or are equal to K_2O halos at Susineva and Luukkolansaari but Cu shows a broader pattern. In the Susineva area, Rb/Sr exhibits scattered anomalies in the periphery of the mineralization as well (Nurmi and Isohanni, 1984, Fig. 6) but at Luukkolansaari the variations in Rb and Sr

are related to lithology. At Kopsa, potassic alteration is revealed by all the variables listed above, excluding Ba (Nurmi, 1984, Table 6). The alteration halo is partly barren but extends over the major Cu ore zone. At Tienpää, the distributions of K_2O, Rb and Ba are also related to potassic alteration, but the alteration envelope is totally outside the Cu halos and evidently represents the deepest barren core level of the mineralization. Unlike in other occurrences, SiO_2 forms at Tienpää a well-defined halo around the stockwork mineralization and indicates silicification of the wall rock.

Figure 12 represents a generalized model of the halo zonality in and around the occurrences of Susineva, Luukkolansaari, Tienpää and Kopsa. It corresponds closely to the results of studies of Phanerozoic porphyry deposits (Olade and Fletcher, 1976a; Boyle, 1982a). The most pronounced difference is the absence or weakness of S (pyrite) halos in the Proterozoic occurrences. Furthermore, only a few studies of Phanerozoic porphyry deposits giving the sequence of the halos as Ag, As, Sb, Zn and Pb have been published; Boyle (1982a), for example, does not put these elements in any particular order (Fig. 2). Beus and Grigorian (1977) give the following zonality patterns towards the core for the elements discussed 1) in the Almalyk porphyry copper deposit (elements between parentheses show equal halos): As — Sb — (Ag, Pb, Zn) — Au — (Cu, Mo), and 2) in epigenetic deposits in general: (Sb, As) — Ag — Pb — Zn — Au — Cu — Mo. The principal differences from the Proterozoic occurrences are the reverse order of As and Sb to Pb and Zn. Moreover, Mo and Cu form equal halos at Almalyk, whereas clear zoning was found in the occurrences studied. In addition, Ag gives broad halos according to Beus and Grigorian (1977), but it is closely related to Cu at Kopsa.

Extensive Ba halos have been reported from Almalyk and many other epigenetic deposits in the U.S.S.R. (Beus and Grigorian, 1977), but in the occurrences studied Ba exhibits no patterns

related to mineralization or else it is controlled by potassic alteration as at Tienpää and in some porphyry deposits (e.g., Woodcock and Hollister, 1978). However, the models are valid only for deposits in which the elements occur as the same minerals. For example, As have been found to form more limited halos when it is present in arsenopyrite instead of, say, tetrahedrite (Beus and Grigorian, 1977). Arsenic is present as arsenopyrite at Kopsa, the only occurrence studied from which As minerals were identified.

The Mo occurrence of Lahnanen was formed under higher temperature (and pressure) conditions than the characteristic porphyry-type occurrences (Nurmi, 1984). The mineralization is suggested to have been formed in two stages. The ore metals were dispersed in the roof of the stock during a late magmatic stage and are now detectable as broad anomalies (Fig. 13). Molybdenum exhibits larger anomalies than do Cu and Sb, which is the exact opposite to the situation in other targets. Sulphur forms the most extensive but scattered pattern. The enriched granodiorite was the source of subsequent mineralization produced by highly K-enriched solutions ascending afterwards from depth. The

small, sharply outlined vein-like showings exhibit only very restricted wall-rock alteration on a scale of centimetres, and no broader primary halos related to individual occurrences were found even by detailed analysis of several of the drill cores intersecting the orebodies.

Effects of tectonics on halo pattern

Structural conditions before, during and after the mineralization may have a considerable impact on the pattern of primary halos. At Luukkolansaari, the halos exhibit variable extension and sequence of elements in different directions at the surface (Fig. 9). Zinc and Au form broad halos trending N-S, whereas the major ore metals, Mo and Cu, show a more widespread W-E pattern. The longish Zn and Au halos evidently mark the passage of ore-forming solutions along a favourable zone where the elements deposited at lower temperatures form broad leakage halos. Molybdenum and Cu halos were probably formed mainly by diffusion. This kind of variation in the sequence of primary halos in different directions is
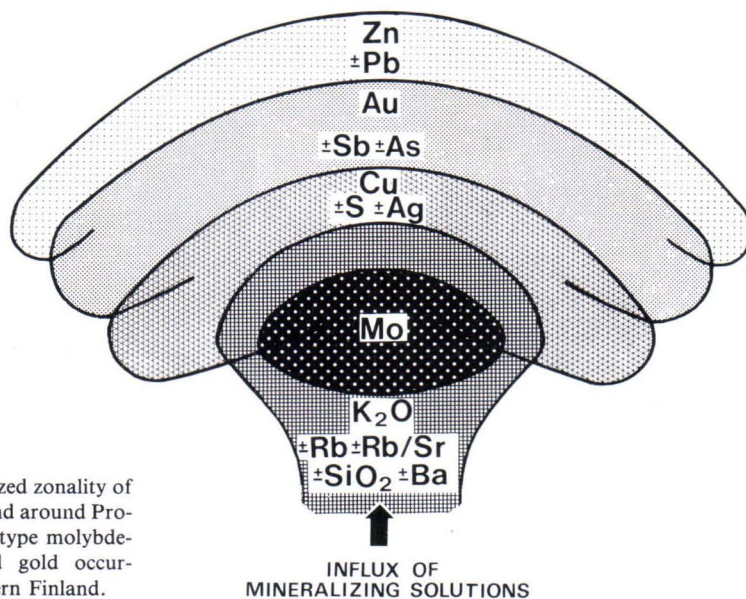

Fig. 12. Generalized zonality of primary halos in and around Proterozoic porphyry-type molybdenum, copper and gold occurrences in southern Finland.
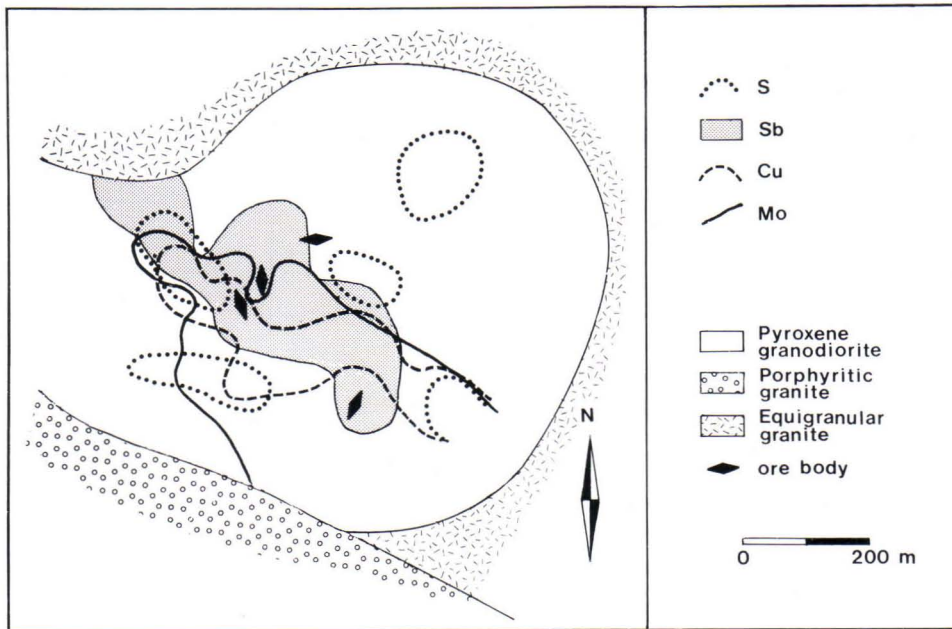
INFLUX OF
MINERALIZING SOLUTIONS

Fig. 13. Molybdenum, Cu, Sb and S anomalies in the pyroxene-bearing granodiorite enclosing the Mo occurrence of Lahnanen (simplified from Nurmi, 1984). Based on analyses of 54 samples.

typical of many epigenetic deposits (Beus and Grigorian, 1977).

The longish Cu and SiO₂ halos surrounding the stockwork occurrence at Tienpää (Fig. 11) are due to the solutions, the influx of which was controlled by a dextral shear zone (Nironen and Csongrádi, 1984). The stockwork mineralization is arranged in an en echelon pattern within the shear zone. Therefore, individual mineralized fissures formed in tension gashes are not parallel to the halos with a more regional control.

The occurrences of Kopsa and Tienpää exhibit asymmetric surface halos (Figs. 10 and 11), which are interpreted to represent different levels of mineralization. They demonstrate that the occurrences may have rotated away from their original position after deposition; the SW part of the Tienpää occurrence and the SE part of the Kopsa occurrence occupied by higher temperature halos were uplifted relative to the other ends.

Anomaly contrast

Anomaly contrasts are evaluated for the elements that form primary halos in and around the occurrences by dividing the contents at the 90th percentile by median contents and, in the case of negative halos, the median contents by contents at the 10th percentile (Table 2). The contrasts are very variable although usually within an order of magnitude. The principal ore metals, Mo and Cu, as well as Au and As at Kopsa, show the highest contrasts, generally from 4 to 7. However, the contrasts are lower at Lahnanen. Sulphur exhibits even higher contrasts, where S halos were detected, excluding the mineralization of Kopsa in which the median contents are also highly anomalous.

Anomaly contrasts are distinctly lower (from 2 to 3) for Au, Zn, Pb, As and Sb, the minor trace elements of the occurrences that form broad halos. Elements associated with wall-rock alteration generally have very low con-

Table 2. Evaluation of anomaly contrasts in the wall rocks of the porphyry-type occurrences studied for elements associated with mineralization. Contents at the 90th percentile devided by median contents.

Element	Occurrence					Mean	Range
	Susi-neva	Luukko-lansaari	Tien-pää	Kopsa	Lahna-nen		
Cu	2.8	8.6	5.8	4.4	2.8	4.9	2.8 — 8.6
Mo	5.3	4.3	—	6.8	1.7	4.5	1.7 — 6.8
Au	3.3	2.3	—	6.1	—	3.9	2.3 — 6.1
Zn	—	1.8	—	2.0	—	1.9	1.8 — 2.0
Pb	—	—	—	1.7	1.4	1.6	1.4 — 1.7
As	2.7	—	—	6.8	—	4.8	2.7 — 6.8
Sb	2.0	—	—	3.8	2.4	2.7	2.0 — 3.8
W	—	—	—	7.4	—	—	—
S	7.8	13	—	2.1	7.4	7.6	2.1 —13
K_2O	1.1	1.2	1.3	2.2	—	1.5	1.1 — 2.2
Na_2O[1]	—	—	—	1.4	—	—	—
SiO_2	—	—	1.04	1.1	—	1.1	1.04— 1.1
Rb	1.2	—	1.2	1.7	—	1.4	1.2 — 1.7
Sr[1]	1.1	—	—	1.3	—	1.2	1.1 — 1.3
Ba	—	—	1.2	—	—	—	—

[1] Negative halos (median contents divided by contents at the 10th percentile).

trasts (1.1 to 1.4) because of the weakness of alteration and the high background contents of these elements. At Kopsa, the contrasts are somewhat higher owing to the more pervasive potassic alteration and the relatively low background contents of K_2O and related elements in tonalite.

Analogous results have been obtained in the studies of Phanerozoic porphyry deposits. Copper and S have anomaly contrasts over 5, and Mo has from 2—5 to over 5 in the deposits connected with the Guichon Creek batholith (Olade and Fletcher, 1976a). Rubidium, Sr, K_2O and Na_2O have contrasts from 1 to 2, when comparing the contents of samples from the potassic zone with all samples (Olade and Fletcher, 1975; Olade, 1977). Rubidium shows a two to threefold increase from fresh rocks to those in potassic or sericitic alteration zones in Chilean porphyry copper deposits (Armbrust et al., 1975). The respective change in the K_2O content is less than two.

Interelement correlation

Correlation coefficients between elements in primary halos are insignificant in all targets but Kopsa. This is principally because samples were taken over large areas around the occurrences, and both barren and weakly mineralized samples were included. Thus, the element contents in the samples are partly governed by magmatic processes and partly by mineralization. Many elements, e.g., Cu, behave in quite a different way in these superimposed processes, and the halos are largely spatially unrelated owing to zoning.

On the other hand, all the samples from Kopsa were invariably mineralized, and elements related to mineralization exhibit significant correlations. Interpreted with factor analysis they exhibit various sulphide associations (Cu-Ag-S, Au-As-Sb and Zn-Pb) and potassic and silicic alteration of the tonalite (Nurmi, 1984, Table 6).

COMPARISON OF LITHOGEOCHEMISTRY WITH TILL AND STREAM-SEDIMENT GEOCHEMISTRY

The applicability of lithogeochemistry has been compared with that of till and stream-sediment geochemistry in the search for Mo-Cu-Au deposits in the area of the Rautio batholith, and with that of till geochemistry in local exploration at Susineva by Nurmi and Isohanni (1984). As shown in the present context lithogeochemistry has contributed to the establishing of the mineral potential of the granodiorite phase of the Rautio batholith and especially of its central parts. Furthermore, it has permitted the history of the crystallization of the batholith to be outlined. Copper gives the best results in regional exploration but the few samples with detectable Mo contents are randomly distributed.

In the regional till geochemical study based on a three times greater number of samples than in the lithogeochemical study, the Susineva occurrence shows up as restricted Mo and Cu anomalies (Nurmi and Isohanni, 1984, Fig. 5). The elements exhibit, however, numerous other anomalies throughout the study area, of which Cu anomalies are concentrated outside the granodiorite, indicating the higher background Cu contents in the surrounding more mafic rocks than the granodiorite, and associated Cu showings.

In organic-rich stream sediments, Mo gives a weak anomaly near the occurrence, but Cu contents are low in the area. The anomaly pattern of Mo is difficult to interpret in detail, because scattered and partly stronger anomalies occur in the stream sediments throughout the granodiorite. They may indicate the mineral potential of the granodiorite on a larger scale.

The distribution patterns of Mo and Cu in the lower part of the till overlying the Susineva occurrence correspond more or less to those in the bedrock (Nurmi and Isohanni, 1984, Fig. 6). The anomalies have shifted somewhat down-ice, and the zonal pattern of the mineralization

is less distinct than on lithogeochemical maps. Molybdenum contents are higher and Cu contents lower in the fine fraction of till than in rock samples (Nurmi and Isohanni, 1984, Fig. 7). This is interpreted to reflect the dissimilar mode of occurrence of the metals in the bedrock: molybdenite in strongly mineralized quartz veinlets and as small pods, and chalcopyrite more disseminated. Thus, till geochemistry seems to give better average of the Mo contents.

At Lahnanen, the Geological Survey has undertaken a detailed till geochemical study with over 300 samples in the same area as the lithogeochemical investigation (Oivanen and Eskola, 1972; Kontas, 1976). Molybdenum gives surprisingly similar distribution patterns in both materials, although the number of rock samples is only one sixth of the till samples (Fig. 14). The variation in Mo contents is slightly higher in till samples, which include some with Mo contents up to several tens of ppm; the till includes material directly from individual occurrences, whereas the rock samples are all from barren granodiorite. The somewhat lower median content in till is due to the partial leach used in the analysis of till samples. Copper anomalies in bedrock and till correspond to each other less well, and the till geochemical map does not indicate the mineral-potential zone. Copper contents are also distinctly lower in till; this is due to the mode of occurrence of Cu in bedrock, where it forms a broad low-contrast anomaly zone but is not concentrated in the Mo showings.

The above examples show that till geochemical maps are often harder to interpret than lithogeochemical maps. This is due to the complex origin of anomalies in till: 1) till is a mixture of material from various sources with different background values; 2) till is often deposited during complex glacial transport
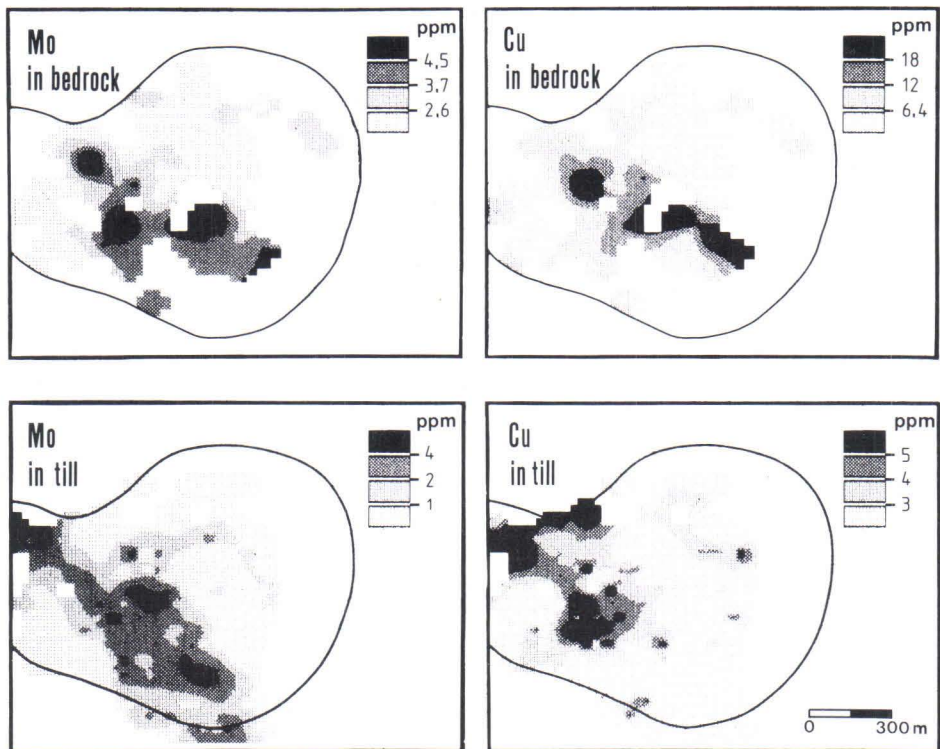
Fig. 14.   Comparison of Mo and Cu anomalies in bedrock and in the fine-fraction of till overlying
the Mo occurrence of Lahnanen. Based on analyses of 54 rock samples and over 300 till samples;
anomaly limits in both materials; 90, 75 and 50 percentiles.

(e.g., Hirvas, 1977; Ekdahl, 1982); and 3) anomalies may be affected by postdepositional hydrogenic processes (e.g., Nurmi, 1976). However, a till sample always represents a larger area than a rock sample and is thus very appropriate when prospecting for elements such as Mo, which often occurs randomly in bedrock and exhibits confined primary halos. Till sampling is more laborious than outcrop sampling, but in areas with a low density of outcrops, till geochemistry may represent a suitable alternative.

Anomalies in stream sediments rich in organic matter are due to secondary enrichment of ore metals and are strongly affected by local geochemical conditions. Stream-sediment studies are evidently best applied at the reconnaissance stage.

CONCLUSIONS

This study demonstrates that lithogeochemistry can be applied successfully at all stages of the exploration for Proterozoic porphyry-type Mo, Cu and Au deposits:

1) On the largest scale lithogeochemistry contributes to the identification of I-type granitoids, potential for porphyry-type mineralization.

2) Productive plutons for porphyry-type deposits cannot be discriminated from barren granitoids by bulk geochemistry; further, the average contents of ore metals are normal outside the mineralized areas. Nevertheless, traces of mineralization can be identified in a batholith with systematic sampling at 1 to 5 samples/km². Productive intrusive phases proved to have an abnormally high variation in Cu contents, although the median content of Cu is higher in phases with more mafic composition. Applications of other ore elements are of more limited value, and more samples will evidently be needed in the identification of granitoids with, for example, Cu-deficient porphyry-type Mo deposits.

3) The anomaly patterns of Cu are scattered on regional scale geochemical maps, but high contents are concentrated in the areas around occurrences and are often associated with more confined anomalies of variables such as Mo, As, K₂O and Rb/Sr. Especially K₂O and Rb/Sr may exhibit large anomalies that were formed during postmagmatic autometasomatic potassic alteration and are not necessarily related to ore deposition. Therefore, evaluation of the mineral potential should be based on simultaneous interpretation of multi-element data.

4) The halo patterns are characteristic of each occurrence, reflecting the extent of the ore-forming processes, the primary composition of mineralizing solutions, the genetic relationship of mineralization to its wall rocks, the composition and structure of wall rocks, temperature and pressure, the present level of erosion, and postdepositional tectonics. Considering the relatively small size and grade of the occurrences, the primary halos have a considerable extent and they can be applied in delineating the most promising parts of the occurrences with studies based on 10 to 40 samples/km². The halos generally exhibit distinct zoning, and the sequence of elements seems to be much the same in different occurrences, although the number of elements forming the halos varies from one mineralization to another. The general sequence of halos towards the core is: $Zn\ (\pm Pb) - Au(\pm Sb \pm As) - Cu(\pm S \pm Ag) - K_2O(\pm Rb \pm Rb/Sr \pm Ba \pm SiO_2) -$ Mo, the elements in parentheses having a more limited general explorational value. The major ore metals, Cu and Mo, are most suitable for explorational purposes, but elements forming the broadest halos may be useful pathfinders for slightly eroded or subsurface deposits. Elements related to wall-rock alteration are of limited importance, exhibiting confined halos in the root and central zones of mineralization. The zonal pattern of halos can be applied in evaluating the mineral potential at depth in a certain deposit or in different deposits having similar characteristics. Effective use of lithogeochemistry should be continued at the subsequent drilling stage of exploration.

5) Anomaly contrasts are highest for the principal ore metals (4 to 7), whereas the elements forming the broadest halos exhibit contrasts from 2 to 3 and those associated with wall-rock alteration from 1 to 2.

6) Correlation coefficients between elements forming halos are low in weakly mineralized samples from around the occurrences because of the prevailing lithological control of the abundances, which is often the reverse of

mineralization and because many elements are spatially unrelated in zoned halos. However, in strongly mineralized samples significant correlations exist, reflecting different associations of sulphides and wall-rock alteration.

7) Granitoids are very suitable targets for lithogeochemical exploration, because the background contents of ore metals are low and constant. It is, therefore, possible to study small changes in element contents and to trace mineral-potential intrusive phases and areas with relatively widely spaced samples. However, the background may vary considerably between different intrusive phases, and lithogeochemical studies should be subjected to detailed geological mapping and classification of samples.

8) Porphyry-type mineralization has a very heterogeneous character and especially ore minerals occurs randomly on outcrop scale. Therefore special emphasis should be laid on taking samples that are as representative as possible.

9) Lithogeochemistry offers an effective and (when samples are readily available) a relatively unexpensive tool for the exploration for porphyry-type deposits. The major disadvantage of lithogeochemistry concerns the availability of sample material. In poorly exposed areas, stream-sediment geochemistry at the reconnaissance stage and till geochemistry in local exploration may be suitable alternatives.

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11—13 *Käkövesi batholith, Puumala:* 11 tonalite, 12 granodiorite, 13 mineralized monzogranite dykes; 21—26 *Lahnanen granitoid complex, Viitasaari:* 21 hypersthene granodiorite (Lahnanen stock), 22 hypersthene granodiorite (Hirvivuori stock), 23 hypersthene monzogranite (Saunamäki and Saarilampi stocks), 24 fine-grained monzogranite, 25 coarse-porphyritic monzogranite, 26 equigranular monzogranite; 31—32 *Rautio batholith, Kalajoki:* 31 granodiorite, 32 granodiorite porphyry; 41—45 *Tienpää tonalite complex, Halsua:* 41 hornblende tonalite, 42 porphyritic tonalite, 43 equigranular tonalite, 44 tonalite porphyry, 45 K-feldspar-bearing tonalite; 51—56 *postorogenic Luonteri (Hirvensalo) stock, Anttola:* 51 fine-grained granodiorite, 52 tonalite, 53 hornblende granodiorite, 54 granodiorite, 55 hornblende monzogranite, 56 monzogranite dykes; 61—63 *Pukala stock, Orivesi:* 61 trondhjemite, 62 granodiorite, 63 monzogranite; 71—72 *Varparanta stock, Enonkoski:* 71 trondhjemite, 72 fine-grained trondhjemite; 81—84 *Palokka granitoid complex, Jyväskylä:* 81 coarse-porphyritic monzogranite, 82 equigranular monzogranite, 83 syenogranite, 84 biotite syenogranite; 91 *late-orogenic Renkajärvi migmatite complex, Renko:* monzogranite; 101—103 *Hämeenkyrö batholith:* 101 granodiorite, 102 monzogranite, 103 monzogranite dykes; 111 *Värmälä stock, Tampere:* granodiorite; 121 *Majajärvi stock, Kankaanpää:* granodiorite; 141 *Kopsa stock, Haapajärvi:* tonalite porphyry; 171 *Äitsaari stock, Ruokolahti:* trondhjemite; 181 *Salosaari stock, Ruokolahti:* tonalite; 211—212 *Mäntsälä stock:* 211 granodiorite, 212 trondhjemite; 221—222 *Aulanko stock, Hämeenlinna:* 221 granodiorite, 222 trondhjemite porphyry; 231 *Silvola stock, Savonlinna:* tonalite; 251—252 *Kalliokangas stock, Evijärvi:* 251 trondhjemite, 252 granodiorite; 261 *Sydänmaa stock, Luhanka:* granodiorite; 271 *Hernemäki stock, Luhanka:* monzogranite.

Appendix

Median contents of selected variables in granitoid phases studied. N = number of samples. (Oxides in percentages, others in ppm.)

Phase No	N	SiO₂	TiO₂	Al₂O₃	FeO*	MgO	CaO	Na₂O	K₂O	P₂O₅	Rb	Sr
11	27	61.7	0.48	15.3	4.2	3.8	3.7	3.7	2.1	0.18	76	690
12	91	66.5	0.29	16.7	2.2	2.1	2.5	4.3	2.6	0.12	81	970
13	4	71.9	0.20	16.5	1.5	1.1	1.6	3.6	4.8	0.06	100	860
21	71	72.3	0.21	14.3	2.9	0.45	2.4	3.7	2.9	0.07	55	260
22	29	72.7	0.22	14.4	2.9	0.46	2.4	3.8	3.0	0.08	73	250
23	24	72.3	0.21	13.9	2.5	0.40	2.3	3.5	3.2	0.07	80	240
24	15	73.3	0.15	12.9	2.0	0.29	1.6	3.3	3.4	0.03	100	180
25	14	70.2	0.33	15.2	2.8	0.98	1.7	2.9	4.7	0.14	180	200
26	47	74.6	0.13	12.9	1.8	0.31	1.2	3.3	3.6	0.04	95	150
31	120	67.8	0.25	16.0	2.4	2.3	2.0	4.2	4.2	0.08	120	540
32	4	68.3	0.19	15.7	1.6	1.7	1.6	3.9	4.5	0.06	130	470
41	3	62.0	0.43	17.4	5.6	3.4	5.2	3.8	1.2	0.15	27	530
42	45	65.5	0.34	16.7	4.0	2.7	3.7	3.6	1.9	0.11	41	490
43	18	65.6	0.32	17.7	3.6	2.4	4.1	3.9	1.6	0.13	37	600
44	4	66.9	0.31	17.4	3.5	2.6	3.9	3.7	1.6	0.12	46	570
45	3	66.1	0.32	17.0	3.5	3.0	3.2	3.5	2.5	0.10	42	430
51	5	59.8	1.9	15.0	7.8	1.9	4.2	3.2	3.8	0.86	120	1300
52	3	53.2	2.3	15.6	9.5	3.0	5.9	3.4	3.0	1.5	96	2300
53	11	57.9	1.8	15.4	7.9	2.0	4.7	3.2	3.7	0.93	100	1200
54	8	58.5	1.9	15.5	7.8	2.3	4.6	3.5	3.4	0.97	98	1900
55	7	63.0	1.4	14.9	6.3	1.6	3.5	3.2	4.0	0.66	110	1200
56	8	69.7	0.54	13.8	3.1	0.80	1.5	2.5	5.1	0.28	130	1000
61	15	68.5	0.20	16.4	1.8	1.6	2.2	4.9	0.93	0.06	19	590
62	14	70.0	0.18	16.2	1.6	1.1	1.8	4.0	3.5	0.06	53	490
63	6	69.5	0.20	16.5	2.0	1.6	1.5	3.9	4.0	0.08	72	540
71	51	65.3	0.31	17.1	2.2	2.0	3.3	4.7	1.1	0.11	31	750
72	4	67.8	0.24	17.1	1.9	1.5	2.5	4.8	1.3	0.08	34	640
81	5	71.6	0.33	13.8	3.3	0.82	1.9	3.2	3.8	0.11	150	210
82	10	67.2	0.40	15.8	3.8	0.80	2.9	3.9	4.1	0.13	120	340
83	16	78.2	0.08	11.6	1.3	0.31	0.60	3.2	4.3	0.04	180	50
84	12	71.1	0.36	14.1	2.6	0.69	1.8	3.2	4.7	0.13	220	230
91	36	73.5	0.15	14.3	1.5	0.29	0.72	2.9	5.5	0.10	290	100
101	37	60.3	0.53	14.4	6.2	2.4	3.8	3.3	3.2	0.21	110	340
102	5	66.5	0.37	15.4	5.7	0.84	2.8	3.8	3.8	0.16	120	350
103	4	67.9	0.31	15.9	4.3	0.38	2.1	3.8	4.5	0.12	130	320
111	16	69.8	0.23	16.2	2.1	1.2	1.8	3.7	3.9	0.07	110	330
121	15	63.2	0.34	17.0	3.5	2.6	4.0	3.5	2.8	0.14	73	830
141	10	61.7	0.34	16.4	5.3	2.4	5.2	2.5	1.7	0.11	65	290
171	21	66.8	0.32	16.5	3.3	2.1	2.6	4.5	1.8	0.21	61	510
181	7	64.0	0.38	15.7	3.8	3.7	3.2	4.3	2.7	0.39	79	780
211	23	67.2	0.41	14.7	4.1	1.2	2.4	3.9	3.4	0.18	85	460
212	4	69.7	0.24	15.3	2.4	1.0	2.6	4.7	1.8	0.11	36	750
221	23	65.9	0.30	16.2	4.1	2.5	3.2	3.7	3.8	0.11	110	550
222	3	75.4	0.17	13.5	1.9	0.43	1.7	3.8	1.2	0.04	140	160
231	15	66.8	0.24	16.8	3.2	1.3	4.6	4.0	1.0	0.10	35	530
251	7	68.3	0.35	15.6	3.2	1.6	2.5	5.1	1.7	0.11	62	360
252	3	71.5	0.35	14.7	2.8	1.0	2.4	4.0	2.7	0.10	53	260
261	18	66.2	0.64	15.3	4.4	1.8	3.0	3.1	4.3	0.24	140	670
271	10	68.9	0.58	13.8	4.8	0.73	2.1	2.6	5.1	0.21	210	210

* Total Fe as FeO

App. contd.

Phase No	N	Ba	Cs	Sc	Cu	Zn	Pb	La	Sm	Th	U
11	27	530	3.5	12	15	47	7.0	28	3.8	6.6	2.1
12	91	710	3.0	5.8	3.6	37	5.3	30	3.4	8.6	2.6
13	4	1100	6.3	1.9	690	92	21	29	3.3	56	19
21	71	960	0.5	4.0	6.1	33	3.6	21	2.6	1.3	0.5
22	29	870	1.0	4.2	6.5	41	5.5	24	3.1	3.8	0.7
23	24	970	1.5	4.4	8.9	44	6.4	27	3.5	6.1	0.9
24	15	1100	1.5	5.5	25	31	5.2	26	2.5	6.5	0.8
25	14	880	7.4	9.5	12	80	13	52	8.4	17	2.7
26	47	1000	1.3	3.0	3.7	29	6.6	28	3.2	9.6	1.7
31	120	630	5.2	5.9	8.9	46	8.0	27	2.8	13	3.0
32	4	640	4.5	4.4	7.6	40	8.0	22	2.1	14	2.9
41	3	420	1.5	18	34	66	6.6	13	2.2	2.0	0.8
42	45	630	2.0	12	23	67	7.5	14	2.0	3.5	1.5
43	18	540	1.8	8.6	16	72	6.9	14	1.7	2.7	1.0
44	4	590	1.9	8.6	37	70	6.6	12	1.6	2.9	1.3
45	3	780	2.0	9.8	19	49	6.3	14	1.9	4.1	1.5
51	5	3400	1.5	15	26	150	12	220	17	11	4.2
52	3	3500	1.2	16	38	200	14	230	21	14	5.2
53	11	2600	2.3	13	26	190	12	190	17	8.6	2.1
54	8	3100	1.4	13	27	160	12	190	18	13	4.7
55	7	3000	1.9	11	19	170	12	180	14	10	2.4
56	8	2500	2.2	3.5	6.9	75	9.7	120	10	12	2.8
61	15	630	0.6	5.5	3.5	17	5.1	29	2.8	6.9	1.8
62	14	1800	0.6	4.3	9.4	22	5.9	28	2.6	7.0	1.9
63	6	1600	0.9	4.6	4.9	29	5.6	32	2.6	8.6	2.0
71	51	450	0.7	5.7	21	51	5.0	15	1.8	2.8	0.9
72	4	460	0.4	4.3	32	48	4.9	14	1.6	2.5	0.9
81	5	630	5.6	11	23	84	11	30	4.1	10	1.9
82	10	1600	3.6	16	6.3	81	7.8	45	6.8	7.1	1.4
83	16	58	1.3	3.9	4.3	46	5.9	20	5.1	14	3.4
84	12	850	7.4	7.3	5.5	90	11	49	4.9	20	2.8
91	36	490	14	3.2	3.9	54	7.4	33	4.6	24	5.9
101	37	790	4.7	14	21	46	11	24	4.2	11	3.8
102	5	1200	4.4	9.6	20	35	10	17	4.6	10	3.9
103	4	1700	1.7	9.0	10	23	8.2	29	4.6	13	5.1
111	16	780	3.7	4.5	5.0	61	9.4	22	3.4	9.1	2.9
121	15	1000	1.9	10	13	39	6.5	28	3.4	7.1	2.1
141	10	450	3.6	17	172	52	13	12	2.3	4.0	1.7
171	21	570	2.9	6.4	5.3	48	4.3	12	1.4	2.5	1.2
181	7	620	2.0	12	2.4	46	5.3	27	3.9	3.4	0.7
211	23	870	2.4	6.5	8.0	41	6.6	21	2.6	7.1	2.6
212	4	630	1.6	4.1	4.2	25	4.1	10	1.3	2.5	1.1
221	23	820	8.1	8.5	9.8	48	7.4	14	2.1	7.1	3.0
222	3	370	26	3.6	6.1	42	5.2	12	1.3	5.3	2.5
231	15	590	1.7	7.9	4.1	28	3.9	15	1.5	2.8	1.1
251	7	430	2.7	7.8	12	49	5.6	16	3.8	4.0	1.4
252	3	920	1.8	5.2	4.0	65	6.2	34	5.4	7.3	2.1
261	18	1000	6.5	12	15	80	12	53	7.9	17	5.1
271	10	950	5.8	14	13	96	12	71	8.9	15	4.9