Geological Survey of Finland

Bulletin 341

The early Proterozoic Zn-Pb-Cu massive sulfide deposit at Attu, SW Finland

Leake S. Hangala

Geologian tutkimuskeskus Espoo 1987



Geological Survey of Finland, Bulletin 341 - Hangala, Leake S.

ERRATA

Page 9, Fig. 2. Only *schists* in the Archean basement in eastern Finland belong to 5, the rest belong to 4 (see Huhma 1986, p. 7).

Page 11, Fig. 3., for km, read m

Page 24, line 5 and in table 7, for breithaupite, read breithauptite

Page 28, second column line 20, for Suzaki, read Sugaki

Page 48, line 8 from below, for 537, read 577.

THE EARLY PROTEROZOIC Zn-Pb-Cu MASSIVE SULFIDE DEPOSIT AT ATTU, SW FINLAND

by

LEAKE S. HANGALA

with 33 figures, 18 tables and 1 appendix

ACADEMIC DISSERTATION

GEOLOGIAN TUTKIMUSKESKUS Espoo 1987 Hangala, L. S. 1987. The early Proterozoic Zn-Pb-Cu massive sulfide deposit at Attu, SW Finland. *Geological Survey of Finland*, *Bulletin 341*. 61 p., 33 figures, 18 tables and 1 appendix.

The stratabound Attu Zn-Pb-Cu massive sulfide deposit occurs in an early Proterozoic Svecofennian domain which covers most of the southern part of Finland and central Sweden. The geology of the surrounding area is dominated by a supracrustal sequence of amphibolites, amphibole gneisses and mica gneisses, which were intruded by synorogenic and late-orogenic plutonic rocks. The orebody is hosted by a tremolite-quartz rock, calc-silicate rocks (diopside-tremolite skarn) and cordierite-anthophyllite rocks. At least two folding phases (F_n and F_{n+1}) and associated metamorphism obliterated the primary features of the ore and changed the mineralogical composition of the wall rocks during the Svecofennian orogeny. Sulfides occur as stratiform or lens-shaped bodies or as dissemination, controlled by F_{n+1} folding. Garnet-pyroxene and sulfur isotope geothermometric determinations suggest that the peak temperature of metamorphism in the Attu area was around 740 °C. Pressures between 4.5–5.1 kb were measured from orthopyroxene-garnet-plagioclase-quartz and sphalerite geobarometers.

Pyrrhotite, sphalerite, galena, pyrite and chalcopyrite are the main sulfide minerals. Ag-, Sb-, Sn- and As-bearing sulfosalts are common and often associated with galena. Sulfides are considered to represent recrystallized equilibrium assemblages formed during metamorphism at a temperature range of ca. 580° to 740 °C. The main gangue minerals are quartz, diopside, tremolite, dolomite, calcite, anthophyllite and cordierite. Geochemically, the ore elements show variation with rock types and depth. Lead is enriched in the calc-silicate rocks and copper in the cordierite-anthophyllite rocks, while zinc predominates in the quartz rock. Metal zonation within the orebody is best indicated by copper and lead; copper contents increase with depth, whereas lead is enriched in the upper parts of the orebody. Lead in the Attu galena has an isotopically well mixed mantle-crustal source. Sulfur isotope ratios suggest that isotopic equilibrium was established between the sulfides and that the bulk of the sulfur in the Attu deposit is of magmatic origin.

The Attu sulfide deposit is of submarine exhalative origin. This is suggested by the mineral association, wall-rock alteration and metal zonation as well as by the similarity with other Svecofennian massive sulfide deposits (e.g., Aijala-Orijärvi-Metsämonttu and Garpenberg) and with other representatives of the world-wide class of stratabound massive sulfide deposits.

Key words: metal ores, sulfides, stratabound deposits, metamorphic rocks, geochemistry, isotopes, metamorphism, Proterozoic, Attu, Parainen, Finland

Leake S. Hangala

Department of Geology, University of Helsinki, Box 115, SF-00171 Helsinki 17, Finland.

ISBN 951-690-269-3 ISSN 0367-522X

Helsinki 1987. Frenckellin Kirjapaino Oy

Dedicated

to

my parents, for their unflinching love and care of their children,

to

the memory of PLAN combatants who have sacrificed in the struggle for national liberation and

to

all those who will carry that struggle to final victory.

CONTENTS

Introduction
Materials and analytical methods 7
Outline of the regional geological setting 8
The Svecofennian domain
Geology of the area around the Attu sulfide deposit
Lithology
Amphibolites and amphibole gneisses 12
Mica gneisses
Cordierite-anthophyllite rocks
Tremolite-quartz rock
Marble and calc-silicate rocks
Granitoid rocks
Geochemistry of the supracrustal rocks
Estimates of the metamorphic conditions
Structures
The Attu sulfide deposit
Orientation of the sulfide orebody 23
Ore minerals
Pyrrhotite
Sphalerite
Chalcopyrite
Pyrite
Galena
Arsenopyrite
Silver-bearing minerals
Other minerals
Metamorphism of the sulfide deposit
Geochemistry of the sulfide deposit
Distribution of the main ore elements
The sphalerite geobarometry
Isotope geochemical studies
Lead isotopes
Sulfur isotopes
Discussion 49
Comparison of the Attu deposit with other massive sulfide deposits
Origin of the wall rocks
Genesis of the Attu sulfide deposit
Summary and conclusions
Acknowledgments
References
Appendix: Chemical analyses of the tremolite-quartz rock, cordierite-anthophyllite rocks.
amphibolites and mica gneisses from Attu.

INTRODUCTION

Attu is an island between longitudes 22° 17' and 22° E and latitudes 60° 12' and 60° 09' N, in the archipelago of southwestern Finland. It belongs administratively to the municipality of Pargas (Parainen). The island of Attu covers an area of approximately 18 sq km, most of which is grown over with forest; and only 15 % of the land is arable. The elevations range from sea level to about 35 m, and there are relatively good outcrops and a few minry tracts. Geologically, Attu belongs to the Svecofennian domain which transects southern Finland in a roughly E-W direction and extends over to central Sweden (Fig.1).

The occurrence of sulfide ore in the northern part of the island of Attu has been known since the 17th century under the name "Attu Silvergruva" (Attu Silver Mine). The name was derived from the silver-bearing galena that was mined there (Pehrman 1932). The age of the Attu mine and the type of ore extracted cannot be exactly verified but could be inferred from



Fig. 1. The location of the Attu Zn-Pb-Cu sulfide deposit in the Svecofennian domain, southern Finland.

the colourful recollection of Holmberg (1858, p. 77–78): "On the estate of Attu is an old trench. It is related that it was dug by the assessor of the Court of Appeal at Turku, Olof Dufva,, who in 1630 had mined silver-ore there. Tilas¹, who visited the place in 1737, did not find any trace of galena, but chalcopyrite and an indication of a green copper mineralization. The mine was then 8 cords (1 cord = 1.75 m) long, 1 cord deep and 1.5 cords wide. Tilas met an old man at the Attu pub. The man was 108 years old and said that the mine was older than he was" (Translated from the Swedish by Prof. Herman Stigzelius).

Pehrman (1932) reported that in 1835 Westling paid a visit to the Attu mine and said he had found pyrite and pyrrhotite but no trace of galena or chalcopyrite. During the period 1890-1891, Mining Engineer H. A. Mueller carried out mining operations at Attu and as a result thereof about 20 tons of ore were shipped to Germany. Mining activities were discontinued, allegedly because they had proved to be uneconomic and the complex ore composition made the ore-enrichment process technically difficult. After 1891 no mining or related activities were reported on the sulfide ore occurrences of Attu. The first reference on the occurrences was made by Pehrman (1927) in his paper on the Ti-Fe ore deposit, at Jermo, south of Attu. The Ti-Fe ore occurrences were discovered in the middle of the 16th century but exploited for only two decades. A more detailed report on the geology and mineralogy of the Attu sulfide deposit was published by Pehrman in 1932.

As a result of the increased demand for metals during the Second World War, the Vuoksenniska Company carried out investigations of the Attu ore between 1942 and 1944. The work included mapping and diamond drilling; altogether 37 boreholes were drilled. With the help of geologists from the Boliden Mining Company in Sweden, Vuoksenniska estimated that the ore reserves at Attu were 230 000 metric tons (Lundén 1964). The deposit was found to be uneconomic and the exploration work was consequently halted. However, in 1956, the Vuoksenniska Company resumed its investigations, which included additional drilling. Further evaluation by this company within the light of the additional information obtained put the ore reserves at 550 000 tons.

In 1958 Vuoksenniska transferred the prospecting rights in the Attu area to the Pargas Kalkbergs Aktiebolag², which carried out mapping and drilling in the area until 1961 under the supervision of Prof. Metzger. Part of the result of this work was reported by Lundén (1964). The actual ore reserves at Attu were estimated by Pargas Kalkberg Aktiebolag to be 1 200 000 tons, and the probable ones 3 000 000 tons (Lundén 1964).

In 1979 Oy Partek Ab entered into an agreement with Outokumpu Oy regarding the Attu sulfide deposit. According to this agreement, Outokumpu Oy was to investigate the technical and economic feasibility of the Attu deposit. Outokumpu Oy carried out investigations of the deposit in 1981 and 1982. The exploratory work included detailed mapping on the scale of 1:4000 at and around the ore deposit as well as a diamond drilling program totalling 3 268 m (Rauhamäki & Karppanen 1982). On the basis of its own investigations, Outokumpu Oy estimated the reserves at the Attu deposit to be 4.3 million tons; 1.5 million being underground and 2.8 million open pit reserves (Table 1).

The estimation was based on the "mining technical" factors, i.e., estimation of the most

Table 1. Estimated ore re-	serves in	the	Attu (deposit
----------------------------	-----------	-----	--------	---------

	Open pit	Underground
Ores	2.8 million tons	1.5 million tons
Waste	4.6 million tons	-
Zn-grade	1.81 %	1.68 %
Pb-grade	1.10 %	0.96 %
Cu-grade	0.14 %	0.21 %
Ag-grade	43 g/t	43 g/t

² renamed and now called Oy Partek Ab.

 $^{^1}$ Daniel Tilas (1712–1772) was a Swedish mining officer who made a study of mineral occurrences in Finland in 1737 and 1738 (Stigzelius 1986).

economic alternatives at given metal prices and working costs (mining, concentrating, transport, melting, etc.). The underground reserves were found not to be economically viable and actually to diminish the proportional importance of the copper ore. Owing to the low level and sharply downward trend of metal prices, it was concluded that the Attu reserves are uneconomic (Rauhamäki & Karppanen 1982).

In 1974 the Department for Economic Geology, Mineralogy and Petrology of the Free University of Amsterdam started a geological and petrological project in the Kemiö-Orijärvi region, southwestern Finland. Within the framework of this project, a report on the geology of the northern part of the island of Attu was compiled (Schellekens 1976, 1980).

In spite of several attempts to mine it, no systematic scientific study of the Attu deposit has been done. The present work seeks to fill that gap. The study was suggested by Professor Ilmari Haapala. On his initiative, the Oy Partek Ab and Outokumpu Oy companies kindly offered me the right and the materials to undertake the work. Its main objectives are to investigate the petrology and geochemistry of the rocks hosting the orebody, to study the mineralogy and geochemistry of the deposit, especially the ore elements, and to explain, on the basis of the results obtained, the genesis of the deposit.

The work was started in the summer of 1984. The author carried out field work in the area during the summers of 1984 and 1985. The study was conducted at the Department of Geology and Mineralogy, University of Helsinki. Various petrographic, geochemical and isotope geochemical methods were used.

MATERIALS AND ANALYTICAL METHODS

Most of the materials used in this work were provided by the Outokumpu Oy Exploration. These include maps, drill-core profiles, thin and polished sections as well as the atomic absorption spectrophotometry (AAS) and the instrumental neutron activation analysis (INAA) analyses of the drill cores. Oy Partek Ab contributed valuable material in the form of drillcore samples, maps, drawing facilities as well as logistical assistance.

More than 200 thin and polished sections were studied under the microscope. As x-ray diffractometer, a Philips wide angle goniometer with a Wallac single analyzer was used. Nickel-filtered CuK radiation and metallic silicon as the internal standard were used throughout.

Major ore elements from drill cores were analyzed in the Geological Laboratory of Outokumpu Oy with the AAS method. Gold and other trace elements were analyzed with the INAA method at the Reactor Laboratory of the Technical Research Centre of Finland. Whole-rock analyses of the surrounding rocks were analysed with a Philips 1400 x-ray fluorescence spectrometer (XRF) at the Research Laboratory of Rautaruukki Oy. Microprobe analyses of the ore minerals were performed with a Camebax Microprobe with a voltage of 20 kV at the Metallurgical Laboratory of Outokumpu Oy in Pori. Electron microprobe mineral analyses for the estimation of metamorphic conditions were done by Dr Hein E. Wever at the Laboratory of the Department for Economic Geology, Mineralogy and Petrology of the Free University of Amsterdam with a Cambridge Microscan-9 Electron microprobe with an accelerating voltage of 20 kV and a specimen current of 25 nA.

Factor analyses of the geochemical data were done at the Geological Survey of Finland with the Factor Analyses Program.

Sulfur isotope determinations were performed at the Laboratory of Economic Geology, Helsinki University of Technology, using the method described by Mäkelä and Tammenmaa (1977).

Lead isotope analyses were done in the Isotope Laboratory of the Geological Survey of Finland following the method described by M.

7

Vaasjoki (1987, pers. commun.). According to this method, the whole rock samples were incinerated in teflon bombs sealed in steel at 170 °C for 24 hours using 300 mg of rock powder mixed with 2 ml of HF and 1 ml of HNO₃. After evaporation with 0.2 ml H₃ClO₄ added and a second evaporation with 3 ml HNO₃ in order to expel all SiF₄ residue, the samples were dissolved overnight in the same teflon vessels at 170 °C in 3 ml of 6.2N HCl, and converted to bromide salts by evaporating with 4 ml 1N HBr.

The sulfide samples were digested in a 1:1 mixture of 6.2N HCl and HNO₃ conc, evaporated to dryness and converted to bromide salts. The chemical purification of the lead was achieved by anion exchange chromatography in HBr solutions followed by anodic electrodeposition (cf., Gulson & Mizon 1979).

The isotopic determinations were carried out on the MS3 thermal ionization solid source mass-spectrometer built at the Geological Survey of Finland. The instrument is equipped with an automated data-acquisition system and uses a VG CA3 chopper amplifier for signal magnification. The analogue signals are digitalized by a Fluke 8500-series digital voltmeter. The MS3 has a 900, 25 cm radius stigmatic magnet giving an effective resolution comparable to a 50 cm radius conventional geometry. During each mass-spectrometric determination, the filament temperature was monitored by an optical pyrometer.

Lead was run at 1 100 °C \pm 50 °C from single rhenium filaments using conventional silica gel-phosphoric acid emitters. Frequent standardization with the CIT, SRM981 and SRM982 standards demonstrate that the ratios reported are on a 2 (95.5 %) confidence level, accurate within \pm 0.07 % for the ²⁰⁷Pb/²⁰⁶Pb ratio and 0.15 % for all other ratios. All the lead results have been normalized to the accepted values of the previously mentioned standards.

OUTLINE OF THE REGIONAL GEOLOGICAL SETTING

The Finnish bedrock is mainly composed of granitoids and greenstone belts of late Archean (about 2.7–2.8 Ga) age and the early Proterozoic Svecokarelian complex (Fig. 2). The Svecokarelian is divided into the Karelian domain in eastern and northern Finland and the Svecofennian domain in southern and western Finland (Simonen 1980, Gaál & Gorbatschev 1987). The Karelian domain consists mostly of epicontinental sediments (e.g., quartzites and dolomites), deposited on the Archean crust 2.45–1.9 Ga ago (cf., Huhma 1986). The Svecofennian supracrustal rocks constitute an orogenic terrain, ca. 1.9 Ga old, which is characterized mainly by volcanic rocks and graywacke-schists deposited in marine environments (Simonen 1980).

The Svecofennian domain

The Svecofennian domain (Figs.1 and 2), is mainly composed of metamorphosed and migmatized supracrustal rocks and plutonic rocks (Hietanen 1975, Latvalahti 1979, Simonen 1980, Schreurs 1985a, b). The predominant supracrustal rocks are micaceous schists and gneisses, amphibolites, quartz-feldspar schists and gneisses (leptites), cordierite-anthophyllite rocks, limestones and calc-silicate rocks. The volcanic rocks often indicate calc-alkaline affinities but tholeiitic trends are also encountered (e.g., Latvalahti 1979, Colley &

Geological Survey of Finland, Bulletin 341



Fig. 2. Main Precambrian units of southern and central Finland (based on Simonen 1980). 1. Jotnian sediments, 2. Rapakivi granites, 3. Svecokarelian plutonic rocks, 4. Svecokarelian schists and gneisses, 5. Presvecokarelian schists, 6. Early Proterozoic layered intrusions, 7. Archean gneisses.

Westra 1987, Kähkönen 1987). Most of the Svecofennian sediments are regarded as products of turbidity currents (Simonen 1980, Gaál 1982, Ojakangas 1986).

The Svecofennian domain has been interpreted as an early Proterozoic volcanic island arc system (Hietanen 1975, Berthelsen 1980, Bowes *et al.* 1984, Gaál 1982, 1986). Recent Nd-isotope studies indicate that the Svecofennides are not underlaid by an Archean basement but that a new crust was generated during the early Proterozoic (Patchett *et al.* 1984, Huhma 1986).

The metavolcanic rocks are basaltic to felsic (amphibolites and quartz-feldspar gneisses). The micaceous schists were mainly sediments of the graywacke-type, interbedded with argillaceous-arenaceous layers and metavolcanic

rocks (Hietanen 1975, Simonen 1960, 1980).

The mica gneisses are commonly mediumgrained, banded or veined and distinctly schistose. The leptites are recrystallized equigranular supracrustal, quartz-feldspar rocks with an average grain size of about 0.5 to 1.0 mm. A more fine-grained equivalent is generally called hälleflinta (Löfgren 1979). The leptites have been generally interpreted as metavolcanic rocks, mainly acid pyroclasts (Latvalahti 1979, Vivallo 1984).

The hornblende amphibolites in the Svecofennian domain occur as thin layers or as thick beds in the mica gneisses. Volcanic rocks like pillow lavas, agglomerates are common. The chemical composition of the amphibolites varies from basaltic to andesitic. The quartzbearing types show transitions to hornblendegneisses and are either metamorphosed dacites or mixtures of volcanic and sedimentary material (Edelman 1985). The volcanic structures and the chemical composition suggest that the amphibolites were originally lavas or tuffs.

Limestones and associated calc-silicate rocks occur as thin lenses or as layers in the quartzfeldspar gneisses and also as thicker layers along the contact between the amphibolites and the mica gneisses. The limestones are mainly calcitic, but dolomitic ones also occur (Simonen 1980, Edelman 1985).

The supracrustal rocks in the Svecofennian domain have undergone intensive deformation, which resulted in polyphase folding (Hopgood et al. 1983, Latvalahti 1979, Campbell 1980, Verhoef & Dietvorst 1980, Schreurs & Westra 1986). It has been indicated (e.g., Gaál & Gorbatschev 1987), that two principal periods of deformation and metamorphism, corresponding roughly to the emplacement times of the early and late Svecofennian granitoids, can be distinguished throughout almost the whole of the Svecofennian domain. In southern Finland, the major phases of deformation, metamorphism and migmatization all occurred in a short period between 1900 and 1885 Ma ago (Hopgood et al. 1983, Gaál 1986, Huhma 1986, Gaál & Gorbatschev 1987). Generally, the main folds and associated foliation trend E-W. The axial planes are commonly steep (e.g., Verhoef & Dietvorst 1980). The Svecofennian rocks are often metamorphosed in low-pressure, hightemperature conditions (Dietvorst 1981, Schellekens 1980, Schreurs 1985, Hölttä 1986).

The metavolcanic and metasedimentary rocks of the Svecofennian domain were intruded by both synorogenic and late-orogenic plutonic rocks. Nurmi and Haapala (1986) have reported that the synorogenic plutonic rocks of Finland display I-type characteristics. They form a differentiated suite of calcic and calcalkaline rocks, ranging in composition from gabbros and diorites through dominant tonalites and granodiorites to granites (Nurmi & Haapala 1986, Front & Nurmi 1987). Geochemical and isotopic studies suggest that the synorogenic plutonic rocks are composed of material newly segregated from the mantle during the early Proterozoic time (Patchett & Kouvo 1986, Huhma 1986, Patchett et al. 1987). The late-orogenic plutonic rocks, on the other hand, exhibit features typical of S-type granites (Simonen 1980, Nurmi & Haapala 1986). Microcline granites, monzo- and syenogranites, and pegmatites constitute the lateorogenic stage.

According to radiometric zircon U-Pb age determinations, the synorogenic plutonic rocks show ages ranging between 1.86 to over 1.9 Ga with a peak value at 1.87–1.89, and the lateorogenic plutonic rocks show ages of 1.8 to 1.85 Ga (Vaasjoki 1981, Hopgood *et al.* 1983, Nurmi & Haapala 1986). The youngest gran-

Table 2. Generalized	stratigraphy	of the	Svecofennian	do-
main after Simonen (1960, 1980)			

GROUP	ROCK TYPES
Upper Svecofennian	Argillaceous and arenaceous sediments
Middle Svecofennian	Mafic and intermediate volcanics (lavas, pyroclastics, epiclastites) intercalated arkoses, graywackes and conglomerates
Lower Svecofennian	Leptites, arkoses,graywackes, arenitic sediments, random calcareous interlayers

ites, the rapakivi granites have U-Pb zircon ages of 1.54 to 1.7 Ga (Kouvo 1958, Vaasjoki 1977).

The Svecofennian domain contains sulfide and iron ore deposits of both economic and sub-economic value. In central Sweden, the domain hosts ore deposits of Cu-Zn-Pb at Falun (Koark 1969), Zn-Pb at Kalvbäck (Hubner 1966) and Zn-Pb-Cu at Saxberg and Garpenberg (Du Rietz 1968, Vivallo 1984). The principal corresponding ore deposits in Finland are Geological Survey of Finland, Bulletin 341 11

the Aijala Cu-Zn deposit, the Metsämonttu and Orijärvi Zn-Cu deposits and the Attu Zn-Pb-Cu deposit (Latvalahti 1979).

It is difficult to establish a full stratigraphic sequence of the whole Svecofennian domain, mainly because of the folding, metamorphism and migmatization. Simonen (1960, 1980) divides the stratigraphy of the Svecofennian domain into three successions: lower, middle and upper Svecofennian subgroups (Table 2).

GEOLOGY OF THE AREA AROUND THE ATTU SULFIDE DEPOSIT

The island of Attu is a westerly extension of the Kisko-Kimito belt, which is part of the Svecofennian domain (Edelman 1960, Schellekens 1980). Reports on the geology of Attu have been presented by Pehrman (1927, 1932) and Edelman (1960), and for the northern part of the island by Schellekens (1976).

Figure 3 gives the geology of the area, about



Fig. 3. Lithological map around the Attu Zn-Pb-Cu sulfide deposit.

1.5 km wide and 2.5 km long around the sulfide deposit, mapped on the scale of 1:4000 for the present study. The geology of the area is dominated by an early Proterozoic supracrustal sequence which consists mainly of amphibolites,

amphibole gneisses, mica gneisses, cordieriteanthophyllite rocks, marble and calc-silicate rocks. These rocks were deformed, metamorphosed and intruded by synorogenic and lateorogenic Precambrian plutonic rocks (Fig. 3).

Lithology

Amphibolites and amphibole gneisses

Amphibolites are dark, homogeneous or banded, fine- to medium-grained rocks with a granoblastic to porphyritic texture. They occur as thin layers in the gneisses or as xenoliths in the granitic gneisses. The banding of the amphibolites is due to variation in contents of plagioclase and hornblende, which are the major minerals (Table 3, Fig. 4). Minor and accessory minerals are quartz, biotite, augite, hypersthene, diopside, cummingtonite and garnet.

Acting as competent bodies during folding, amphibolites could endure metamorphism, so that certain primary volcanic rocks (pillow lavas, agglomerates and porphyrites) preserved their primary textures (Fig. 5, see Schellekens 1976, Edelman 1985).

Amphibole gneisses form a transition from banded mica gneisses to banded amphibolites. They also occur as intercalations in mica gneisses. They are generally fine-grained, banded and granoblastic with a marked foliation resulting from the alignment of amphibole crystals. Plagioclase (andesine), hornblende and quartz are the major minerals (Table 3, Fig. 4). Hypersthene, biotite and K-feldspar constitute the minor minerals. Secondary and accessory minerals are chlorite, carbonate, garnet, cummingtonite, apatite, sericite, opaque and prehnite.

Mica gneisses

Rocks designated as mica gneisses include biotite gneisses, amphibole-biotite gneisses and hypersthene-biotite gneisses. They display a great diversity in appearance, as they vary from homogeneous to banded and from fine- to medium-grained. The banding is caused by variations in grain size and mineral content and it ranges in scale from 0.1 cm to 1 dm in width. Medium-grained, garnet-rich quartz-feldspar veins, which run parallel to the banding, are encountered in the banded biotite gneiss type. With the increase in the amount of leucosome, the migmatitic mica gneiss gradually changes into gneissose granite. The contacts between the banded veined biotite gneiss and the granite are gradual, whereas those between the homogeneous biotite gneiss and the granite are sharp.

The main minerals of the biotite gneisses are plagioclase (andesine), quartz and biotite (Table 3, Fig. 4). Hornblende, hypersthene and garnet occur in subordinate amounts and in variable



Fig. 4. Modal ratio of quartz (Q), plagioclase (Pl) and hornblende (Hbl) for the amphibolites, amphibole gneisses and biotite gneisses from Attu.





13



Fig. 6. A calc-silicate rock from Attu with forsterite (fo), dolomite (do), serpentine (se) and talc (ta). 2.5x, nicols crossed. (Attu-23-RAB-80).

proportions. Chlorite, muscovite, sericite and prehnite are the most common minor minerals while zircon, epidote, opaques and carbonate occur as accessory minerals.

Table 3. Average modal mineral compositions for biotite gneisses, amphibole gneisses and amphibolites from Attu. Total number of thin sections are given in brackets (calculated to 1000 points for each section)

	Mica gneisses (15)	Amphib. gneisses (14)	Amphibolites (12)
Quartz	33.5	21.0	3.9
Plagioclase	34.4	34.2	37.0
K-Feldspar	2.9	2.3	-
Biotite	20.0	3.8	4.3
Hornblende	3.0	33.5	52.1
Pyroxene	2.1	1.5	1.7
Chlorite	0.6	0.6	-
Muscovite	0.4	-	-
Garnet	2.5	1.0	-
Opaque	0.5	0.1	0.3
Others	0.1	2.0	0.7

In the Attu area two types of biotite gneisses could be recognized: a fine-grained type with a granoblastic texture, and a medium-grained type which contains plagioclase (An_{43}) as megacryst and which has a significant amount of hornblende and orthopyroxene. The hypersthene-biotite gneiss occurs intercalated in the mica gneiss sequence. Biotite and hypersthene are the major mafic minerals.

Cordierite-anthophyllite rocks

Cordierite-anthophyllite rocks commonly occur as host rocks of the ores. They are generally coarse-grained, massive or schistose and occasionally porphyroblastic. As the quartz and cordierite content increases and the anthophyllite content decreases, the rock changes into a cordierite gneiss. Cordierite-anthophyllite rocks consist of large cordierite poikiloblasts with radial aggregates of anthophyllite. The poikiloblastic cordierite grains range in diameter from 0.2 to 0.5 mm. Quartz, biotite, microcline and garnet are common inclusions in cordierite. Pinitization and sericitization are regular phenomena. Quartz and biotite are common and occur in varying proportions.

Cordierite-anthophyllite rocks are considered to be altered rocks which have undergone varying degrees of Mg-Fe metasomatism (e.g., Eskola 1914). Similar rocks in Finland have been described by, e.g., Eskola (1914) and Latvalahti (1979) from the Orijärvi and Metsämonttu ore deposits and in Sweden by Vivallo (1984) and Wolter and Seifert (1984).

Tremolite-quartz rock

Tremolite-quartz rock (quartzite) is a quartz-rich (SiO₂ about 82 wt.%), coarsegrained, banded and distinctly foliated rock. The banding is the result of variation in the contents of quartz, tremolite and diopside. Tremolite-quartz rock is the main host rock of the ore body and a shaft has therefore been made in it to mine the underlying Zn-Pb-Cu deposit (Fig. 3). Quartz, the principal mineral, occurs as large, tabular grains, which are often preferentially orientated. Tremolite, which occurs occasionally with diopside and anthophyllite, is the prominent mafic mineral. Common accessory minerals are carbonate, zircon and spinel.

The mafic minerals are often found as inclusions in the quartz, mostly concentrated at the grain boundaries or in small interstitial aggregates. The amphibole lenses have been boundinaged and quartz as well as sulfide minerals are concentrated in the boundinaged area. Mafic and sulfide minerals are also found concentrated in lenses or on planes of the cleavage fractures parallel to the foliation of the host rock.

The tremolite-quartz rock is a metamorphosed and deformed rock which has been enGeological Survey of Finland, Bulletin 341 15

riched, through metasomatism, in Ca, Mg and Fe.

Marble and calc-silicate rocks

Marble in the mapped area occurs as a lens of about 50 m wide and 850 m long (Fig. 3). The rock is medium- to coarse-grained and contains both dolomite and calcite. Sulfide ore minerals are found associated with both dolomitic and calcitic marbles. As a result of metamorphism and hydrothermal fluid activity, dolomite has reacted with diopside or talc to form forsterite and calcite:

 $CaMgSi_2O_6 + 3 CaMg(CO_3)_2 = 2 Mg_2SiO_4 + 4 CaCO_3 + 2CO_2$

1 Diopside + 3 Dolomite = 2 Forsterite + 4 Calcite + 2CO₂

It has been reported by Winkler (1979, p. 124) that this reaction holds at temperatures above $650 \,^{\circ}$ C. The forsterite has altered to serpentine.

Calc-silicate rocks are found in association with sulfides or as wall rocks. They are fine- to medium-grained, foliated and generally banded. Dolomite, tremolite, diopside, forsterite, calcite, scapolite, quartz and plagioclase occur as the main minerals. Serpentine is chiefly an alteration product of forsterite and/or diopside. Talc, together with carbonate, occurs as an alteration product of forsterite and tremolite. Figure 6 shows forsterite occurring together with dolomite, serpentine, and talc. Finegrained quartz-feldspar fragments are also found in the calc-silicate rocks, accessory minerals being epidote, titanite, green spinel and grossular.

Granitoid rocks

Granitoid rocks found in the mapped area include massive microcline granite, the domi-

nant granitoid rock, gneissose granite and migmatitic granitoid rocks. According to Edelman (1985), most of the granitoid rocks were formed through a number of processes, such as metamorphism, metasomatism, anatexis and/or intrusion.

Microcline granite shows a great textural variability. Two types are especially common, namely a grey, coarse-grained and porphyritic type, and a red-coloured type with an aplitic texture. The microcline granite consists of microcline, quartz, plagioclase, biotite, hornblende and occasionally garnet. Gahnite has been found in the grey microcline granite. Microcline often occurs as megacrysts. Chlorite, sericite, epidote and calcite are common secondary minerals while zircon, apatite, graphite and opaque constituents occur as accessory minerals. The gneissose granitoid is homogeneous, medium-grained and moderately foliated. Leucocratic veins are abundant in the mapped area. According to Simonen (1960, 1980), the microcline granites are late- to postorogenic and they are considered to be the youngest Precambrian rocks in the area.

Geochemistry of the supracrustal rocks

The average chemical composition of the amphibolites, mica gneisses, tremolite-quartz rock and cordierite-anthophyllite rocks are given in Table 4. Appendix 1 gives whole rock analyses of these rocks. In Figure 7, the major oxides are plotted against SiO_2 . The total Fe content is computed to FeO after subtracting the sulfide iron.

The composition of the host and altered wall rocks (tremolite-quartz rock, cordierite-anthophyllite rocks and calc-silicates rocks) at the Attu sulfide deposit reflects the effect of the interaction between these wall rocks and hydrothermal solutions. The hydrothermal solutions deposit altered the existing chemical balance and caused a general redistribution of the chemical elements. The wall rocks were mainly enriched in Mg, Fe, Al, Zn, Cu and Pb, and depleted in Na and Ca.

The SiO₂ content in the **amphibolite** from Attu ranges between 47 and 62 wt.% (Table 4). In the AFM and Al₂O₃-FeO+TiO₂-MgO diagrams (Fig. 8), the amphibolite specimens plot into both tholeiitic and calc-alkaline fields, whereas in the Na₂O+K₂O vs. SiO₂ diagram (Fig. 9), some amphibolite specimens show an alkaline character. However, in the MnO-TiO₂-P₂O₅ diagram (Fig.10), most of the amphibolite specimens plot in the field of island arc tholeiites. The amphibolite is enriched in FeO, MgO and CaO, and has a medium content of Zr and Ti (Table 4). Schreurs (1985) noted that the FeO and MgO contents in the amphibolites from the West Uusimaa area increase with increasing metamorphism.

The Ti and Zr contents of the Attu amphibolites and mica gneisses are plotted against each other in Figure 11. The average Ti content is 0.4 wt.% whereas that of Zr is 105 ppm. These values are consistent with the composition of both tholeiitic basaltic and calc-alkaline rocks (Pearce & Cann 1973). Sr is enriched relative to Rb.

The petrographic and geochemical evidence suggest that the Attu amphibolites were primarily lavas or tuffites of basaltic to andesitic composition. Edelman (1985) came to a similar conclusion in his description of the amphibolites from the Attu area.

The mica gneisses are characterized by high SiO₂, Al₂O₃, K₂O and Na₂O values as well as by low Ti and Mn contents. The SiO₂ content ranges from 67.3 to 76.2 wt. %, whereas that of Al₂O₃ is from 11.7 to 15.2 wt.% (Table 4). In the AFM diagram (Fig. 8), the mica gneisses plot into the calc-alkaline field, whereas in the N₂O+K₂O vs. SiO₂ diagram the mica gneisses are sub-alkalic. The Sr, Rb, Y, Ce, Cs, Rb and

CaO

0

0





Fig. 7. Variation diagrams of major oxides vs. SiO₂ for amphibolites, mica gneisses, cordierite-anthophyllite rocks and tremolite-quartz rock.



Fig. 8. (a) AFM diagram and (b) Jensen (1976) Al₂O₃-FeO+Fe₂O₃+TiO₂-MgO plot for amphibolites and mica gneisses from Attu. Explanations to symbols as in figure 7.

18

Table 4. Average chemical composition of the host rocks of the Attu sulfide deposit; tremolite-quartz rock (1), cordierite-anthophyllite rocks (2), amphibolites (3) and mica gneisses (4) $FeO_t = Total$ iron, N = number of samples. Oxides, Zn, Pb, Cu and S in per cent, trace elements in ppm.

	1	2	3	4
N	(10)	(11)	(12)	(8)
SiO ₂	81.5	53.2	55.5	72.7
Al ₂ O ₃	0.2	17.2	15.7	13.3
MgO	3.9	11.2	4.2	2.1
CaO	2.9	0.3	8.0	1.5
Na ₂ O	0.3	0.5	2.1	2.5
K ₂ O	0.0	1.9	1.4	2.0
FeO,	1.9	10.6	9.9	3.8
MnÒ	0.1	0.2	0.1	0.1
TiO ₂	0.0	0.6	0.4	0.2
P_2O_5	0.0	0.0	0.2	0.0
CO ₂	0.1	0.1	0.1	0.1
S	3.8	1.7	0.3	0.0
Zn	1.8	0.7	0.0	0.0
Pb	0.5	0.3	0.0	0.0
Cu	0.1	0.4	0.0	0.0
TOTAL	99.4	99.0	99.8	98.3
Cr	221	171	104	111
Zr	10	17	78	226
Ni	17	18	30	16
Ba	25	35	222	473
Sn	10	116	19	10
Sr	14	13	213	102
Rb	10	18	40	79
V	10	13	163	19
Cl	0	0	62	0
Ce	5	20	28	52
Cs	13	12	13	19
Ta	18	10	10	15
La	18	18	0	0
Th	8	5	5	0
U	0	5	0	2
Y	0	0	8	31



19



Fig. 10. Analyses of the Attu amphibolite plotted on a Mullen (1982) MnO \times 10-TiO₂-P₂O₅ \times 10 discriminant diagram. CAB = calc-alkaline basalts, IAT = island arc tholeiites, MORB = mid ocean ridge and marginal basin basalts, OIT = ocean island tholeiites, OIA = ocean island alkalic basalts.

La contents are variable. The mica gneisses are considered to be metamorphic derivates of geosynclinal turbiditic sediments, namely graywackes and argillites.

The cordierite-anthophyllite rocks are characterized by a marked enrichment in Al_2O_3 , MgO, FeO, Zn, K_2O and Cu, and depletion in CaO and Na₂O (Table 4). The cordierite-anthophyllite rocks are geochemically



Fig. 9. Na_2O+K_2O vs. SiO_2 plot for the Attu amphibolites and mica gneisses. The subalkaline/alkaline boundary is based on Colley & Westra 1987. Symbols as in figure 7.

Fig. 11. Ti vs. Zr for the amphibolites and mica gneisses from Attu. Symbols as in figure 7.

and mineralogically similar to those in the Orijärvi area, as described by Latvalahti (1979), Schippers (1983), and Schreurs and Westra (1985). In both the AFM and Jensen Cation Plot diagrams (Fig. 8), the cordierite-anthophyllite rocks indicate a tholeiitic affinity.

Many workers (e.g., Latvalahti 1979, Schippers 1983) have suggested that the cordierite-anthophyllite rock is a product of metamorphism of hydrothermally altered chloritebearing volcanic rocks. This conclusion is based on the model proposed by Vallance (1967). A similar origin which suggests pre-metamorphic exhalative activities, is thought for the Attu cordierite-anthophyllite rock. The tremolite-quartz rock is chemically characterized by a high SiO₂ content, averaging 82 wt.%. The rock is depleted in Al₂O₃, alkalis and REE contents while slightly enriched in CaO and MgO. The high but variable FeO and MgO contents are well reflected in the AFM diagram (Fig. 8). Allen (1979) interpreted low K_2O values in metamorphic felsic rocks as indicative of K_2 depletion during granulite metamorphism.

The ore metal contents (Zn, Pb, Cu) in the tremolite-quartz rock are significantly higher than in other rocks owing to the hydrothermal mineralization.

Estimates of the metamorphic conditions

Temperatures of 600° to 800 °C at pressures between 3-5.5 kb have been reported in the Svecofennian domain of southwest Finland (e.g. Schreurs 1985a, b, Schreurs & Westra 1985, Hölttä 1986). To date, these are among the highest grades of regional metamorphism in the Svecofennian domain. Various independent geothermometric and geobarometric methods were used to establish these metamorphic conditions. Schreurs (1985) and Schreurs and Westra (1985) applied the mineralogical changes and prograde mineral reactions in the West Uusimaa complex and obtained internally consistent results. The cordierite-garnet geothergeobarometer applied by mometer and Schellekens (1980) to the gneisses of Attu suggested metamorphism in the amphibolite and lower granulite facies. The sphalerite geobarometer study on the Attu sulfide deposit gave pressure in the range of 4.0 to 4.2 kb (Törnroos 1982).

In this study, geothermometric and geobarometric methods based on the composition of co-existing minerals were used to estimate the conditions of metamorphism of the rocks of the Attu area. The thin sections of the analysed samples were examined for any sign of disequi-

The winds where a

librium such as mineral zonation, symplectites, coronas, exsolution or obvious alteration. After careful examination, specimen 51-LSH-85 (mica gneiss) appeared most promising and was consequently selected for mineral analyses.

The mineral analyses were carried out in the Mineralogical Laboratory of the Free University in Amsterdam. The main elements were measured with reference to a set of natural and synthetic standards. The mineral homogeneity was carefully examined by analysing at least three grains of one mineral. Each grain was analysed at three or four points. The modal composition of the analysed specimen is given in Table 5 and that of analysed minerals in Table 6.

Table 5. Modal composition of the analysed sample Ref No. 51-LSH-85, x = 6675.87, y = 573.42

Plagioclase (% anor 83)	46
Quartz	. ++
Amphibole	32
Orthopyroxene	10
Garnet	7
Biotite	2
Ilmenite	2
Total	99

Table 6. Electron microprobe analyses for plagioclase (plag), amphibole (amph), grunerite (gru) garnet (ga) and orthopyroxene (opx). $X_{mg} = Mg/(Mg+Fe)$; $X_{an} = Ca/(Ca+Na+K)$. x = 6675.87, y = 573.42. Cation numbers on the basis of 8 for plag, 23 for amph, 12 for ga and 6 for opx (O) (Analyst, H. E. Wener)

	Plag	Amph	Gru	Ga	Opx
SiO ₂	46.87	40.86	50.57	37.90	48.71
TiO ₂	-	0.73	0.02		0.04
Al ₂ O ₃	33.48	11.79	0.82	20.92	0.53
FeO	-	25.69	37.07	31.82	41.33
MnO	-	0.19	0.73	1.83	0.78
MgO	-	4.88	8.14	1.89	8.51
CaO	16.88	11.02	0.46	7.08	0.67
Na ₂ O	1.89	1.24	0.08	0.02	0.09
K ₂ O	0.05	1.45	0.00	-	-
Total	99.17	97.85	97.89	101.45	100.66
Si	2.169	6.414	7.915	3.004	1.986
Ti	—	0.086	0.002	-	0.001
Al	1.826	2.181	0.151	1.954	0.025
Fe	-	3.373	4.853	2.108	1.410
Mn	-	0.025	0.097	0.123	0.027
Mg	-	1.142	1.898	0.223	0.517
Ca	0.837	1.854	0.077	0.601	0.029
Na	0.170	0.376	0.025	0.003	0.007
K	0.003	0.290	0.000	-	-
Total	5.004	15.741	15.019	8.016	4.003
Xmg	-	-	0.280	0.096	0.268
X _{an}	0.826	-	-	-	-

The temperature was calculated at a given pressure of 5 kb with garnet-orthopyroxene

thermometer of Sen and Bhattacharya (1984). This thermometer is based on the partitioning of Mg and Fe^{2+} between coexisting garnet and orthopyroxene which can be represented by the reaction:

$3 \text{ MgSiO}_3 + \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} = 3 \text{ FeSiO}_3 + \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}.$

A value of 740 °C was obtained for the temperature of metamorphism by this method. The plagioclase – Ca-amphibole thermometer calibrated by Spear (1980) gave a value of 725 °C for the same specimen. Pressure was calculated from the Fe-reaction of the orthopyroxenegarnet-plagioclase-quartz assemblage (Perkins & Chipera 1985) at an assumed temperature of 750 °C. A value of 5.1 kb was obtained for the pressure.

The obtained temperature and pressure estimates for the Attu gneisses are in excellent agreement with those reported by other workers for regional metamorphism in the southwest part of the Svecofennian domain (cf. Schellekens 1980, Törnroos 1982, Schreurs & Westra 1985, Hölttä 1986). They are also constant with the isotope geothermometry and sphalerite geobarometry results calculated in this study.

Structures

At least two folding phases, F_n and F_{n+1} , could be recognized in the area studied (Fig. 12). The existence of F_n folds is not always noticeable, since the F_n and F_{n+1} axial planes are sub-parallel. F_n folds are distinguishable only if found together in the same outcrop with F_{n+1} folds.

The style of deformation varies from one rock type to another. In general, the older F_n folding is characterized by rootless intrafolial folding. Associated with F_n is a penetrative axial plane schistosity (S_n), defined by preferred orientation of micas and other minerals and transposed layering, probably associated with metamorphic segregation. S_n has been deformed by open to isoclinal F_{n+1} folds (Fig.12) with E-W striking axial planes dipping at high angles southward. These structural features are more abundant and evidently pronounced in banded mica gneiss and amphibole gneiss.

The calc-silicate rocks, limestones and ironformation interlayers often show symmetric folding with gently dipping axial planes.

Leucocratic veins in the banded mica gneiss were deformed into small lenses with pinch and swell structures. Microcline granite forms a sharp contact with the banded mica gneiss and in places crosscuts the foliation. This suggests





Fig. 12. Deformation phase relationships in mica gneiss from Attu. $F_n =$ older, rootless isoclinal fold; $F_{n+1} =$ younger folding phase; $S_n =$ penetrative schistosity and AP = axial plane of F_{n+1} . (x = 6676.12, y = 573.58)

that the banding of mica gneiss is probably older than both the intrusion of the microcline granite and F_{n+1} folding. This conclusion is in agreement with the observations of the S₂ in the Kemiö area described by Verhoef and Dietvorst (1980).

The prominent structural features in the tremolite-quartz rock are the penetrative E-Wstriking, subvertical schistosity (S_n) and the fractures subparallel to it. The fractures were apparently formed during the F_{n+1} folding phase. Sulfide and mafic minerals are concentrated in the fracture planes. A major fold found in the area studied is about 80 m north of the shaft, where the foliated tremolite-quartz rock is isoclinically folded. The fold axis plunges about 75° W. On the hinge zone of the fold, there are tensional fractures parallel to the axial plane, filled with pegmatitic material and sulfide minerals. The fold is interpreted as an F_{n+1} fold, and the fracturing subparallel to S_n as a result of F_{n+1} folding. The dominant, roughly E–W trending foliation is thus mostly a composite structure in the limb areas of F_{n+1} folds.

The orientation and style of both F_n and F_{n+1} at Attu conform to structural observations from other southwestern parts of the Svecofennian domain (cf., Latvalahti 1979, Verhoef & Dietvorst 1980, Staal & Williams 1983, Edelman 1985). The similarity in the orientation and style of the F_n and F_{n+1} folds indicates that both generations are a response to a continuous progressive deformation (Verhoef & Dietvorst 1980). The structural features at the Attu sulfide deposit indicate that F_{n+1} folding affected both the orebody and the country rock.

THE ATTU SULFIDE DEPOSIT

Orientation of the sulfide orebody

The orientation of the orebody is schematically presented in a three-dimensional block diagram (Fig. 13), which is based on the data obtained from the drill cores. The longitudinal axis of the orebody plunges about 45° WSW (250°/45°), subparallel to the axis of the F_{n+1} folds. The strike of the lenticular orebody is 75° and it dips 80° south. The plunge of the longitudinal axis steepens with depth. The length of the longitudinal axis is unknown, whereas that of the short axis ranges from 40 to 80 m.

The form of the orebody is in accordance with the prevailing structural features of the area, i.e., the orebody is elongated parallel to the F_{n+1} fold axis, foliation and lineation of the area. On the basis of the evidence cited, it is suggested that the present form of the orebody is controlled mainly by F_{n+1} folding.

The sulfide mineralization occurs mostly as stratabound, massive, lenticular bodies elongated parallel to the bedding and dominant schistosity or as dissemination. The massive ore is composed of about 50-90 % sulfide minerals, which is in agreement with the definition of a massive sulfide deposit as given by Hutchison (1973) and Sangster and Scott (1976).

The main host rock is a tremolite-quartz rock, which shows banding and a gneissic texture. The ore is also hosted by the cordieriteanthophyllite and calc-silicate (diopside- and tremolite-skarn) rocks (Fig. 14). The main host rock and the adjacent mineralized wall rocks constitute an alteration pipe (cf., Gilmour 1976, Large 1977, Franklin *et al.* 1981).



Fig. 13. The orientation of the Attu orebody schematically presented in a three-dimensional form between profiles 102 and 116.

Ore minerals

Well over 20 ore minerals have been identified in the Attu sulfide deposit (Table 7). The dominant ore mineralogy consists mainly of varying proportions of intimately intergrown pyrrhotite, sphalerite, galena, chalcopyrite and pyrite (Fig. 15). Arsenopyrite occurs in association with pyrite, marcasite, loellingite and electrum. Other minor ore minerals are magnetite, ilmenite, molybdenite, and rutile.

Various sulfosalts, such as Ag-bearing tetrahedrite (argentian tetrahedrite), tennantite, kesterite, boulangerite, pyrargyrite, bournonite and sinnerite, are found. Also breithaupite and hessite are encountered in association with galena. Native elements Ag, Au and Bi have been found. The main gangue minerals are quartz, diopside, tremolite, dolomite, calcite, anthophyllite and cordierite. The mode of occurrence of the sulfides ranges from fine-grained, poor dissemination to

Table 7. Ore minerals and metals found at the Attu sulfide deposit.

Main minerals	Minor minerals					
		Sulfosalts O				
pyrrhotite sphalerite galena chalcopyrite pyrite	arsenopyrite magnetite marcasite loellingite	tetrahedrite boulangerite tennantite bournonite pyrargyrite kesterite sinnerite	ilmenite mackinawite hessite breithaupite rutile molybdenite electrum metallic Ag metallic Au metallic Bi			



Fig. 14. Cross-sections of profiles (a) 102 and (b) 108 of the Attu sulfide deposit. 1. tremolite quartz rock, 2. cordierite-anthophyllite rocks, 3. calc-silicate rocks, 4. massive ore. 5. other country rocks (Modified from Rauhamäki and Karppanen 1982).



Fig. 15. The main sulfide minerals in the Attu deposit, suggesting crystallization under equilibrium conditions: sphalerite (sph), pyrrhotite (po), galena (ga), chalcopyrite (cp), pyrite (py), and arsenopyrite (ap). (a) Attu-305 137.33, 12.5x, (b) Attu-133 195.55-196.55, 50x.

(b)

26 Geological Survey of Finland, Bulletin 341

coarse-grained, pyrrhotite-dominated, rich massive or network orebody. The sulfides are thought to represent equilibrium assemblages, as can be inferred from the boundaries between the sulfide grains (Fig. 15). Inclusion and exsolution textures are common. Oxidation and hydration phenomena were not observed. Recrystallization and remobilization of the sulfides into fractures have taken place. The metamorphism has also caused the coarsening of the sulfide grains.

Pyrrhotite

Pyrrhotite is the main iron sulfide mineral in the Attu deposit. It is generally non-magnetic and occurs as large anhedral masses or granular grains disseminated between the silicate grains. Pyrrhotite has also been found in fracture fillings or as elongated grains following the mineral lineation of the host rock, suggesting a common deformational event with the enclosing host rock. It forms assemblages and intergrowth with other sulfides, especially sphalerite, chalcopyrite and, to a certain extent, pyrite (Figs. 15 and 16). Alteration to marcasite has also taken place.

Five pyrrhotite samples from the Attu deposit were studied by XRD. The d-values for the reflections 200, 201, 202 and 220 as well as the unit cell dimensions are given in Table 8. Using the method of Arnold (1962, 1966) and Arnold and Reichen (1962), the intensity of 202 peak was used to calculate the Fe content of the pyrrhotite; the mean is 47.69 atomic per cent. For a_0 and c_0 , the values obtained are 6.888 and 5.749, respectively.

27

Hexagonal pyrrhotite is the common type found at the Attu deposit, which is confirmed by its single 202 reflection, non-magnetism, atomic per cent iron content and absence of the lamellae intergrowth between the monoclinic and hexagonal types (see Vokes 1969, Plimer & Finlow-Bates 1978).

According to Sangster (1972), Sangster and Scott (1976) and Nold (1983), most of the pyrrhotite occurring with sphalerite in the Precambrian massive sulfide ores is formed from primary pyrite. Vokes (1976) shares the same opinion about the formation of pyrrhotites in the Scandinavian massive deposits. Accordingly, the pyrrhotite in the Attu deposit is considered to be a product of increasing metamorphism, mostly formed from primary pyrite.

Sphalerite

Sphalerite is economically the most important base metal sulfide mineral in the deposit. It occurs as irregular masses of anhedral grains, which commonly show a preferential association with pyrrhotite and chalcopyrite. In the massive ore, the sphalerite content may exceed 50 %. Macroscopically, sphalerite is chocolatebrown, while under reflected light it displays a light to medium gray colour. Sphalerite does not show any zoning under transmitted light.

In addition to its occurrence as crack filling,

Sample No.	d ₂₀₀	d ₂₀₁	d ₂₀₂	d ₂₂₀	a _o	c _o	at.% Fe
1.	2.982	2.647	2.068	1.725	6.894	5.738	47.50
2.	2.983	2.644	2.070	1.724	6.890	5.743	47.69
3.	2.978	2.648	2.073	1.720	6.879	5.775	47.96
4.	2.976	2.637	2.068	1.722	6.876	5.739	47.60
5.	2.981	2.648	2.070	1.723	6.888	5.751	47.68
I/I _o	32	42	102	27	-	-	-
Average	-	-	-	-	6.888	5.749	47.69

Table 8. Unit cell dimensions and composition of pyrrhotite from Attu.

1 = 2-LSH-85, 2 = Attu-304 73.80, 3 = Attu-304 93.70, 4 = Attu-308 172.05, 5 = Attu-310 25.05.

sphalerite has also replaced carbonates and silicates in the host rock. Chalcopyrite and pyrrhotite inclusions are common. The paragenetic association of sphalerite with other sulfide minerals as given in Figure 15 suggests that these minerals were formed under similar equilibrium conditions.

Table 9 shows the chemical composition of the sphalerite. Its average Fe content is 8.83 wt.% and 7.4 atomic per cent, corresponding to the formula $(Zn_{0.85}Fe_{0.15})S$.

Wiggins and Craig (1980) have suggested that most of the natural sphalerites coexisting with pyrite, pyrrhotite and chalcopyrite contain < 0.5 wt.% Cu. Several of these sphalerites are assumed to have equilibrated at temperatures above 400 °C. The average Cu content in the Attu sphalerite is < 0.2 wt.% (Table 9).

Table 9. Average chemical composition (microprobe analyses) of pyrrhotite (po), pyrite (py), sphalerite (sph) and chalcopyrite (cp). ns = number of samples analyzed, tp = total number of analyzed points, n = not analyzed

	po	ру	sph	ср
ns tp	(7) (20)	(6) (14)	(10) (25)	(5) (15)
Fe	60.67	45.83	8.83	30.44
Zn	0.00	0.00	55.83	0.00
Cu	0.01	0.02	0.19	33.40
Co	0.00	0.01	0.00	0.01
Ni	0.02	0.01	0.00	0.01
Mn	0.00	0.00	0.17	0.00
Cd	0.00	0.00	0.19	0.00
Hg	n	n	0.05	n
As	0.05	0.07	0.00	0.01
S	38.83	52.37	34.56	34.58
TAL	99.58	98.52	99.82	98.48
Fe	47.70	33.38	7.40	25.34
Zn	0.00	0.00	42.17	0.00
Cu	0.00	0.01	0.00	24.44
Co	0.00	0.15	0.00	0.01
Ni	0.01	0.00	0.15	0.00
Mn	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.00	0.00
Hg	-	-	0.12	-
As	0.00	0.04	0.00	0.07
S	52.26	66.42	50.09	50.14
	ns tp Fe Zn Cu Co Ni Mn Cd Hg As S TAL Fe Zn Cu Co Ni Hg As S	po ns (7) tp (20) Fe 60.67 Zn 0.00 Cu 0.01 Co 0.00 Ni 0.02 Mn 0.00 Cd 0.00 Hg n As 0.05 S 38.83 TAL 99.58 Fe 47.70 Zn 0.00 Cu 0.00 Co 0.00 Ni 0.01 Mn 0.00 Co 0.00 Ni 0.01 Mn 0.00 Cd 0.00 Hg - As 0.00 S 52.26	po py ns (7) (6) tp (20) (14) Fe 60.67 45.83 Zn 0.00 0.00 Cu 0.01 0.02 Co 0.00 0.01 Ni 0.02 0.01 Mn 0.00 0.00 Cd 0.00 0.00 Hg n n As 0.05 0.07 S 38.83 52.37 TAL 99.58 98.52 Fe 47.70 33.38 Zn 0.00 0.00 Cu 0.00 0.01 Co 0.00 0.01 Co 0.00 0.00 Mn 0.00 0.00 Mn 0.00 0.00 Mn 0.00 0.00 Hg - - As 0.00 0.04 S 52.26 66.42 <td>po py sph ns (7) (6) (10) tp (20) (14) (25) Fe 60.67 45.83 8.83 Zn 0.00 0.00 55.83 Cu 0.01 0.02 0.19 Co 0.00 0.01 0.00 Mn 0.02 0.01 0.00 Mn 0.00 0.00 0.17 Cd 0.00 0.00 0.17 Cd 0.00 0.00 0.19 Hg n n 0.05 As 0.05 0.07 0.00 S 38.83 52.37 34.56 TAL 99.58 98.52 99.82 Fe 47.70 33.38 7.40 Zn 0.00 0.01 0.00 Co 0.00 0.15 0.00 Ni 0.01 0.00 0.00 Ni 0.01 0.00</td>	po py sph ns (7) (6) (10) tp (20) (14) (25) Fe 60.67 45.83 8.83 Zn 0.00 0.00 55.83 Cu 0.01 0.02 0.19 Co 0.00 0.01 0.00 Mn 0.02 0.01 0.00 Mn 0.00 0.00 0.17 Cd 0.00 0.00 0.17 Cd 0.00 0.00 0.19 Hg n n 0.05 As 0.05 0.07 0.00 S 38.83 52.37 34.56 TAL 99.58 98.52 99.82 Fe 47.70 33.38 7.40 Zn 0.00 0.01 0.00 Co 0.00 0.15 0.00 Ni 0.01 0.00 0.00 Ni 0.01 0.00

Chalcopyrite

Chalcopyrite is the only significant Cu-bearing mineral found at the Attu deposit. It often occurs as coarse-grained or irregular crystals, which form mutual boundaries with other sulfides, mainly pyrrhotite and sphalerite (Figs. 15, 16 and 20). Small-sized, elongated and rounded chalcopyrite inclusions, which in places have a similar crystallographic orientation, were observed within sphalerite and pyrrhotite.

The average grade of Cu in the Attu deposit is 0.14 %. Cu tends to concentrate more in the cordierite-anthophyllite rocks, which form the footwall of the orebody. Monomineralic chalcopyrite veins are also found in the quartz-rich or pegmatitic parts of the tremolite-quartz rock.

The amount of Cu increases within the ore body with increasing depth, thereby displaying a phenomenon of metal zonation (Large 1977).

Suzaki *et al.* (1975) have shown that chalcopyrite has a small solid solution field, extending from a nearly stoichiometric CuFeS₂ to a slightly Fe-rich composition. The solubility of Zn in chalcopyrite solid solution generally decreases with decreasing temperature (Hutchinson & Scott 1981, Kojima & Sugaki 1985). The chemical composition of chalcopyrite from Attu (Table 9) corresponds to the formula $(Cu_{0.49}Fe_{0.51})S_2$.

Pyrite

Pyrite is the common iron sulfide mineral in most volcanogenic massive sulfide deposits (Solomon 1976, Sangster & Scott 1976, Franklin *et al.* 1981). Pyrite is stable up to 743 °C, at which level it breaks down to hexagonal 1C pyrrhotite and sulphur (Kullerud & Yoder 1959, Craig & Vaughan 1981). Studies on the pyrrhotite-pyrite solvus indicate that the stability of pyrite depends on the coexisting pyrrhotite composition, temperature, pressure and activities of FeS and sulfur (Arnold 1962, Toulmin & Barton 1964, Scott & Barnes 1971). The pyrrhotite superstructures below 300 °C complicate the



Fig. 16. Paragenesis of chalcopyrite (cp), sphalerite (sph) and pyrrhotite (po) from the Attu sulfide deposit. (Attu-304 73.85, 12.5x).



rig. 1/. Mutual inclusions of galena (ga) and pyrite (py) from the Attu sulfide deposit. (Attu-301 92.50, 25x).

situation. In the presence of sulfur- and ironbearing solutions, pyrite remains stable and unchanged in composition, whereas pyrrhotite reacts and changes to a more iron- or sulfur rich modification. Simple oxidation enriches pyrrhotite with sulfur and even causes it to change to pyrite or marcasite. Marcasite can be converted to pyrite at a temperature as low as $150 \,^{\circ}$ C in the presence of excess sulfur, but above 400 $^{\circ}$ C in the absence of sulfur (Craig & Scott 1974).

Contrary to most other massive sulfide deposits, pyrite is not a prominent iron sulfide mineral in the Attu deposit. This is probably partly due to metamorphism, which has caused the primary pyrite to be converted into pyrrhotite. As a major mineral, pyrite occurs as euhedral grains, forming sharp contacts with other sulfide minerals. Mutual inclusions of pyrite in sphalerite and galena are common (Fig. 17).

The average cell parameter a_0 obtained for pyrite by XRD is 5.418 Å. The microprobe analyses are given in Table 9. The analyses show that the Attu pyrite has a low Co content equivalent to 0.01 wt.%.

Galena

Pb is economically the second most important base metal in the Attu sulfide deposit. The average Pb grade is 1.1 %. Lead ore occurs in massive form or as impregnations, preferentially in the diopside calc-silicate rocks. Under reflected light, galena forms anhedral masses with its distinct characteristic cleavage triangles (Fig. 17). Inclusions of Ag-bearing tetrahedrite, electrum, chalcopyrite, sphalerite and sulfosalts are common.

The importance of galena as a host of minerals that contain appreciable quantities of other elements, especially Ag, Sb, As, Cu, Zn, Sn, Cd, Fe, Se and Te, has been discussed by a number of authors (e.g., Ramdohr 1980, Sack & Loucks 1985). In the Attu deposit, galena hosts Ag-bearing tetrahedrite, kesterite, tennantite, boulangerite, bournonite and pyrargyrite. The presence of tetrahedrite in the Attu galena was reported earlier by Pehrman (1932). In his spectrographic studies on the galena from the Attu deposit, Vaasjoki (1956) reported that galena has high Ag, Bi and Sn contents. He attributed the high Sn content in the galena to a relatively high temperature of formation of the galena-bearing assemblage. Microprobe studies of the galena (Table 10) suggest that most of the Ag crystallized as an independent mineral and that only a trace amount of about 0.07 wt.% of Ag occurs in galena. No Sn has been detected in the lattice of galena from Attu. The presence of Ag-bearing minerals in the galena is generally regarded as a result of the breakdown of high temperature solid solutions (Craig 1967).

Table 10. Average chemical composition (microprobe analyses) of galena.

_	1.147			
	We	ight %	Atomic %	
	Pb	87.54	49.85	
	Zn	0.22	0.30	
	Sb	0.06	0.06	
	Ag	0.07	0.08	
	Au	0.00	0.00	
	S	13.54	49.71	
	TOTAL	101.43		

Arsenopyrite

An As-rich zone occurs at the depth of 190–200 m in the Attu deposit. Arsenopyrite, sphalerite and pyrrhotite are the main ore minerals and loellingite is an accessory mineral. Arsenopyrite occurs as euhedral grains, and in places it forms large irregular bodies with cata-

Table 11. Average chemical composition of the Attu arsenopyrite.

	Wei	ght %	Atomic %	
	Fe	34.41	33.94	
	Cu	0.02	0.01	
	Co	0.03	0.03	
	Ni	0.02	0.02	
	As	44.60	32.79	
	S	19.33	33.21	
TO	TAL	98.40		

clastic texture. Mutual intergrowth and inclusions with other sulfides prevail, suggesting a cogenetic origin (Fig. 15b). Although electrum is found associated with arsenopyrite, no Au has been detected in the solid solution of arsenopyrite (Table 11).

Silver-bearing minerals

On the whole, the Ag content of the Attu massive sulfide ores is quite low, averaging only about 43 g/t. Argentian tetrahedrite (freibergite) and electrum are the principle silverbearing minerals. Other silver-bearing minerals are hessite, pyrargyrite and metallic Ag which have been met with in association with galena.

Under reflected light, the color of tetrahedrite ranges from yellow brown to grayish. It has been found in fractures as independent anhedral grains, but more often it occurs in galena as inclusions of about 50–100 μ m in diameter (Fig. 18). The microprobe analyses of tetrahedrite are given in Table 12. The order of metal abundance is Sb > Ag > Cu. The average Fe content is 5.6 wt.%, while that for Zn is 0.59 wt.%. The formula obtained for the Attu tetrahedrite is {(Ag_{4.00}Cu_{5.42}Fe_{1.87}Zn_{0.17}Sn_{0.17}) (Sb_{4.17}As_{0.16})}S₁₃, corresponding to **freibergite** (Riley 1974, Ramdohr 1980).

Reciprocal relationships between the contents of As, Sb, Cu and Ag in tetrahedrite have been observed by, among others, Miller and Craig (1983), and Sack and Loucks (1985). The As content rises as that of Sb decreases, the copper content decreases with increasing Ag and the Sb content increases with increasing Ag. Hackbarth and Petersen (1984) suggested that the observed patterns in tetrahedrite could be produced during the process of hydrothermal ore deposition. Tetrahedrite deposited nearest to the source of the solutions is enriched in Cu and As because these elements are precipitated preferentially in tetrahedrite relative to Ag and Sb. Ag and Sb become residually enriched in the solution relative to Cu and As as crystallization proceeds.

Pyrargyrite and hessite are rarely present, but have been met with in galena as inclusions of no more than 10 μ m in diameter. Metallic Au occurs in association with arsenopyrite as well as in fractures. The Ag content in metallic Au is 15.2–28.8 wt.%, while the Au content in metallic Ag is about 18.8 wt.%. Microprobe studies performed on the galena hosting Agbearing minerals indicate that the galena contains only 0.08 wt.% of Ag. This suggests that most of Ag crystallized as separate Ag minerals.

Electrum occurs in association with arsenopyrite and chalcopyrite, or as granular grains in fractures (Fig. 19). Under reflected light, electrum is pale yellow to light yellow, depending on the Ag/Au ratio. The Ag-rich grains are difficult to distinguish from arsenopyrite while the Au-rich grains resemble chalcopyrite in appear-

Table 12. Average chemical composition of tetrahedrite (tetra), boulangerite (bou), kesterite (kes), bournonite (bn) and electrum (elec). Abbreviations ns and tp as in Table 9. (Analyst, V. Polvi)

		tetra	bou	kes	bn	elec
	ns tp	(6) (13)	(4) (12)	(2) (6)	(2) (7)	(4) (16)
W	Cu	18.49	0.01	27.80	14.03	0.16
e	Zn	0.59	0.02	11.80	0.03	0.13
i	Fe	5.62	0.02	1.74	0.34	0.47
g	Sb	27.24	24.15	0.00	18.95	0.21
h	Bi	0.00	0.00	0.00	0.00	0.14
t	Pb	0.00	57.07	0.00	40.79	0.00
	Sn	0.12	0.00	27.34	0.00	-
%	Ag	23.16	0.01	0.53	0.76	56.40
	As	0.66	0.04	0.61	4.12	0.23
	Au	0.00	0.13	0.00	0.16	41.20
	S	22.38	17.95	29.22	20.22	0.0
TO	TAL	98.26	99.40	99.05	99.03	99.40
	Cu	18.81	0.15	24.26	17.34	0.35
Α	Zn	0.58	0.02	10.01	0.04	0.29
t	Fe	6.51	0.04	1.73	0.48	1.06
0	Sb	14.47	19.13	0.00	12.23	0.71
m	Bi	0.00	0.00	0.00	0.00	0.01
i	Pb	0.00	26.56	0.00	15.46	0.00
С	Sn	0.06	0.00	12.77	-	0.00
	Ag	13.88	0.01	0.27	0.55	68.54
%	As	0.57	0.05	0.45	4.31	0.41
	Au	0.00	0.06	0.00	0.06	28.16
	S	45.12	53.98	50.52	49.52	0.38



Fig. 18. Tetrahedrite (tre) inclusions in galena (ga) and at the contact of galena and sphalerite (sph) from the Attu sulfide deposit. (Attu-133 126.55–127.66, 50x).



Fig. 19. Electrum (e) in association with arsenopyrite (ap), chalcopyrite (cp), sphalerite (sph) and pyrrhotite (po) from the Attu sulfide deposit. (Attu-133 195.55–196.55(4), 50x).

ance. The high reflectance is, however, a sharp diagnostic feature. The amounts of Ag and Au in the electrum vary from grain to grain, averaging 56.40 wt.% Ag and 41.20 wt.% Au. The electrum contains Zn, Fe, Sb, Bi, As and S, but they amount to no more than 1.5 wt.% (Table 12).

Other minerals

Kesterite, boulangerite, bournonite and Pbbearing sinnerite occur as small grains in association with sphalerite and galena. According to microprobe analyses, the formulas for the Attu boulangerite and bournonite are $(Pb_{5.41}Sb_{3.90}-Au_{0.01}As_{0.01})S_{11}$ and $(Pb_{0.94}Cu_{1.05}Sb_{0.74}As_{0.26})S_3$, respectively.

Kesterite was first found by Z. V. Orlova in the Kester deposit, Yakutia, USSR in 1956. It is a Zn analogue of stannite (Kissin & Owens 1975, Hall et al. 1978). To date, this mineral has not been reported in Finland. It was reported recently by Moh (1986) and Osadechii (1986) that kesterite and cernyite (Cu₂CdSn₄) form a close intergrowth and that these two end members are structurally analogous but crystallized in different space groups. The formula of the Attu kesterite is {Cu_{1.92}(Zn_{0.79}Fe_{0.14})- $As_{0.04}Sn_{1.02}$ S₄. It has Ag and As contents of 0.53 and 0.61 wt.%, respectively (Table 11), which has not been taken into account in the foregoing formula. Other minerals and native metals met with in the the Attu sulfide deposit are listed in Table 7.

Metamorphism of the sulfide deposit

Deformation and metamorphism have modified the shape and geometry of the Attu orebody, obliterated primary features of the ore minerals and changed the mineralogical and chemical composition of the hydrothermally altered host rocks.

Ore minerals, such as galena, chalcopyrite and arsenopyrite, have migrated into fracture zones and cracks. In places, these minerals also form parallel, thin to large monomineralic veins in wall rocks. Sulfosalts, like tetrahedrite, frequently accompany galena in these veins. In many places, arsenopyrite grains have a cataclastic texture.

The granoblastic texture, mutual intergrowths and inclusions of the Attu sulfides reflect recrystallization under metamorphic conditions, as observed by many other workers elsewhere (e.g., McDonald 1967, Vokes 1969, 1976; Mookherjee 1976, Secord & Brown 1986). Similarly, the coarse grain size of the ore minerals suggests metamorphic effects (Stanton 1972). Recrystallization is believed to have taken place under equilibrium conditions, as can be deduced from the contacts of the sulfide grains (Fig. 15) and from sulfur isotope studies. The main factor in causing recrystallization and coarsening of the sulfides during metamorphism is, according to Vokes (1969), the thermal energy provided by metamorphism.

Equally common is variation of the grain size within a single thin section, a phenomenon reported by Deb (1980) to have resulted from metamorphic effects. Chalcopyrite and pyrrhotite occur as lamellae or inclusions in sphalerite. These inclusions form parallel dots and small, thin, needle-like grains, which have a similar orientation (Fig. 20). Arsenopyrite and pyrrhotite form long veins in fractures of the host rock (Fig. 21). The chalcopyrite and pyrrhotite blebs in sphalerite are thought to be a product of exsolution formed as a result of high temperature recrystallization during metamorphism, as has been reported elsewhere (see McDonald 1967, Kojima & Sugaki 1984, 1985; Sugaki et al. 1987).

Most of the Attu pyrrhotite is considered to be a product of metamorphism due to desulfurization of primary pyrite. This is consistent with many observations in metamorphosed



Fig. 20. Chalcopyrite exsolution lamellae in sphalerite from the Attu sulfide deposit assumed to have been formed at higher metamorphic temperatures. (Attu-304 52.10 (1), 50x).



Fig. 21. Pyrrhotite and arsenopyrite (white) from the Attu sulfide deposit occurring as veins because of deformation processes associated with metamorphism (Attu-304 52.10 (2), 50x).

Precambrian ores (e.g., Sangster & Scott 1976, Plimer 1978).

The effect of metamorphism on the chemical composition of sulfide minerals in most metamorphosed massive sulfide deposits is indicated by the variation of the Fe content in sphalerite and by the Co/Ni ratio in pyrite, which increases with increasing grade of metamorphism (e.g., Mookherjee 1976, Boctor 1980). At Attu, these phenomena are not marked, suggesting that the ore minerals have crystallized in approximately isothermal metamorphic conditions. Metamorphism also had a profound effect on the mineralogical composition of the associated wall rocks.

Geochemistry of the sulfide deposit

The essential chemical constituents of the ore at the Attu deposit are Zn, Pb, Cu, Fe and S. Ag and Au are the only precious metals observed. Other significant metals are Sn, As and Sb. In addition, metals such as Co, Cr, Bi, Ba and Mo occur in minor quantities.

The relationships between the elements associated with the deposit were studied with a correlation matrix (Table 13) and a varimax rotated factor analysis (Table 14). Antimomy shows significant correlation coefficients with As, Ag and Pb, whereas Pb shows with Cu, Ag, Sb and Zn. Au shows moderate correlation coefficients with Ag and Sb.

Several models with different numbers of factors and variables were tested. The model presented in Table 13 with 20 variables and 4 factors explains 68.3 per cent of the total variance in the data (Table 14). The first factor has high positive loadings of La, Sm and Th, moderate positive loadings of U and Na, and a moderate negative factor of Zn. It thus reflects lithologic variation. As, Sb and Ag are associated with factor 2. Factor 3 explains the occurrences of the major sulfides, the associated minor minerals and sulfosalts. This has been reflected by the high loadings of Pb, Cu, Ag and the moderate loadings of Sb, Zn and Au. Fe, Co and Ni are associated with factor 4.

Distribution of the main ore elements

The distribution and ratios between Zn-Pb-Cu, Ag-Pb-Au, Ag-As-Au and Co-Ni-Cu in the ore host rocks (tremolite-quartz rock, calcsilicate and cordierite-anthophyllite rocks) are given in Figures 22 and 23. Zn predominates in

ingher	unan 0.50	Dora races	a. oquare	loot fullet		0,			0			
	Cu	Zn	Ni	Co	Pb	Ag	Fe	As	Sb	Au	Ba	S
Zn	0.52	1.00										
Ni	-0.24	-0.22	1.00									
Co	0.35	0.13	0.37	1.00								
Pb	0.73	0.61	-0.24	0.11	1.00							
Ag	0.47	0.44	-0.10	-0.26	0.72	1.00						
Fe	0.10	0.21	0.41	0.65	-0.01	-0.18	1.00					
As	0.05	0.28	0.06	-0.49	0.36	0.77	-0.29	1.00				
Sb	0.23	0.41	-0.02	-0.44	0.60	0.86	-0.23	0.89	1.00			
Au	0.41	0.21	-0.02	-0.09	0.49	0.53	-0.27	0.44	0.50	1.00		
Ba	-0.26	-0.08	0.19	-0.12	-0.08	0.25	0.10	0.39	0.30	0.07	1.00	
S	0.54	0.64	-0.11	0.14	0.41	0.43	0.33	0.30	0.36	0.38	0.05	1.00

Table 13. Correlation matrix between selected elements for 62 samples from the Attu sulfide deposit. Values equal to or higher than 0.50 hold faced. Square root values used for S; values for other elements after logarithmic transformation.

36

Geological Survey of Finland, Bulletin 341



Fig. 22. Variation of Pb, Cu and Zn ratios in the (a) tremolite-quartz rock, (b) calc-silicate rocks and (c) cordieriteanthophyllite rocks from the Attu sulfide deposit. Fig. 23. Variation of (a) Pb, Au and Ag; (b) As, Au and Ag; (a) (c) Ni, Cu and Co ratios in calc-silicate rocks, tremolitequartz rock and cordierite-anthophyllite rocks from the Attu sulfide deposit.





Fig. 24. Variation in the contents of selected elements with depth between the interval of 5 and 150 m of drill core no. 309 from the Attu sulfide deposit (See figure 14). The geology of the drill core is also given. Symbols as in Fig. 14.

38

Geological Survey of Finland, Bulletin 341



Fig. 25. Variation in the contents of selected elements with depth between the interval of 360 and 480 m of drill core no. 311 from the Attu sulfide deposit. Symbols for the geology of the drill core as in figure 14.

Table 14. Factor loadings in a 4-factor model, after varimax rotation (loadings less than 0.25 excluded). Based on 62 samples from the Attu sulfide deposit. Square root values used for S; values for the other elements after logarithmic transformation.

XX 111		Fac			
Variable	1	2	3	4	Communality
La	0.93	-	-0.28	-	0.95
Sm	0.91	_	-0.30	-	0.92
Th	0.81	0.30	-0.30	-	0.84
Na	0.58	—	-	0.37	0.48
As	-	0.89	0.29	-	0.90
Sc	-	-0.83	_	0.30	0.79
Sb	-	0.79	0.56	—	0.95
U	0.56	0.65	-	-	0.75
Ba	0.40	0.42	-	0.26	0.40
Pb	_	_	0.96	_	0.95
Cu	_	_	0.74	_	0.63
Ag	_	0.61	0.70	_	0.96
Zn	-0.46	_	0.54	_	0.56
Au	-	0.30	0.46	_	0.33
S	-	0.26	0.39	-	0.32
Fe	_	_	_	0.77	0.64
Co	-0.26	-0.53	_	0.66	0.81
Ni	-	-	_	0.61	0.47
Rb	0.44	_	—	0.60	0.59
Cs	0.42	-	_	0.54	0.51
Cumulative percentage of total variance	26.3	49.7	60.9	68.3	
Eigenvalue	5.2	4.7	2.3	1.5	I

the tremolite-quartz rock, Pb is mostly associated with calc-silicate wall rocks, while the Cu has a close affinity with the cordierite-anthophyllite rocks. Ag occurs with Pb in the calcsilicate rocks but they occurs also together in the cordierite-anthophyllite rocks. Ni and Co do not show any significant variation with the rock type.

Figure 24 indicates that the geochemical distribution of the ore elements in the Attu orebody shows variation with depth. To elucidate the variation with depth, the average distribution of Zn, Pb, Cu, Ag, Au, Fe, S, Ba, As and Sb between the depth intervals of 5 to 150 m of drill core No. 309 (profile 102), and between the depth interval of 355 to 480 m of drill core no. 311 (profile 113) (Fig. 13), was studied in detail. The results are given together with the lithology of the two depth intervals in Figures 24 and 25.

Cu contents increase with depth, whereas Pb is enriched in the upper parts of the deposit. The distribution of Zn throughout the orebody remains more or less constant (Fig. 26). Figure 26 is compiled from the average values of each profile (see Figure 13, profiles 102A to 116).

The decrease in the Pb content and the simultaneous increase in the Cu values with increasing depth constitute a sequence of metal zonation, a common phenomenon in volcanogenic massive sulfide deposits (Solomon 1976, Large 1977, Large 1980, Finlow-Bates 1980, Susaka & Crerar 1982). Crerar et al. (1985) emphasized that the transport, deposition and zoning of hydrothermal ores are controlled by three main factors: (1) the crystal chemistry and stability of the mineral phase, (2) the physiochemical properties of aqueous electrolyte solutions at high temperature and pressure, and (3) the thermodynamics and molecular properties of aqueous species of metals. Large (1977) discussed in detail the sequence of metal zonation in the volcanic-hosted deposits on the basis of mineral equilibria, and the variation of the metals as a result of changes in the physical chemistry of the solution. He interpreted base metal zonation as being primarily the result of temperature with influences of pressure as well as sulphur and oxygen concentrations in the hydrothermal solution. Barnes (1979) states that the least soluble mineral in a particular solution will be deposited first near the source of the metal-carrying solution, followed by others in order of increasing solubility. Barnes and Czamanske (1967) gave the mobility of common ore metals in the decreasing order of Hg>Pb>Cu>Zn>Sn>Ni>Fe>Co which is related to the free energy of sulfide complex formation. A similar decreasing order of stability of the chloride complexes of ore-forming metals at 25 °C was reported earlier by Helgeson (1964).

The sequence of metal zonation at the Attu sulfide deposit is reflected in the systematic in-



Fig. 26. Variation with depth in the average contents of Zn, Pb and Cu along the longitudinal axis of the Attu sulfide deposit.

crease of Cu/Pb, the moderate increase of Cu/Zn and the decrease of Pb/Zn with depth (Fig. 27). Fe is present throughout the sequence in the form of pyrrhotite and/or pyrite. Galena and sphalerite are supposed to have precipitated later and therefore deposited at a considerable distance from the vent, while chalcopyrite and iron sulfides would have precipitated at the top or in the proximity of the vent.

The geochemical distribution of Zn is such that it occurs in all three rock types and at all mineralized depths studied. It is relatively more abundant, however, in the tremolite-quartz rock. Sphalerite is the major Zn-bearing mineral but, according to the microprobe studies, Zn has been detected also in the kesterite (11.80 wt.%), tetrahedrite (0.59 wt.%), galena (0.22 wt.%) and electrum (0.13 wt.%).

Pb content is often high in the diopside calcsilicate wall rocks. Galena is the principal Pb ore mineral. The significant Pb-bearing sulfosalts met with are boulangerite and bournonite. Cu ores tend to concentrate in the cordierite-anthophyllite rocks, as also observed by Latvalahti (1979) at Metsämonttu.



Fig. 27. The variation of the ratios Pb/Zn, Cu/Pb and Cu/ Zn with depth along the longitudinal axis of the orebody at the Attu sulfide deposit indicating metal zoning.

The occurrence of Ag is closely linked to Pb because Ag is normally contained within galena: partly as sulfosalt inclusions in galena and partly as solid solution in the crystal lattice. The main Ag-bearing ore minerals are tetrahedrite and electrum. Electrum has been found in association with arsenopyrite and chalcopyrite (Fig. 21). The average Ag content in the electrum is 58.40 wt.% and that of Au 41.20 wt.%.

As a result of the close association of Ag and Pb, the sulfide orebody is relatively enriched in Ag above the +350 level (vertical distance from the surface), where Pb ores are more pronounced. The Ag values have not been found to exceed 120 ppm while the average value is 45 ppm. Au has an average value of 0.15 ppm, with the highest measured value being 0.90 ppm.

Arsenopyrite is the main As-bearing mineral at the Attu deposit. Loellingite occurs mostly as an accessory mineral. In addition to arsenopyrite and loellingite, As has been detected in the bournonite (4.12 wt.%), tetrahedrite (0.66 wt.%) and in kesterite (0.61 wt.%). As-bearing sulfosalts tennantite and sinnerite have been observed to be present in trace amounts.

Although cassiterite and/or stannite have been reported to occur in the ores and the associated wall rocks of several massive sulfide deposits (e.g. Bell 1982, Petersen 1986), kesterite is the only Sn-bearing mineral met with at the Attu deposit. Analytical data of Sn could not generally be used because the content of Sn was not within detection limits. However, high Sn values are associated with Pb, As and Sb, reflecting the presence of kesterite. Petersen (1986) suggested that the presence of cassiterite in a sulfide deposit indicates high $f(O_2)$ in the hydrothermal solutions. Correspondingly, its absence, as at the Attu deposit, might suggest low $f(O_2)$ content in the ore-bearing solutions.

Kesterite occurs in association with chalcopyrite and/or as inclusions in galena. The intimate association of kesterite with galena and Cu ores suggests that Sn was deposited at the same time as these base metals and by similar mechanisms.

No particular systematic enrichment or distribution of Ba was observed in the sulfide orebody. However, relatively high Ba values, of about 900 ppm were met with in the cordierite-anthophyllite footwall rocks along drill core No. 309 (Fig. 24).

The contents of Cr, Co and Ni in the orebody average around 300 ppm Cr, 25 ppm Ni and 30 ppm Co. About 0.15 wt.% Co is contained within the pyrite, possibly as a solid solution in the crystal lattice. A similar amount of Ni has also been detected within the sphalerite (Table 9).

Ag, Sb, Sn and As occur in sulfosalts which are associated with galena. As a result, their inter-elemental correlations are more pronounced (Table 13).

THE SPHALERITE GEOBAROMETRY

The concept of the sphalerite geobarometer is based on the variation of the FeS content of sphalerite in equilibrium with Fe sulfides as a function of pressure, temperature and activity of FeS (a_{FeS}). The theory behind the sphalerite geobarometer has evolved through the investigations of Barton and Toulmin (1966), Scott and Barnes (1971), and Scott (1973). The pressure dependence of the composition of sphalerite in equilibrium with pyrite and pyrrhotite has been expressed by Hutchison and Scott (1981) as $p(kb) = 42.30-32.10 \log$ mole per cent FeS. The concept is now firmly established in the literature as confirmed by its increasing application to metamorphosed sulfide deposits (e.g., Scott 1976, Scott *et al.* 1977, Brown *et al.* 1978, Boctor 1980, Hutchison & Scott 1980, Sangameshwar & Marshall 1980, Sundblad *et al.* 1984). Törnroos (1982) applied the sphalerite geobarometer to some metamorphosed sulfide ore deposits in Finland, including the Attu deposit.

For the application of the sphalerite geobarometer in this study, the following criteria suggested by Scott (1976) were adhered to:

(1) Sphalerite must have equilibrated with pyrite and hexagonal pyrrhotite. At the Attu sulfide deposit, the equilibrium condition can be inferred from the mutual triple contact of the sulfides (Fig. 28).

(2) The temperature of formation or metamorphism must have been higher than the abrupt reversal in the slope of the pyrite + hexagonal pyrrhotite (265 °C at 1 bar) and lower than the upper limit of the temperature-dependent region.

(3) The microprobe analyses of sphalerite in contact with pyrite and pyrrhotite must be precise. In this study, precise microprobe analyses of sphalerite in contact with pyrite and pyrrho-

tite were carried out and the results are presented in Table 15 and Figure 29.

(4) The sphalerite grains must be homogeneous. Heterogeneous sphalerite grains and grains that contain chalcopyrite exsolutions were avoided. According to Hutchison and Scott (1981), Cu contaminants may be problematical to the geobarometer, whereas trace amounts of Mn and Cd in the sphalerite solid solution have been reported by Craig and Scott (1974) to have no effect on the pressure dependence of FeS in the sphalerite. The maximum content of Mn in the analyzed sphalerites is 0.4 wt.% and that of Cd 0.3 wt.%. The analyzed sphalerites are almost free of Cu (Table 15). Sphalerite was therefore found to be essentially homogeneous with respect to Cu, Fe, Zn, Mn and Cd contents, indicating attainment of equilibrium in the Zn-Fe-S system under uniform pressure (Deb 1980). The FeS mole per cent in sphalerite ranges between 14.8 to 15.1 (Table 15). The average FeS contents of sphalerite in three specimens range



Fig. 28. Sphalerite (sph)-pyrrhotite (po)-pyrite (py) assemblage from the Attu sulfide deposit. The triple contact of the sulfides suggest that the assemblage has equilibrated. (Attu-2-LSH-85, 25x).

1	2	3
5	4	5
56.3	57.2	57.7
8.6	8.7	8.6
0.1	0.3	0.2
0.1	0.2	0.2
0.0	0.0	0.0
0.1	0.2	0.1
33.6	33.5	33.7
98.8	100.2	100.5
15.1	15.1	14.8
4.5	4.5	4.7
47.4	47.2	47.5
	1 5 56.3 8.6 0.1 0.1 0.0 0.1 33.6 98.8 15.1 4.5 47.4	$\begin{array}{c ccccc} 1 & 2 \\ \hline 5 & 4 \\ \hline 56.3 & 57.2 \\ 8.6 & 8.7 \\ 0.1 & 0.3 \\ 0.1 & 0.2 \\ 0.0 & 0.0 \\ 0.1 & 0.2 \\ 33.6 & 33.5 \\ \hline 98.8 & 100.2 \\ \hline 15.1 & 15.1 \\ 4.5 & 4.5 \\ 47.4 & 47.2 \\ \hline \end{array}$

Table 15. Average microprobe analyses of sphalerite in contact with pyrite + hexagonal pyrrhotite in weight percentages.

1 = Attu-133/155.55 - 156.55,

2 = Attu-133/176.55 - 177.55,

3 = Attu-2-LSH-85, po pyrrhotite.

from 14.8 to 15.1 mole per cent FeS (Table 15), but the range of the separate analyses is markedly wider (Fig. 29).

The sphalerite geobarometer gives a total average 15.0 mole per cent FeS, corresponding to the pressure of 4.5 kb for the Attu sulfide de-



15

MOLE % FeS

Fig. 29. Frequency histogram of the FeS content of sphalerites from Attu in contact with pyrite + hexagonal pyrrho-

PRESSURE (kb)

5

14

13

6

4

3

40

30

17

tite (e.g., Fig. 28).

16

FREQ

* 10

ISOTOPE GEOCHEMICAL STUDIES

Lead isotopes

Lead isotope analyses were performed on the sulfide minerals galena, sphalerite, pyrrhotite and chalcopyrite as well as for tremolite-quartz rock, amphibolite and mica gneiss as whole rock analyses. The results are presented in Table 16.

In the Pb-Pb diagram of ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb (Fig. 30), the sulfide isotopic composition is shown together with the whole rock analyses. An isochron calculated for whole rock analyses gives an age of 1894±24 Ma. This age is comparable to that obtained by previous workers (e.g., Kouvo 1958, Patchett & Kouvo 1986, Huhma 1986). Galena, sphalerite and pyrrhotite have an identical isotopic composition within experimental error, and therefore they plot at a single point in the ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb diagram (Fig. 30). This suggests that these sulfides in the Attu deposit are from the same source (M. Vaasjoki 1986, pers. commun.). The different lead isotopic composition of chalcopyrite may be due to the addition of radiogenic lead to chalcopyrite after its deposition, as has been observed in many Precambrian ore deposits (cf., Gulson 1986). The isotopic values for the whole rock analyses lie on one line and this is interpreted to mean that the three supracrustal

		Lead isotopic ratio						
Sample No. Attu-	mineral/ rock	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb				
GO11	galena	15.660	15.327	35.192				
309/40.1	sphalerite	15.686	15.323	35.180				
303/86.0	pyrrhotite	15.657	15.333	35.175				
303/144.5	chalcopyrite	16.065	15.383	35.218				
1-LSH-85	guartz rock	15.595	15.249	34.929				
32-LSH-85	amphibolite	18.436	15.566	35.883				
28-LSH-85	mica gneiss	23.906	16.210	38.978				

Table 16. Lead isotopic data and model ages for the Attu deposit

Model ages in Ma and milieu indices from the Attu galena

Stacey and Kramers Age μ W 1792 9.91 36.60	ramers	Cumming and Rickards					
Age	μ	W	Age	μ	W		
1792	9.91	36.60	1722	10.72	40.19		

Isochron age for the whole rock: 1894±24 Ma



Fig. 30. 207 Pb/ 204 Pb vs. 206 Pb/ 204 Pb diagram showing lead isotopic composition for galena, sphalerite, pyrrhotite, chalcopyrite and whole rock (tremolite-quartz rock, amphibolite and mica gneiss) analyses from Attu. The whole rock isochron gives an age of 1894 ±24 Ma.

rocks have identical initial lead.

The galena model ages, milieu indices μ and W for both the two-stage model of Stacey and Kramers (1975) and the linear uranium accretion model of Cumming and Rickard (1975) have been calculated, and the results are given in Table 16. The calculated galena model ages of 1792 and 1722 Ma, respectively, correspond with those obtained by Vaasjoki (1981) for the same deposit.

It has been shown in earlier studies (Vaasjoki 1981, Rickard 1978) that the lead isotopic data of the Svecofennian galenas in Finland form groups that are geographically and geologically distinct. On the ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb diagram, these isotopic groups define an orogenic trend. In a recent study, Huhma (1986, pp. 36–38, Fig. 21) used both the two-stage model of Stacey and Kramers (1975) and the plumbotectonic model of Doe and Zartman (1979) to interpret this orogenic trend (Fig. 31). He attributed this trend to a varying degree of mixing. According to this model, the mixing, which involved a mantle component and an Archean upper crustal component, took place about 1.9 Ga ago (T_2). An Archean upper crustal component differentiated about 3.0 Ga ago (T_1). A high U/Pb ratio in the Archean upper crustal component generated relatively radiogenic lead during the time between T_1 and T_2 .

Variable mixing during the 1.9 Ga orogeny is now manifested as lead isotope provinces (e.g., Outokumpu, Pyhäsalmi, Pihtipudas, Orijärvi) on a line in the ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb diagram. The lead isotopic data from Attu were fitted into Huhma's diagram (Fig. 31). In this



Fig. 31. Lead isotopic composition of the Attu galena plotted on Huhma (1986) $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram illustrating the lead isotopic evolution in the mantle and continental crust. Mixing which involved a mantle component and an Archean upper crustal component took place 1.9 ago (T₂). An Archean upper crustal component differentiated from the mantle about 3.0 Ga ago (T₁). Finnish galenas exhibit lead isotope provinces (e.g., Outokumpu, Pyhäsalmi, Pihtipudas, Orijärvi) on a line. Lead isotope composition of the Attu galena plots close to the Orijärvi province.

diagram, the Attu isotopic data plot into the Orijärvi province, suggesting that the lead in the Orijärvi and Attu deposits could be from the same or a similar source. These data fall within the range for stratabound and vein galena mineralizations from the contemporary formations of southwest Finland, as measured by Vaasjoki (1981) and those of Bergslagen, central Sweden, reported by Johansson and Rickard (1985). Johansson and Rickard have concluded that the homogeneity of the ore leads in those stratabound deposits suggests that (1) the ores were formed on a similar large

Geological Survey of Finland, Bulletin 341

47

scale, and (2) the lead was derived from a large common source, which was isotopically well mixed. According to the model in Figure 31, much of the lead in the galenas from Attu had Archean upper crustal sources. The equation

$$f = \frac{C^{MA} \times (R^{M} - R^{MA})^{3}}{C^{C} \times (R^{C} - R^{M}) + C^{MA} (R^{M} - R^{MA})}$$

derived from Faure (1977, p. 98), gives the weight fraction f of the crustal component in the mixture. In the case of Attu, this value is 8.7 %.

Sulfur isotopes

Because several factors influence the sulfur isotope composition, the interpretation of sulfur isotope data is often difficult. Ohmoto (1972) and Ohmoto and Rye (1979) stated that the δ^{34} S-values for the sulfides depend largely on $f(O_2)$, pH, T and the bulk sulfur isotope composition in the fluids. In a number of recent studies, sulfur isotope data have been used; (1) to determine the temperature of sulfide deposition or metamorphism, (2) to determine the mechanism of sulfide deposition and (3) to determine the origin of sulfur (Rye & Ohmoto 1974, Sangster 1976, Franklin et al. 1981, Cole & Ohmoto 1986, Ohmoto 1986). The successful determination of these factors is based on the assumption that the isotopic equilibrium between the sulfide species has been established and preserved. The sensitivity of sulfur isotope fractionation to temperature among the common sulfide minerals follows the order pyritegalena > sphalerite(pyrrhotite)-galena > pyrite-chalcopyrite > pyrite-pyrrhotite(sphalerite) (Rye & Ohmoto 1974). In a recent study, Ohmoto (1986) reported that, under conditions of isotopic equilibrium, the relationships $\delta^{34}S$ among H₂S, ZnS, and PbS should be: $\delta^{34}S_{ZnS} >$ $\delta^{34}S_{H_sS} > \delta^{34}S_{PbS}$. Isotopic equilibrium among co-existing sulfides occurs when m_{H,S} >> Σm_{metals} , whereas the reverse relationship m_{H_2S} $<< \Sigma m_{metals}$ would imply isotopic disequilibrium among co-existing sulfides.

Sulfur isotope δ^{34} S-values are determined for galena, sphalerite, pyrrhotite and pyrite from the Attu deposit. The results are presented in Table 17 and Figure 32.

Table 17 and Figure 32 show that the Attu sulfides have light $\delta^{34}S^{\circ}/_{oo}$ values close to 0, with a narrow range from -1.0 to $0.9 \ \delta^{34}S^{\circ}/_{oo}$, with an average of $0.1 \ \delta^{34}S^{\circ}/_{oo}$. Within and between co-existing sulfides, there is a systematic and constant variation in the $\delta^{34}S$ values. All the sulfides have $\delta^{34}S$ values close to each other, except for the galena which has a distinctly lower value than the other minerals. This confirms the existence of the relationship $\delta^{34}S_{ZnS} > \delta^{34}S_{PbS}$ in the Attu deposit, suggesting that isotopic equilibrium between the two sulfides was established (Ohmoto 1986).

The calculated isotopic temperatures from pyrite-galena, sphalerite-galena and pyrrhotite-galena pairs, based on equations reported in Ohmoto and Rye (1979), are given in Table 17. The pairs sphalerite-galena and pyrrhotite-

 $[\]overline{{}^{3}C^{MA}, C^{C}, R^{MA}, R^{C}}$ are the Pb concentrations and $\overline{{}^{206}Pb/{}^{204}Pb}$ isotope ratios of mantle- and crustal-derived materials, respectively, and R^{M} is the $\overline{{}^{206}Pb/{}^{204}Pb}$ ratio in the mixture. $C^{C} = 15$ ppm and $C^{MA} = 1$ pmm (see e.g. Weaver and Tarney 1980 and Sun 1980), $R^{C} = 16.3$ and $R^{MA} = 14.71$ (see Huhma 1986). For the galena from Attu, $R^{M} = 15.66$.

a 1		δ ³⁴	5°/00	Temperature in °C			
Sample	ру	ga	sph	ро	py-ga	sph-ga	po-ga
6/19.50	0.5	-	0.8	0.6	-	_	-
16/70.80	0.3	-	0.5	0.2	-	—	—
17/88.00	0.5	-0.5	0.5	-	737	577	—
21/105.00	0.4	-0.6	0.4	0.6	737	577	500
100/30.10	0.7	-	-	0.9	-	_	-
309/40.10	0.3	-0.8	-	0.2	737	-	577
2-LSH-85	-	-1.0	-	0.0	-	-	577

Table 17. Sulfur isotope data for the Attu deposit. (ga = galena, po = pyrrhotite, py = pyrite, sph = sphalerite).



Fig. 32. Range of δ^{34} S values of pyrite, pyrrhotite, sphalerite and galena from the Attu deposit.

galena give a temperature mostly at 577 °C, while pyrite-galena gives a constant value of 737 °C. The explanation for the different temperatures is that different sulfide assemblages attain isotopic equilibrium at different temperatures. The temperature range of 537 °C to 737 °C, however, indicates amphibole-granulite facies regional metamorphism. It is worth noting that the temperature 737 °C is consistent with the values obtained in this study by the garnet-orthopyroxene (740 °C) and plagioclase – Ca-amphibole (725 °C) thermometers.

The sulfur isotopic ratios of the Attu deposit,

as given in Figure 32, are all close to 0, a value reported by many authors to imply a magmatic origin of the sulfur (e.g., Ohmoto 1986). However, the prevalent current opinion is that the major source of sulfur for the submarine exhalative deposits is the direct reduction of coeval sea-water sulfate, especially during circulation in the ore-forming hydrothermal cell (e.g., Franklin *et al.* 1981, Ohmoto 1986). Therefore, the narrow range of sulfur isotope ratios in the Attu deposit is taken to mean that the sulfur was derived from a homogenized source.

DISCUSSION

Comparison of the Attu deposit with other massive sulfide deposits

The Attu deposit exhibits geological characteristics typical of those of the worldwide class of stratabound massive sulfide deposits. The general features of these deposits have been reviewed by, among many others, Sangster (1972), Hutchinson (1973), Sangster and Scott (1976) and Franklin et al. (1981). By 1983, more than a thousand volcanogenic stratabound massive sulfide deposits had been recognized (Ohmoto & Skinner 1983). They occur throughout geological time from Archean to Present and are found on all continents. They are considered to have been formed on the sea floor from discharged hydrothermal solutions. Among the most important characteristic features of the stratabound massive sulfide deposits are stratiform mineralization, alteration of the footwall rocks, and zonation of metals within the mineralization. Massive sulfide deposits are the major source of most of the world's Cu, Zn, Pb, Ag, and Au, and produce significant quantities of Sn, Se, Bi as well as other minor metals (Franklin et al. 1981). They rank second only to porphyry coppers in economic importance among nonferrous metallic mineral deposits (Rose et al. 1977).

On the basis of metal content, Hutchison (1973) identified two distinct groups of stratabound massive sulfide deposits, namely, the Cu-Zn group and the Zn-Pb-Cu group. Sangster and Scott (1976) proposed a division based on rock association: (1) deposits of predominantly volcanic association, (2) those of predominantly sedimentary association, and (3) those of volcanic-sedimentary association. The most cited classification is, however, the one that includes the tectonic environment and ore element association, which broadly divide the massive sulfide deposits into the Kuroko-type and the Cyprus-type. Deposits of the Kurokotype mineralization are mostly associated with felsic volcanics and occur in a calc-alkaline island-arc environment. They predominantly consist of Cu-Zn-Pb-Ag ores. The Cyprustype deposits are generally associated with mafic volcanics in an ophiolite sequence and are generally Cu-rich, often Pb-deficient and have variable Au and Ag contents. They occur at an accretionary plate margin or back arc basin (Constantinou & Govett 1973). Another example of mafic association is the Besshi-type Curich massive sulfide deposits, which are hosted in tholeiitic volcanics within a thick greywacke sequence in a tectonic setting of an immature oceanic island arc (Mitchell & Bell 1973, Klau & Large 1980).

The bulk of the ore-forming solutions in stratabound massive sulfide deposits is derived from seawater. The hydrothermal system involves the convection of seawater by a convection cell, driven by the heat of a cooling, subvolcanic igneous body (e.g., Barnes 1979). The seawater depth at which submarine hydrothermal discharges occur range from very deep to shallow. This is taken to mean that the formation of the stratabound massive sulfide deposits does not require a specific depth of water (cf. Franklin et al. 1981). Ore metals are generally assumed to be leached from rocks through which the hydrothermal solutions have flown and/or to be generated directly from a magmatic source. A substantial portion of the sulfur is from seawater sulfate reduced to sulfide species or/and directly from a magmatic source (Ohmoto 1986).

Geologically, the Attu sulfide deposit belongs to the same Svecofennian domain as the stratabound massive sulfide deposits of Aijala-Metsämonttu-Orijärvi in southwest Finland (Latvalahti 1979) and the metallogenic province of central Sweden, including the Garpenberg and Falun deposits (e.g., Frietsch *et al.* 1979, Vivallo 1984). The domain has been interpreted as an early Proterozoic island-arc system where calc-alkaline magmatism predominated, although rocks with a tholeiitic affinity also occur (e.g., Hietanen 1975, Gaál 1982, Schreurs 1985a, b; Ehlers *et al.* 1986). Sulfide minerals

occur both as stratiform Zn-Pb-Cu massive and Cu-disseminated mineralizations in a metavolcanic-metasedimentary sequence. Major ore minerals in the massive sulfide deposits in the Svecofennian domain are commonly sphalerite, galena, chalcopyrite, pyrite, pyrrhotite, magnetite and minor Ag-bearing minerals. Wall rocks are hydrothermally altered with Mg enrichment and depletion in Na and Ca. The massive sulfide deposits of the Aijala-Metsämonttu-Orijärvi area and central Sweden were strongly deformed and metamorphosed under the amphibolite/granulite facies during the Svecofennian orogeny. A volcanogenic origin has been proposed for these massive sulfide deposits in southwest Finland and central Sweden - Garpenberg - (Latvalahti 1979, Vivallo 1984).

Like the Garpenberg deposit, the Attu deposit displays a number of similarities as well as dissimilarities when compared with the Canadian Precambrian massive sulfide deposits or with the Phanerozoic Kuroko deposits of Japan (Table 18). The similarities are, generally speaking, mostly expressed as stratiform mineralization, mineralogy, metal zonation within the deposits and the fact that the wall rocks have undergone a certain degree of alteration.

Figure 33 compares the variations in the ratios of Pb-Cu-Zn of the Attu deposit with those of Metsämonttu, Garpenberg, the Precambrian deposits of Canada and the Kuroko deposits. Ohmoto et al. (1983) concluded that the principal parameters that determine the amounts and proportions of minerals and metals in volcanogenic massive sulfide deposits are: (1) the thermal history of an oreforming system, (2) the dominant type of country rocks, and (3) the composition of seawater, particularly its oxygen and sulfate contents. The differences in these factors can explain both the contrast between Precambrian and Phanerozoic deposits, and between deposits associated with mafic volcanics and with felsic rocks. Variation in the metal ratios in Fig-

	Attu deposit	Kuroko deposits	Canadian Deposits
Age	Early Proterozoic	Miocene	Archean
Host rock sequence	Volcanic-sedimentary Submarine Shallow water	Felsic volcanics Shallow-water	Greenstone belt
Type of volcanism and tectonic setting	Calc-alkaline island-arc	Calc-alkaline mature island arc	Tholeiitic Archean rift zones
Major sulfides	Pyrrhotite, sphalerite galena, pyrite, chalcopyrite	Chalcopyrite, sphalerite galena, tetrahedrite- tennantite, pyrite	Sphalerite, chalcopyrite, pyrite pyrrhotite, +-galena
Barite	Absent	Major	Trace
Stratigraphic mineralization zoning	Increasing of Zn-Pb and decreasing of Cu upwards	Increasing of Zn-Pb and decreasing of Cu upward	Increasing of Zn-Pb and decreasing of Cu upward
Wall rock alteration	Mg, Fe enrichment and depletion of Ca and Na in the footwall	Mg and SiO2 enrichment and depletion of Na in both foot- and hangingwall	Mg metasomatism and depletion of Na, Ca and SiO ₂ in the footwall
Metamorphism	Amphibolite facies	None	Greenschist to amphibolite facies

Table 18. Comparison between the Attu, Kuroko and the Canadian Archean massive sulfide deposits.

Fig. 33. Pb-Cu-Cu ratios for (a) the Attu sulfide deposit compared to those of (b) Metsämonttu (Drawn from Latvalahti 1979), (c) the Precambrian deposits of Canada, Kuroko deposits of Japan and the Garpenberg sulfide ores from central Sweden (Drawn from Vivallo 1984).



51



ure 33 is, therefore, a reflection of the differences in one or more of the aforementioned parameters.

Compared with the Kuroko deposits, Precambrian deposits that developed from, and in, reduced seawater would contain pyrrhotite, rare sulfates, high ratios of sphalerite/pyrite, sphalerite/chalcopyrite, Zn/Cu, Zn/Ba, and Au/Ag, and δ^{34} S close to 0. The deposits developed in areas dominated by basaltic rocks tend to have higher Cu/Zn, Cu/Pb, and Au/Ag ratios, compared with the Kuroko deposits (Lambert & Sato 1974, Franklin *et al.* 1981, Ohmoto *et al.* 1983).

Carbonate-rich sediments are the predominant sedimentary facies at the Attu deposit, contrary to the Kuroko deposits where anhydrite, gypsum, barite and iron-rich minerals are the common facies. Mixing of the ore-forming fluids with cold seawater is an effective mechanism for the precipitation of anhydrite, gypsum and pyrite (Ohmoto *et al.* 1983). As in the case of many Canadian Archean sulfide deposits or metamorphosed deposits such as Mount Isa, Sulurian, McArthur River, no barite or gypsum has been found in association with the Attu ore minerals. It has been said (e.g., Sangster & Scott 1976) that the absence of gypsum, barite and iron-rich sedimentary facies in the Precambrian massive sulfide deposits reflects the evolution of the seawater from Precambrian to Phanerozoic. Large (1980) stated that sulfate species are favored at low temperatures and high oxygen and sulfur concentrations. This view was shared by Cameron (1982), who noted that sulfate was a minor component of Archean and early Proterozoic seawater. In contrast, barite has, however, been reported from some Precambrian sulfide deposits in Finland, such as the Vihanti Zn ore deposit (Rouhunkoski 1968) and the Zn-Cu deposits of the Pyhäsalmi-Pielavesi district (Helovuori 1979, Huhtala 1979). Tucker (1982) suggested that the presence of carbon-rich sediments as the dominant chemical sediments associated with the Precambrian massive sulfide deposits implies that the partial pressure of CO₂ could have been higher in the Proterozoic seawater.

Origin of the wall rocks

The Attu Zn-Pb-Cu mineralization occurs in a metavolcanic-metasedimentary association. The volcanic suite is represented by the amphibolites and the cordierite-anthophyllite rocks, whereas tremolite-quartz rock, marbles and calc-silicate rocks constitute the chemical sedimentary sequence.

The genesis of the cordierite-anthophyllite rocks has attracted the interest of many petrologists ever since the classical study by Eskola (1914), who proposed a syn-metamorphic Mgmetasomatic process for the origin of such rocks. Reservations for the nature of such a process were expressed by a number of authors, among them Tuominen and Mikkola (1950), James *et al.* (1978), Schermerhorn (1978), Treloar *et al.* (1981) and Spear and Schumacher (1982).

In the Attu deposit, the cordierite-antho-

phyllite rocks occur as a footwall of the sulfide ore. The rocks are thought to be derived from hydrothermally altered, chlorite-bearing seafloor volcanic rock, analogous to the model proposed by Vallance (1967) and later advocated by other researchers (e.g. Berge 1978, Baker & Groot 1983, Schippers 1983).

As a result of the reaction between the volcanic rock and hydrothermal solutions, destruction of the primary minerals, mainly feldspars, and a general redistribution of elements in the altered wall rock took place. The rock was enriched in Mg, Fe, Zn, Pb, and Cu, and depleted in Na and Ca. Regional metamorphism in the amphibole facies during the Svecofennian orogeny, culminating in southern Finland about 1.81–1.83 Ga ago (Korsman *et al.* 1984, Hölttä 1986) isochemically transformed the previously altered chlorite-bearing rock into a cordierite-anthophyllite assemblage. Greenwood (1963) and Schreurs and Westra (1985) noted that under metamorphic conditions of granulite facies, anthophyllite breaks down to orthopyroxene:

 $Mg_7Si_8O_{22}(OH)_2 \rightarrow 7 MgSiO_3 + SiO_2 + H_2O$

anthophyllite \rightarrow 7 enstatite + quartz + H₂O

In its mineralogical and geochemical composition, the cordierite-anthophyllite rocks at Attu are quite similar to those observed in the hydrothermally altered rocks genetically associated with Precambrian volcanogenic massive sulfide deposits, e.g., at the Coronation mine in Canada (Whitmore 1969), Bergslagen, in central Sweden (Wolter & Seifert 1984), and Orijärvi (Latvalahti 1979).

The tremolite-quartz rock, the main host rock of the sulfide ores, is interpreted to be a metamorphosed chert mixed with carbonate material. It was probably deposited as exhalative hydrothermal silica on the sea floor. Metasomatism and subsequent high-grade regional metamorphism led to the formation of calc-silicate minerals, such as tremolite and diopside.

The marble is both of dolomitic and calcitic composition and has low contents of Al_2O_3 , SiO_2 and FeO_2 . According to Vivallo (1984), low Al_2O_3 and SiO_2 contents suggest that the marbles are of chemical origin with little contamination of volcanoclastic material and iron oxides.

The calc-silicate rocks (skarns) occur as altered wall rocks of the orebody. In addition to dolomite and calcite, they consist of coarsegrained Ca-Mg-Fe silicates, mainly tremolite, diopside and minor forsterite, talc and serpentine. Calc-silicate rocks are interpreted as metamorphosed impure dolomitic limestones, which were initially altered during the process of ore deposition. High temperature regional metamorphism caused the breakdown of tremolite/ diopside and dolomite to form forsterite and calcite (Winkler 1979).

Genesis of the Attu sulfide deposit

Textural and mineralogical evidence suggests a pre-metamorphic origin for the Attu stratiform deposit. The similarities, as shown in the geological setting, ore mineralogy, wall rock alteration and stratiform mineralization with other stratabound massive sulfide deposits (e.g., Orijärvi, Garpenberg, Kuroko), suggest a submarine exhalative origin for the Attu deposit. The ore metals were deposited in a submarine environment dominated by chemical sediments and sea-floor volcanic rocks. Hydrothermal solutions affected the adjacent wall rocks by altering their chemical and mineralogical composition. In analogy with many Precambrian sulfide deposits (e.g., Garpenberg) and in contrast to the Pyhäsalmi-Pielavesi sulfide deposits and the Kuroko deposits, the presence of carbonate-rich sedimentary rocks and absence of gypsum and barite at the Attu deposit are indicative of a compositional difference between the Proterozoic and the Tertiary sea water.

Under progressive regional metamorphism and deformation during the Svecokarelian orogeny, the primary features of the sulfides and their host rocks were coevally obliterated, as reflected by the recrystallization textures in the ore minerals and the chemical and mineralogical changes in the wall rocks. The peak of metamorphism in the Attu area was at the amphibolite- to granulite-facies transition, with the temperature peak at about 740 °C and the pressure between 4.5 and 5.1 kb. These values were calculated in the present study and are in agreement with earlier regional observations (Schellekens 1980, Törnroos 1982, Schreurs 1985, Hölttä 1986).

The main ore mineral species, pyrrhotite, sphalerite, galena, pyrite and chalcopyrite, at the Attu sulfide deposit are typical constituents of stratabound massive sulfide deposits (Sangster & Scott 1976, Franklin *et al.* 1981). Pyrrhotite is mainly considered to be a metamorphic product of pyrite, although the existence of primary pyrrhotite is not ruled out (see Plimer & Finlow-Bates 1978).

Study of the structural features at the Attu deposit indicates that the ores, together with the country rocks, were affected by at least two folding phases, Fn and Fn+1 Similar tectonic phenomena have been described from other parts of the Svecofennian domain (e.g., Verhoef & Dietvorst 1980). Ore minerals recrystallized under equilibrium conditions as can be deduced from their contacts as well as from sulfur isotope studies. The orientation of the longitudinal axes of the ore mineral grains parallel to the foliation and lineation of the enclosing host rock, the grain size of the ore minerals, their granoblastic texture and the grain boundaries are features that reflect deformation and recrystallization under metamorphic conditions and therefore confirm the pre-deformation and pre-metamorphic genesis of the Attu orebody.

Chalcopyrite and pyrrhotite inclusions are common in the Attu sphalerite. According to the experimental data published by Wiggins and Craig (1980) and Kojima and Sugaki (1984), sphalerite dissolves significant amounts of both chalcopyrite and pyrrhotite at temperatures higher than 600 °C. Such inclusions have various shapes such as lamellae, blebs, dots, dust and vermiculae (e.g., Sugaki *et al.* 1987). Below 500 °C, the solubility of copper in sphalerite solid solution is generally low (Kojima & Sugaki 1985, Sugaki *et al.* 1987).

Hexagonal pyrrhotite with an average Fe content of 47.7 atomic % is the dominant iron sulfide at the Attu deposit. Lamellar intergrowth between monoclinic pyrrhotite and hexagonal pyrrhotite is rare. This suggests that the equilibration temperature was above 254 °C, the upper stability limit of monoclinic pyrrhotite (Kissin & Scott 1982).

The whole rock lead isochron from the Attu supracrustal rocks yield an isochron age of about 1.89 Ga, which is in agreement with that obtained for the Svecofennian supracrustal suites (e.g., Huhma 1986). The model age of 1.79-1.72 Ga provided by the plumbotectonic model for the Attu Pb is much lower than the geologic age. The galena, sphalerite and pyrrhotite show an identical lead isotope composition. This suggests that the ore metals are from the same source. According to a two-stage mixing model, the identical isotope composition occurs in the Pb of the galena from both Attu and Orijärvi (Fig. 31). The Pb in both places, therefore, are derived from a similar mantle-crustal source (Huhma 1986). Johansson and Rickard (1985), commenting on the homogeneity of the ore leads in the stratabound deposits of southwest Finland and central Sweden, suggested that the ores were formed by similar processes and that they have a large common source, which was isotopically well mixed. Accordingly, the ore metals in the Attu sulfide deposit are interpreted to have been derived from orebearing fluids that extracted materials from a well mixed mantle-crustal source, which precipitated them on the sea floor. The bulk of the ore-forming solution is considered to be hydrothermally circulated seawater.

The range of the δ^{34} S values in the Attu sulfides is narrow, close to 0. This is often interpreted to indicate a magmatic origin of the sulfur (e.g., Ohmoto 1972, 1986). The narrow range shown by the sulfur isotope ratio of the Attu sulfides suggests a well homogenized source of the sulfur. Isotopic equilibrium among the sulfides was established at a temperature range of 580 °-740 °C, as proposed by sulfur isotope thermometric determinations.

Most of the sulfosalts found at the Attu deposit are Ag-, As-, Sb-, and Sn-bearing. They commonly occur as inclusions in the galena. Au occurs as native element or electrum, in association with arsenopyrite and chalcopyrite. The intimate association of the sulfosalts with galena, and arsenopyrite with chalcopyrite indicate that the metals that constitute the sulfosalts were probably deposited at the same time as the main ore metals of the deposit and by similar mechanisms. The occurrence of Sn-bearing kesterite instead of cassiterite is interpreted to suggest low $f(O_2)$ in hydrothermal solutions (cf. Petersen 1986).

SUMMARY AND CONCLUSIONS

The geology of the Attu area is dominated by a supracrustal sequence of amphibolites, amphibole gneisses and mica gneisses, which were intruded by synorogenic to late-orogenic Precambrian plutonic rocks. The Attu Zn-Pb-Cu sulfide ores are hosted in tremolite-quartz rock, calc-silicate rocks (diopside-, tremolite skarn) and cordierite-anthophyllite rocks.

The amphibolites are interpreted to represent former lavas of basaltic to andesitic composition. The quartz rock is considered to be a metamorphosed chert, probably deposited as exhalited hydrothermal silica on the sea floor. The cordierite-anthophyllite rock is thought to have been derived during regional metamorphism from hydrothermally altered chloritebearing volcanic rocks. As a result of the interaction of the wall rocks and the hydrothermal solution, the wall rocks were altered and chemically enriched in magnesium, iron and ore metals and depleted in sodium and calcium.

The sulfide ores occur as stratiform massive, lenticular bodies or as disseminations. The main ore minerals are pyrrhotite, sphalerite, galena, chalcopyrite and pyrite. Arsenopyrite, magnetite and ilmenite occur in subordinate amounts. Significant sulfosalts met with are argentian tetrahedrite, Sn-bearing kesterite, boulangerite, bournonite, tennantite and pyrargyrite. Gold occurs mainly as electrum. Anhydrite, gypsum and barite are virtually absent. The main gangue minerals are quartz, diopside, tremolite, dolomite, calcite, anthophyllite and cordierite.

The Attu sulfide deposit displays a metal zonation along the longitudinal axis of the orebody. The Cu content increases with increasing depth while that of Pb increases upwards. No systematic zonation has been recognized with regard to Zn. Iron is present throughout the sequence in the form of pyrrhotite and/or pyrite. Cu shows a preferential association with the cordierite-anthophyllite rock while Pb is mostly associated with the calc-silicate rocks.

During the Svecofennian orogeny, about 1.9–1.87 Ga ago, the Attu deposit was deformed and regionally metamorphosed at the amphibolite-granulite transition. At least two folding phases, F_n and F_{n+1} , could be recognized in the Attu area. The parallel orientation of the sulfide mineral grains with the F_{n+1} fold axis, the foliation and the lineation of the host rock suggest that the present form of the Attu orebody is controlled by F_{n+1} folding.

Geothermometric and geobarometric determinations suggest that the peak temperature of metamorphism was around 740 $^{\circ}$ C and the pressure 4.5–5.1 kb.

The whole rock lead isochron gives an age of 1.89 Ga for the Attu supracrustal rocks. The model age of 1.79–1.72 Ga yielded by the plumbotectonic model is much lower than the geologic age of 1.9 Ga. The common lead isotopic data of the galena, sphalerite and pyrrhotite have identical isotopic composition, indicating that the sulfides are from the same source. A two-stage mixing model suggests that the lead in the Attu galena has an isotopically well mixed mantle-crustal source.

On the basis of the grain boundaries and the sulfur isotope thermometric determinations, the Attu sulfides are considered to represent equilibrium assemblages established during regional metamorphism at temperatures from 580° to 740 °C. Isotopic equilibrium among the ore minerals has also been attained. The sulfur isotope study suggests a homogeneous source for the sulfur in the Attu deposit.

The Attu Zn-Pb-Cu sulfide ores were deposited on the sea floor in a reduced milieu of the Svecofennian island arc environment about 1.9 Ga ago. Carbonate-rich sediments and seafloor volcanic rocks dominated the depositional environment. The mineralogical composition, wall rock alteration, metal zonation and the geotectonic setting suggest that the metamorphosed, stratabound Attu Zn-Pb-Cu stratiform mineralization is a submarine exhalative sulfide deposit of a proximal type.

In its mineralogical, geochemical, textural and lithological features, the Attu deposit displays characteristics similar to the Orijärvi and Garpenberg deposits in particular, and to those of the world-wide family of stratabound massive sulfide deposits in general.

ACKNOWLEDGMENTS

This work was carried out at the Department of Geology and Mineralogy, University of Helsinki, under the guidance of Professor Ilmari Haapala. Professor Haapala followed with keen interest the development of this thesis from infancy to maturity. I wish to express my deep gratitude to him for all the support that he gave me in various ways throughout this study. His constructive criticism on various drafts of the thesis proved quite valuable.

The years I have spent at the Department of Geology have been, in many ways enriching. I am indebted to my colleagues and staff at the Department for all the assistance given me and for the friendly and warm atmosphere which was conducive to the successful completion of this work. I owe special thanks to Mr. M. Nironen, for his patient and courteous cooperation at different stages of writing which broaden my understanding of tectonics and related problems; to Ms. M. Ahokas for drawing the maps and figures; to Mr. L. Rämö for preparing many of the petrographic sections; and to Mr. O. Rantala for introducing me to the use of the personal computer.

I am grateful to Oy Partek Ab for giving me permission and providing some of the materials needed to conduct the research work at the Attu deposit; to Outokumpu Oy, for thin and polished sections, drill-core analyses, microprobe determinations and other research materials; to Dr. M. Vaasjoki, of the Geological Survey of Finland, for lead isotope determinations; to Dr. H. E. Wener, of the Department of Economic Geology, Mineralogy and Petrology of the Free University of Amsterdam, for the mineralogical analyses required for the estimation of the metamorphic conditions; to Mr. J. Tammenmaa, of the Laboratory of Economic Geology, Helsinki University of Technology, for sulfur isotope measurements; to Mr. K. Rasilainen, of the Geological Survey of Finland, for factor analyses of geochemical data; and to Professor L. K. Kauranne, Director of the Geological Survey of Finland, for arranging the publication of the thesis in the Survey's Bulletin series.

I thank Professor Jaakko Siivola, Dr. Pekka Nurmi, Messrs E. Rauhamäki, T. Karppanen and E. Lundén, who critically read and constructively commented on an earlier draft of this manuscript. Mr. Paul Sjöblom checked the language of the manuscript. It is needless to state, however, that I alone bear the final responsibility for the views presented.

I would like to thank, most profoundly, the Finnish International Development Agency (FINNIDA), Ministry for Foreign Affairs of Finland, for the scholarship given to me through SWAPO. In particular, Fellowship Officer Helena Kuivila and Assistant Director Pertti Majanen have been helpful in many ways. The practical administration of the scholarship was carried out by Finn Church Aid, and I therefore wish to extend my thanks to Pirkko Seitsonen, Yrjö Höysniemi and Laura Torvinen, all from Finn Church Aid.

My fellow SWAPO students in Finland meant a lot to me. Their solidarity, unity of purpose and patriotic commitment were not only a great source of encouragement and inspiration, but also provided a sense of security and optimism. To them, I extend my fraternal salutations and only say: *A luta continua*.

Finally, I want to extend my deepest gratitude to SWAPO, which not only encouraged me to pursue my research work, but also offered me practical assistance and thereby provided the stimulus for me to carry on the task of studying.

REFERENCES

- Allen, A. R., 1979. Metasomatism of a depleted granulite facies terrain in the Arunta Block, Central Australia – Geochemical evidence. Contrib. Mineral. Petrol. 31, 85–98.
- Arnold, R. G., 1962. Equilibrium relations between pyrrhotite and pyrite from 325° to 743 °C. Econ. Geol. 57, 72-90.
- Arnold, R. G., 1966. Mixtures of hexagonal and monoclinic pyrrhotite and the measurement of the metal content of pyrrhotite by X-ray diffraction. Am. Mineral. 51, 1221–1227.
- Arnold, R. G. & Reichen, L. E., 1962. Measurement of the metal content of naturally occurring, metal-deficient, hexagonal pyrrhotite by an X-ray spacing method. Am. Mineral. 47, 105–111.
- Baker, H. J. & Groot, P. A., 1983. Proterozoic seawaterfelsic volcanics interaction W.Bergslagen, Sweden. Evidence for high REE mobility and implications for 1.8 Ga seawater compositions. Contrib. Mineral. Petrol. 82, 119-130.
- Barnes, H. L., 1979. Solubilities of ore minerals. In Geochemistry of Hydrothermal Ore Deposits, 2nd. edit., ed. by H. L. Barnes, 404–460. John Wiley & Sons, New York.
- Barnes, H. L. & Czamaske, G. K., 1967. Solubilities and transports of ore minerals. *In* Geochemistry of hydrothermal ore deposits. 1st ed., ed. by H. L. Barnes, 334-381. Holt, Rinnehart and Winston, New York.
- Barton, P. B., Jr. & Toulmin, P., III, 1966. Phase relations involving sphalerite in the Fe-Zn-S system. Econ. Geol. 61, 815-849.
- Bell, H., 1982. Stratabound sulfide deposits, wall-rock alteration, and associated tin-bearing minerals in the Carolina slate belt, South Carolina and Georgia. Econ. Geol. 77, 294–311.
- Berge, J. W., 1978. A re-examination of the association of magnesium and massive sulfide ores. Geol. Fören. Stockh. Förh. 100, 155–170.
- Berthelsen, A., 1980. Towards a planspatic tectonic analysis of the Baltic shield. 26th Congr. Geol. Int. Abstr. 3, 1405.
- Boctor, N. Z., 1980. Sphalerite geobarometry in Bodenmais ore, Bavaria. Am. Mineral. 65, 1031–1037.
- Bowes, D. R., Halden, N. M., Koistinen, T. J. & Park, A, F., 1984. Structural features of basement and cover rocks in the eastern Svecokarelides, Finland. In Precambrian Tectonics Illustrated, ed. by A. Kröner and E. Greiling, 147–171. E. Schweizerbart'ssche Verlagsbuchhandlung, Stuttgart.
- Brown, P. E., Essene, E. J. & Kelly, W. C., 1978. Sphalerite geobarometry in the Balmat-Edwards district, New York. Am. Mineral. 63, 250–257.

- Cameron, E. M., 1982. Sulphate and sulphate reduction in early Precambrian oceans. Nature 296, 145–148.
- Campbell, D. S., 1980. Structural and metamorphic development of migmatites in the Svecokarelides, near Tampere, Finland. Trans. R. Soc. Edinburgh: Earth Sci. 71, 185–200.
- Cole, R. D. & Ohmoto, H., 1986. Kinetics of isotopic exchange at elevated temperatures and pressures. *In* Stable isotope geochemistry of ore deposits. Reviews in Mineralogy 16, ed. by Valley, W. J., Taylor, P. H. and O'Neil, R. J., 41–90.
- Colley, H. & Westra, L., 1987. The volcano-tectonic setting and mineralization of the early Proterozoic Kemiö-Orijärvi-Lohja belt, SW Finland. J. Geol. Soc. London. In press.
- Constantinou, G. & Govett, G. J. S., 1973. Geology, geochemistry, and genesis of Cyprus sulfide deposits. Econ. Geol. 68, 843–858.
- Craig, J. R., 1967. Phase relations and mineral assemblages in the Ag-Bi-Pb-S system. Mineral. Deposita 1, 278-306.
- Craig, J. R. & Scott, S.D., 1974. Sulfide phase equilibria. In Sulfide Mineralogy. Mineralogical Society of America, Short Course Notes, 1.Cs 1–110. ed. by P. H. Ribbe.
- Craig, J. R. & Vaughan, D., 1981. Ore microscope and ore petrography. John Wiley & Sons, New York, 406 p.
- Crerar, D., Wood, S., Brantley, S. & Bocarsly, A., 1985. Chemical controls on solubility of ore-forming minerals in hydrothermal solutions. Can. Mineral. 23, 333–352.
- Cumming, G. L. & Rickard, J. R., 1975. Ore lead isotope ratios in a continuously changing Earth. Earth Plan. Sci. Letters 28, 155–171.
- Deb, M., 1980. Genesis and metamorphism of two stratiform massive sulfide deposits at Ambayi and Deri in the Precambrian of Western India. Econ. Geol. 75, 572-591.
- Dietvorst, E. J. L., 1981. Pelitic gneisses from Kemiö, southwest Finland: a study of retrograde zoning in garnet and spinel. Ph. D. Thesis, Free University of Amsterdam.
- Doe, B. R. & Zartman, R. E., 1979. Plumbotectonics, The Phanerozoic. In Geochemistry of hydrothermal ore deposits, 2nd edit., ed. by H. L. Barnes, 22–70. John Wiley & Sons, New York.
- Du Rietz, T., 1968. Huvuddragen av Garpenbergstraktens, bergbyggna. Sveriges Geol. Undersökning. Ser. C. No. 631, 22 p.
- Edelman, N., 1960. The Gullkrona region, SW Finland. Bull. Comm. Geol. Finlande 187, 87 p.

- 58 Geological Survey of Finland, Bulletin 341
- Edelman, N., 1985. Explanation to the maps of Pre-Quaternary rocks, Sheet 1034. Summary in English on Pre-Quaternary rocks of the Nauvo (Nagu) map-sheet area. Geol. Surv. Finland, Espoo. 47 p.
- Ehlers, C., Lindroos, A. & Jaanus-Järkkälä, M., 1986. Stratigraphy and geochemistry in the Proterozoic mafic volcanic rocks of the Nagu-Korpo area, SW Finland. Precambrian Res., 32. 297–315.
- Eskola, P., 1914. On the petrology of the Orijärvi region in southwestern Finland. Bull. Comm. Gèol. Finlande 40. 277 p.
- Faure, G., 1977. Principles of Isotope Geology. John Wiley & Sons, New York, 464 p.
- Finlow-Bates, T., 1980. The chemical and physical controls on the genesis of submarine exhalative orebody and their implications for formulating exploration concepts. A review. Geol. Jb. D40, Hanover, 131–168.
- Franklin, J. M., Lyndon, J. W. & Sangster, D. F., 1981. Volcanic-associated massive sulfide deposits. Econ. Geol. 75th Anniversary Vol., 485–627.
- Frietsch, R., Papunen, H., & Vokes, F. M., 1979. The ore deposits in Finland, Norway and Sweden – a review. Econ. Geol. 74, 975–1001.
- Front, K & Nurmi, P. A., 1987. Characteristics and geological setting of synkinematic Svecokarelian granitoids in southern Finland. Precambrian Res., 35, 207–224.
- Gaál, G., 1982. Proterozoic tectonic evolution and late Svecokarelian plate deformation of the Central Baltic Shield. Geol. Rundschau 71, 158-170.
- Gaál, G., 1986. 2200 Million years of crustal evolution: The Baltic Shield. Bull. Geol. Soc. Finland 58, Part 1, 149–168.
- Gaál, G. & Gorbatschev, R., 1987. An outline of the Precambrian of the Baltic Shield. Precambrian Res., 35, 15-52.
- Gilmour, P., 1976. Some transitional types of mineral deposits in volcanic and sedimentary rocks. *In* Handbook of stratabound and stratiform ore deposits, 1. ed. by Wolf, K. H., 111–160. Elsevier, Amsterdam.
- Greenwood, J. H., 1963. The synthesis and stability of anthophyllite. Jour. Petrol. 4, 317–351.
- Gulson, B. L., 1986. Lead isotopes in Mineral exploration. Elsevier, Amsterdam, 245 p.
- Gulson, B. L. & Mizon, K. J., 1979. Lead isotopes as a tool for gossan assessment in base metal exploration. J. Geochem. Explor. 11, 299-320.
- Hackbarth, C. J. & Petersen, U., 1984. A fractional crystallization model for the deposition of argentian tetrahedrite. Econ. Geol. 79, 448–460.
- Hall, S. R., Szymanski, J. T. & Stewart, M. J., 1978. Kesterite Cu₂(Zn,Fe)SnS₄, and stannite Cu₂(Fe,Zn)SnS₄, structurally similar but distinct minerals. Can. Mineral. 16, 131–137.
- Helgeson, H. C., 1964. Complexing and hydrothermal ore depositions. Macmillen, New York. 129 p.
- Helovuori, O., 1979. Geology of the Pyhäsalmi ore deposit, Finland. Econ. Geol. 74, 1084-1101.
- Hietanen, A., 1975. Generation of potassium-poor magma in the northern Sierra Nevada and the Svecofennian of Finland. J. Res. U. S. Geol. Surv. 3, 631–645.

- Holmberg, J. H., 1858. Materialier till Finlands geognosi. Birdrag till Finlands naturkännedom, etnografi och statistik 4, Finska Litteratursällkapet XXV, 254 p.
- Hölttä, P., 1986. Observations on the metamorphic reactions and PT conditions in the Turku granulite area. In Development of deformation, metamorphism and metamorphic blocks in eastern and southern Finland. ed. by K. Korsman. Geol. Surv. Finland, Bull. 339. 43–58.
- Hopgood, A. M., Bowes. D. R., Kouvo, O. & Halliday, A. N., 1983. U-Pb and Rb-Sr isotopic study of polyphase deformed migmatites in the Svecokarelides, southern Finland. *In* Migmatites, melting and metamorphism, Shiva Geology Series, ed. by Atherton, M. P. and Gribble, C. D., 80–92.
- Hubner, H., 1966. Die Geologie der Sulfiderzlagerstätte Kalvbäcken. Sveriges Geol. Unders. 615, 85 p.
- Huhma, H., 1986. Sm-Nd, U-Pb and Pb-Pb isotopic evidence for the origin of the Early Proterozoic Svecokarelian crust in Finland. Geol. Surv. Finland, Bull. 337. 48 p.
- Huhtala, T., 1979. The geology and zinc-copper deposits of the Pyhäsalmi-Pielavesi district, Finland. Econ. Geol. 74, 1069–1083.
- Hutchison, R. W., 1973. Volcanogenic sulphide deposits and their metallogenic significance. Econ. Geol. 68, 1223-1246.
- Hutchison, M. N. & Scott, S. D., 1980. Sphalerite geobarometry applied to metamorphosed sulfide ores of the Swedish Caledonides and U. S. Appalachians. Norges Geol. Unders. 360, 59–71.
- Hutchison, M. N. & Scott, S. D., 1981. Sphalerite geobarometry in the Cu-Fe-Zn-S system. Econ. Geol. 76, 143-153.
- James, R. S., Grieve, R. A. & Pauk, L., 1978. The Petrology of cordierite-anthophyllite gneisses and associated mafic and pelitic gneisses at Manitouwadge, Ontario. Am. J. Sci. 278, 41–63.
- Jensen, L. S., 1976. A new cation plot for classifying subalkalic volcanic rocks. Miscellaneous paper 66. Canadian Ministry of Natural Resources, Division of Mines, Ontario.
- Johansson, A. & Rickard, D., 1985. Some new lead isotope determinations from Proterozoic sulfide ores of central Sweden. Mineral. Deposita 20, 1–7.
- Kähkönen, Y., 1987. Geochemistry and tectonomagmatic affinities of the metavolcanic rocks of the early Proterozoic Tampere Schist Belt, southern Finland. Precambrian Res. 35, 295-311.
- Kissin, S. A. & Owens, R. D., 1975. New data on stannite and related sulphide minerals. Can. Mineral. 13, 309.
- Kissin, S. A. & Scott, S. D., 1982. Phase relations involving pyrrhotite below 350 °C. Econ. Geol. 77, 1739–1754.
- Klau, W. & Large, E. D., 1980. Submarine exhalative Cu-Pb-Zn deposits: A discussion of their classification and metallogenesis. Geol. Jb. D40, Hanover, 13-58.
- Koark, H. J., 1969. Zur Altersstellung un Entstehung der Sulfiderze vom Typus Falun. Geol. Rundschau, 57, 123–146.
- Kojima, S. & Sugaki, A., 1984. Phase relations in the central portion of the Cu-Fe-Zn-S system between 800° and 500 °C. Mineral. Jour. 12, 15–28.

- Kojima, S. & Sugaki, A., 1985. Phase relations in the Cu-Fe-Zn-S system between 500 °C and 300 °C under hydrothermal conditions. Econ. Geol. 80, 158–172.
- Korsman, K., Hölttä, P., Hautala, T. & Wasenius, P., 1984. Metamorphism as an indicator of evolution and structure of the crust in eastern Finland. Geol. Surv. Finland, Bull. 328. 40 p.
- Kouvo, O., 1958. Radioactive age of some Finnish pre-Cambrian minerals. Bull. Comm. Geol. Finlande 182. 70 p.
- Kullerud, G. & Yoder, H. S., 1959. Pyrite stability relations in the Fe-S system. Econ. Geol. 54, 533-572.
- Lambert, I. B. & Sato, T., 1974. The Kuroko and associated ore deposits of Japan: A review of their features and metallogenesis. Econ. Geol. 69, 1215–1236.
- Large, D. E., 1980. Geological parameters associated with sediment-hosted, submarine exhalative Pb-Zn deposits: An empirical model for mineral exploration. Geol. Jb. D40, Hanover., 59–129.
- Large, R. R., 1977. Chemical evolution and zonation of massive sulfide deposits in volcanic terrains. Econ. Geol. 72, 549-572.
- Latvalahti, U., 1979. Cu-Zn-Pb ores in the Aijala- Orijärvi area, southwest Finland. Econ. Geol. 74, 1035–1059.
- Löfgren, C., 1979. Do leptites represent Precambrian island arc rocks ? Lithos 12, 159–165.
- Lundén, E., 1964. Malmbildningen på Attu, Storstrand. Unpublished M.Sc. Thesis, Åbo Akademi, 30 p.
- Mäkelä, M. & Tammenmaa, J., 1977. A system for precise sulfur isotope analysis by a small mass spectrometer. Report of Investigation No. 20, Geol. Surv. Finland. 22 p.
- McDonald, J. A., 1967. Metamorphism and its effects on sulphide assemblages. Mineral. Deposita 2. 200–220.
- Miller, W. J. & Craig, R. J., 1983. Tetrahedrite-tennantite series compositional variations in the Cofer Deposit, Mineral District, Virginia. Am. Mineral. 68, 227–234.
- Mitchell, A. H. G. & Bell, J. D., 1973. Island-arc evolution and related mineral deposits. J. Geol. 81, 381-405.
- Moh, G. H., 1986. Current ore petrology: Microscopy, Genesis, analyses and experimentation. Neues Jahrbuch Miner. Abh. 153, 245–324.
- Mookherjee, A., 1976. Ores and metamorphism: temporal and genetic relationships. *In* Handbook of stratabound and stratiform ore deposits, 4. ed. by Wolf, K. H., 203–260 Elsevier, Amsterdam.
- Mullen, D. E., 1983. MnO/TiO₂/P₂O₅: a minor element discriminant for basaltic rocks of oceanic environments and its implications for petrogenesis. Earth and Planetary Sci. Lett. 62, 53–62.
- Nold, J. L., 1983. The Holden Mine, a metamorphosed volcanogenic deposit in the Cascade range of Washington. Econ. Geol. 78, 944–953.
- Nurmi, P. A. & Haapala, I., 1986. The Proterozoic granitoids of Finland: granite types, metallogeny and relation to crustal evolution. Bull. Geol. Soc. Finland 58, Part 1, 203-233.
- Ohmoto, H., 1972. Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. Econ. Geol. 67,

551-579.

Ohmoto, H., 1986. Stable isotope geochemistry of ore deposits. In Stable isotopes in high temperature geological processes. Reviews in mineralogy 16, 491–559.

59

- Ohmoto, H. & Rye, R. O., 1979. Isotopes of sulfur and carbon. *In* Geochemistry of Hydrothermal Ore Deposits 2nd ed. ed. by H. L. Barnes, 509–567. John Wiley & Sons, New York.
- Ohmoto, H. & Skinner, B. J., 1983. The Kuroko and related volcanogenic massive sulfide deposits: Introduction and summary of new findings. Econ. Geol. Monograph 5, 1–8.
- Ohmoto, H., Mizukami, M., Drummond, S. E., Eldrije, C. S., Pisutha-Arnond, U & Lenagh, T. C., 1983. Chemical processes of Kuroko formation. Econ. Geol. Monograph 5, 570-604.
- Ojakangas, R. W., 1986. An early Proterozoic metagraywacke-slate turbidite sequence: The Tampere schist belt, southwestern Finland. Bull. Geol. Soc. Finland 58, 241–261.
- Orlova, Z. V., 1956. Collection of chemical analyses of ores and minerals from mineral deposits in the northeastern USSR – Trudy Vses. Inst. Magadan 2, 76, in Am. Mineral. 43, 1222–1223.
- Osadechii, E. G., 1986. Solid solutions and phase relations in the system Cu₂SnS₃-ZnS-CdS at 850° and 700 °C. Neues Jahrbuch Miner. Abh. 155. 23–38.
- Patchett, P. J. & Kouvo, O., 1986. Origin of continental crust of 1.9–1.7 Ga age: Nd isotopes and U-Pb zircon ages in the Svecokarelian Terrain of South Finland, Contrib. Mineral. Petrol. 92, 1–12.
- Patchett, P. J., Gorbatschev, R., Kouvo, O. & Todt, W., 1984. Origin of continental crust of 1.9–1.7 Ga age: Nd isotopes in the Svecokarelian terrain of Sweden and Finland. GSA meeting 1984. Abstract no. 47262.
- Patchett, P. J., Gorbatschev, R. and Todt, W., 1987. Origin of continental crust of 1.9–1.7 Ga age: Nd isotopes in the Svecofennian orogenic terrains of Sweden. Precambrian Res., 35, 145–160.
- Pearce, J. A. & Cann, J. R., 1973. Tectonic setting of basic volcanic rocks determined using trace element analyses. Earth Plan. Sci. Lett., 19, 290-300.
- Pehrman, G., 1927. Om en titanjärnmalm och omgivande bergarter på Attu landet in sydvästra Finland. Acta Acad. Aboensis, Math. Phys. 5, 5–81.
- Pehrman, G., 1932. Über eine Sulfidlagerstätte im südwestlichen Finnland. Acta Acad. Aboensis Math. Phys. 6, 5-52.
- Perkins, D. III & Chipera, S. J., 1985. Garnet-orthopyroxene-plagioclase-quartz barometry: refinement and application to English River subprovince and the Minnesota River Valley. Contrib. Mineral. Petrol. 89, 69-80.
- Petersen, E. U., 1986. Tin in volcanogenic massive sulfide deposits: An example from the Geo Mine, Manitouwadge District, Ontario, Canada. Econ. Geol. 81, 323-342.
- Plimer, I. R., 1978. Proximal and distal stratabound ore deposits. Mineral. Deposita 13, 345–353.

60

- Plimer, I. R. & Finlow-Bates, T., 1978. Relationship between primary iron sulphide species, sulphur source, depth of formation and age of submarine exhalative sulphide deposits. Mineral. Deposita 13, 399-410.
- Ramdohr, P., 1980. The ore minerals and their intergrowths. Second Ed. Pergamon Press, Oxford. 1174 p.
- Rauhamäki, E. & Karppanen, T., 1982. Attu-perussuunnitelma, 2. Geologia. Internal report, Outokumpu Oy, Kaivosteknillinen ryhmä (In Finnish). 1–9.
- Rickard, D.T., 1978. The Svecokarelian anomalous ore lead line. Geol. Fören. Stockh. Förh. 100, 19–29.
- Riley, J. F., 1974. The tetrahedrite-freibergite series, with reference to the Mount Isa Pb-Zn-Ag ore body. Mineral. Deposita 9, 117–124.
- Rose, A. W., Barnes, H. L., Burnham, C. W. & Ohmoto, H., 1977. Report on workshops on Research Frontiers in Exploration for Non-Renewable Resources Research and Technology: Washington, D. C., Natl. Sci. Found., 164 p.
- Rouhunkoski, P., 1968. On the geology and geochemistry of the Vihanti zinc ore deposit, Finland. Bull. Comm. Geol. Finlande 236. 121 p.
- Rye, R. O. & Ohmoto, H., 1974. Sulfur and carbon isotopes in ore genesis: A review. Econ. Geol. 69, 826–842.
- Sack, R. O. & Loucks R. R., 1985. Thermodynamic properties of tetrahedrite-tennantites: constraints on the interdependence of the Ag=Cu, Fe=Zn, Cu=Fe, and As=Sb exchange reactions. Am. Mineral. 70, 1270– 1289.
- Sangameshwar, S. R. & Marshall, B., 1980. Sphalerite geobarometry of deformed sulphide ores from the C. S. A. mine, Cobar, Australia. Mineral. Deposita 15, 305–314.
- Sangster, D. F., 1972. Precambrian volcanogenic massive sulfide deposits in Canada: a review – Pap. Geol. Surv. Canada, 72–22, 44 p. Ottawa.
- Sangster, D. F., 1976. Sulphur and lead isotopes in stratabound deposits. In Handbook of stratabound and stratiform ore deposits 2. ed. by Wolf, K.H. 219–266, Elsevier, Amsterdam.
- Sangster, D. F. & Scott, S. D., 1976. Precambrian stratabound massive Cu-Zn-Pb sulfide ores of North America. In Handbook of stratabound and stratiform ore deposits 6. ed. by Wolf, K. H. 129–222, Elsevier, Amsterdam.
- Schellekens, J. H., 1976. Report on the geology of the island Attu (northern part), southwest Finland. M. A. thesis, Free University, Amsterdam. 59 p.
- Schellekens, J. H., 1980. Application of the garnet-cordierite geothermometer and geobarometer to gneisses of Attu, SW Finland; an indication of P and T conditions of the lower granulite facies. N. Jb. Miner. Mh.,1, 11-19.
- Schermerhorn, L. J. G., 1978. Epigenetic magnesium metasomatism or syngenetic chlorite metamorphism at Falun and Orijrvi. Inst. Mining Metallurgy Trans. 87. 162–167.
- Schippers, M., 1983. The cordierite-anthophyllite rocks of Orijärvi, Finland. Internal report, Free University of Amsterdam, 53 p.
- Schreurs, J., 1985a. The West Uusimaa low pressure thermal dome, sw Finland. Doctoral thesis, Free University

of Amsterdam, 177 p.

- Schreurs, J., 1985b. Prograde metamorphism of metapelites, garnet-biotite thermometry and prograde changes of biotite chemistry in high grade rocks of West Uusimaa, southwest Finland. Lithos 18, 69–80.
- Schreurs, J. & Westra, L., 1985. Cordierite-orthopyroxene rocks: the granulite facies equivalents of the Orijärvi cordierite-anthophyllite rocks in West Uusimaa, southwest Finland. Lithos 18, 215–228.
- Scott, S. D., 1973. Experimental calibration of the sphalerite geobarometer. Econ. Geol. 68, 466–474.
- Scott, S. D., 1976. Application of the sphalerite geobarometer to regionally metamorphosed terrains. Am. Mineral. 61, 661–670.
- Scott, S. D. & Barnes, H. L., 1971. Sphalerite geothermometry and geobarometry. Econ. Geol. 66, 653-669.
- Scott, S. D., Both, R. A. & Kissin, S. A., 1977. Sulfide petrology of the Broken Hill region, New South Wales. Econ. Geol. 72, 1410–1425.
- Secord, K. T. & Brown, P. E., 1986. Geology and geochemistry of the Ore Hill Zn-Pb-Cu massive sulfide deposit, Warren, New Hampshire. Econ. Geol. 81, 371–387.
- Sen, S. K. & Bhattacharya, A., 1984. An orthopyroxenegarnet thermometer and its application to the Madras charnockites. Contrib. Mineral. Petrol. 88, 64–71.
- Simonen. A., 1960. Plutonic rocks of the Svecofennides in Finland. Bull. Comm. géol. Finlande 189, 101 p.
- Simonen, A., 1980. The Precambrian in Finland. Geol. Surv. Finland, Bull. 304, 58 p.
- Solomon, M., 1976. 'Volcanic' massive sulphide deposits and their host rocks- A review and explanation. In Handbook of strata-bound and stratiform ore deposits 6. ed. by Wolf, K. H. 21–54, Elsevier, Amsterdam.
- Spear, F., 1980. NaSi = CalAl exchange equilibria between plagioclase and amphiboles: an empirical model. Contrib. Mineral. Petrol. 72, 33-41.
- Spear, F. S. & Schumacher, J. C., 1982. Origin of cordierite-anthophyllite rocks. *In* Amphiboles, Petrology and experimental phase relations. ed. by Vebler, D. R. and Ribbe, P. H. Reviews in Mineralogy 9B. Min. Soc. Am.
- Staal, C. R. van & Williams, P. F., 1983. Evolution of Svecofennian-mantled gneiss dome in SW Finland, with evidence for thrusting. Precambrian Res., 21, 101–128.
- Stacey, J. S. & Kramers, J. D., 1975. Approximation of terrestrial lead isotope evolution by a two-stage model. Earth Planet. Sci. Lett. 26, 207–221.
- Stanton, R. L., 1972. Ore Petrology. Mcgraw-Hill Book Company, New York. 713 p.
- Stigzelius, H., 1986. Mineral exploration and geological surveys in Finland before 1886. Geol. Surv. Finland, Bull. 336, 9–19.
- Sugaki, A., Shima, H., Kitakaze, A. & Harada, H., 1975. Isothermal phase relations in the system Cu-Fe-S under hydrothermal conditions at 350 °C and 300 °C. Econ. Geol. 70, 806-823.
- Sugaki, A., Kitakaze, A. and Kojima, S. 1987. Bulk composition of intimate intergrowths of chalcopyrite and sphalerite and their genetic implications. Mineral. Deposita 22, 26–32.

- Sun, S. S. 1980. Lead isotopic study of young volcanic rocks from mid-ocean ridges, ocean islands and island arcs. Phil. Trans. R. Soc. Lond. A 297, 409-445.
- Sundblad, K., Zachrisson, E., Smeds, S.-A., Berglund, S. & Ålinder, C., 1984. Sphalerite geobarometry and arsenopyrite geothermometry applied to metamorphosed sulfide ores in the Swedish Caledonides. Econ. Geol. 79, 1660-1668.
- Susaka, N.J. & Crerar, D. A., 1982. Factors controlling mineral zoning in hydrothermal ore deposits. Econ. Geol. 77, 476–482.
- Törnroos, R., 1982. Sphalerite geobarometry of some metamorphosed sulphide ore deposits in Finland. Geol. Surv. Finland, Bull. 323. 42p.
- Toulmin, P. & Barton, P. B. Jr, 1964. A thermodynamic study of pyrite and pyrrhotite. Geochim. Cosmochin. Acta 28, 641-671.
- Treloar, P. J., Koistinen, T. J. & Bowes, R. D., 1981. Metamorphic development of cordierite-amphibole rocks and mica schists in the vicinity of the Outokumpu ore deposit, Finland. Trans R Soc Edinburg Earth Sc, 72, 201–215.
- Tucker, M. E., 1982. Precambrian dolomites: petrographic and isotopic evidence that they differ from Phanerozoic dolomites. Geology 10, 7–12.
- Tuominen, H. V. & Mikkola, T., 1950. Metamorphic Mg-Fe enrichment in the Orijrvi region as related to folding. Bull. Comm. Finlande 150, 67-92.
- Vaasjoki, M., 1977. Rapakivi granites and other postorogenic rocks of Finland: their age and lead isotopic composition of certain associated galena mineralizations. Geol. Surv. Finland, Bull. 294. 64 p.
- Vaasjoki, M., 1981. The lead isotopic composition of some Finnish galenas. Geol. Surv. Finland, Bull. 316, 30 p.

- Vaasjoki, O., 1956. A comparison of the minor base metal contents of some Finnish galenas. Bull. Comm. Finlande 172, 47–53.
- Vallance, T. G., 1967. Mafic rock alteration and isochemical development of some cordierite-anthophyllite rocks. Jour. Petrol. 8, 84–96.
- Verhoef, P. N. W. & Dietvorst, E. J. L., 1980. Structural analysis of differentiated schists and gneisses in the Taalintehdas area, Kemiö island, SW Finland. Bull. Geol. Soc. Finland 52, 147–164.
- Vivallo, W., 1984. The geology and origin of Zn-Pb-Cu sulfide deposit Garpenberg, central Sweden. Doctoral Thesis, Department of Geology, Stockholm University.
- Vokes, F. M., 1969. A review of the metamorphism of sulphide deposits. Earth-Sci. Rev. 5, 99-143.
- Vokes, F. M., 1976. Caledonian massive sulfide deposits in Scandinavia. A comparative review. *In* Handbook of stratabound and stratiform ore deposits, 6. ed. by Wolf, K. H., 79–127. Elsevier, Amsterdam.
- Weaver, B. L. & Tarney, J., 1980. Continental crust composition and nature of the lower crust: constraints from mantle Nd-Sr isotope correlation. Nature 286, 342–346.
- Whitmore, D. R. E., 1969. Geology of the Coronation copper deposit. Geol. Survey Canada Paper 68 – 5, 37–54.
- Wiggins, L. B. & Craig, J. R., 1980. Reconnaissance of the Cu-Fe-Zn-S system: Sphalerite phase relationships. Econ. Geol. 75, 742–751.
- Winkler, G.F. H., 1979. Petrogenesis of metamorphic rocks. Fifth Edition. Springer-Verlag, Berlin. 348 p.
- Wolter, H. U. & Seifert, F., 1984. Mineralogy and genesis of cordierite-anthophyllite rocks from the sulfide deposit of Falun, Sweden. Lithos 17, 147-152.

APPENDIX

Chemical analyses of the tremolite-quartz rock, cordierite-anthophyllite rocks, amphibolites and mica gneisses from Attu in wt.% if not otherwise stated.

Sample										
No.	1	2	3	4	5	6	7	8	9	10
SiO ₂	83.89	84.41	90.00	69.17	80.73	96.08	81.16	79.14	73.68	76.52
Al ₂ O ₃	0.23	0.20	0.07	0.34	0.11	0.04	0.23	0.14	0.09	0.11
MgO	1.66	1.66	1.53	0.70	4.41	0.41	10.14	7.75	3.98	6.78
CaO	1.90	1.68	1.31	0.67	5.24	0.41	4.15	4.05	2.18	7.10
Na ₂ O	0.36	0.53	0.03	1.36	0.15	0.09	0.12	0.09	0.37	0.29
K ₂ O	0.01	0.01	0.01	0.02	0.00	0.02	0.03	0.03	0.03	0.01
FeO,	1.84	1.78	0.66	3.42	2.24	0.96	2.47	2.25	0.80	2.40
MnÓ	0.05	0.05	0.03	0.07	0.09	0.02	0.12	0.05	0.12	0.07
TiO ₂	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.00
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.11	0.15	0.22	0.05	0.18	0.11	0.07	0.07	0.22	0.18
S	4.21	3.92	3.10	10.39	2.87	0.66	0.84	2.67	6.78	2.36
Zn	1.83	2.49	0.28	7.87	0.62	0.57	0.30	0.37	1.95	1.23
Pb	0.69	0.57	0.15	0.43	0.65	0.07	0.19	1.01	0.48	0.40
Cu	0.17	0.13	0.06	0.15	0.15	0.01	0.04	0.09	0.23	0.14
TOTAL	99.41	99.20	99.59	98.11	99.50	99.42	99.73	99.81	99.81	99.53
Trace elemen	nts in ppm									
Cr	310	240	240	230	320	280	110	130	140	210
Zr	10	10	10	10	10	10	10	10	10	10
Ni	20	20	20	30	10	20	10	10	20	10
Ba	20	20	30	20	30	0	30	250	20	10
Sn	10	10	10	20	10	10	10	20	10	10
Sr	10	10	10	20	10	10	0	50	10	10
Rb	10	0	0	10	10	0	0	10	10	0
V	10	10	0	0	0	10	0	10	0	10
Cl	0	0	0	0	0	0	0	0	0	0
Ce	0	0	10	0	10	20	10	10	0	0
Cs	10	20	0	30	30	0	0	10	10	10
Ta	20	20	30	30	10	30	10	10	10	10
La	20	20	30	30	10	30	10	10	10	10
Th	20	0	0	0	30	0	0	30	0	0
U	0	0	0	0	0	0	0	0	0	0
Y	0	0	0	0	0	0	0	0	0	0
$FeO_t = total$	liron									
1. 1-LSH-85	5	2. 2-LSH	-85	3. 4-LS	SH-85	4. A	ttu-11/92.00	5	5. 5-LSH-8	5
6. 6-LSH-85	;	7. 8-LSH	-85	8. Attu	1-9/98.00	9. A	ttu-19/72.00	10). Attu-22/	107.50

Table (i). Chemical analyses of the tremolite-quartz rock from Attu

Sample							_	0	0		
No.	1	2	3	4	5	6	7	8	9	10	11
wt.%											
SiO ₂	59.38	60.62	47.82	58.99	55.24	50.06	48.60	52.42	44.62	57.82	50.11
Al_2O_3	15.42	16.52	19.12	15.15	16.21	19.26	17.00	18.52	18.88	16.51	16.75
MgO	9.25	8.76	13.01	9.59	10.21	13.85	11.96	10.31	12.55	10.84	12.85
CaO	0.36	0.21	0.36	0.17	0.53	0.41	0.25	0.15	0.37	0.18	0.19
Na ₂ O	0.25	0.16	0.45	0.38	0.97	0.49	0.58	0.72	0.45	0.42	0.54
K ₂ O	1.65	0.75	2.43	1.21	2.12	2.11	1.77	2.00	2.86	1.52	2.34
FeO	8.25	8.81	11.21	9.24	10.03	9.98	11.86	12.68	12.12	10.43	12.00
MnO	0.21	0.23	0.04	0.08	0.11	0.09	0.08	0.38	0.42	0.08	0.12
TiO ₂	0.23	0.34	0.57	0.37	0.62	0.72	0.56	0.43	0.83	0.78	0.68
P_2O_5	0.01	0.00	0.02	0.03	0.04	0.00	0.02	0.01	0.00	0.02	0.00
CO ₂	0.10	0.12	0.12	0.08	0.23	0.07	0.32	0.22	0.01	0.21	0.08
S	2.21	1.65	2.02	1.74	1.53	0.97	2.99	2.21	0.87	1.01	1.11
Zn	1.11	0.96	0.81	0.12	0.67	0.20	0.86	0.75	1.02	0.08	0.54
Pb	0.65	0.43	0.41	0.52	0.21	0.00	0.32	0.32	0.64	0.00	0.15
Cu	0.70	0.23	0.53	0.54	0.43	0.14	0.21	0.25	0.54	0.00	0.27
TOTAL	99.69	99.79	98.95	98.21	99.56	98.35	98.38	99.55	98.30	99.76	98.63
Trace elen	nents in p	pm									
Cr	90	200	215	150	180	220	120	179	110	217	200
Zr	10	20	10	25	20	10	22	20	20	10	15
Ni	30	25	10	20	10	10	25	30	10	15	20
Ba	35	40	35	45	40	30	45	25	30	30	35
Sn	150	100	200	100	110	115	90	95	125	85	105
Sr	15	10	14	10	20	14	10	10	15	10	12
Rb	25	15	10	20	30	15	15	20	10	15	25
V	10	10	15	10	15	15	10	15	20	10	10
Cl	0	0	0	0	0	0	0	0	0	0	0
Ce	25	20	25	15	20	20	15	25	20	20	15
Cs	10	10	10	15	10	15	10	15	10	10	15
Ta	10	10	10	10	10	10	10	10	10	10	10
La	20	20	25	20	25	15	20	20	10	15	15
Th	5	10	10	0	10	5	5	10	0	5	0
U	5	0	5	5	0	10	0	0	5	10	10
Y	0	0	0	0	0	0	0	0	0	0	0
E O	1										

App. contd. Geological Survey of Finland, Bulletin 341

Table (ii). Chemical analyses of the cordierite-anthophyllite rocks from Attu

 $FeO_t = total$

1. 11-LSH-85	2. 13-LSH-85	3. 14-LSH-85	4. 19-LSH-85	5. Attu-17/82.00
6. Attu-19/113.80	7. Attu-20/69.50	8. Attu-21/112.68	9. Attu-22/138.80	10. Attu-101/23.19
11. Attu-303/86.00				

Comm10												
No.	1	2	3	4	5	6	7	8	9	10	11	12
wt.%												
SiO ₂	47.89	50.42	61.14	53.81	54.03	60.91	49.9	52.62	57.50	57.50	61.76	59.05
Al ₂ O ₃	19.67	15.98	9.57	16.21	16.65	13.12	18.96	15.98	17.94	16.01	12.69	15.86
MgO	4.42	4.53	4.25	6.42	4.55	4.47	4.54	5.86	2.16	3.12	2.98	3.33
CaO	10.27	9.65	9.89	8.30	8.59	2.27	9.89	8.12	8.21	9.03	3.17	7.98
Na ₂ O	2.01	2.45	0.08	2.58	1.76	1.65	2.34	2.58	2.64	2.21	2.45	2.34
K ₂ O	1.47	1.38	0.82	1.37	1.10	2.46	1.71	1.63	0.96	0.71	1.79	0.82
FeO.	11.95	10.99	11.39	8.11	10.60	12.45	11.08	8.12	8.31	8.00	10.64	7.49
MnÒ	0.15	0.16	0.13	0.11	0.12	0.10	0.17	0.14	0.14	0.14	0.13	0.15
TiO ₂	0.27	0.58	0.21	0.71	0.42	0.31	0.37	0.42	0.59	0.34	0.45	0.38
P_2O_5	0.25	0.14	0.11	0.28	0.14	0.07	0.07	0.08	0.21	0.07	0.36	0.10
CO_2	0.11	0.18	0.26	0.15	0.04	0.11	0.04	0.18	0.11	0.11	0.26	0.18
S	0.04	1.78	0.38	0.42	0.60	0.29	0.03	0.02	0.04	0.04	0.01	0.04
Zn	0.02	0.11	0.03	0.05	0.02	0.04	0.02	0.01	0.03	0.02	0.01	0.02
Pb	0.00	0.21	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.13	0.01	0.02	0.01	0.03	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	98.52	98.69	98.28	98.54	98.68	98.19	99.02	95.76	98.84	97.30	96.70	98.11
Trace element	ts in ppm											
Cr	60	30	120	28	120	160	120	160	110	130	100	120
Zr	20	10	100	110	50	230	70	40	60	100	70	80
Ni	20	10	20	100	20	40	40	30	20	10	20	30
Ba	110	10	170	400	120	360	270	140	160	570	180	170
Sn	20	10	10	20	20	20	10	10	20	20	10	20
Sr	150	20	30	420	180	70	300	290	190	140	180	160
Rb	80	0	30	40	40	110	20	10	20	100	10	20
V	340	30	80	210	260	80	230	190	180	40	160	150
Cl	90	0	0	30	70	180	0	0	60	280	0	30
Ce	0	10	20	20	0	40	20	10	80	80	20	30
Cs	30	10	0	20	20	20	0	0	10	10	20	20
Ta	0	0	10	0	10	10	0	10	10	0	10	0
La	0	0	0	0	0	0	0	0	0	0	0	0
Th	0	0	10	0	10	20	0	0	10	0	0	10
U	0	10	10	0	0	0	0	0	0	0	0	0
Y	0	0	0	10	20	10	0	0	0	50	10	0

App. contd. Geological Survey of Finland, Bulletin 341

Table (iii). Chemical analyses of the amphibolites from Attu

 $FeO_t = total$

1. 43-LSH-852. Attu-10/21.503. Attu-121/272.804. Attu-301/78.505. Attu-303/110.006. Attu-115/207.807. 57-LSH-858. 38-LSH-859. 52-LSH-8510. 46-LSH-8511. 28-LSH-8512. 41-LSH-85

1 76.22 12.06 1.45 2.35 2.45 1.85 2.75	2 75.30 12.65 1.58 1.01	3 74.32 11.66 1.77	4 75.24 12.18	69.77	6	7	67.32
76.22 12.06 1.45 2.35 2.45 1.85	75.30 12.65 1.58 1.01	74.32 11.66 1.77	75.24 12.18	69.77	72.25	71.34	67 32
76.22 12.06 1.45 2.35 2.45 1.85	75.30 12.65 1.58 1.01	74.32 11.66 1.77	75.24 12.18	69.77	72.25	71.34	67 32
12.06 1.45 2.35 2.45 1.85	12.65 1.58 1.01	11.66 1.77	12.18	1100			01.52
1.45 2.35 2.45 1.85	1.58 1.01	1.77		14.89	13.60	14.25	15.17
2.35 2.45 1.85	1.01		2.00	2.13	2.55	1.32	3.98
2.45		0.81	0.77	2.45	1.11	0.99	2.21
1.85	2.07	2.21	1.38	2.74	2.11	2.99	3.65
2 70	3.16	2.11	1.69	0.77	1.55	3.21	1.31
2.19	3.04	3.27	4.28	4.54	4.88	3.21	4.11
0.02	0.09	0.05	0.11	0.04	0.06	0.06	0.12
0.09	0.02	0.12	0.49	0.14	0.23	0.05	0.13
0.02	0.02	0.02	0.01	0.03	0.02	0.02	0.03
0.07	0.07	0.07	0.03	0.23	0.14	0.15	0.08
0.04	0.02	0.02	0.03	0.02	0.03	0.04	0.03
0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
99.32	99.04	96.44	98.22	98.76	98.55	97.65	98.15
s in ppm							
110	110	100	90	120	130	120	110
270	190	220	270	190	250	200	220
10	20	10	20	20	10	20	20
400	310	520	550	760	430	450	360
10	10	0	10	10	10	10	10
90	100	60	60	250	40	110	102
50	90	90	90	70	130	30	80
20	20	10	10	60	10	10	10
0	0	0	0	0	0	0	0
70	40	70	60	30	40	60	50
20	10	20	20	20	10	30	20
10	0	20	10	10	10	10	20
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0
10	10	0	0	0	0	0	0
10	10	50	60	10	60	30	20
	0.02 0.09 0.02 0.07 0.04 0.02 0.00 0.00 99.32 s in ppm 110 270 10 400 10 90 50 20 0 70 20 10 0 10 10 10 10 10 10 10 10	0.02 0.02 0.02 0.02 0.07 0.07 0.04 0.02 0.02 0.01 0.00 0.00 0.01 0.00 0.02 0.01 0.00 0.00 99.32 99.04 s in ppm 110 110 110 270 190 10 20 400 310 10 10 90 100 50 90 20 20 0 0 70 40 20 10 10 0 0 0 10 10 10 10 10 10 10 10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table (iv). Chemical analyses of the mica gneisses from Attu

1. 27-LSH-852. 24-LSH-853. 32-LSH-854. 22-LSH-855. 15-LSH-856. 27-LSH-857. 21-LSH-858. Attu-17/61.80



Tätä julkaisua myy

VALTION PAINATUSKESKUS MARKKINOINTIOSASTO

Postimyynti

PL 516 00101 HELSINKI 10 Puh. 90-539 011

Kirjakauppa

Annankatu 44 00100 HELSINKI 10 Puh. 90-173 41

Denna publikation säljes av

STATENS TRYCKERICENTRAL MARKNADSFÖRINGSAVDELNINGEN

Postförsäljning

PB 516 00101 HELSINGFORS 10 Tel. 90-539 011

Bokhandel

Annegatan 44 00100 HELSINGFORS 10 Tel. 90-173 41

This publication can be obtained from

GOVERNMENT PRINTING CENTRE MARKETING DEPARTMENT

Bookshop Annankatu 44 00100 HELSINKI 10 Phone 90-173 41

Orders from abroad: AKATEEMINEN KIRJAKAUPPA Keskuskatu 1 SF-00100 Helsinki 10

> ISBN 951-690-269-3 ISSN 0367-522X