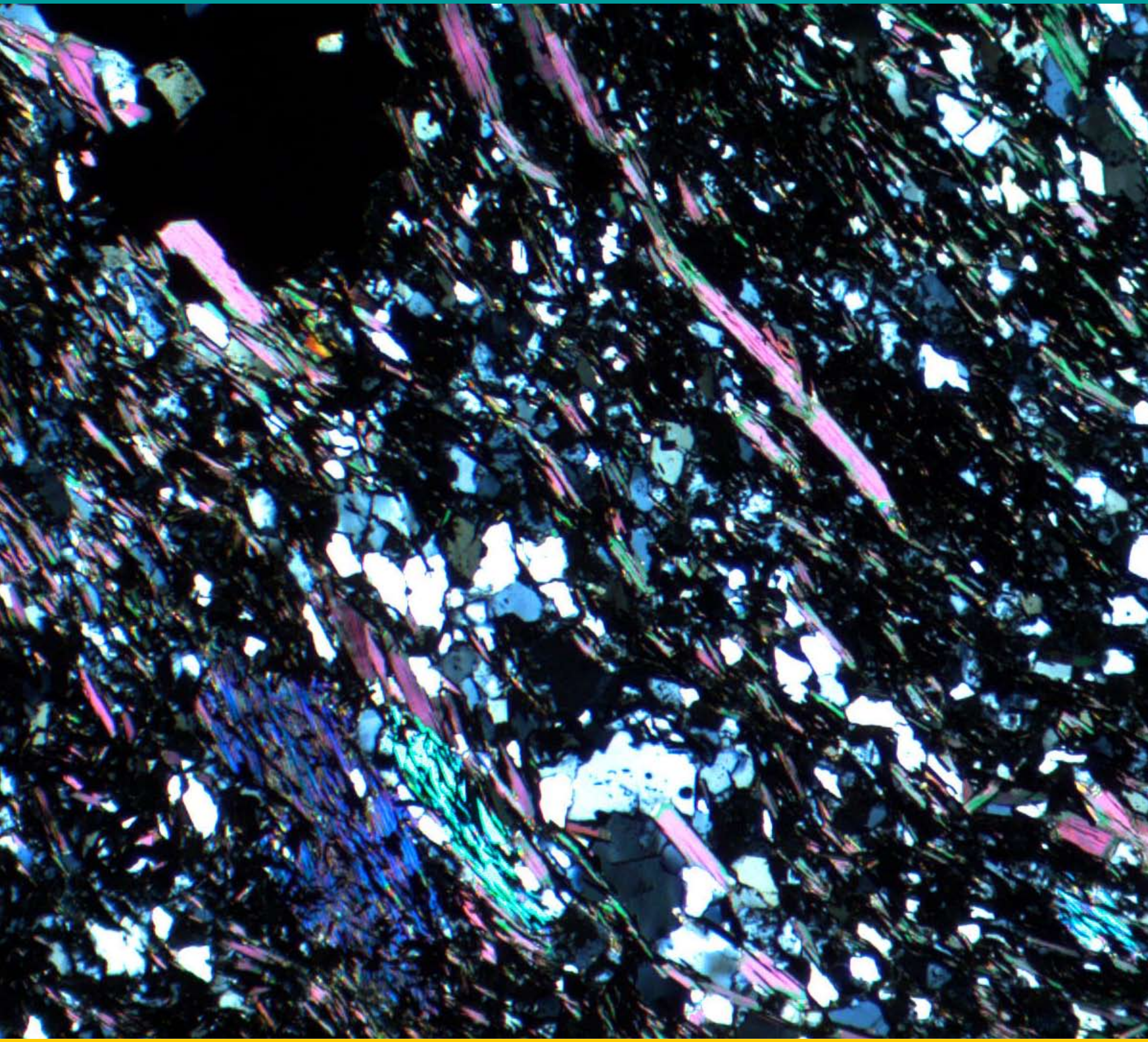
GEOLOGICAL SURVEY OF FINLAND

Report of Investigation 173

2008



Chemical composition of metamorphosed black shale and carbonaceous metasedimentary rocks at selected targets in the Vihanti area, western Finland

GTK

Kaj Västi

GEOLOGIAN TUTKIMUSKESKUS

Tutkimusraportti 173

GEOLOGICAL SURVEY OF FINLAND

Report of Investigation 173

Kaj Västi

CHEMICAL COMPOSITION OF METAMORPHOSED BLACK SHALE AND CARBONACEOUS METASEDIMENTARY ROCKS AT SELECTED TARGETS IN THE VIHANTI AREA, WESTERN FINLAND

Espoo 2008

Västi, K. 2008. Chemical composition of metamorphosed black shale and carbonaceous metasedimentary rocks at selected targets in the Vihanti area, western Finland, *Geological Survey of Finland, Report of Investigation 173*, 22 pages, 6 figures and 4 tables.

Altogether 645 drill core samples, including 272 black schists (in this study *"black schist"* is used synonymously with *"metamorphosed black shale"*) from 10 exploration targets in the Vihanti area, western Finland, were selected for chemical analyses. Black schist formations are located within the Paleoproterozoic Svecofennian supracrustal sequences, intruded by syn- and late-orogenic plutonic rocks. The lower part of the supracrustal sequence is dominated by migmatitic mica gneisses, whereas the upper part is characterized by volcaniclastic metasedimentary and metavolcanic rocks. Most black schist formations are related to the migmatitic lower part of the supracrustal sequence. Three deposits (Kenkisuo, Mari and Häkkilänpalo), however, are in close association with volcanic or volcaniclastic sedimentary rocks.

Black schists vary greatly in graphitic carbon and sulphur concentrations, the range being 1% – 32% and 1.3% – 18%, respectively. Median C and S concentrations for 9 black schist formations vary from 1.9% to 14.7%, and from 3.4% to 8.5%, respectively. Trace metals (Co, Cu, Pb, Zn, Mo, Ni, V, Cr, U) typically enriched in black schists show rather similar concentrations compared to other black schist occurrences in Ostrobothnia and eastern Finland, but notably higher values compared to the average North American shale. Median Co, Cu, Pb and Zn concentrations vary between 16 – 52 ppm, 121 – 841 ppm, 12 – 194 ppm and 188 – 2,630 ppm, respectively. V, Ni and Mo, also displaying strong or good correlation with C and S, show median concentrations between 200 – 1,090 ppm, 149 – 631 ppm and 6 -160 ppm, respectively. Median Cr contents vary from 27 to 189 ppm, and U contents from 14 to 32 ppm.

C/S ratios, as well as V/(V+Ni) and V/Cr ratios, were used in determining paleoenvironmental conditions for accumulation of organic-rich mud. Median C/S ratios for individual black schist formations are mostly <1 and always <3. V/(V+Ni) ratios vary typically between 0.6 and 0.7, the lowest value being 0.4. C/S ratios less than 1 and V/(V+Ni) ratios between 0.6 and 0.7 indicate anoxic conditions for the black schist accumulation. V/Cr ratios between 2.4 and 19.4 further support anoxic depositional environments for black shale accumulation. However, because of the low metal contents, small volume, and minor or non-existent addition of hydrothermal metalliferous solutions into accumulated black shales, interest in black shale is of a scientific rather than economic nature.

Key words (GeoRef Thesaurus, AGI): metasedimentary rocks, black schists, geochemistry, chemical composition, carbon, sulfur, trace metals, depositional environment, Proterozoic, Paleoproterozoic, Vihanti, Finland

Kaj Västi
Geological Survey of Finland
P. O. BOX 1237
FI-70211 Kuopio, Finland

E-mail: kaj.vasti@gtk.fi

ISBN 978-952-217-051-4 (PDF)
ISSN 0781-4240

Vammalan Kirjapaino Oy 2008

Västi, K. 2008. Chemical composition of metamorphosed black shale and carbonaceous metasedimentary rocks at selected targets in the Vihanti area, western Finland, *Geologian tutkimuskeskus, Tutkimusraportti 173*, 22 sivua, 6 kuvaa ja 4 taulukkoa.

Kymmenestä mustaliuskekerrostumia sisältävästä malmitutkimuskohteesta Vihannin ympäristössä kerättiin yhteensä 645 kairansydännäytettä analysoitaviksi. Näytteistä 272 oli mustaliuskeita. Mustaliuskeet liittyvät svekofennisiin liuskemuodostumiin, joita syn- tai myöhäiskinemaattiset syväkivet leikkaavat. Liuskemuodostumien alaosa koostuu pääasiassa migmatiittisista kiillegneisseistä. Liuskemuodostumien yläosassa vulkaniklastiset metasedimentit ja metavulkaniitit ovat yleisiä. Suurin osa mustaliuske-esiintymistä liittyy liuskemuodostumien migmatiittiseen alaosaan. Kolmessa kohteessa – Kenkisuolla, Marissa ja Häkkilänpalossa – mustaliuskeet esiintyvät kuitenkin vulkaniittien tai vulkaniklastisten sedimenttikivien yhteydessä.

Mustaliuskeiden (grafiittinen) hiili ja rikkipitoisuus vaihtelevat paljon: hiilipitoisuus on 1–32 % ja rikkipitoisuus 1,3–18 %. Yhdeksän mustaliuske-esiintymän mediaanihiilipitoisuus vaihtelee välillä 1,9–14,7 % kun taas mediaanirikkipitoisuus on 3,4–8,5 %. Mustaliuskeisiin tyypillisesti rikastuneiden hivenmetallien (Co, Cu, Pb, Zn, Mo, Ni, V, Cr, U) pitoisuudet ovat jokseenkin samanlaiset verrattuna muihin mustaliuskeisiin Pohjanmaalla ja Itä-Suomessa, mutta huomattavasti suuremmat verrattuna tavalliseen pohjoisamerikkalaiseen liuskeeseen. Koboltin, kuparin, lyijyn ja sinkin mediaanipitoisuudet vaihtelevat vastaavasti välillä 16–52 ppm, 121–841 ppm, 12–194 ppm ja 188–2630 ppm. Hiilen ja rikin kanssa hyvin korreloivien vanadiinin, nikkelin ja molybdeenin mediaanipitoisuudet puolestaan vaihtelevat välillä 200–1090 ppm, 149–631 ppm ja 6–160 ppm. Kromin mediaanipitoisuus on 27–189 ppm ja uraanin 14–32 ppm.

Mustaliuskeiden kerrostumisympäristössä vallinneiden olosuhteiden määrittämisessä käytettiin C/S-, V/(V+Ni)- ja V/Cr-suhteita. Mustaliuskemuodostumien mediaani-C/S -suhteet ovat useimmiten <1 ja aina <3. V/(V+Ni)-suhde vaihtelee tavallisesti välillä 0,6–0,7 alhaisimman arvon ollessa 0,4. Alhaisten C/S- ja korkeiden V/(V+Ni)-suhteiden perusteella mustaliuskeet kerrostuivat hapettomissa olosuhteissa. Lisätukea tälle olettamukselle antaa korkea (2,4 – 19,4) V/Cr-suhde. Koska tutkittujen mustaliuske-esiintymien metallipitoisuudet ja volyymi jäävät pieniksi, on niillä kuitenkin enemmän tieteellistä kuin taloudellista mielenkiintoa.

Asiasanat (Geosanasto, GTK): metasedimentit, mustaliuskeet, geokemia, kemiallinen koostumus, hiili, rikki, hivenmetallit, kerrostumisympäristö, proterotsooinen, paleoproterotsooinen, Vihanti, Suomi

Kaj Västi
Geologian tutkimuskeskus
PL 1237
FI-70211 Kuopio

Sähköposti: kaj.vasti@gtk.fi

CONTENTS

1. INTRODUCTION

This study is closely related to the Vihanti-Pyhäsalmi project (stage 1), which commenced at the beginning of 1992 and finished in 1997. Although the emphasis of the field activity at the early stage was on bedrock mapping, exploration activities also started within the first year. In the initial stage, prospecting was targeted in the northwestern part of the Vihanti-Pyhäsalmi Zn-Cu-Pb province. Exploration targets were chosen mainly on the basis of geophysical (electromagnetic, magnetic) anomalies and/or mineralized boulders found by professional or amateur prospectors. For practical purposes, all targets lack outcrops and only a couple have been investigated, in part by the mining company of Outokumpu. Geophysical ground survey measurements and geochemical till samplings with percussion drilling machines were conducted across most targets before drilling began.

There are very few earlier studies of the chemistry of the black schists of this area. Rouhunkoski (1968) shows some analyses from the country rocks of the Vihanti mine. Ruskeeniemi et al. (1986) and Loukola-Ruskeeniemi et al. (1997) have reported analyses from four other black shales in western Finland. Note that in the following text the term *"black schist"* is used in the sense of the term *"metamorphosed black shale"*.

As stated above, the study area is located in the Vihanti-Pyhäsalmi Zn-Cu-Pb province, and for practical reasons it is here called the Vihanti area (Fig. 1). This province is the northwestern part of the Raahe-Ladoga Ore Zone, known as the main Sulphide Ore Belt in Finland (Kahma 1973, 1978). Many small, unexploited sulphide deposits, both VMS- and SEDEX-type, are known in the Vihanti-Pyhäsalmi ore zone. So far, however, only two large volcanic-hosted massive Zn-Cu-Pb deposits have been exploited. The Pyhäsalmi mine, located ca. 95 km southeast of Vihanti, is still active, while the Vihanti mine was closed in 1992. Zinc was by far the most important metal in the Vihanti mine, and more than 75% of ore reserves were hosted by three main lodes: Ristonaho, Välisaari and Lampinsaari (Autere et al. 1991). Altogether 28.1 Mt of ore, averaging 5.12% Zn, 0.48% Cu, 0.36% Pb, 25 ppm Ag and 0.49 ppm Au was mined between 1954 and 1992 (Kousa et al. 1997). In addition to the above-mentioned ore types, a few unexploited Au deposits and a couple of peridotite-serpentinite hosted Ni-Cu ores occur in or in close vicinity to the Vihanti-Pyhäsalmi Zn-Cu-Pb zone.

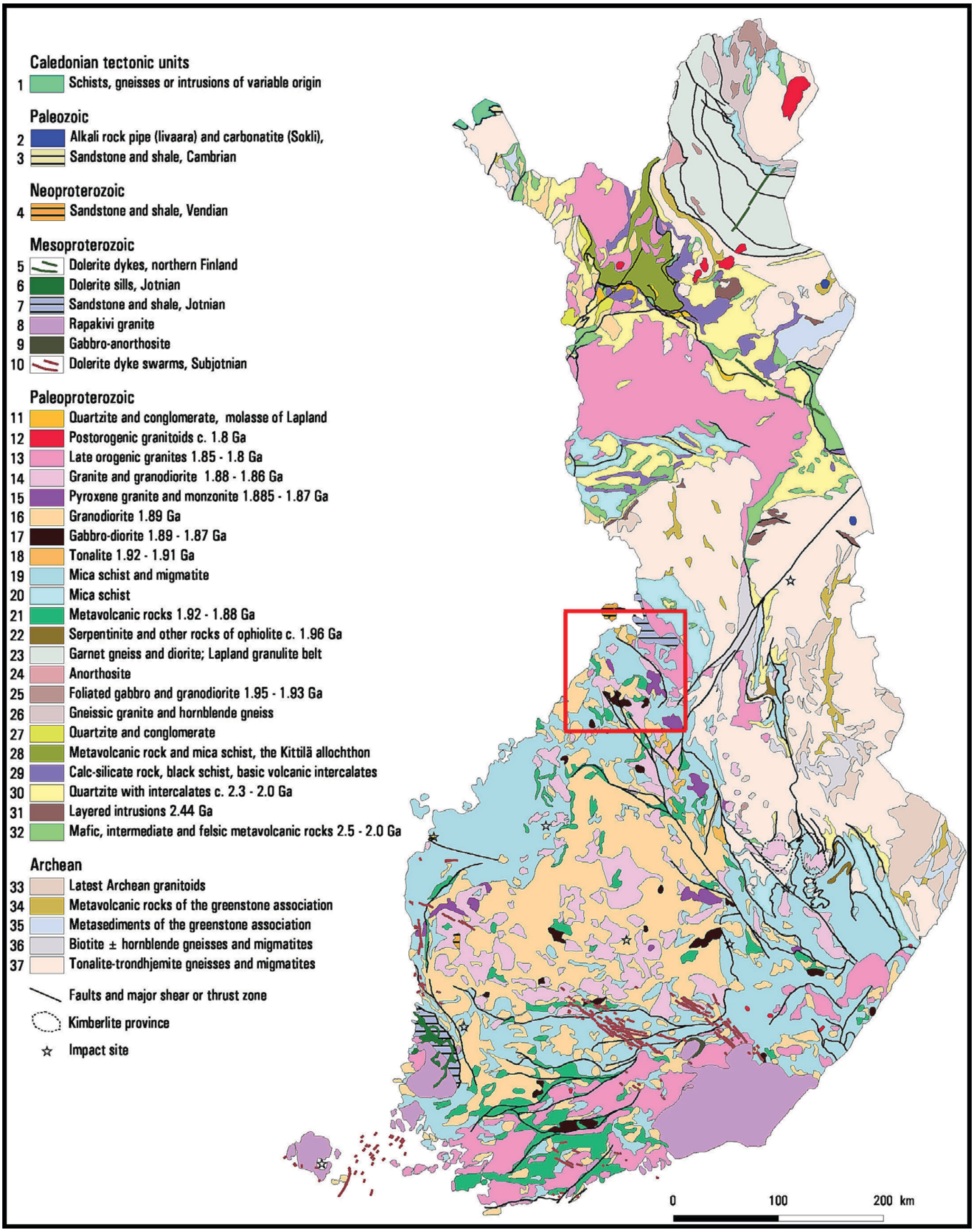


Figure 1. Location of the black schist study area (red square) on the bedrock map of Finland (K. Korsman, T. Koistinen, J. Kohonen, M. Wennerström, E. Ekdahl, M. Honkamo, H. Idman & Y. Pekkala, editors, 1997).

2. SAMPLES AND ANALYTICAL METHODS

During the exploration work, a total of 645 drill core samples, including 272 black schist samples, were picked up for analyses from 38 drill holes and ten prospecting targets in the Vihanti area and the surrounding country (Fig. 2, 3). The selection of samples was carried out macroscopically. Drill cores were split in two, and one half was taken for analysis. The majority of drill core samples were 0.5 –1.0 m long, with a minimum of 0.1 m and maximum of 1.75 m. Analyses were performed at the chemical laboratories of the Geological Survey of Finland using a variety of methods. All samples were analysed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Carbon concentration was determined with a combustion technique, utilising a LECO-analyser. Altogether 81 samples, including 36 black schists from 31 drill holes were analysed with X-ray fluorescence (XRF). Atomic absorption spectrometry and graphite furnace (GFAAS) were used in determining Au concentrations from 184 samples. The analytical methods used in this study are shown in Table 1.

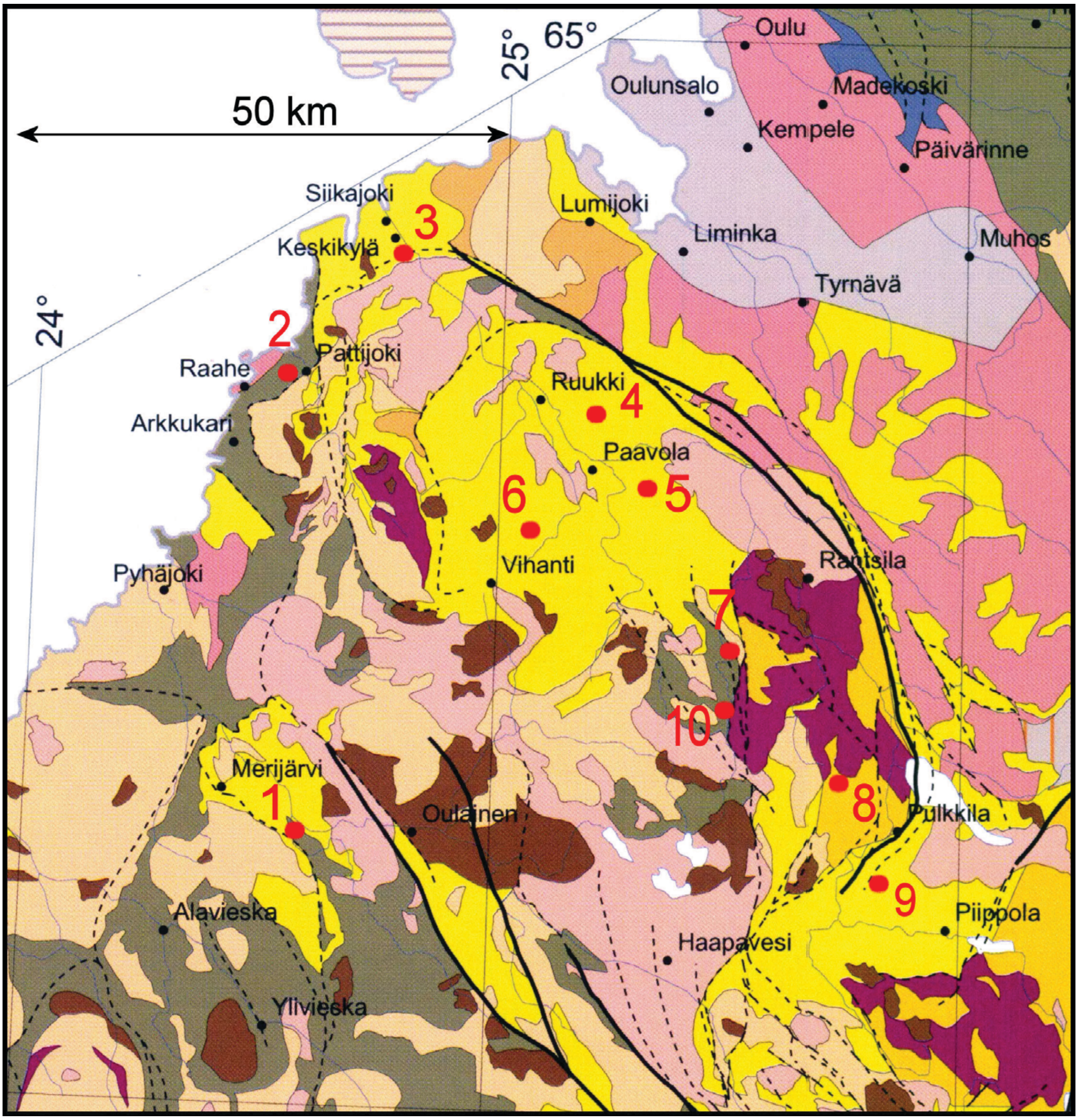


Figure 2. Location of the sampling sites on the structure – lithology, metamorphism and metallogeny map of the Raahe-Ladoga Zone, Map2: Metamorphism (Korsman, K. & Glebovitsky, V., editors, 1999). Greyish-brown refers to lower to medium amphibolite facies rocks, yellow to upper amphibolite facies connected with granitoids of ca. 1.89-1.87 Ga, and brownish yellow to high-T/medium-P or low-P granulite facies connected with granitoids of ca. 1.89-1.87 Ga. Sampling sites: 1 Kenkisuo, 2 Mari, 3 Hirvasperä, 4 Koiramaa, 5 Niemelä, 6 Ilvesneva, 7 Häkkilänpalo, 8 Viitastenjärvi, 9 Lamparekaarrot, 10 Honkisalo

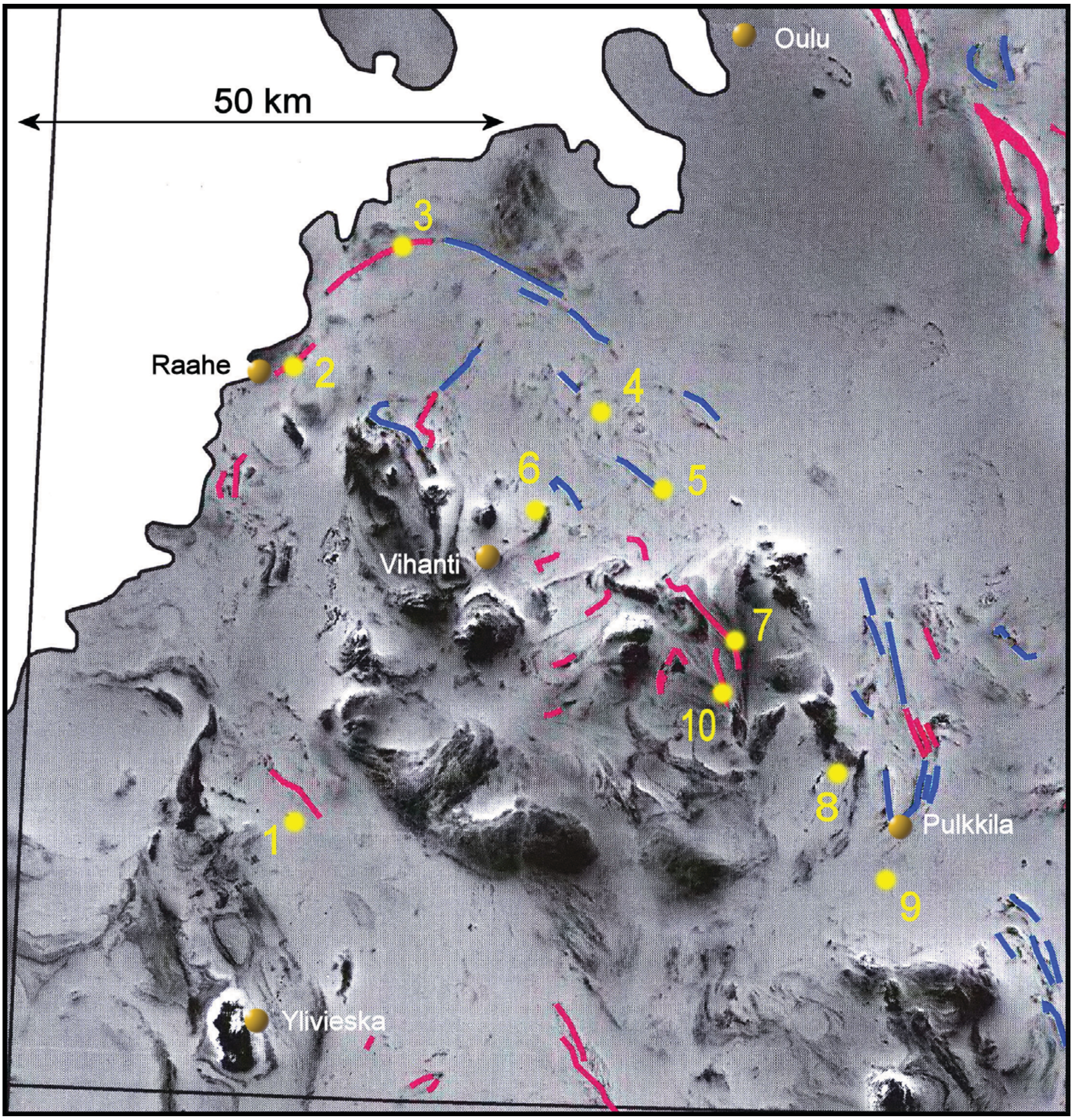


Figure 3. Part of the airborne total intensity magnetic map showing observed (red) and interpreted (blue) black schist formations in the study area (Arkimaa et al., 2000). See Fig. 2 for names of sampling sites.

Table 1. Analytical methods.

Method	Elements	Number of samples
ICP-AES (inductively coupled plasma-atomic emission spectrometry)	Ag, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, S, Sb, Ti, V, Zn	645
XRF (pressed powder pellets)	Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, S, Ba, Bi, Ce, Cl, Ga, La, Nb, Rb, Sc, Sn, Sr, Th, U, Y, Zr	81
LECO S/C-analyser (combustion technique)	C	645
GFAAS (Aqua regia leach, Hg-coprecipitation)	Au	184

3. LITHOLOGICAL VARIATION ASSOCIATED WITH BLACK SCHISTS AND OTHER CARBONACEOUS ROCKS

The separate target areas are located within the Paleoproterozoic Svecofennian supracrustal rocks, intruded by syn- and late-orogenic intrusive rocks (Fig. 1, 2). The supracrustal rocks are divided into the lower sequence, dominated by migmatitic mica gneisses and the upper sequence, which consists characteristically of volcaniclastic metasedimentary and metavolcanic rocks. Metamorphic grade varies from the upper amphibolite facies to the lower or medium amphibolite facies (Korsman & Glebovitsky 1999). Black schist deposits at Kenkisuo, Mari and Häkkilänpalo are in close association with the lower or medium amphibolite facies volcaniclastic metasedimentary and/or metavolcanic rocks, whereas black schists elsewhere are closely related to migmatitic mica gneisses in the upper amphibolite facies terrain.

A brief lithological description of the surroundings of the black schist formations and other carbonaceous rocks is given below. The location of the analysed samples at each study area is expressed in Finnish grid coordinates KKJ2 or KKJ3. When samples represent one single drill hole, the coordinates are in italics. Centrally-located coordinates are given when samples represent two or more drill holes.

3.1 Kenkisuo, Merijärvi *(7131.54N; 2527.60E)*

Graphite-rich intercalations (~ 0.2–2 m thick) are closely related to ca. 60 m thick amphibolite formation, enclosed by mica gneiss. Narrow granite pegmatite dykes crosscut both the amphibolite and mica gneiss. Samples selected for analysis are graphite-rich black schists or hornblende bearing and pyrrhotite-rich black schists, which often show a brecciated structure (Nikander 1999). Besides the high graphitic carbon and sulphur contents, the black schist at Kenkisuo contains on the average more Cu, Mo, Ni, V and Zn than other black schists in the study area.

3.2 Mari, Raahe *(7156.617N; 2525.549E)*

According to Nikander (2004), the Mari formation consists of fine-grained mica schists, siltstones, conglomerates, carbonate rocks, skarns, chert and mafic volcanics intruded by plutonic rocks. Siltstone, carbonate rock and skarn contain variably graphite, iron sulphides and minor sphalerite, chalcopyrite and iron oxides. Analysed black schist samples, which originally were logged as siltstones, are fine grained, grey or dark grey in colour and quartz-plus-feldspar-rich, containing occasionally also tremolite and phlogopite. The thickness of the black schist intercalations vary from less than 1 m to almost 10 m. Due to the calcite and, in all probability, apatite occurring in the graphite- rich siltstones, these rocks show relatively high calcium and phosphorus contents compared to other black schist occurrences.

3.3 Hirvasperä, Siikajoki (7188.10N; 2536.02E)

At the Hirvasperä area, black schists (sometimes chlorite- and/or amphibole-bearing) and mica schists are enclosed within migmatitic mica gneisses close to the contact of a porphyritic granite massif (Iisalo 1997). A few narrow pegmatite granite dykes crosscut the metasedimentary rocks. Graphite-bearing rocks contain variably iron sulphides and sometimes minor calcite veins. Base metal contents, as well as graphitic carbon and sulphur contents, are lower at Hirvasperä compared to other study areas.

3.4 Koiramaa, Ruukki (7172.02N; 2557.50E)

At Koiramaa, 0.5–20 m thick black schist layers occur in close association with mica schist and quartz-feldspar gneiss intercalations within the extensive migmatitic mica gneiss formation in the Ruukki-Vihanti area (Västi 1997). Phlogopite-, cordierite- and muscovite gneiss intercalations are also met with black schists. A few narrow granodiorite and mafic dykes crosscut the metasedimentary rocks. The sulphur content at Koiramaa is roughly double compared to that of carbon. Iron sulphides predominate but also sphalerite and chalcopyrite occur here and there. In places, mica schists/gneisses and quartz-feldspar gneisses are graphite-bearing and considered black schists.

3.5 Niemelä, Ruukki (7165.39N; 2562.80E)

Lithological features in the Niemelä study area closely resemble those of the Koiramaa and Hirvasperä region. Black schist (1–9 m thick), mica schist and cordierite gneiss intercalations are enclosed within migmatitic mica gneisses (garnet-bearing in places) intruded occasionally by pegmatite granite veins. Black schist at Niemelä contains, however, more graphite than the above-mentioned occurrences. The average Cr content is higher, too. On the other hand, V concentration is rather low, although slightly higher than at Mari, Hirvasperä and Ilvesneva. Pyrite is the most common sulphide in black schists. Pyrrhotite, chalcopyrite and sphalerite are more rare (Västi 1995).

3.6 Ilvesneva, Ruukki *(7160.798N; 2551.658E)*

As in the above-mentioned regions, thin (<1 m) black schist and cordierite gneiss intercalations occur within migmatitic mica gneiss. Black schists are often pyrrhotite- and/or pyrite-rich causing magnetic and electro-magnetic anomalies. Graphitic carbon and base metal contents are low, compared to other black schist occurrences in the Vihanti area.

3.7 Häkkilänpalo, Rantsila *(7149.109N; 2571.501E)*

In the Häkkilänpalo area, relatively thin (~ 1–3.5 m) black schist interlayers are closely related to amphibolites, quartz-feldspar gneisses, cordierite gneisses, diopside gneisses, chlorite gneisses, chlorite-muscovite gneisses and diopside-tremolite skarns (Västi 1998b). In places, amphibolites show porphyritic texture and are considered metavolcanic rocks. Chlorite-, cordierite-, quartz-feldspar- and chlorite-muscovite gneisses may also contain at least some volcanic substance, while diopside gneisses and skarns were originally carbonate-bearing sedimentary rocks. Fine- to medium-grained tonalites and granites crosscut the supracrustal sequence. Black schist at Häkkilänpalo is graphite-rich, closely resembling the Kenkisuo black schist. Zn and Cu contents are, however, distinctly lower.

3.8 Viitastenjärvi, Pulkkila (7135.86N; 3439.34E)

The Viitastenjärvi formation lithologically resembles the Lampinsaari rock assemblage in Vihanti. It consists primarily of quartz-feldspar gneisses and fine-grained mica gneisses, enclosed within migmatitic mica gneisses close to the contact of a large pyroxene granite massif. Numerous intercalations of cordierite gneiss, amphibolite, carbonate rock, diopside- and tremolite skarn, quartz rock and black schist occur within quartz-feldspar gneisses and fine-grained mica gneisses (Västi 1998a). Narrow granitic dykes crosscut the sequence. Except in black schists, graphite typically occurs widely in diverse rock types, especially in quartz-feldspar gneisses, cordierite gneisses and carbonate rocks, which at the same time contain variably iron sulphides. Pyrrhotite and pyrite are the main sulphide minerals. Chalcopyrite and sphalerite are less common. The mean graphitic carbon content of the Viitastenjärvi black schist is lower compared to the other black schist occurrences in this study.

3.9 Lamparekaarrot, Pulkkila *(7125.00N; 3443.835E)*

Black schists at Lamparekaarrot occur as thin (0.2–2.7 m) intercalations within migmatitic mica gneisses, which also may be variably graphite-bearing. Crosscutting pegmatite granite dykes occur in places. Black schists are rich in iron sulphides, and they also contain on the average more Zn and Cu than other black schist occurrences investigated in this study. On account of the relatively high Ca-content, the black schist of this area presumably contains some carbonate.

3.10 Honkisalo, Rantsila (7143.60N; 2571.98E)

Honkisalo is located ca. 6.5 km south of Häkkilänpalo, within the same metavolcanic-metasedimentary rock association (Fig. 2, 3). Cummingtonite- and hyperstene-bearing rocks, quartz-feldspar gneisses, diopside gneisses, diopside-tremolite skarns and muscovite rocks are the most common rock types in this area.

Muscovite rocks are medium- to coarse-grained, massive or sometimes weakly oriented and light grey or grey in colour. They are graphite- and sulphur-bearing, containing 1.04%–2.95% (median 1.28%) graphitic carbon and 2.89%–8.20% (median 4.87%) sulphur (Västi 1998b). Trace metal concentrations, as well as Fe, Ca and C concentrations, are lower than in the ordinary black schists. SiO_2, Al_2O_3, Na_2O and K_2O contents (57.0%, 15.3%, 1.6% and 3.5%, respectively), however, are higher on average. Median trace element concentrations for the muscovite rock are shown in Table 3. Because the analysed muscovite rock is not considered ordinary black schist, it will not be discussed later in this work.

4. GEOCHEMISTRY OF THE BLACK SCHISTS

According to the Glossary of Geology (Jackson 1997) black shale (schist) is *a dark, thinly laminated carbonaceous shale, exceptionally rich in organic matter (5% or more carbon content) and sulfide (esp. iron sulfide, usually pyrite), and commonly containing unusual concentrations of certain trace elements (U, V, Cu, Ni). Fossil organisms (principally planktonic and nektonic forms) are commonly preserved as a graphitic or carbonaceous film or as pyrite replacements.* Tyson (1987) defined black shales as *dark-coloured, fine-grained mudrocks having the sedimentological, palaeoecological and geochemical characteristics associated with deposition under oxygen-deficient or oxygen-free bottom waters.*

The enrichment of most trace metals seems to be directly related to the euxinic conditions of black shale or black schist (originally mud rocks or sapropels) deposition. The process of enrichment is due to 1) precipitation as a sulphide, 2) incorporation as a trace element in pyrite and 3) complexation with organic matter. The third factor being dominant, most trace metals show a positive correlation when plotted against organic carbon (Vine & Tourtelot 1970). Brumsack (1980), however, stated that this might only reflect that organic matter preservation and metal enrichment are controlled by the anoxic depositional environment, not by a relationship between them. The important role of plankton in trace metal enrichment was stressed by Piper (1994), who showed that the similarity in several minor element ratios in many black shale occurrences to minor element ratios in modern plankton demonstrates that these rocks deposited in environments where marine chemistry was nearly identical to the oceans of today.

According to Tyson (1987) the preservation of trace metal rich organic matter is controlled by five factors: *1) Sediment texture and grain size:* Organic matter is preferentially concentrated in fine-grained sediments due to similar settling velocities. The low porosity and permeability of fine-grained sediments enhance organic matter preservation by restricting the contact of organic matter with potential oxidants. *2) Water depth:* Bathymetry is an important control on the organic carbon content of black shales, since the proportion of organic matter surviving the sedimentation process decreases with increasing residence time in the water column. Mixing of the water column (by wind or temperature variations) in the bottom waters may also have an influence on the preservation of organic matter. Although shallow water models have been proposed for many black shales (e.g. Coveney et al. 1991), most geologists consider that black shales represent deep sea facies. *3) Sedimentation rate:* Although there are practically no means to measure absolute sedimentation rates, it is thought that black shale accumulation rates are exceedingly slow. *4) Primary production and rate of organic matter supply to the sediment:* The abundance of organic matter in black shales has led many researchers to suggest that they deposited in basins with elevated organic productivity. In Tyson's (1987) opinion, however, organic rich sediments even in areas of high productivity will not accumulate unless other preservative factors are fulfilled. *5) Bottom-water oxygenation:* Generally, all black shale models and trace metal enrichment are related to anoxic bottom waters caused by restricted water circulation or the decay of abundant organic matter.

4.1 Black schists of the Vihanti area

In Finnish geological literature, the classification of black schists has varied somewhat during the last decades. Peltola (1960) and Loukola-Ruskeeniemi (1999) regarded the sedimentary rocks containing >1% graphite (organic carbon) and >1% S as black schists. Kukkonen et al. (1985) proposed a black schist classification which divides the rocks into three groups on the basis of graphitic carbon and S concentrations:

1. ordinary black schists containing <10% C and S
2. graphite schists containing >10% C and very little S

3. graphite-sulphide schists containing >10% S and variable amounts of C.

In this study, the metasedimentary rocks containing >1% of both graphitic C and S were considered black schists. Generally speaking they are heterogeneous, fine- to coarse-grained, granoblastic-lepidoblastic and grey or black in colour. Metamorphic grade varies from lower to upper amphibolite facies. Quartz, feldspars and biotite are the main silicate minerals. Sometimes Ca-Mg silicates and phlogopite (at Mari), chlorite (at Hirvasperä), garnet and cordierite (at Niemelä, Häkkilänpalo and Viitastenjärvi) occur as the major minerals. Graphite and iron sulphides are the most common opaque minerals. Sphalerite and chalcopyrite are present here and there, although rare. However, the relative amounts of the major silicates, as well as the amounts of graphite and iron sulphides, vary greatly. Chemically, the black schists are highly enriched especially in Fe_2O_3, S, C and many trace metals (Cd, Co, Cu, Cr, Mg, Mn, Mo, Ni, Pb, U, V, Zn) compared to the median composition of mica gneisses/schists or to the average black shale of Vine and Tourtelot (1970).

4.1.1 Major elements

Whole rock analyses show that median concentrations for SiO_2, Al_2O_3, TiO_2, Fe_2O_3, MgO, MnO, CaO, Na_2O, K_2O and P_2O_5 in nine black schist deposits vary from 39.6 to 57.7 wt%, 6.94 to 13.35 wt%, 0.36 to 0.65 wt%, 9.52 to 26.8%, 2.69 to 8.19%, 0.03 to 0.08%, 0.44 to 5.38%, 0.42 to 1.76 wt%, 1.14 to 3.8 wt% and 0.05 to 0.34%, respectively. These contents are close to other black schist occurrences but slightly lower (e.g. SiO_2, Al_2O_3, TiO_2, Na_2O, K_2O) compared to mica gneisses (Table 2). However, these figures should be viewed critically, because only a few (1–4) samples represent some of the black schist deposits. The more comprehensive set of samples was analysed by ICP-AES, yielding definitely a more reliable result (cf. Table 3). The TiO_2/Al_2O_3 ratio in black schist and mica gneisses is ~0.05, which might indicate that the clastic component in the black schists has fairly the same chemical composition and source as the mica gneisses. Increased Fe concentrations are solely consequences of high sulphide contents (mainly pyrite and pyrrhotite). However, except in sulphides, Fe is also distributed in biotite, chlorite and phlogopite.

4.1.2 Carbon and sulphur

The median C concentrations vary from 1.9% to 14.7% (Tables 2, 3). Sporadic black schist samples show, however, remarkably large variation in graphitic C concentrations varying from ~1% to 32%. Especially high C contents occur at Kenkisuo and Häkkilänpalo while at Viitastenjärvi and Ilvesneva graphitic C remains in much lower levels. Compared to other black schist occurrences in Ostrobothnia and eastern Finland, the median C concentrations are rather similar with a few exceptions, but for the most part richer compared to the average black shale of North America (Vine & Tourtelot 1970). On the other hand, many Phanerozoic black shales, e.g. Cambrian Alum shale in Sweden, Devonian Chattanooga shale in the U.S.A. (Leventhal 1991) and Carboniferous black shales in the Midwest United States (Coveney et al. 1991), show high organic C concentrations (2.7% to 20.6%, 1% to 10% and 8% to 15%, respectively). Brumsack (1980) and Gavshin and Zakharov (1996) have described Jurassic-Cretaceous black shale formations from the Atlantic Ocean and West Siberia where mean C_{org} concentrations are 6.18% and 8.0%, respectively (highest values 35.57% and 18.18%, respectively). Recent sapropels from the Black Sea contain 6.47% C_{org} (mean) while samples from the Gulf of California have a C content between 3.55% and 5.51% (Brumsack 1989).

Sulphur contents of the black schists analysed in this work are greater than in most Phanerozoic or Precambrian black shales or schists (cf. Henderson 1977, Cameron & Garrels 1980, Brumsack 1980, 1989, Berner & Raiswell 1983, Davis et al. 1988). Practically all sulphur is distributed in iron sulphides because of the fact that other sulphides are rare and occur only sporadically. The median S concentrations vary from 3.4% at Hirvasperä to 8.5% at Lamparekaarrot. Excluding one S-rich (18%) sample, the variation in S concentration is in the range of 1.32% – 12.1%. However, except between separate occurrences, there are also notably large variations in the S concentrations within some individual deposits. For instance at Koiramaa, graphite-rich black schist is also rich in S (7.59%), while biotite-rich and quartz-feldspar-rich rocks contain much less sulphur (3.62% and 2.98%, respectively). Sulphur concentrations of the black schists analysed in this study are comparable to other black schist deposits in Ostrobothnia and eastern Finland. Black schists in the Haukipudas-Kiiminki area (Ahtonen 1996), Kaustinen (Loukola-Ruskeeniemi et al. 1997) and Hammaslahti (Loukola-Ruskeeniemi 1992) show lower and similar S contents than the Hirvasperä, Niemelä and Viitastenjärvi deposits (Tables 2, 3).

The median C/S ratios vary from 0.3 to 2.6. The lowest values are met at Ilvesneva, Viitastenjärvi, Koiramaa and Lamparekaarrot (0.3, 0.4, 0.5 and 0.5, respectively). The highest C/S ratios occur at Häkkilänpalo (2.6), Niemelä (1.5) and Kenkisuo (1.4). These ratios are comparable to other black schist occurrences in Ostrobothnia and eastern Finland. It

Table 2. Median whole rock chemical compositions of black schists and mica gneisses. (Elements Si ↔ Zr analysed by XRF, elements Ag ↔ V by ICP-AES, C with a LECO-analyser, Au by GFAAS).

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
SiO2 %	39,6	57,7	56,25	46,85	43,8	53,95	44,4	47,8	55,2	63
TiO2	0,36	0,65	0,56	0,62	0,48	0,51	0,46	0,58	0,55	0,71
Al2O3	8,14	6,94	12,3	11,2	9,93	13,35	9,21	11,2	13,3	14,9
Fe2O3	19,5	11,3	10,59	18,9	26,8	9,52	13,65	23,3	12,4	6,97
MnO	0,06	0,03	0,08	0,07	0,08	0,05	0,07	0,07	0,06	0,06
MgO	3,75	4,11	5,56	4,87	3,92	5,6	8,19	2,69	4,64	3,67
CaO	1,45	5,38	0,44	1,76	0,89	0,52	1,44	2,95	3,26	1,78
Na2O	0,83	1	1,38	1	1,23	0,7	0,48	0,42	1,76	2,33
K2O	1,97	2,13	3,8	2,11	2,23	3,78	1,14	1,17	2,15	3,22
P2O5	0,16	0,34	0,1	0,13	0,09	0,05	0,16	0,13	0,24	0,14
S	6,97	6,11	3,77	7,2	10,7	4,74	5,53	8,91	4,75	1,92
C tot	14,7	6,29	5,62	5,11	5,27	6,99	14,95	4,9	3,22	0,18
Ba ppm	203	135	583	264	224	481	203	145	426	500
Bi	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Ce	48	31	67	48	59	76	23	43	82	80
Cl	<60	<60	<60	120	70	125	105	90	110	120
Ga	<20	<20	22	23	<20	25	<20	<20	24	25
La	<30	<30	<30	<30	<30	46	<30	<30	44	37
Nb	<10	8	<10	10	11	14	<10	10	14	13
Rb	44	35	118	92	120	124	50	65	81	99
Sc	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Sn	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Sr	72	44	72	67	63	76	40	91	116	131
Th	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
U	18	32	15	20	14	15	15	30	14	<10
Y	51	45	28	39	30	39	23	52	54	26
Zr	98	116	140	120	89	143	101	122	133	176
Ag	<1	3	<1	2	<1	<1	<1	1	<1	<1
As	<30	30	<30	<30	<30	<30	<30	<30	<30	<30
Cd	13	14	2	15	4	6	8	38	6	<0,5
Co	33	16	26	31	52	40	27	51	33	20
Cu	294	409	244	351	255	231	165	841	274	109
Ni	481	385	240	382	374	322	365	491	317	103
Sb	<15	n.d.	<13	<15	<13	<15	<15	<15	<15	<15
Pb	15	40	188	26	28	194	16	12	14	<10
Zn	1590	1239	296	1860	635	196	732	2630	389	163
Cr	89	68	103	162	133	163	108	189	92	69
Mo	153	73	33	74	21	39	96	160	55	<5
V	1090	294	465	823	595	397	802	968	719	135
Au ppb	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

1. Kenkisuo, Merijärvi (n=3)
2. Mari, Raahe (n=2)
3. Hirvasperä, Siikajoki (n=6)
4. Koiramaa, Ruukki (n=10)
5. Ilvesneva, Ruukki (n=1)
6. Niemelä, Ruukki (n=4)
7. Häkkilänpalo, Rantsila (n=4)
8. Lamparekaarrot, Pulkkila (n=1)
9. Viitastenjärvi, Pulkkila (n=5)
10. Mica gneisses from four deposits (n=9)

is widely known (cf. e.g. Berner & Raiswell 1984, Calvert & Carlin 1991) that black schists accumulated in euxinic bottom waters usually show C/S ratios of <1 while deposits accumulated in normal oxygenated seawater have a constant ratio of ~3 (Berner & Raiswell 1983).

4.1.3 Manganese and phosphorus

Manganese contents are low in all black schist occurrences, with the median concentration varying from 133 to 479 ppm. Higher phosphorus contents occur only at Mari, where median and average P and

Table 2. continued

	11.	12.	13.	14.	15.	16.	17.	18.
SiO2 %	52,4	43,78	51,18	53,53	43,02	45,82	54,6	n.d.
TiO2	0,75	0,51	0,38	0,57	0,5	0,36	0,57	0,33
Al2O3	11,8	10,37	11,7	10,57	10,52	11,97	14,3	13,23
Fe2O3	12,07	26	14,78	10,84	12,67	12,93	10,3	2,86
MnO	0,07	0,05	0,05	0,05	0,07	0,31	0,07	0,02
MgO	3,81	1,44	3,47	3,35	8,1	2,8	4,76	1,16
CaO	1,46	1,57	2,29	4,09	9,25	1,62	3,87	2,1
Na2O	1,29	2,14	1,42	1,13	0,62	0,63	0,9	0,94
K2O	2,99	1,92	2,67	2,18	1,23	3,43	3,82	2,41
P2O5	0,16	0,09	0,13	0,17	0,12	0,14	0,15	n.d.
S	3,94	13,13	7,1	6,65	5,42	8,9	4,21	n.d.
C tot	4,28	4,8	7,4	4,31	6,36	7,7	n.d.	3,2
Ba ppm	300	n.d.	350	249	253	330	540	300
Bi	n.d.	n.d.	n.d.	<30	<30	n.d.	n.d.	n.d.
Ce	n.d.	n.d.	50	59	45	38	n.d.	n.d.
Cl	n.d.	n.d.	n.d.	100	150	70	n.d.	n.d.
Ga	n.d.	n.d.	n.d.	<20	<20	n.d.	n.d.	20
La	n.d.	n.d.	n.d.	34	30	35	31	30
Nb	n.d.	n.d.	n.d.	11	10	n.d.	n.d.	n.d.
Rb	n.d.	n.d.	n.d.	96	67	n.d.	105	n.d.
Sc	n.d.	n.d.	15	<30	<30	15	21	10
Sn	n.d.	n.d.	n.d.	<20	<20	n.d.	n.d.	n.d.
Sr	n.d.	n.d.	80	148	151	70	85	200
Th	n.d.	n.d.	8,5	<10	<10	8	10	n.d.
U	15	n.d.	16,5	19	16	16	12	n.d.
Y	15,7	n.d.	25	46	32	20	n.d.	30
Zr	n.d.	n.d.	105	150	97	100	170	70
Ag	<1	n.d.	<1	0,6	0,7	1	3	<1
As	12	n.d.	n.d.	<30	<30	n.d.	9	n.d.
Cd	4,9	n.d.	n.d.	19,3	5,3	15	n.d.	n.d.
Co	27,4	n.d.	35	20,7	21,1	50	40	10
Cu	225	3500	280	236	253	610	340	70
Ni	180	n.d.	380	264	378	380	400	50
Sb	9	n.d.	n.d.	62,1	7,9	n.d.	2,1	n.d.
Pb	39,5	100	<14	14	8,1	38	90	20
Zn	311	700	1460	2245	889	2370	1250	<300
Cr	133,5	n.d.	105	145	121	140	330	100
Mo	25,6	n.d.	50	24	68	60	n.d.	10
V	357	952	540	423	762	740	n.d.	150
Au ppb	0,6	n.d.	n.d.	<2	<2	18	15	n.d.

11. Northern Ostrobothnian schist area (Ahtonen, 1996)
12. Vihanti mine dh 640 (Rouhunkoski, 1968)
13. Outokumpu region (Loukola-Ruskeeniemi, 1999)
14. Ordinary black schist, dh R2500 Outokumpu (Västi, unpubl. data)
15. Calcareous black schist, dh R2500, Outokumpu (Västi, unpubl. data),
16. Talvivaara black schist, Ni<0.1% (Loukola-Ruskeeniemi and Heino, 1996)
17. Hammaslahti hanging wall black schist (Loukola-Ruskeeniemi, 1992)
18. Average North American black shale (Vine and Tourtelot, 1970).

n.d. = not determined or no data available

P_2O_5 are 941 ppm and 0.34%, respectively (Tables 2, 3). This P enrichment probably indicates small amounts of apatite in graphite-bearing siltstones. The median Mn and P contents for mica gneisses and most black schists in Ostrobothnia and eastern Finland show rather similar contents. Black schists at Pattijoki and Talvivaara, however, are remarkably richer in manganese, and Pattijoki is also rich in

Table 3. Median chemical concentrations of black schists compared to some other black schist occurrences in Finland and the average North American black shale. (Study areas 1-5 and 7-11: elements As ↔ S and Ag analysed by ICP-AES, C with a LECO-analyser, Au by GFAAS).

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
As ppm	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Ca %	0,8	1,9	0,2	0,4	0,2	0,1	0,4	1,9	0,5	0,2	0,2
Cd ppm	11,8	9,4	2,0	9,5	0,6	3,3	4,6	30,6	1,8	<0,5	<0,5
Co	43	25	18	26	31	30	27	50	26	29	19
Cr	89	63	80	27	111	163	98	189	95	47	73
Cu	354	348	153	307	121	190	172	355	188	110	75
Fe %	14,1	7,1	5,5	9,7	11,3	5,3	8,7	13,3	7,9	7,6	5
Mg	1,3	0,7	2,6	2,1	1,9	2,5	3,4	1,7	1,8	1,9	1,8
Mn ppm	279	133	479	375	407	275	285	357	229	231	449
Mo	128	44	6	49	11	39	113	112	39	12	<5
Ni	631	352	149	342	209	257	395	479	259	99	80
P	671	941	557	587	499	286	424	814	536	582	602
Pb	19	30	35	21	18	62	17	12	12	12	10
Ti %	0,1	0,1	0,1	0,1	n.d.	0,1	0,01	0,2	0,1	0,02	0,1
V ppm	1080	220	200	524	345	391	840	810	483	44	118
Zn	1590	762	239	968	347	188	302	2075	336	92	133
S %	8,3	6,1	3,4	6,7	6,2	4,2	5,7	8,5	4,3	4,9	1,3
C	11,5	6,8	2,3	3,3	1,9	6,2	14,7	4,5	1,9	1,3	0,2
Ag ppm	<1	2,4	<1	1,4	<1	1,8	<1	<1	<1	<1	<1
Au ppb	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
C/S	1,4	1,1	0,7	0,5	0,3	1,5	2,6	0,5	0,4	0,3	0,2
V/(V+Ni)	0,6	0,4	0,6	0,6	0,6	0,6	0,7	0,6	0,7	0,3	0,6
V/Cr	12,1	3,5	2,5	19,4	3,1	2,4	8,6	4,3	5,1	0,9	1,6

1. Kenkisuo, Merijärvi (n=11; *Ag: n=7*)
2. Mari, Raahe (n=10)
3. Hirvasperä, Siikajoki (n=56; *Mo: n=48, Ti: n=25, Au: n=18*)
4. Koiramaa, Ruukki (n=93; *Cr: n=47, Au: n=43*)
5. Ilvesneva, Ruukki (n=8)
6. Niemelä, Ruukki (n=22; *Cr: n=4, Ag analysed by FAAS*)
7. Häkkilänpalo, Rantsila (n=12)
8. Lamparekaarrot, Pulkkila (n=6; *Cr: n=1*)
9. Viitastenjärvi, Pulkkila (n=54; *Ti: n=5, Ag: n=24*)
10. Muscovite rock, Honkisalo, Rantsila (n=40)
11. Mica gneiss from five targets (n=61; *Cr: n=53, Mo: n=56, Ti: n=27, Ag: n=60, Au:n=34*)

n.d. = not determined or no data available

phosphorus (Table 3). The generally low Mn content can be attributed to permanently anoxic ocean basins (Calvert & Pedersen 1996).

4.1.4 Cobalt, copper, lead and zinc

Median cobalt, copper, lead and zinc concentrations in the target areas vary between 16–52 ppm, 121–841 ppm, 12–194 ppm and 188–2,630 ppm, respectively. These values are remarkably higher than those of the Phanerozoic black shales of Vine and Tourtelot (1970) or the mica gneisses in this study (Tables 2, 3). Cambrian Alum shales from Sweden show on average a higher Pb content, lower Cu and Zn contents and a comparable Co content (Leventhal 1991), while Cretaceous black shales from the Atlantic Ocean (Brumsack 1980) have concentrations very similar to the black schists in this study. Recent sapropels from the Black Sea and the Gulf of California contain much less Cu and Zn, but roughly the same amount of Pb and Co (Brumsack 1989). Co-, Cu-, Pb- and Zn-concentrations are comparable to other black schist occurrences elsewhere in Ostrobothnia and eastern Finland. Some exceptions, however, occur. For instance, at Talvivaara the amounts of the above-mentioned elements are systematically higher. On the other hand, Pb and Co contents are lower in the black schists of the deep drill hole R2500 at Outokumpu (Table 3).

Table 3. continued

	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.
As ppm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9,0	n.d.	<30	<30	n.d.
Ca %	3,2	3,7	2,9	2,3	1,9	1,8	2,8	1,3	2,9	6,6	1,5
Cd ppm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15	19,3	5,3	n.d.
Co	25	35	35	10	21	33	40	100	21	21,1	10
Cr	65	120	130	75	110	110	330	140	145	121	100
Cu	285	120	400	100	230	350	340	870	236	253	70
Fe %	11	8,1	6,5	4,6	6,9	9,5	7,9	10,2	7,6	8,9	2
Mg	1,3	1,9	1,8	1,5	2,5	2,0	2,9	1,8	2,0	4,9	0,7
Mn ppm	260	500	5550	375	420	340	542	2500	387	542	150
Mo	30	65	50	15	54	58	n.d.	50	24	68	10
Ni	425	320	300	140	310	350	400	720	264	378	50
P	525	670	1200	775	600	700	655	690	742	524	n.d.
Pb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	90	43	14	8,1	n.d.
Ti %	0,2	0,2	0,2	0,3	0,2	0,3	0,3	0,2	0,3	0,3	0,2
V ppm	550	885	545	330	540	540	n.d.	670	423	762	150
Zn	715	430	605	255	1500	1800	1250	3210	2245	889	<300
S %	9	5,2	8,7	2,7	5,1	6,5	4,2	9,2	6,7	5,4	n.d.
C	3,9	15,5	4,2	5,3	6,3	6,6	n.d.	7,5	4,3	6,4	3,2
Ag ppm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3	1	0,6	0,7	n.d.
Au ppb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15	17	<2	<2	n.d.
C/S	0,4	3	0,5	2	1,2	1	n.d.	0,8	0,6	1,2	n.d.
V/(V+Ni)	0,6	0,7	0,6	0,7	0,6	0,6	n.d.	0,8	0,6	0,7	0,8
V/Cr	8,5	7,4	4,2	4,4	4,9	4,9	n.d.	4,8	2,9	6,3	1,5

12. Vihanti mine, 13. Vihanti, Kuuhkamo, 14.Pattijoki, 15. Kaustinen, 16. Keretti mine, 17. Vuonos mine, 18. Hammaslahti, 19. Talvivaara black schist (Ca<3.13%), 20. Dh R2500 Outokumpu (ordinary black schist), 21. Dh R2500 (calcareous black schist), 22. Average North American black shale.
(12–15 data from Loukola-Ruskeeniemi et al., 1997; 16-19 from Loukola-Ruskeeniemi, 1992; 20–21 unpublished data by Västi; 22 from Vine and Tourtelot, 1970).

4.1.5 Vanadium, nickel and molybdenum

Median vanadium, nickel and molybdenum concentrations for black schists vary between 200 – 1,090 ppm, 149 – 631 ppm and 6 – 160 ppm, respectively, greatly exceeding the mean contents (60, 20, 1.5 ppm, respectively) of the upper crust. The highest V, Ni and Mo contents occur at Kenkisuo, Lamparekaarrot and Häkkilänpalo, where deposits are also rich in other trace metals, excluding Pb (Tables 2, 3). Except for the northern Ostrobothnian schist area (Ahtonen 1996), the black schist occurrences in this study show very similar V and Ni concentrations compared to other black schists elsewhere in Ostrobothnia and eastern Finland but remarkably higher values compared to the average North American shale of Vine and Tourtelot (1970) and recent sapropels in the Gulf of California and in the Black Sea (Brumsack 1989). However, some carbon-rich Cambrian Alum shales in Sweden contain vanadium up to 3,100 ppm (Leventhal 1991) and some Carboniferous black shales in the United States mid-continent contain up to 5,970 ppm (Coveney and Martin, 1983).

According to Lewan and Maynard (1982), the sedimentary geochemistry of vanadium and nickel are very similar. These metals are preferentially concentrated in tetrapyrrole complexes because of their availability in anaerobic environments, favourable electron configurations and small atomic radii. Vanadium is present as a dissolved vanadate (V^{+5}) ion in oxygenated seawater. Under reducing acidic conditions typical of euxinic basins, vanadate is reduced to a vanadyl (V^{+4}) ion by organic compounds or H_2S. The solubility of Ni is not, however, influenced by the redox potential, but under anoxic conditions, the availability of H_2S causes nickel sulphide formation (Lewan & Maynard 1982). Breit and Wanty (1991) noted that the vanadyl ion is also readily adsorbed by clay particles when reduced to V^{+3} during burial. V^{+3} is stable in clay structure and will survive weathering, also recrystallizing to coarse-grained micas in graphitic schists.

The V/(V+Ni) ratio has been useful in determining the paleoenvironmental conditions in which black shales were deposited. Lewan's (1984) values of porphyrins differ from those of Hatch and Leventhal

(1992) because their results were derived from whole rock samples.

The median V/(V+Ni) ratios of the black schists in this study typically vary between 0.6 and 0.7 (Table 3). The low value (0.4) at Mari can most likely be explained by the scarcity of micas. V/(V+Ni) ratios are great enough to indicate anoxic depositional conditions for the accumulation of black schists of this work (cf. Wignall 1994, Fig. 4.3, p. 42). In addition, Dill (1986) assumed that V/Cr ratios over 2 also indicate anoxic environmental conditions for black schist deposition. V/Cr ratios between ca. 2.4 and 19.4 for the black schists in this study also support anoxic conditions for black schist accumulation.

Median molybdenum concentrations show considerable variation in the black schists in this study. In some deposits, its content is double compared to that of other black schist occurrences in Ostrobothnia or in eastern Finland. Great variation in Mo content is met in Phanerozoic and recent black shale and sapropel deposits too. Leventhal (1991) reported a mean 50 ppm Mo concentration for the Devonian black shale in the United States. Brumsack (1980, 1989) has published results for Cretaceous black shales from the Atlantic Ocean and for recent sapropels from the Gulf of California and the Black Sea, which show Mo contents of the same order as the black schists in this study. On the other hand, Cambrian Alum shale in Sweden and Carboniferous Mecca shale in the USA have mean Mo contents of 280 and 1,160 ppm, respectively (Leventhal 1991, Coveney & Martin 1983).

According to Coveney and Martin (1983), molybdenum is one of the most highly enriched trace metals in black shales. It is also one of the most abundant trace metals in the modern oceans, with an average concentration of 10.6 ppb (Brumsack 1989). Vine and Tourtelot (1970) and Leventhal (1991) noted the correlation of Mo with organic C, although modern marine plankton contains only little Mo. Brumsack (1989) and Coveney et al. (1991) suggested that the source for Mo is seawater. It was initially adsorbed into organic matter, but later it precipitated as a sulphide, possibly a trace metal in pyrite (Huerta-Diaz & Morse 1992). The importance of the relation between pH and retention of Mo by peat was documented by Bertine (1972) and Coveney et al. (1991). They noted that peat can retain Mo up to 2,400 ppm at pH=4, 1,000 ppm at pH=7 and essentially none at pH=8. Hence Mo is soluble in ocean water (pH=8.1) as MoO_4^{2-}, but is retained by organic matter in contact with acidic solutions.

4.1.6 Other elements

Median cadmium and chromium concentrations are rather similar compared to other black schist occurrences in Ostrobothnia and eastern Finland, varying between 0.6 – 38 and 27 – 189 ppm, respectively. It should be noted, however, that the highest chromium value was represented by only one sample at Lamparekaarrot. The median Cr concentration at Niemelä may also be misleading, because only four samples were analysed for chromium.

Silver and gold contents in most black schist deposits are below the detection limit (<1 ppm and <10 ppb, respectively). At Koiramaa, Niemelä and Mari, median Ag concentrations are slightly above the detection limit, varying from 1.4 to 2.4 ppm (note: at Niemelä, Ag was analysed by FAAS). Although a few sporadic samples contain 11 – 32 ppb Au, median Au concentrations for all black schist occurrences fall below the detection limit (Table 3).

Uranium concentrations were determined for 36 samples only. The contents range from below the detection limit (<10 ppm) up to 40 ppm, with median values between 14 and 32 ppm. Median yttrium and zirconium concentrations vary from 23 to 54 ppm and from 89 to 143 ppm, virtually identical with other black schist deposits in Ostrobothnia and eastern Finland but slightly higher than in the average North American black shale (Table 2).

4.2 Correlations between selected elements

Various authors have reported on the good correlation of organic carbon with the majority of trace metals (e.g. Vine & Tourtelot 1970, Brumsack 1989, Leventhal 1991). In the black schist deposits investigated in this study, there is generally strong or good positive correlation between graphitic carbon and the trace metals V, Ni and Mo. However, at Kenkisuo and Häkkilänpalo, C correlates negatively against Ni and V. Chromium shows strong positive correlation against C at Niemelä, Ilvesneva, Koiramaa and Hirvasperä, but strong negative correlation at Kenkisuo (Fig. 5, Table 4). At Ilvesneva, Lamparekaarrot, Niemelä, Hirvasperä and Koiramaa there is strong or good positive correlation between Co and C, and good negative correlation at Häkkilänpalo, Mari and Kenkisuo. Cu shows strong positive correlation against C only at Ilvesneva and Hirvasperä. Pb shows good positive correlation against C at Niemelä, Kenkisuo and Lamparekaarrot, while Zn shows strong positive correlation only at Ilvesneva and strong negative correlation at Kenkisuo (Table 4). There is also strong positive or negative correlation between

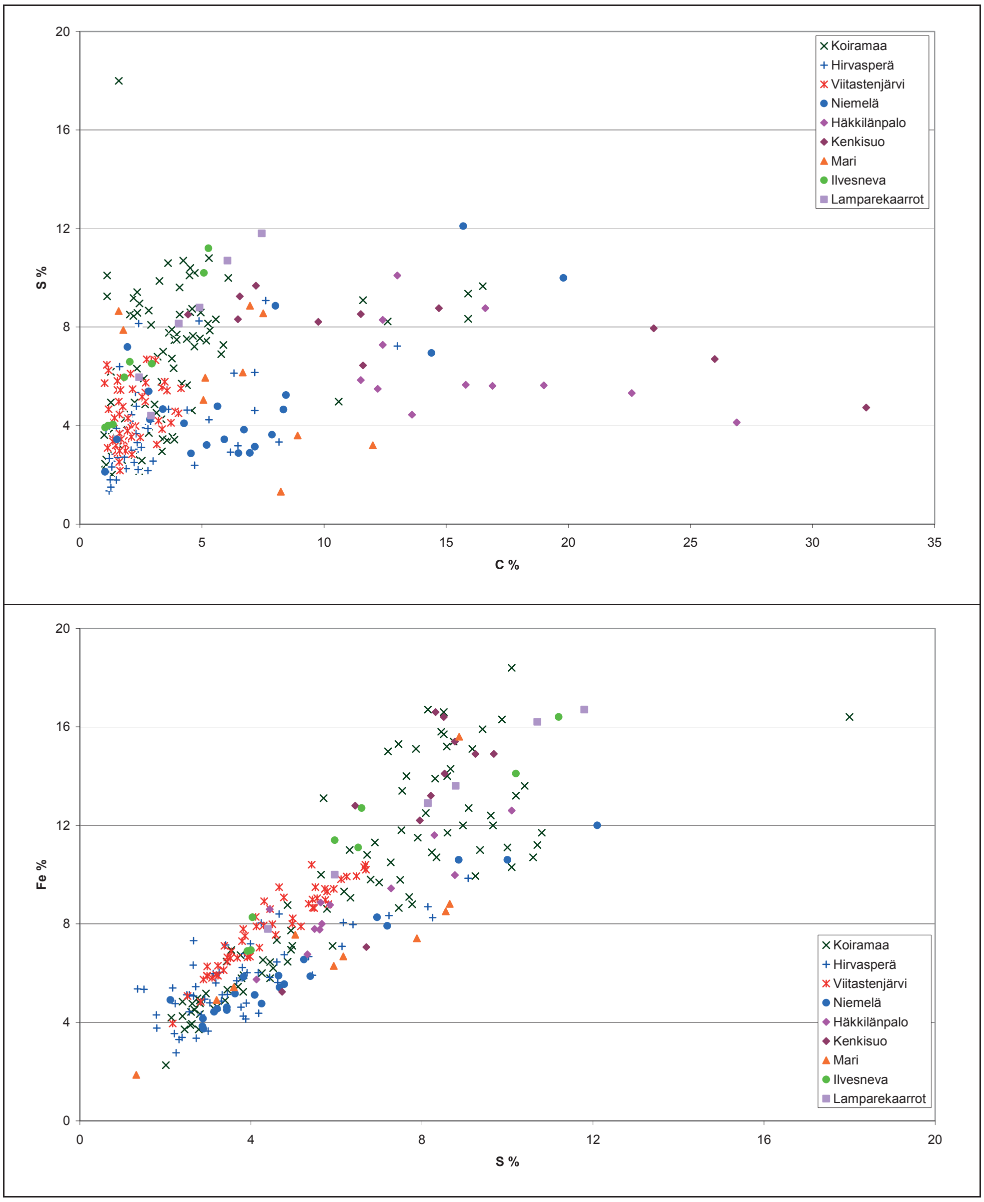


Figure 4. Plot of S against C and Fe against S for black schists analysed in this study.

S and C in most black schist deposits. At Ilvesneva, Lamparekaarrot, Niemelä and Hirvasperä the correlation is positive, but it is negative at Kenkisuo, Mari and Häkkilänpalo (Fig. 4, Table 4).

Fe and Co show strong positive correlation against S in all black schist deposits. Excluding the Mari area, there is strong positive correlation between Ni and S, too (Fig. 4, 6; Table 4). V correlates strongly against S at Ilvesneva, Niemelä, Koiramaa, Kenkisuo, Lamparekaarrot and Hirvasperä. Mo and Cr also show good correlation against S in some occurrences. The correlation between Pb and S is good at Niemelä, Viitastenjärvi, Lamparekaarrot and Kenkisuo. However, at the last-mentioned site, Pb correlates negatively with S. Zn shows strong positive correlation against S at Kenkisuo, Koiramaa and Ilvesneva (Table 4).

Correlations between trace metals are mostly strong and positive. The two most conspicuous deposits are again Kenkisuo and Häkkilänpalo, where Mo, Ni and V, as well as C, often correlate negatively with other metals. At Kenkisuo Mo shows strong negative correlation with Cr, V and Zn, while V shows strong negative correlation with Mo and Pb. On the other hand in most occurrences there is strong or good positive correlation between V and Cr and between V and Zn. Mo correlates positively with Pb at Mari, Ilvesneva, Kenkisuo and Niemelä, but negatively at Lamparekaarrot. Ni shows strong positive correlation with Fe and Co at all deposits except Mari (Fig. 6; Table 4).

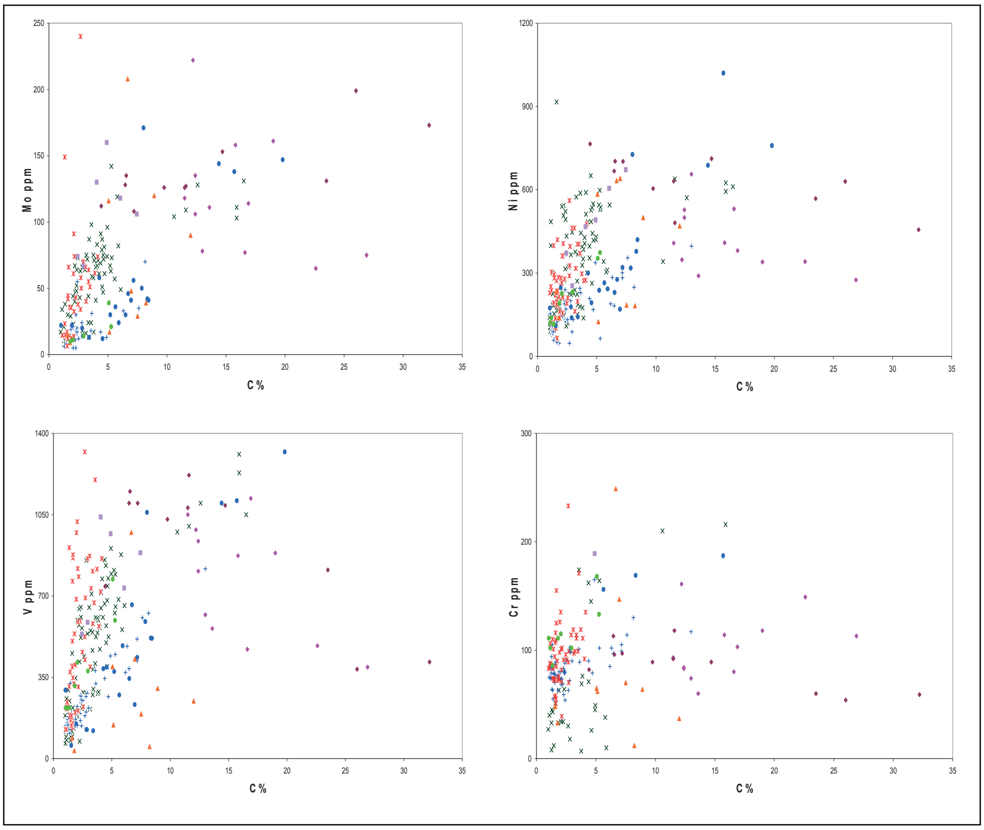


Figure 5. Plot of Mo, Ni, V and Cr against graphitic C for black schists. Symbols as in Fig. 4.

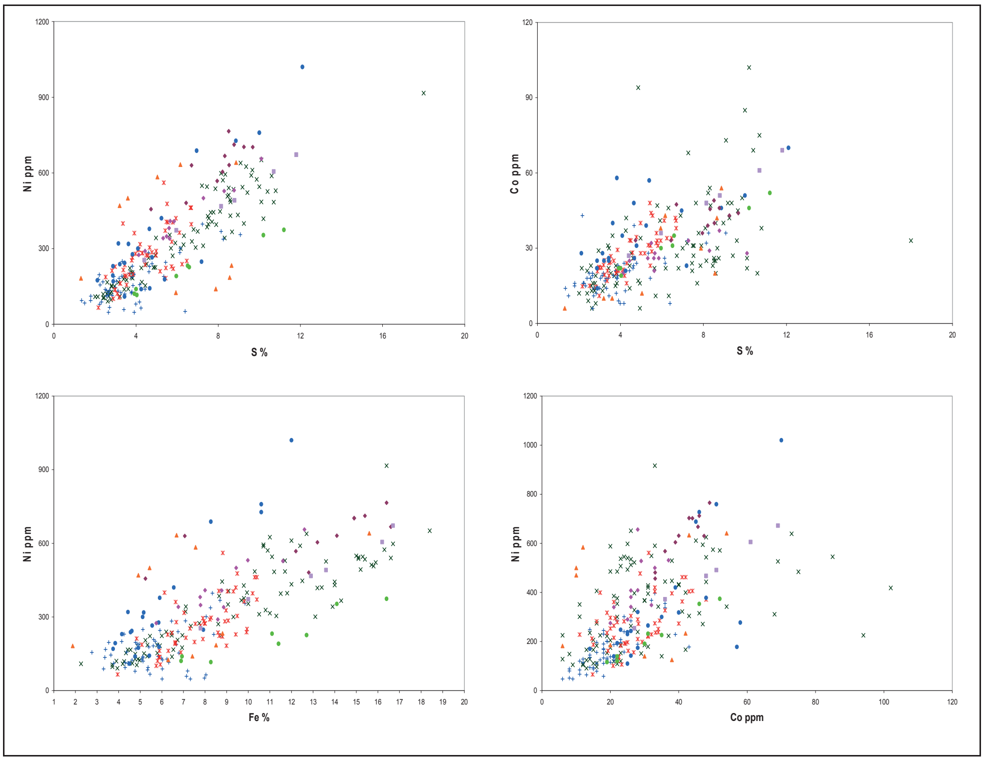


Figure 6. Plot of Ni and Co against S and Ni against Fe and Co for black schists. Symbols as in Fig. 4.

Table 4. Correlation coefficients for the selected elements of black schists.

	1. Kenkisuo			**2.** Mari			**3.** Hirvasperä			**4.** Koiramaa			**5.** Ilvesneva		
	C	S	Fe	C	S	Fe	C	S	Fe	C	S	Fe	C	S	Fe
S	**-0.77**		**0.85**	**-0.61**		**0.81**	**0.52**		**0.77**	0.38		**0.85**	**0.98**		**0.95**
Fe	**-0.91**	**0.85**		-0.29	**0.81**		0.42	**0.77**		0.33	**0.85**		**0.89**	**0.95**	
Co	-0.44	**0.58**	0.45	**-0.50**	**0.76**	**0.73**	0.43	**0.52**	0.39	0.43	0.49	0.37	**0.95**	**0.99**	**0.96**
Cr	**-0.79**	0.41	**0.71**	0.04	0.31	0.41	**0.63**	0.40	0.37	**0.69**	0.19	0.03	**0.80**	**0.81**	**0.68**
Cu	-0.37	0.42	0.17	0.47	0.01	**0.53**	**0.70**	**0.60**	**0.54**	0.48	0.47	0.48	**0.94**	**0.97**	**0.92**
Mo	**0.79**	**-0.63**	**-0.80**	0.39	-0.32	-0.15	**0.67**	0.36	0.41	**0.69**	0.48	0.47	**0.82**	**0.75**	**0.53**
Ni	**-0.66**	**0.83**	**0.70**	0.38	-0.07	0.36	**0.69**	**0.71**	0.39	**0.52**	**0.94**	**0.88**	**0.98**	**0.99**	**0.94**
Pb	**0.67**	**-0.54**	**-0.79**	0.45	-0.43	-0.17	0.40	0.49	0.48	0.17	0.31	**0.54**	-0.14	-0.15	-0.27
V	**-0.77**	**0.64**	**0.79**	0.21	0.05	0.21	**0.94**	**0.53**	0.44	**0.80**	**0.64**	**0.70**	**0.94**	**0.94**	**0.86**
Zn	**-0.78**	**0.78**	**0.86**	0.42	-0.36	-0.16	0.08	0.09	0.18	0.38	**0.68**	**0.76**	**0.82**	**0.76**	**0.56**
	Mo	Ni	V	Mo	Ni	V	Mo	Ni	V	Mo	Ni	V	Mo	Ni	V
Co	0.00	**0.91**	-0.02	-0.09	0.13	0.33	0.19	**0.74**	0.43	0.31	0.42	0.47	**0.68**	**0.99**	**0.92**
Cr	**-0.64**	0.18	**0.88**	**0.69**	**0.65**	**0.94**	0.21	0.46	**0.74**	0.37	0.41	0.47	**0.96**	**0.82**	**0.92**
Cu	-0.18	0.34	0.18	**0.51**	**0.86**	**0.59**	**0.59**	**0.61**	**0.62**	0.34	**0.55**	**0.52**	**0.85**	**0.97**	**0.98**
Mo		-0.33	**-0.72**		**0.78**	**0.89**		**0.64**	**0.56**		**0.57**	**0.84**		**0.79**	**0.96**
Ni	-0.33		0.26	**0.78**		**0.79**	**0.64**		**0.68**	**0.57**		**0.74**	**0.79**		**0.95**
Pb	**0.88**	-0.22	**-0.80**	**0.94**	**0.75**	**0.86**	0.36	**0.56**	0.33	0.25	0.37	0.38	**0.92**	-0.17	-0.11
V	**-0.72**	0.26		**0.89**	**0.79**		**0.56**	**0.68**		**0.84**	**0.74**		**0.96**	**0.95**	
Zn	**-0.81**	0.42	**0.90**	**0.98**	**0.81**	**0.85**	0.24	0.22	0.15	**0.52**	**0.75**	**0.72**	**0.99**	**0.78**	**0.88**

	6. Niemelä			**7.** Häkkilänpalo			**8.** Viitastenjärvi			**9.** Lamparekaarrot		
	C	S	Fe	C	S	Fe	C	S	Fe	C	S	Fe
S	**0.69**		**0.97**	-0.46		**0.90**	0.25		**0.94**	**0.95**		**0.99**
Fe	**0.70**	**0.97**		**-0.66**	**0.90**		0.25	**0.94**		**0.93**	**0.99**	
Co	**0.59**	**0.67**	**0.71**	**-0.55**	**0.60**	0.43	0.32	**0.81**	**0.78**	**0.95**	**0.99**	**0.99**
Cr	**0.86**	**0.65**	**0.72**	0.38	-0.45	**-0.61**	0.37	0.35	0.44			
Cu	-0.02	-0.03	-0.03	-0.30	0.34	0.44	0.28	0.35	0.32	-0.09	0.05	0.08
Mo	**0.81**	**0.78**	**0.84**	-0.42	-0.26	-0.12	0.34	0.28	0.28	0.46	**0.57**	**0.61**
Ni	**0.86**	**0.88**	**0.91**	**-0.51**	**0.98**	**0.89**	0.46	**0.68**	**0.68**	**0.94**	**0.99**	**0.99**
Pb	**0.79**	**0.60**	**0.64**	-0.30	0.36	0.45	0.07	**0.57**	0.41	**0.65**	**0.58**	0.44
V	**0.90**	**0.72**	**0.79**	**-0.57**	-0.05	0.08	**0.54**	0.27	0.33	**0.51**	**0.57**	**0.58**
Zn	-0.05	-0.23	-0.31	-0.11	-0.24	-0.17	0.34	0.16	0.17	-0.05	0.20	0.28
	Mo	Ni	V	Mo	Ni	V	Mo	Ni	V	Mo	Ni	V
Co	**0.59**	**0.71**	**0.66**	0.12	**0.59**	0.09	0.11	**0.54**	0.23	**0.56**	**0.99**	**0.57**
Cr	**0.77**	**0.78**	**0.83**	0.44	-0.47	0.15	**0.80**	**0.63**	**0.80**			
Cu	0.08	0.04	0.05	0.49	0.25	0.28	**0.56**	**0.67**	0.39	**0.61**	0.05	0.28
Mo		**0.93**	**0.92**		-0.24	**0.67**		**0.66**	**0.85**		**0.53**	**0.86**
Ni	**0.93**		**0.92**	-0.24		0.03	**0.66**		**0.74**	**0.53**		**0.53**
Pb	**0.77**	**0.83**	**0.78**	0.43	0.32	0.48	-0.31	0.20	-0.11	**-0.57**	**0.60**	0.15
V	**0.92**	**0.92**		**0.67**	0.03		**0.85**	**0.74**		**0.86**	**0.53**	
Zn	-0.20	-0.22	-0.23	**0.83**	-0.31	0.49	0.40	0.26	0.43	**0.71**	0.19	0.46

5. CONCLUSIONS

The thickness of the Paleoproterozoic black schist intercalations investigated in this work usually varies between 0.1 and 3 m, but may reach 20 m in places. They show medium to high median graphite and sulphur concentrations, with the mean values varying between 1.9%–14.7% and 3.4%–8.5%, respectively. Pyrrhotite and pyrite are by far the most common sulphides, whereas chalcopyrite and sphalerite occur sporadically and are totally absent in some places. The base metal contents (especially Zn) of the black schists studied in this work are on the average lower compared to those which are closely related to the exploited sulphide ore deposits, or to the gigantic Talvivaara Ni-Cu-Zn deposit under construction just now (tables 2, 3). To some degree, Kenkisuo and Lamparekaarrot, however, show similar Zn, Ni and Cu values compared to the black schists of the Vihanti, Outokumpu, Hammaslahti and Talvivaara areas.

C/S-, V/(V+Ni)- and V/Cr ratios have been useful in determining depositional conditions and environments for organic-rich muds. Median C/S ratios for the black schists studied in this work are in most cases <1, varying between 0.3 and 2.5, while the V/(V+Ni)- and V/Cr ratios vary from 0.4 to 0.7 and from 2.7 to 20, respectively. These values very much resemble the ratios obtained from the analyses of black schists of eastern Finland and Ostrobothnia. Low C/S ratios, as well as sufficiently high V/(V+Ni)- and V/Cr ratios, indicate anoxic depositional environments for metalliferous organic-rich mud (black schist) accumulation.

Black schists at Kenkisuo, Mari and Häkkilänpalo differ from other black schist occurrences in that they are closely related to volcanic rocks of lower to medium amphibolite facies, while other black schists occur in upper amphibolite and high-T / medium-P or low-P granulite facies terrains. Differences with other black schist deposits are distinctly expressed in correlation coefficients, too.

Concerning the above-mentioned occurrences, C/S ratios for some separate samples may lie between 6.2 and 6.8, with median values being high as well. In a few cases at Kenkisuo and Mari, high C/S- and low V/(V+Ni) ratios (0.2–0.5) are met in the same samples, which might suggest that at least occasionally dysoxic or even oxic conditions prevailed in those depositional environments. On the other hand, V/Cr ratios are sufficiently great to support anoxic conditions. At Häkkilänpalo, some samples show high (3–6.5) C/S ratios, too. However, both V/(V+Ni) and V/Cr ratios are sufficiently great to suggest the existence of anoxic depositional environments for the accumulation of organic matter.

Black schist intercalations at Hirvasperä, Koiramaa, Ilvesneva, Niemelä and Lamparekaarrot occur within migmatitic mica gneisses. Zn, Cu and Ni contents are lowest at Hirvasperä, Ilvesneva and Niemelä and highest at Lamparekaarrot. V/(V+Ni)-, V/Cr- and C/S ratios suggest anoxic depositional environments for all above-mentioned black schist formations. The high C/S value at Niemelä is, however, an exception, being a consequence of sulphide-poor and graphite-rich black schists. The high V/Cr value at Koiramaa is accounted for by the very low (<detection limit) Cr-contents of many samples.

Graphite-bearing rocks at Viitastenjärvi are mainly mica-poor quartz-feldspar gneisses, cordierite gneisses and fine-grained mica gneisses. They are graphite-poor, the sulphur-content being roughly double. Base metal contents are also low. C/S, V/(V+Ni) and V/Cr ratios are, however, similar compared to most other black schist occurrences in the Vihanti area, suggesting anoxic conditions in depositional environments.

The relatively low Cu, Ni and Zn contents of the black schists analysed in this study suggest that these metals precipitated from seawater in anoxic conditions. Except at Mari, Kenkisuo and Häkkilänpalo, it is most likely that no hydrothermal metalliferous solutions were incorporated in accumulating black shales. Due to the low base metal content and small volume of the separate black schist formations, their significance is purely scientific and not economic.

6. ACKNOWLEDGMENTS

I wish to thank Kirsti Loukola-Ruskeeniemi for reviewing the manuscript. Her constructive comments and corrections markedly improved the paper. The English Centre Helsinki revised the English, which is gratefully noted.

REFERENCES

Ahtonen, N. 1996. Pohjois-Pohjanmaan liuskejakson mustaliuskeiden geokemia, mineralogia ja petrofysiikka malminetsinnän kannalta. Pro gradu tutkielma, Oulun yliopisto, Geotieteiden ja tähtitieteen laitos. 77 p. (in Finnish)

Arkimaa, H., Hyvönen, E., Lerssi, J., Loukola-Ruskeeniemi, K. & Vanne J. 2000. Suomen mustaliuskeet aeromagneettisella kartalla – Proterozoic black shale formations and aeromagnetic anomalies in Finland, 1:1 000 000. Espoo: Geologian tutkimuskeskus – Geological Survey of Finland.

Autere, I., Pelkonen, K. & Pulkkinen, K. 1991. Outokumpu Finnmines Oy:n Vihannin kaivos. Summary: Outokumpu Finnmines Oy's Vihanti zinc mine. Vuoriteollisuus – Bergshanteringen, n:o 2, 81–88.

Berner, R. A. & Raiswell, R. 1983. Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. Geochimica et Cosmochimica Acta 47, 855–862.

Berner, R. A. & Raiswell, R. 1984. C/S method for distinguishing freshwater from marine sedimentary rocks. Geology 12, 365–368.

Bertine, K. K. 1972. The deposition of molybdenum in anoxic waters. Marine Chemistry 1, 43–53.

Breit, G. N. & Wanty, R. B. 1991. Vanadium accumulation in carbonaceous rocks: A review of geochemical controls during deposition and diagenesis. Chemical Geology 91, 83–97.

Brumsack, H.-J. 1980. Geochemistry of Cretaceous black shales from the Atlantic Ocean (DSDP LEGS 11, 14, 36 and 41). Chemical Geology 31, 1–25.

Brumsack, H.-J. 1989. Geochemistry of recent TOC-rich sediments from the Gulf of California and the Black Sea. Geologische Rundschau 78, 851–882.

Calvert, S. E. & Karlin, R. E. 1991. Relationships between sulphur, organic carbon, and iron in the modern sediments of the Black Sea. Geochimica et Cosmochimica Acta 55, 2483–2490.

Calvert, S. E. & Pedersen, T. F. 1996. Sedimentary geochemistry of manganese: Implications for the environment of formation of manganiferous black shales. Economic Geology 91, 36–47.

Cameron, E. M. & Garrels, R. M. 1980. Geochemical composition of some Precambrian shales from the Canadian Shield. Chemical Geology 28, 191–197.

Coveney, R. M., Jr. & Martin, S. P. 1983. Molybdenum and other heavy metals of the Mecca quarry and Logan quarry shales. Economic Geology 78, 132–149.

Coveney, R. M., Jr., Watney, W. L. & Maples, C. G. 1991. Contrasting depositional models for Pennsylvanian black shale discerned from molybdenum abundances. Geology 19, 147–150.

Davis, H. R., Byers, C. W. & Dean, W. E. 1988. Pyrite formation in the Lower Cretaceous Mowry shale: Effect of organic matter type and reactive iron content. American Journal of Science 288, 873–890.

Dill, H. 1986. Metallogenesis of Early Paleozoic Graptolite Shales from the Graefenthal Horst (Northern Bavaria-Federal Republic of Germany). Economic Geology 81, 889–903.

Gavshin, V. M. & Zakharov, V. A. 1996. Geochemistry of the Upper Jurassic-Lower Cretaceous Bazhenov Formation, West Siberia. Economic Geology 91, 122–133.

Hatch, J. R. & Leventhal, J. S. 1992. Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pensylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, Kansas, U.S.A. Chemical Geology 99, 65–82.

Henderson, J. B. 1977. Archean geology and evidence of ancient life in the Slave Structural Province, Canada. In: Ponnamperuma, C. (ed.) Chemical evolution of the Early Precambrian. New York, San Francisco, London: Academic Press, 41–54.

Huerta-Diaz, M. A. & Morse, J. W. 1992. Pyritization of trace metals in anoxic marine sediments. Geochimica et Cosmochimica Acta 56, 2681–2702.

Iisalo, E. 1997. Sinkkimalmitutkimukset Siikajoen Hirvasperällä, ktl 2441 12, vuosina 1994–1996. Geological Survey of Finland, unpublished report M19/2441/97/3/10. 7 p. (in Finnish)

Jackson, J. A. (ed.) 1997. Glossary of geology. Alexandria, Virginia: American Geological Institute.

Kahma, A. 1973. The main metallogenic features of Finland. Geological Survey of Finland, Bulletin 265. 28 p.

Kahma, A. 1978. The main sulphide ore belt of Finland between Lake Ladoga and the Bothnian Bay. Bulletin of the Geological Society of Finland 50, 39–43.

Korsman, K. & Glebovitsky, V. (eds.) 1999. Structure-lithology, metamorphism and metallogeny of the Raahe-Ladoga Zone. Map 2: Metamorphism 1:1 000 000. Geological Survey of Finland.

Korsman, K., Koistinen, T., Kohonen, J., Wennerström, M., Ekdahl, E., Honkamo, M., Idman, H. & Pekkala, Y. (eds.) 1997. Suomen kallioperäkartta – Berggrundskarta över Finland – Bedrock map of Finland 1:1 000 000. Geological Survey of Finland.

Kousa, J., Luukas, J., Mäki, T., Ekdahl, E., Pelkonen, K., Papunen, H., Isomäki, O.-P., Penttilä, V.-J. & Nurmi, P. 1997. Geology and mineral deposits of central Ostrobothnia. Geological Survey of Finland, Guide 41, 43–67.

Kukkonen, I., Sarapää, O. & Heino T. 1985. Black schists, their origin, composition and occurrence. Geological Survey of Finland, Report of Investigation 69, 70–84. (in Finnish, English abstract)

Leventhal, J. S. 1991. Comparison of organic geochemistry and metal enrichment in two black shales: Cambrian Alum Shale of Sweden and Devonian Chattanooga Shale of United States. Mineralium Deposita 26, 104–112.

Lewan, M. D. 1984. Factors controlling the proportionality of vanadium to nickel in crude oils. Geochimica et Cosmochimica Acta 48, 2231–2238.

Lewan, M. D. & Maynard, J. B. 1982. Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. Geochimica et Cosmochimica Acta 46, 2547–2560.

Loukola-Ruskeeniemi, K. 1992. Geochemistry of Proterozoic metamorphosed black shales in eastern Finland, with implications for exploration and environmental studies. Academic Dissertation, University of Helsinki, Geological Survey of Finland. 86 p.

Loukola-Ruskeeniemi, K. 1999. Origin of Black Shales and the Serpentinite-Associated Cu-Zn-Co Ores at Outokumpu, Finland. Economic Geology, vol. 94, 1007–1028.

Loukola-Ruskeeniemi, K. & Heino, T. 1996. Geochemistry and genesis of the black shale-hosted Ni-Cu-Zn deposit at Talvivaara, Finland. In: A group of papers devoted to the metallogeny of black shales. Economic Geology 91, 80–110.

Loukola-Ruskeeniemi, K., Kuronen, U. & Arkimaa, H. 1997. Geochemical comparison of metamorphosed black shales associated with the Vihanti zinc deposit and prospects in western Finland. Geological Survey of Finland, Special Paper 23, 5–13.

Nikander, J. 1999. Malmitutkimukset Merijärven Kenkisuolla karttalehdellä 2432 07, vuosina 1997–1998. Geological Survey of Finland, unpublished report M19/2432/-99/1/10. 4 p. (in Finnish)

Nikander, J. 2004. Pattijoen alueen geologia Raahe-Laatokka – vyöhykkeen luoteisosassa. In: Kousa, J. & Luukas, J. (eds.) Vihannin ympäristön kallioperä- ja malmitutkimukset vuosina 1992–2003. Geological Survey of Finland, unpublished report M10.4/2004/2, 109–118. (in Finnish)

Peltola, E. 1960. On the black schists in the Outokumpu region in Eastern Finland. Bulletin de la Commission Geologique de Finlande 192. 107 p.

Ruskeeniemi, K., Sarapää, O. & Rehtijärvi, P. 1986. Chemical composition of Proterozoic carbon-bearing metasediments in Finland. Geologi, v. 38, 90–95. (in Finnish)

Tyson, R. V. 1987. The genesis and palynofacies characteristics of marine petroleum source rocks. In: Brooks, J. R. V. & Fleet, A. J. (eds.) Marine petroleum source rocks. Geological Society, Special Publication, v. 26, 47–68.

Västi, K. 1995. Geokemiallisen sinkki-kupariaiheen tutkimukset Ruukin Niemelässä 1992–1994. Geological Survey of Finland, unpublished report M19/2443/-95/1/10. 8 p. (in Finnish)

Västi, K. 1997. Tutkimustyöselostus Ruukin kunnassa valtausalueella Koira1 (Kaivosrekisterinro 6262/1) suoritetuista sinkkimalmitutkimuksista vuosina 1995–1996. Geological Survey of Finland, unpublished report M06/2443/-97/1/10. 6 p. (in Finnish)

Västi, K. 1998 a. Tutkimustyöselostus Pulkkilan kunnassa valtausalueilla Viita 1 (Kaivosrekisterinro 6263/1), Viita 2 (Kaivosrekisterinro 6263/2) ja Viita 3 (Kaivosrekisterinro 6413/1) suoritetuista sinkki- ja kuparimalmitutkimuksista vuosina 1993–1996. Geological Survey of Finland, unpublished report M06/3412/-98/1/10. 6 p. (in Finnish)

Västi, K. 1998 b. Sinkki- ja kuparimalmitutkimukset Rantsilan Honkisalon ja Ruukin Rankisen kylän välisellä vyöhykkeellä vuosien 1993–1997 välisenä aikana. Geological Survey of Finland, unpublished report M19/2434,3412/-98/1/10. 16 p. (in Finnish)

Wignall, P. B. 1994. Black shales. Oxford: Calderon Press. 123 p.

www.gtk.fi
info@gtk.fi

Black shales (schists) are dark-coloured carbonaceous rocks, which were originally deposited as organic-rich mud on oxygen-deficient or oxygen-free ocean bottoms. They often are enriched in many trace metals, even to such an extent that economic mining activity is possible. Black shales are also often met in close association with massive zinc and copper deposits, which in some cases is thought to have had a possible role (as cap rock) in the deposition of these types of ores.

ISBN 978-952-217-051-4 (PDF)
ISSN 0781-4240