

Environmental impact of mineralised black shales

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ABSTRACT

Black shales are sedimentary rocks containing > 0.5% of organic carbon. They host polymetallic deposits which have been mined for Cu, Ni, Zn, Mn, P, Mo, V, U, Au and PGE (platinum group elements). Even sub-economic occurrences provide potential risk of acid rock drainage when exposed to oxic surface environment. The natural acid neutralisation potential varies depending on the adjacent rock units, especially on the presence of calcareous rocks. The chemical and mineralogical composition of black shale is reflected in the quality of the surface waters and groundwater. Cu, Ni, Pb, U and Zn are recognised as major pollutants though the environmental impact is characteristically polymetallic just like the black shale occurrences. Hence, the environmental impacts have to be evaluated in each occurrence.

The Proterozoic Ni–Zn–Cu–Co deposit at Talvivaara, Finland, is reviewed in more detail as an example of a large, low-grade deposit that is currently exploited with open pit mining and a bioleaching process, together with the Proterozoic Central African Copperbelt, the Cambrian U–Mo deposits in Sweden, the Cambrian Ni–Mo–PGE deposits in China and the Cambrian–Ordovician U deposits in South-Korea, the Devonian Ni–Zn–PGE occurrences in Yukon, Canada, and Kentucky, USA, and the Permian Cu–Ag deposits in Poland and Germany. The mineralised horizons may be merely few centimetres thick like in Yukon or hundreds of metres thick like at Talvivaara. Both natural and anthropogenic environmental impacts of black shales are reviewed world-wide, and based on the overview of the state-of-the-art an integrated research approach is suggested for the comprehensive assessment of the risk.

Black shales are natural sources of soil and water contamination. At Talvivaara, the geochemical background includes higher than average concentrations of Ni, Cu, Zn and Mn in glacial till, peat, surface waters and groundwater as well as in stream and lake sediments. Bioaccumulation by plants has been reported in China and Korea. Even endemic diseases have been proposed to be linked with the contamination derived from the weathering and leaching of harmful elements from black shale. Anthropogenic actions exposing the black shale bedrock and associated soils to oxic conditions further intensifies acid rock drainage.

Regional or nation-wide mapping of the black shales is recommended to detect potential risk areas. Finland has recently completed the country-wide mapping program of black shales with airborne geophysics integrated with geological, petrophysical and geochemical studies. The black shale database is actively used in regional planning and by environmental authorities, research institutes and consulting companies. In the case of the historical black shale mining areas like in the Kupferschiefer in Germany, restoration measures have been applied to prevent further acid mine drainage. In active and future mining projects, a comprehensive environmental impact assessment with effective monitoring programmes and closure plans play a crucial role in the prevention of acid mine drainage from the black shale -associated deposits.

1. Introduction

Sulphide oxidation at oxygenated environment and subsequent migration of trace elements and sulphate from the sulphide-rich bedrock and soil to surface waters, known as acid rock drainage, has gained attention in the past decades (e.g., Blowes et al., 2003; Nordstrom,

2011). The public awareness of geogenic contamination has grown as a consequence of the potential human exposure. Chronic exposure even to low concentrations of As and Cr derived from soil has been suggested to elevate the risk of developing certain types of cancer (Zhao et al., 2014; Núñez et al., 2016). The results from a black shale area with elevated Ni and low Ca concentrations in bedrock and soil indicate that

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the use of dug well water, as well as the consumption of local mushrooms, slightly affects the Ca concentration of the blood serum of local residents. Low Ca values in the black shale bedrock and soil are reflected as lower Ca concentrations in blood serum than in the reference area in the same municipality with a lower sulphide and higher Ca content in the bedrock and the overlying glacial till (Loukola-Ruskeeniemi et al., 2003; Kantola et al., 2000, 2008; Kousa et al., 2011).

Black shales commonly host sub-economic, low-grade sulphide occurrences and may provide a source of base and precious metals, U, Mo, Ni, Mn, V, Hg, Sb, and W (Fan, 1983; Coveney and Glascock, 1989; Oszczepalski, 1989; Grauch and Huyck, 1990; Coveney and Chen, 1991; Pašava, 1993; Loukola-Ruskeeniemi et al., 1991; Leventhal, 1993; Wignall, 1994; Pašava et al., 1996; Loukola-Ruskeeniemi, 1999; Coveney, 2000; Fan et al., 2004; Coveney and Pašava, 2004; Shpirt et al., 2007; Polgári et al., 2012). As black shales are enriched in a variety of harmful elements, including radionuclides, they represent potential sources of soil, groundwater and surface water contamination.

The abundance of organic matter and sulphide minerals makes black shale susceptible to chemical weathering (Blowes et al., 2003; Nordstrom, 2011). When black shale outcrops, it is exposed to oxic conditions. Hence, sulphides are prone to oxidation and dissolution, liberating protons and trace metals (Jambor, 1994). As a consequence of low-pH drainage, even the more resistant silicate mineral phases are susceptible to alteration and dissolution, contributing to the metal load of the drainage waters. Fractures in the rock promote their weathering (Jin et al., 2013). The natural weathering processes are enhanced by anthropogenic actions that bring the black shale to the surface, such as mining, excavation, road construction and forestry. Therefore, as with any anthropogenic actions on sulphide-rich rocks, the disturbance of black shale enhances the release and mobility of the associated metals (Nordstrom, 2011).

Even though not within the scope of this work, it is worth to mention that, in the geological time scale, black shale plays a role in the carbon cycle and the oxygenation and de-oxygenation of the environment.

Characterisation of the sulphide mineralogy and rock assemblages of each black shale deposit and occurrence is needed to evaluate their pollution risk. In this review, we compare eight well-known black shale deposits where environmental studies have been carried out and where the concentrations of both S and C_{org} in the black shale exceeds 1%, namely

- the Proterozoic Talvivaara Ni–Zn–Co–Cu deposit in Finland,
- the Proterozoic Cu–Co and Ni deposits in Zambia, in the Central African Copperbelt,
- the Cambrian U–Mo occurrences in the alum shale units in Sweden,
- the Cambrian Niutitang Ni–Mo–platinum group element (PGE) deposits in China,
- the Cambrian–Ordovician Okchon U deposit in South Korea,
- the Devonian Ni–Zn–PGE occurrences in Yukon, Canada,
- the Devonian U-bearing black shale occurrences in Kentucky, USA, and
- the Permian Kupferschiefer Cu–Ag deposits in Poland and Germany

(please see the references for each deposit in the figure caption of Fig. 1 and in more detail in sections 5–7 below).

2. Materials and methods

We have compiled data for the selected black shale units in Tables 1 and 2 that work as the core of this review. The selected mineralised black shale occurrences contain > 1% of both organic carbon and sulphur and either the black shale layer or organic matter in general has played an important role in the ore formation processes. A brief description of the different black shale occurrences is necessary to

understand the geochemical processes and to evaluate their environmental impacts as the thickness, ore mineralogy and the composition of wall rocks control the potential acid rock drainage. The numeric data is presented in tables and figures. Sampling and analytical methods for the data presented in Tables 1–3 are given in detail in the original publications cited.

In Section 5 below, we describe the environmental impacts of the Talvivaara black shale deposit in Finland in both pre-mining and active mining phases. Large geochemical databases serve as a basis for geochemical baseline studies. They were acquired with nation-wide surveys and are maintained by the Geological Survey of Finland (Salminen and Tarvainen, 1995). Before the nation-wide mapping program started, pilot studies were carried out in the Talvivaara region because the chemical characteristics of the bedrock and overlying glacial till exhibit contrasting geochemical characteristics for black shale and the adjacent quartzite and granitoid areas (Gustavsson et al., 2012). These data have subsequently been applied to depict the geochemical background of Ni and Cu in glacial till, stream sediments and stream water. The exploitation of the Talvivaara Ni–Zn–Cu–Co deposit began in 2008, and sampling performed before that is thus considered to represent pre-mining conditions. Thereafter, the evaluation of the environmental impacts of mining activities is based on scientific articles and public monitoring data provided by the mining company in their web-pages.

The present paper is the result of team work where the main responsibilities were divided as follows: Annika Parviainen was responsible for the literature study of the environmental impacts and the compilation of the tables and Fig. 7 while Kirsti Loukola-Ruskeeniemi was responsible for the compilation of Figs. 1–6. Kirsti Loukola-Ruskeeniemi was responsible for the black shale research, both geochemical and environmental, in the Talvivaara black shale deposit and other sites in Finland. The nation-wide black shale mapping program of Finland was carried out by geophysicists Eija Hyvönen, Hilikka Arkimaa, Jouni Lerssi and Meri-Liisa Airo, geologist Kirsti Loukola-Ruskeeniemi and research assistant Satu Vuoriainen from the Geological Survey of Finland. The international review is based on Kirsti Loukola-Ruskeeniemi's experience from international black shale projects during 1987–2008: the UNESCO International Geological Correlation Programme Projects (IGCP) 254, 357 and 429 related to mineralised black shales and their environmental impacts (e.g., Pašava and Gabriel, 1988), project “Ore deposits in black shale basins” between Finland and the Soviet Union /Russia and the European Union research project BIOSHALE which compared ore geology and environmental impacts of black shales in the Talvivaara deposit in Finland with the Lubin mine in Poland (<http://www.brgm.eu/project/bioshale-search-sustainable-way-of-exploiting-black-shale-ores-using-biotechnologies>).

3. Black shales and the associated sulphide deposits

Black shales are dark-coloured mudrocks containing organic matter and silt- and clay-size mineral grains that accumulated together (Swanson, 1961). In the IGCP 254 of UNESCO titled “Metalliferous Black Shales”, conducted during 1987–1992, a definition was agreed that a black shale should contain > 0.5% organic carbon (Huyck, 1990). Many researchers were of the opinion that a black shale should contain over 1% of both organic carbon and sulphur to represent specific depositional conditions but since in a black shale unit the content of organic carbon can vary, 0.5% was agreed to represent the minimum concentration within the unit. Black shales can be classified due to their Ca, Al and Si content (Loukola-Ruskeeniemi, 1992) and they comprise a heterogeneous group of polymetallic rocks (e.g., Tourtelot, 1979). Based on the U. S. Geological Survey black shale standard SDO-1 (Devonian Ohio Shale from Kentucky), the definition of a mineralised, so called ‘metalliferous’ black shale is (Huyck, 1990): “A metalliferous black shale is a black shale that is enriched in any given metal by a factor 2x (except Be, Co, Mo, and U, for which 1x is sufficient) relative to the U.S. Geological Survey Standard SDO-1.”

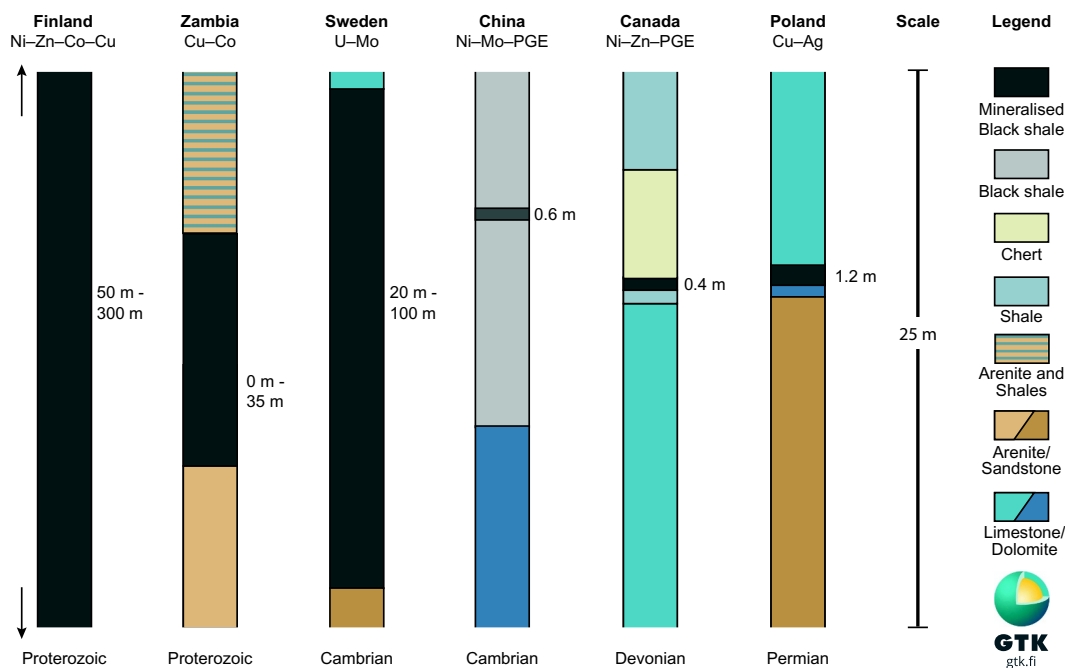


Fig. 1. The relative maximum thickness of mineralised black shale in typical profiles of the Palaeoproterozoic Talvivaara Ni–Zn–Cu–Co deposit in Finland (modified from Loukola-Ruskeeniemi and Lahtinen, 2013), Proterozoic Cu–Co black shale in Zambia (modified from McGowan et al., 2006), Cambrian U–Mo alum shales in Sweden (modified from Andersson et al., 1985), Cambrian Ni–Mo–PGE black shale in China (modified from, e.g., Han et al., 2015), Devonian Ni–Zn–PGE black shale in Yukon (modified from Hulbert et al., 1992), and Permian Cu–Ag black shale in Poland (modified from, e.g., Pieczonka et al., 2015).

The unifying feature of black shale is deposition as fine-grained, laminated sediment on the sea bottom with a high supply of organic matter. A key issue in the formation of black shale is the preservation of organic matter in the sediment, which usually requires deposition in low-oxygen or euxinic bottom waters. However, formation in oxic conditions has been recently described as well (Reynaud et al., 2018). At present, the deposition of organic- and sulphur-rich mud occurs, for example, in the Black Sea (Kaiser et al., 2017). Piper and Calvert (2009) studied two modern marine basins with anoxic bottom conditions. The hydrography and trace metal and phytoplankton nutrient budgets exhibit that the rate of burial of labile organic matter promotes anoxic conditions in the sediment pore waters that enhances the retention of trace metals deposited from the water column. High supply of clay minerals (up to 30%) with large reactive surface area contribute to the sorption and preservation of organic matter and metals (Kennedy et al., 2002). Macquaker and Bohacs (2007) show that the deposition and burial of mud is a more dynamic and complex process than traditionally thought, and findings from hydrocarbon exploration in deep sea (> 200 m depth) indicate that mud rich in organic carbon is formed by a combination of processes such as pelagic settling, hemipelagic deposition and turbidity currents.

The sources of metals include seawater-derived material (e.g., Mao et al., 2002; Lehmann et al., 2003, 2007 and 2016; Wallis, 2007; Xu et al., 2012, 2013; Pagès et al., 2018; Morel and Price, 2003; Piper and Calvert, 2009; Slack et al., 2015) and hydrothermal and/or multiple metal sources (Loukola-Ruskeeniemi, 1991; Hulbert et al., 1992; Coveney et al., 1994; Lott et al., 1999; Steiner et al., 2001; Jiang et al., 2007; Pašava et al., 2008; Och et al., 2013; Young et al., 2013). The post-depositional diagenetic and metamorphic processes have an impact on the mineralogy of black shale and the distribution of trace elements (e.g., Piper and Calvert, 2009; Rimstidt et al., 2017). In addition, organic compounds and biomineralization (mineral production by organisms) may have a role in the genesis of the ore and fluxes at the sediment-water interface during early diagenesis may have an impact on the trace element concentrations (Piper and Calvert, 2009; Rimstidt et al., 2017; Pérez-Huerta et al., 2018). Fine-grained organic-rich mud

with low permeability and a locally reducing environment may capture the ore-forming fluids underneath and the hydrothermal fluids may then precipitate in and below this trap. As a potential zone of weakness during tectonic deformation, a black shale unit may act as a thrust surface and locally allow the flow of fluids (Loukola-Ruskeeniemi, 1992). Moreover, microbial activity, specifically sulphate-reducing bacteria, may trigger the precipitation of sulphide minerals, and the accumulation of metals may be promoted by porphyrins that bind metals to form complexes (Greenwood et al., 2013).

Black shales host sulphide deposits but are also associated with many other types of deposits because both black shale and massive sulphide deposit in most cases require isolation from oxic conditions to be preserved. In addition to sulphide deposits, black shales are a source rock for hydrocarbons (e.g., Sethi and Schieber, 1998) and shale gas deposits (Zou, 2013).

For the review, we selected eight black shale deposits and occurrences containing > 1% organic carbon and over 1% sulphur. The deposits represent different metamorphic grades and different geological terrains. In the Sections 5, 6 and 7 below, we have divided the deposits into groups according to the main metal (Ni, Cu, U), though the deposits are actually polymetallic (Table 1).

4. Weathering of black shale under natural conditions and due to anthropogenic actions

Black shale occurrences should be considered as sources of acid rock drainage when they are exposed to oxic conditions. Natural weathering profiles and excavations have been studied in black shale areas worldwide, for example in China, Korea, Sweden and the United States (Falk et al., 2006; Fang et al., 2002; Lavergren et al., 2009b,b; Ling et al., 2015; Liu et al., 2017; Park et al., 2010; Peng et al., 2004, 2014; Petsch et al., 2005; Tang et al., 2018; Xu et al., 2013; Yu et al., 2012). These studies show that black shales are sources of harmful elements in soils and adjacent water systems, and translocation occurs to plants and agricultural products cultivated on black shale-associated soils.

Recent studies demonstrate that besides chemical and mechanical

Table 1
Age, depositional environment and thickness of selected black shale deposits around the world. Additionally, mean (unless mentioned otherwise), min. and max. values of organic C, S and metals of main economic interest and main ore forming minerals are given.

Location and name of the black shale deposit	Depositional environment	Intercalating rocks	Thickness of the sequence	Mean organic C and S content (Min–Max)	Main sulphides and U minerals	Estimated ore reserves	Element concentrations in black shales (Min–Max)
Finland Talvivaara <i>Palaeoproterozoic</i>	Stratified oxic/anoxic, restricted marine basin	Black meta-carbonate rocks (calc-silicate rocks rich in graphite and tremolite)	50–800 m	Organic C: Median 8.2% (2.4–13.2%) ¹ S: Median 9.0% (2.4–26.0%) ¹	Pyrite, pyrrhotite, chalcocopyrite, sphalerite, galena, alabandite, molybdenite, pentlandite, ullmannite, stannite, uraninite, thucholite	Ni–Zn–Co–Cu 2053 Mt (0.22% Ni, 0.13% Cu, 0.50% Zn, and 0.02% Co) ²	Talvivaara ore (556 samples): median As 86 mg/kg (4–891), Cd 16 (< 1–41), Co 189 (15–653), Cu 1340 (163–5190), Mn 2750 (694–59,300), Mo 58 (6–96), Ni 2415 (102–6690), Pb 47 (5–437), U 17 (2–30), V 660 (120–1190), Zn 4955 (941–11,000) ¹
China Niutang Formation <i>Cambrian</i>	From a shallow shelf environment to a deep basinal facies of black shale	Phosphorite	Mineralised layer 5–20 cm, rarely up to 2 m	Organic C: ● 10% (0.7–15%) ³ ● 7.7% (2.6–11.5%) ⁴ S: -	Bravoite, vaesite, pyrite, Millerite, gersdorffite, MoSC ⁵	Ni–PGE–Mo–U No estimates available	Non-mineralised black shale: Ni (28–1280 mg/kg), Mo (4.3–177) ³ Mineralised black shale: Ni up to 53400 mg/kg, Mo up to 87300 ³ Mineralised black shale: As 8969 mg/kg (3340–18054), Cd 481(87–879), Co 281 (109–437), Cu 2304 (740–3847), Mo 38508 (7346–84922), Ni 48345 (14688–70292), Pb 333 (137–599), Sb 284 (72–564), U 295 (73–520), V 189 (62–552), Zn 48345 (5532–116712) ³
Canada Yukon <i>Devonian</i>	Epicratonic marine basin, proximal to the transition zones between shallow and deep water sedimentary environments	–	Ni–Zn–PGE-rich layer from few cm to 40 cm	Organic C: 1.9% (1.3–2.5%) ⁶ S: 28% (20–33%) ⁶	Vaesite, pyrite, marcasite, sphalerite, wurzite, melnicovite	Ni–Zn–PGE No mining activities, Other anthropogenic actions (e.g., road construction, excavation)	Nick Property mineralization: As (0.19–0.42%), Ba (0.2–0.5), Ni 5.3 (2.3–2.8), Mo (0.1–0.4), Re (1.0–6.1), Se (0.06–0.24), V (0.037–0.088), Zn 0.73 (0.4–1.2), U (40–108 mg/kg) ⁶ Taiga Property: Up to Ni 5.21%, Au 100 µg/kg, Pt 560, 244 Pd ⁷
Poland and Germany (Saxony-Anhalt)	Intracontinental or cratonic Central European Basin	–	Average 0.3 m with up to 1.2 m, footwall and	Organic C: ● 0.3–30% ⁹	Bornite, chalcocopyrite, pyrite, chalcocite, covellite, neodigenite, native Ag.	Germany Cu–Ag (Pb, Zn, Au, V, Mo,	Ni-rich black shale occurrences: Ni 3.6 % (1.2–7.0), As 6037 mg/kg (646–10690), Cd 21.6 (3.2–100), Co 154 (35–330), Cu 298 (89–560), Mo 1995 (390–3300), Pb 23.4 (7–58), Tl 217 (27–390), U 150 (3.8–650), Zn 6515 (230–23000) ⁸ Pitchy shale: Cu 7.1 wt.% (1.8–39), Pb 0.1 (0.04–0.5), Zn 0.06 (0.8–0.1), Ag 286 mg/kg

(continued on next page)

Table 1 (continued)

Location and name of the black shale deposit Age	Depositional environment	Intercalating rocks	Thickness of the sequence	Mean organic C and S content (Min–Max)	Main sulphides and U minerals	Estimated ore reserves	Element concentrations in black shales (Min–Max)
Kupferschiefer Permian			hanging wall ore up to 50 m	Poland (7.5–8.0%) Lubin 7.3% S: -	galena, sphalerite, loellingite, tetraahedrite, tennantite, idaite etc.	Ni, Co, Se, Re, Cd, Tl, Ge, and Te) (242 Mt) ¹⁰ Poland Cu–Ag–Au–Pb (Ni–Co–Mo) Lubin 379 Mt (Cu 1.32%, Ag 54.5 g/Mg) ¹⁷ Rudna 432 Mt (Cu 1.88%, Ag 62.52 g/Mg) ¹¹ Polkowice–Sieroszowice 409 Mt (Cu 2.3% and As 62 g/Mg) ¹¹ Cu ¹²	(120–3500), Au 1.5 (< 0.6–10), Hg 15 (1–53), Pt 0.1 (0.01–0.9) ⁹
Zambia Central African Copperbelt Proterozoic	Deep sea	–	<ul style="list-style-type: none"> 0.5–20 m (0.5–35 m)¹² from a few m to 80 m, lenses of dark carbonaceous quartz-rich rock vary from 1 to 10 m¹³ 	Organic C: <ul style="list-style-type: none"> 9–17%¹³ S: -	<ul style="list-style-type: none"> Pyrite, bornite, chalcocopyrite, chalcocite, malachite, chrysocolla, cuprite¹² Pyrite, bravoite, vaesite, millerite, chalcocopyrite, molybdenite, pyrrhotite, carrollite¹³ 	<ul style="list-style-type: none"> Ni (Cu–PGE)^{13,40} Mt (1.07% Ni)¹³ 	<ul style="list-style-type: none"> Cu 2–3%, (up to 20%)¹² Ni up to 17 %, Cu 2.5, Co 0.2, Fe 7, Mo 5000 mg/kg, U 20, Ir 24 µg/kg, Os 15, Ru 66, Rh 66¹³
Sweden Alum shales Late Cambrian to early Ordovician	Deep and shallow-marine environment of the Baltoscandian Platform over an extensive period of tectonic stability	Bituminous limestones; occasional chert bands and phosphorite nodules	Degerhamn 17 m, Ranstad (Billingen) 22–24 m Hällekis: 22 m	Organic C: <ul style="list-style-type: none"> 10% (up to 20%)¹⁴ 12% (5–20%)¹⁵ (2.7–20.6%)¹⁷Ranstad: 15%¹⁷Hällekis: 15% (8–28%)¹⁸ S: <ul style="list-style-type: none"> (4.6–8.4%)¹⁴ 5.5% (4.6–10.4%)¹⁵ (3.4–8.26%)¹⁶ Ranstad: 15% ¹⁷ Hällekis: 5.9% (4.9–8.4%) ¹⁸	Pyrite, chalcocopyrite, sphalerite, galena, brannerite, uraninite	Degerhamn: alum salt Ranstad: U No estimates available	<ul style="list-style-type: none"> As (59–212 mg/kg), Co (19–46), Cr (59–93), Cu (103–224), Mo (104–396), Ni (96–357), Pb (25–139), Th (10–14), U (31–8000), V (303–1464), Zn (36–1190)^{15,19} Co (22–39 mg/kg), Cr (55–210), Cu (69–210), Mo (47–350), Ni (110–510), Pb (28–140), U (22–410), V (380–3100), Zn (28–600)¹⁶ Degerhamn: As 121 mg/kg (91–138), Cd 5.5 (1.3–13), Cu 117 (97–158), Ni 107 (88–147), Zn 277 (77–623) ²⁰ Ranstad: As 106 mg/kg, Cd 2.5, Cu 110, Mn 250, Mo 340, Ni 200, Pb 14, Sb 5, U 300, Zn 130 ¹⁷ Okchon Metamorphic Belt: U (~0.03%), V (~0.3%), Ba (~1.4%) and Mo (~0.04%) ²¹
South Korea Okchon black shales Cambrian-Ordovician	Okchon sea basin	Coaly slates, lenses of phosphatic nodules	20–40 m	Organic C: 21% S: 2.3%	Pyrite, pyrrhotite, chalcocopyrite, uranothorite,	U No estimates available	(continued on next page)

Table 1 (continued)

Location and name of the black shale deposit <i>Age</i>	Depositional environment	Intercalating rocks	Thickness of the sequence	Mean organic C and S content (Min–Max)	Main sulphides and U minerals	Estimated ore reserves	Element concentrations in black shales (Min–Max)
USA Appalachian basin black shales <i>Devonian</i>	Euxinic sea basin	Siltstone, sandstone and limestone ²⁵	0–30 m ²⁵	Organic C: 3–6% ²⁶ S: 2–5% ²⁶	Pyrite, marcasite,	U	Deog-Pyung: Cd 6.3 mg/kg, Mo 136, Se 8.6 ²² Chu-Bu: As 3.0 mg/kg (0.5–6.2), Ba 1900 (240–4100), Cd 1.1 (0.5–3.9), Cu 38 (16–57), Mo 8 (1–23), Pb 17 (5–38), U 18 (5.4–47), V 199 (64–435), Zn 126 (27–417), Se 17.7 (1.5–33.9), S 451 (48–854) ^{23,24} Duk-Pyung: As 42 mg/kg (5.0–110), Ba 2110 (110–6000), Cd 10.9 (1.0–36), Cu 240 (120–430), Mo 213 (18–650), Pb 124 (19–440), U 83 (3–616), V 938 (70–1900), Zn 394 (42–1100), Se 1.9 (1.6–2.3), S 215 (15–753) ^{23,24} As 20–40 mg/kg, Co 20–40, Cu 40–70, Ni 80–150, U 10–40, V 150–300 ²⁶
					brannerite, uraninite, ekamite, and thorutite	No estimates available	

¹ Loukola-Ruskeeniemi and Lahtinen, 2013.

² Talvivaara Mining Company, 2012.

³ Shi et al., 2014.

⁴ Han et al., 2015.

⁵ Kao et al., 2001.

⁶ Hulbert et al., 1992.

⁷ Butterworth and Caulfield, 1997.

⁸ Goodfellow et al., 2010.

⁹ Kucha, 1990.

¹⁰ Borg et al., 2012.

¹¹ KGHM Polska Miedz (<http://kghm.com/>).

¹² McGowan et al., 2016.

¹³ Capistrant et al., 2015.

¹⁴ Andersson et al., 1985.

¹⁵ Lecomte et al., 2017.

¹⁶ Leventhal, 1991.

¹⁷ Allard et al., 1991.

¹⁸ Sanei et al., 2014.

¹⁹ Schovsbo, 2002.

²⁰ Falk et al., 2006.

²¹ Kim et al., 2015.

²² Kim et al., 1993.

²³ Lee et al., 1998.

²⁴ Park et al., 2010.

²⁵ Roen, 1984.

²⁶ Leventhal and Hosterman, 1982.

Table 2

Environmental impacts of mining of black shale deposits. Information on mining activities as well as mean, min. and max. values of selected trace elements in mine waste, soil, stream sediment, lake sediment, groundwater and surface water samples subjected to anthropogenic pollution in black shale areas are given. *Natural contamination in Korea, as available data on anthropogenic pollution are scarce.

Location and name of the deposit Mining activity Ore enrichment processes	Mean concentrations in mine waste or by-products (Min–Max)	Mean concentrations in anthropogenic (*natural) soil/sediment pollution (Min–Max)	Mean concentrations in (*natural) surface water bodies and in groundwater (Min–Max)
Finland Talvivaara 2008 – present Crushing, grinding, heap bioleaching	Production waste: Cd 1.0 mg/kg, Co 10.0, Cr 14, Cu 5.0, Fe 30,500, Mn 4840, Ni 420, Pb 5.1, Th 1.3, U 58, Zn 160 ¹	Lake sediments: Fe 68,300 mg/kg (47,000–88,000), Mn 3800 (2400–5100), Ni 760 (460–980), Zn 850 (370–1400), S 68,000 (43,000–110,000) ²	Groundwater: pH (4.4–8.8), SO ₄ (< 0.3–9500 mg/L), As (< 0.4–3.3 µg/L), Cd (< 0.1–2.2), Co (0.1–65), Cu (0.5–1200), Ni (0.5–6400), Pb (0.25–1.3), Zn (0.25–20,000), Al (1.5–6500), Fe (< 10–790,000), (U < 0.5–8.7) ³ Lake water (Salminen, Kalliojärvi): As (< 1.0 µg/L), Cd (< 0.03–1.7), Cu (< 0.1–7.3), Mn (86–37000), Ni (1.4–4700), Pb (< 0.5–1.4), Zn (< 5.0–780), U (< 1.0–240) ³ Lake water (Kivijärvi, Lumijärvi, Ylä-lumijärvi): As (< 1.0–42 µg/L), Cd (0.03–170), Cu (< 0.1–170), Mn (600–85000), Ni (28–1700000), Pb (< 0.5–45000) ³ Lake water (Kuusijärvi): pH 9.1 (6.5–11.2), SO ₄ 3500 mg/L (1800–6100), Na 690 mg/L (435–956), Co 4 µg/L (2–30), Cu 9 (0.6–80), Fe 370 (110–6910), Mn 263 (80–5850), Ni 36 (10–510), Zn 64 (10–890) ⁴ Lake water (Kalliojärvi and Ylä-lumijärvi): pH 6.1 (4.4–7.5), SO ₄ 136 mg/L (42–330), Na 3.6 (1.39–457), Co 4 µg/L (< 0.2–10), Cu 23 (< 1.2–30), Fe 2230 (80–18,600), Mn 3600 (110–30,500), Ni 19 (10–80), Zn 35 (< 20–130) ⁴ Stream water (Kalliojoki, Kivijoki, Tuhkajoki): pH 6.2 (5.1–7.2), SO ₄ 328 mg/L (44–473), Na 63 (4.9–282), Cu 20 µg/L (< 0.12–40), Fe 921 (240–2010), Mn 449 (100–1350), Ni 11 (10–20), Zn 24 (10–70) ⁴ Drainage pipe: pH 7.9 (6.5–10.4), SO ₄ 2434 mg/L (1700–3620), Na 452 mg/L (343–622), Cu 4.3 µg/L (2–40), Fe 4403 (180–837,000), Mn 1704 (170–303,000), Ni 27 (10–220), U, 0.02 (< 0.02–0.04), Zn 27 (10–60) ⁴
China Niutitang Formation Hunan: U mining Zunyi: Ni–Mo mining, 1985 – No reported data available on the ore enrichment processes	No reported data available	Soil: As (21–110 mg/kg), Cd (0.4–1.4), Cu (62–99), Hg (0.16–0.60), Mo (51–130), Ni (64–199), Pb (19–25), Zn (139–270), V (572–1221) ⁵	Surface water: pH 5.6 (3.0–7.8), As 1.0 µg/L (0.3–4.2), Cd 41.7 (2.1–297), Co 51.7 (0.05–298), Cu 3.9 (0.2–9.3), Ni 261 (22.8–1531), Pb 0.4 (0.02–2.6), Zn 873 (12.6–4087), U 147 (0.01–1372) ⁶
Canada Yukon, Nick Property No reported mining activity on black shale deposits	No reported data available	No reported data available	Eagle Plain excavation, stream water: pH 3.1 (2.8–4.4), Al 66.3 (44–84 mg/L), Fe 133 (3.0–459), Mg 86 (6.0–105), Mn 2.6 (1.5–3.3), Zn 4.8 (2.2–7.0) ⁷ Keno Hill stream water: pH 5.4–7.3, As (80–220 µg/L), Cd (35–2720), Cr (2–10), Co (15–149), Cu (< 1–94), Pb (5–131), Fe (121–25,500), Mo (12–28), Ni (40–621), Zn (3970–96,200) ⁸
Poland Kupferschiefer Lubin 1968 - (estimated closure in 2059) Rudna 1974 - (2045) Polkowice-Sieroszowice 1968 - (2054) Cu smelting	Zelazny Most tailings: As 25 mg/kg (12–37), Cd (< 0.5–0.7), Cu 1309 (1300–1318), Co 16 (5–27), Cr 34 (31–37), Fe 5550 (5200–5900), Ni 282 (275–288), Pb 245 (206–283), Zn 53 (30–75) ⁹ Zbiornik Gilow tailings: As 24 mg/kg (19–29), Cd (< 0.5–0.5), Co 13 (12–14), Cu 1126 (1084–1165), Cr 60 (55–65), Ni 580 (567–592), Pb 221 (219–2222), Zn 47 (32–61) ¹⁰	Stream sediments: As (< 5–49 mg/kg), Cd (< 0.5–2.9), Cu (22–4409), Co (2–62), Cr (3–114), Fe (4000–200,500), Ni (88–826), Pb (8–570), Zn (8–700) ^{9,10} Soil: Cd 4 mg/kg, Cu 7400, Cr 54, Mn 587, Ni 33, Pb 1960, Zn 675 ¹¹	No reported data available

(continued on next page)

Table 2 (continued)

Location and name of the deposit Mining activity Ore enrichment processes	Mean concentrations in mine waste or by-products (Min–Max)	Mean concentrations in anthropogenic (*natural) soil/sediment pollution (Min–Max)	Mean concentrations in (*natural) surface water bodies and in groundwater (Min–Max)
Germany Kupferschiefer 1200–1969 (1990), mining peak in mid-20 th century <i>Cu smelting during the mining peak</i>	Theisen sludge: Cu 16 g/kg, Cd 0.54, Fe 24, Zn 209, Pb 131 ¹²⁻¹³ Theisen sludge: Zn 207 g/kg, Pb 35, Cu 11, Cd 0.34, As 5.1, Ag 0.44, U 0.022, S 143 ¹⁴	Mansfeld river sediments: As (13–3200 mg/kg), Cu (92–11,400), Cd (5–23), Ni (10–176), Pb (57–7510), Sb (2–695), U (4–60), Zn (580–39,000) ¹⁴ East-Thuringia soil: As 28 mg/kg (9–112), Co 49 (13–60), Cu 49 (24–149), Mo 5.3 (BDL–23), Ni 84 (48–170), Pb 19(9–23), S 4740 (936–14,012), U 13 (2–40), Zn 101 (80–164) ¹⁵	Sangerhausen surface water: pH (7.6–7.9), As 75 µg/L (< 50–90), Cu 180 (80–360), Pb 70 (60–80), Mo 53 (30–70), Ni 30 (< 30–30), Sb 8 (< 5–10), Zn 713 (410–1050) ¹⁶ Mansfeld surface water: pH (7.3–8.0), As (< 0.5–3.4 µg/L), Cu (3.2–510), Cd (2.8–44), Ni (3.8–110), Pb (< 0.5–940), Zn (< 10–17,860) ¹⁷ East-Thuringia groundwater: pH 4.1 (3.5–5.7), S 2208 mg/L (505–5601), As 4.8 µg/L (< 0.05–33), Cd 115 (1.5–513), Co 5070 (48–20,550), Cu 669 (2–3433), Fe 3281 (< 20–29,370), Mn 183,067 (3767–808,000), Ni 21,206 (540–69,580), Pb 2.1 (< 0.1–13), U 338 (BDL–3263), Zn 4808 (48–20,360) ¹⁵ Chambishi stream water: Ni up to 730 µg/L, Zn 180 ²⁰ Chambishi groundwater: pH 9.5, SO ₄ 1820 mg/L, Co 12 µg/L, Cu 6, Fe 70, Mg 670, Mn 13 ¹⁸
Zambia Central African Copperbelt ● Cu-mining from the 20 th century to present ● Mine development phase in the Enterprise Ni deposit	Chambishi tailings: Co (790–6175 mg/kg), Cu 795–9979, Fe (14067–321614) ¹⁸	Kitwe soil: pH 4.8 (4.1–8.0), S 400 mg/kg (40–4500), As 3.1 (0.04–255), Co 57 (2.0–606), Cu 1501 (34–27,410), Pb 15 (4.0–480), Zn 34 (4.0–450) ¹⁹	
Sweden Alum shales Skåne (S Sweden): Alum mining from the 17 th to the 20 th century Degerhamn: Alum mining from the 18 th to the 20 th century Kvarnatorp: Hydrocarbons 1942–1966 (from associated limestones) Ranstad: U and V mining 1965–1976 Degerhamn: burning, water leaching of alum salts, Ranstad: crushing, H ₂ SO ₄ leaching followed by ion-exchange and solvent extraction ²¹	Degerhamn: As 93 mg/kg (33–201), Cd 0.8 (0.2–2.2), Cu 77 (39–157), Ni 47 (21–115), Zn 41 (7.0–88) ²² Ranstad: As 102 mg/kg, Cd 0.6, Cu 110, Mn 110, Mo 330, Ni 130, Pb 13, Sb 5, U 64, Zn 100 ²¹ Kvarnatorp: As 79 mg/kg, Mo 163, Ni 70, U 235, V 650 ²³	No reported data available	Degerhamn groundwater: pH (4.1–7.3), As (< 1–10 µg/L) Cd (< 0.05–18.7), Cu (< 1–1050), Ni (0.5–862), Zn (4.3–1300) ²² Degerhamn groundwater: pH 6.5 (4.1–7.7), S 257 mg/L (8.9–662), As 2.5 µg/L (< 0.4–9.5), Cd 3.1 (0.1–20), Co 98 (0.01–892), Cu 83 (0.2–552), Fe 487 (0.6–5650), Mn 500 (1.1–1860), Mo 37 (0.5–228), Ni 207 (0.1–1640), Pb 0.4 (< 0.01–2.5), Sr 425 (30–1830), U 54 (2.7–198), Zn 76 (1.7–1580) ²⁴ Degerhamn groundwater: U 39 µg/L (0.2–196) ²⁵ Degerhamn stream water: U 33 µg/L (13–82) ²⁵ Ranstad leachates: pH (3–8.4), As (< 2–43,000 µg/L), Cd (20–60), Cu (1–91,000), Mn (480–87,000), Ni, (< 2–75,000), Mo (2900–130,000), Zn (< 20–38,000), Pb (< 1–15,000) ²¹ Kvarnatorp groundwater: pH (3.2–12.2), Fe (0.007–1130 mg/L), Mo (< 1–935), Ni (< 0.5–2420), U (< 0.01–1760 µg/L) ²³ Kvarnatorp pit lake: pH 6.0 (3.2–7.8), As 0.70 µg/L (< 0.6–1.4), Cd 0.3 (0.02–1.1), Co 7.8 (0.4–27), Cr 0.5 (0.08–1.0), Cu 2.0 (0.6–4.0), Li 310 (220–480), Mo 5.3 (0.2–9.1), Ni 42.6 (1.3–130), Pb 0.7 (0.05–1.9), U 30.2 (4.9–83), V 4.4 (< 0.05–16), Zn 38.3 (2.2–140), ²⁶ Groundwater: pH 6.6 (4.9–7.9), Cr (0.10–1.27 µg/L), Cu (0.36–18.9), Fe (13.1–698), Mn (0.58–1160), Pb (0.12–2.52), Zn (1.82–1430), V (BDL–2.25), U (BDL–21.3), SO ₄ (1400–160,800) ³⁰ *Groundwater: pH 7.2 (6.0–8.2), Cr (ND–5 µg/L) Cu (ND–312 µg/L), Fe (ND–130), Mn (ND–84), Pb (ND–17), Zn (ND–996), V (ND–2), SO ₄ (3600–130,900) ²¹ *Surface water: pH 7.4 (4.1–9.9), Cu (Not Detected–18 µg/L), Fe (ND–67), Mn (ND–282), Pb (ND–12), Zn (ND–138), V (ND–3) ³¹ No reported data available
South Korea Okchon black shales Sporadic U mining No reported data available of the ore enrichment processes	No reported data available	No reported data available *Soil: Cd 1.2 mg/kg, Mo 20, Se 1.5 ²⁷ *Soil, Chu-Bu: As 40 mg/kg (5–340), Ba 1570 (490–15,000), Cd 1.6 (0.2–20.1), Cu 64 (23–217), Mo 15 (1–240), Pb 48 (18–182), U 29 (2–450), Zn 172 (50–1100), S 4000 (2000–7300) ²⁸⁻²⁹ *Soil, Duk-Pyung: As 30 mg/kg (9–61), Ba 996 (93–6380), Cd 0.7 (0.2–7.2), Cu 99 (36–403), Mo 34 (1–134), Pb 57 (12–370), U 78 (5–780), Zn 186 (60–841), S 2200 (900–4800) ²⁸⁻²⁹	
	No reported data available		

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Table 2 (continued)

Location and name of the deposit Mining activity Ore enrichment processes	Mean concentrations in mine waste or by-products (Min–Max)	Mean concentrations in anthropogenic (*natural) soil/sediment pollution (Min–Max)	Mean concentrations in (*natural) surface water bodies and in groundwater (Min–Max)
USA Appalachian basin black shales No reported mining activity on black shale deposits		Stream sediments, road cut: median As 56 mg/kg (38–98), Co 36 (11–105), Cr 75 (27–92), Cu 30 (12–75), Mn 970 (135–1750), Mo 78 (3.0–215), Ni 61 (16–340), Pb 42 (25–68), V 335 (87–490), Zn 210 (81–800) ³² Soil, road cut: median As 53 mg/kg (43–57), Co 5.7 (5.1–5.9), Cr 125 (105–140), Cu 56 (43–63), Mn 52 (44–54), Mo 96 (86–110), Ni 15 (12–18), Pb 23 (21–28), Sb 6.6 (5.6–7.4), U 23 (20–24), V 465 (395–525), Zn 38 (27–39) ³²	

BDL: below detection limit; ND: not detected.

¹ Tuovinen et al., 2018.

² Leppänen et al., 2017.

³ Terrafame report, 2017; Terrafame report, 2018.

⁴ Publically available data by Terrafame Ltd.

⁵ Pašava et al., 2003.

⁶ Peng et al., 2009b.

⁷ Lacelle et al., 2007.

⁸ Kwong et al., 1997.

⁹ Sun, 1999.

¹⁰ Sun et al., 2000.

¹¹ Helios Rybicka et al., 1994.

¹² Daus and Weiß, 2001.

¹³ Schubert et al., 2003.

¹⁴ Wennrich et al., 2004.

¹⁵ Carlsson and Büchel, 2005.

¹⁶ Bozau et al., 2017.

¹⁷ Bobarowski and Bozau, 2006.

¹⁸ Sracek et al., 2010.

¹⁹ Ettler et al., 2011.

²⁰ Ntengwe et al., 2006.

²¹ Allard et al., 1991.

²² Falk et al., 2006.

²³ Bäckström and Sartz, 2015.

²⁴ Lavergren et al., 2009a.

²⁵ Åström et al., 2009.

²⁶ Allard et al., 2011.

²⁷ Kim and Thornton, 1993a.

²⁸ Lee et al., 1998.

²⁹ Park et al., 2010.

³⁰ Woo et al., 2002.

³¹ Chon and Oh, 2000.

³² Tuttle et al., 2009.

weathering, bioweathering plays an important role in the degradation of black shale exposed to oxic conditions. Microorganisms may utilise the organic matter during black shale weathering as a carbon source controlling the oxidation of sedimentary organic matter (Petsch et al., 2005). Matlakowska et al. (2012) and Włodarczyk et al. (2016) studied the bioweathering of the Kupferschiefer black shales in Poland and found that the oxidation of the fossil organic matter by indigenous lithobiotic, heterotrophic and neutrophilic bacteria accounts for the release of various organic compounds, which in turn can promote the weathering of sulphides. Subsequently, trace elements and S associated with sulphides are mobilised, affecting the leachate waters and precipitation of secondary minerals (Matlakowska et al., 2012; Włodarczyk et al., 2016). However, other studies show that chemical weathering processes have higher influence on the oxidation of the rock than the organic matter degradation by microbial activity (Chi Fru et al., 2016). Laboratory experiments prove that an indigenous consortium of bacteria is involved in the oxidative bioweathering of fossil organic matter (bitumens and kerogen) and may promote the mobilisation of fossil

organic carbon from the rock (Seifert et al., 2011; Stasiuk et al., 2017). The mobilisation of organic carbon is documented in the form of oxidised organic compounds, such as monohydroxy and dihydroxy alcohols, aldehydes, monocarboxylic and dicarboxylic acids and esters due to microbial activity (Stasiuk et al., 2017).

The potential for acid rock drainage and soil pollution should be evaluated case-specifically due to the heterogeneity of black shale occurrences (Tables 1 and 2). Table 2 summarises the environmental impacts of the selected black shale deposits with reported metal concentrations in the mining waste, in by-products or in environmental recipients like in soil, river sediments and water bodies. Fig. 1 highlights that the environmental impacts of black shale may vary due to the volume of sulphide-rich units. Considering the vast extent of many of the black shale deposits, extending over hundreds of kilometres, they have the potential to produce acidity in large areas if they outcrop at the surface. Besides the thickness of the metal-rich sequence, the chemical characteristics of under- and overlying rocks and their hydraulic properties contribute to the issue. Typically, black shales occur in cyclic

Table 3

Environmental impact of black shales in Talvivaara under pre-mining conditions. Median, min. and max. values of selected trace elements in glacial till, stream sediment, lake sediment, surface water, peat and dug well water samples in the black shale area are given.

Sample material		Cu	Fe	Mn	Ni	Pb	Zn	Cd	Al	As	Co	U
Till mg/kg (N = 586) ¹	Min	8.0			6.0		14					
	Max	2900			3100		17,900					
	Median	70			56		150					
Well-decomposed organic stream sediments mg/kg (N = 88) ²	Min	4.0	9390	73	7.0	7.0	17					
	Max	660	398,000	4600	2600	195	9800					
	Median	57	51,300	375	93	38	350					
Poorly decomposed organic sediments “peat” mg/kg (N = 100) ²	Min	5.0	6100	91	15	11	68					
	Max	7200	364,000	22,000	4550	564	10,100					
	Median	63	83,750	615	106	81	348					
Surface lake sediments mg/kg (N = 56) ³	Min	23	8280	93	48	2.61	180	0.39	5720	0.57	6.5	0.54
	Max	217	292,000	79,500	1080	845	2500	16	25,500	50	113	4.7
	Median	61	45,950	666	173	24	907	4.8	14,450	3.8	29	1.5
Stream water µg/L (N = 51) ²	Min	1.0	0.26	0.02	2.0	1.0	0.02					
	Max	130	7.9	0.77	920	5.3	3.6					
	Median	1.2	1.9	0.07	7.8	< 1.00	0.03					
Stream water µg/L (N = 26) ³	Min	0.4	170	14	0.5	0.07	1.1	< 0.02	40	0.13		
	Max	12	4650	973	1.6	1.6	530	0.54	1370	1.1		
	Median	1.6	1260	82	0.17	0.17	49	0.18	260	0.29		
Lake water µg/L (N = 9)	Min	0.83	320	5.6	1.69	0.05			0.01	BDL	BDL	BDL
	Max	4.51	910	156	65.5	2.3			177	0.46	3.5	0.09
	Median	2.61	410	25	14.8	0.27			94	0.24	1.6	0.06
Peat mg/kg (N = 25) ¹	Min	29	2620	6.80	18	0.43	36				1.4	0.61
	Max	316	109,000	77	612	24	4360				36	11
	Median	180	53,300	33	244	1.3	1490				20	3.7
Dug well µg/L (N = 4) ³	Min	2.00	< 30	1.00	10	< 0.03	26	0.22	7	< 0.05		
	Max	80	290	143	91	2.1	628	3.68	416	0.09		
	Median	17	75	84	51	0.93	385	2.2	289	0.05		
*Dug well µg/L (N = 9) ⁴	Min											
	Max	220	140	91	82	1.5	130	0.04	990	0.31	7.4	0.23
	Median	34	84	8.0	1.9	0.49	24	0.68	40	0.09	0.25	0.05
*Well drilled into bedrock µg/L (N = 39) ⁴	Min											
	Max	360	17,000	1400	26	8.7	500	0.19	130	0.61	0.73	4.5
	Median	31	150	8.0	0.80	0.45	16	0.01	< 20	0.07	0.07	0.03

¹ Parviainen et al., 2014 (originally from the database of the Geological Survey of Finland).

² Gustavsson et al., 2012.

³ Loukola-Ruskeeniemi et al., 1998.

⁴ Karppinen et al., 2012.

* Samples collected in 2011–2012. The mining activities commenced in 2008.

alternation with phyllites, sandstones and limestones / dolomites, making up between 10% and 20% of the succession, rarely over 50%. Hence, the surrounding rock units reflect the quantity of the natural neutralisation capacity.

5. Nickel deposits and occurrences

5.1. Talvivaara deposit, Finland

The Talvivaara black shales deposited during 2.1–1.9 Ga and are characterised by a large amount of organic matter and sulphur (Table 1). In general, the Palaeoproterozoic of northern and eastern parts of Finland and the related formations in Karelia and the Kola peninsula in NW Russia contain the highest total amounts of accumulation and preservation of organic matter in sedimentary rocks reported so far (Loukola-Ruskeeniemi, 1991; Loukola-Ruskeeniemi, 1999; Melezhik et al., 1999). The Talvivaara deposit consists of two polymetallic ore bodies: Kuusilampi and Kolmisoppi (Ervamaa and Heino, 1983; Loukola-Ruskeeniemi, 1995; Loukola-Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi and Lahtinen, 2013; Kontinen, 2012; Kontinen and Hanski, 2015; Makkonen et al., 2017). The medium-grade regional metamorphism caused recrystallization of the sulphide phases and reduction of organic matter to graphite.

The tectonic deformation and isoclinal folding shaped and multiplied the black shale layers so that the two ore bodies are now up to 330 m thick even though the original thickness may have been < 50 m (Figs. 1 and 2). The whole black shale formation reaches a maximum

thickness of over 800 m, including ore-grade (> 0.07% Ni) and barren black shales (< 0.07% Ni). The Talvivaara mine that exploits the Kuusilampi orebody has been operating since 2008, and the total estimated low-grade mineral resources are over 2000 Mt. (0.22% Ni, 0.13% Cu, 0.50% Zn and 0.02% Co, Talvivaara Mining Company, 2012). However, the Kolmisoppi ore body is in part located under Lake Kolmisoppi which may limit the possibility to exploit it.

The black shale containing abundant graphite and sulphides is principally composed of quartz and phlogopitic biotite, with rutile, apatite, zircon, feldspar, tremolite, diopside, sphene, muscovite and spessartine garnet as common accessory minerals (Loukola-Ruskeeniemi and Lahtinen, 2013; Tuovinen et al., 2016). Pyrite [FeS₂] and pyrrhotite [Fe_(1-x)S] are the dominant sulphide minerals, whereas chalcocopyrite [FeCuS₂], sphalerite [ZnS], galena [PbS], alabandite [MnS], molybdenite [MoS₂], pentlandite [(Fe,Ni)₉S₈], ullmanite [NiSbS] and stannite [Cu₂FeSnS₄], together with uraninite [UO₂] and thucholite [a mixture of hydrocarbons, uraninite and sulphides], occur in minor amounts (Table 1; Loukola-Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi and Lahtinen, 2013).

5.1.1. Pre-mining conditions and the impact of current mining at Talvivaara

The Talvivaara-type mineralised black shales commonly lie in topographic depressions in Finland due to their susceptibility to erosion during the last glaciations. They are usually covered by glacial till, peat and lakes, but exposed outcrops also occur in the Talvivaara area because the formation was originally that thick. Substantial amounts of Ni-rich and Ca-poor black shale material were abraded and transported

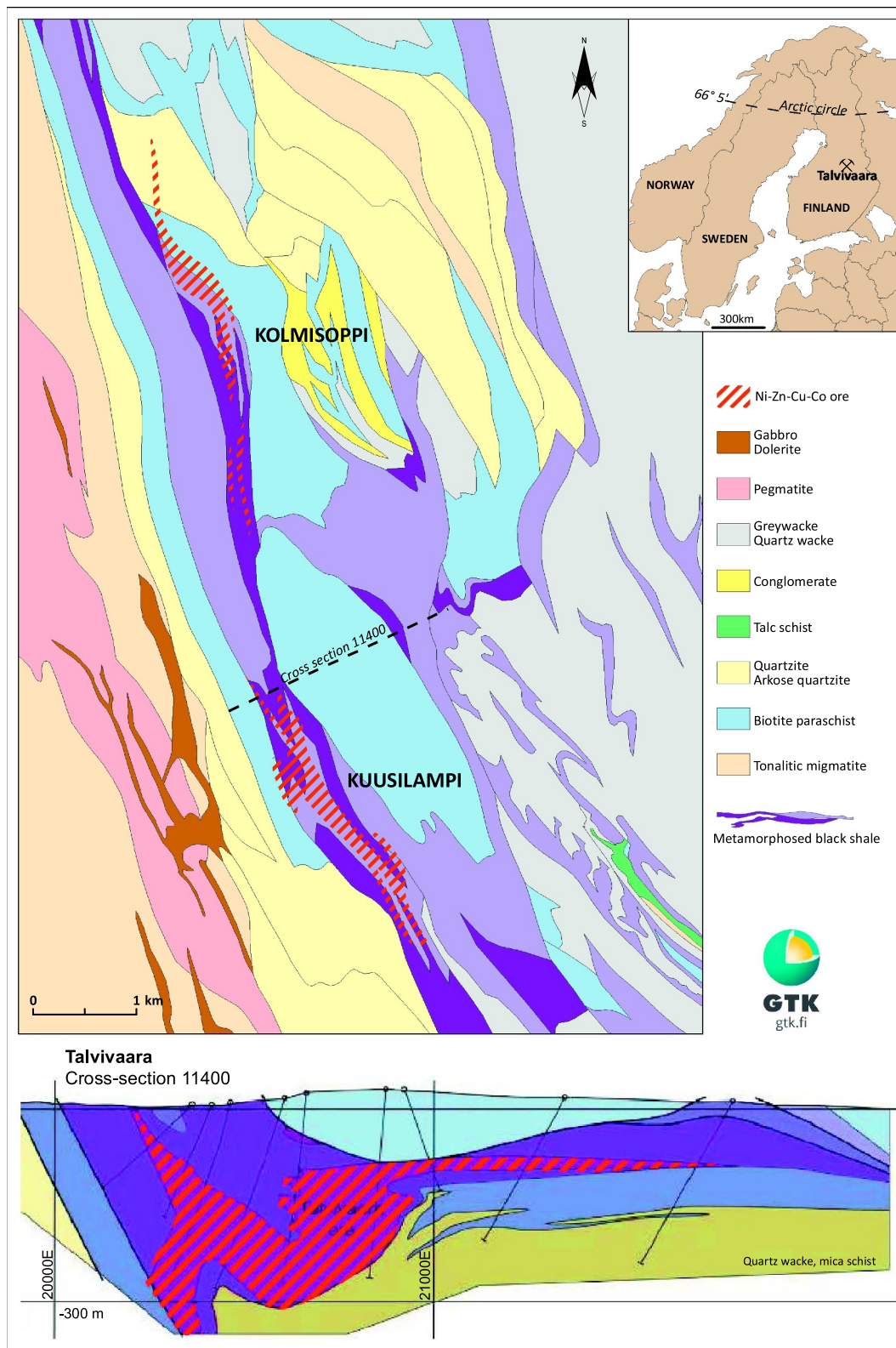


Fig. 2. Geological map of the Talvivaara area, generalised and modified from the digital geological map database of Finland (DigiKP, Geological Survey of Finland, 2017). At present, open pit mining continues in the Kuusilampi ore body. Cross-section 11400 showing the depth of the deposit is modified from Makkonen et al. (2017).

during the glaciations. This is evidenced by geochemical maps of glacial till, which show the distribution of ground black shale material far from the original bedrock source (Loukola-Ruskeeniemi et al., 2003). Similarly, the soil geochemistry is well-correlated with the underlying

bedrock concentrations (Table 3; Gustavsson et al., 2012), and many studies show the influence of mineralised black shale on the overlying till and peat cover (e.g., Loukola-Ruskeeniemi et al., 1998; Mäkinen et al., 2010; Parviainen et al., 2014). The till deposited over black shale

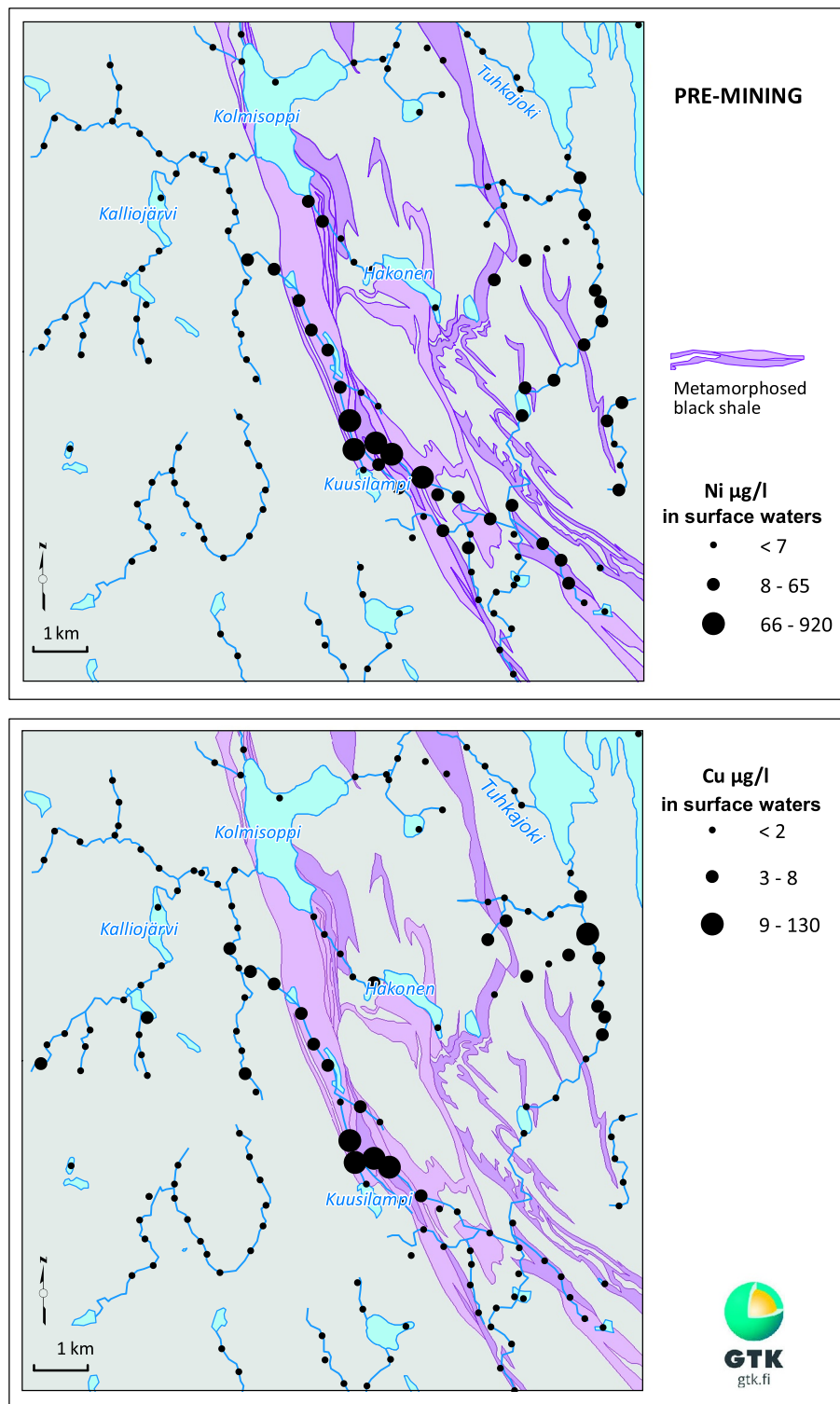


Fig. 3. Nickel and copper concentrations in surface waters in the Talvivaara area before mining activities. However, it is already obvious that three pilot quarries have impacted the water quality in streams, lakes and rivers (Gustavsson et al., 2012). The distribution of metamorphosed black shale is modified from the digital map database of the Geological Survey of Finland (DigiKP, 2017).

bedrock contains approx. 2-, 3- and 5-fold higher values of Cu, Ni and Zn, respectively, than the till in the surrounding granite gneiss, quartzite and mica schist areas (e.g., Parviainen et al., 2014). The peat deposits in the study site are affected by both the underlying mineralised rocks and by the acid rock drainage from black shale outcrops. Elevated pre-mining concentrations of, for instance, Fe, Ni, Zn and S were found towards the bottom layers under acidic conditions (Mäkilä et al., 2012;

Parviainen et al., 2014).

Weathering of black shale and associated soils have an impact also on the local water geochemistry. Fig. 3 displays Ni and Cu concentrations in surface waters prior to the mining activities.

Consequently, especially Ni and Zn concentrations in stream and lake sediments in the mineralised areas reflect the chemical composition of the bedrock (Table 3): the median concentrations of Cu, Fe, Ni

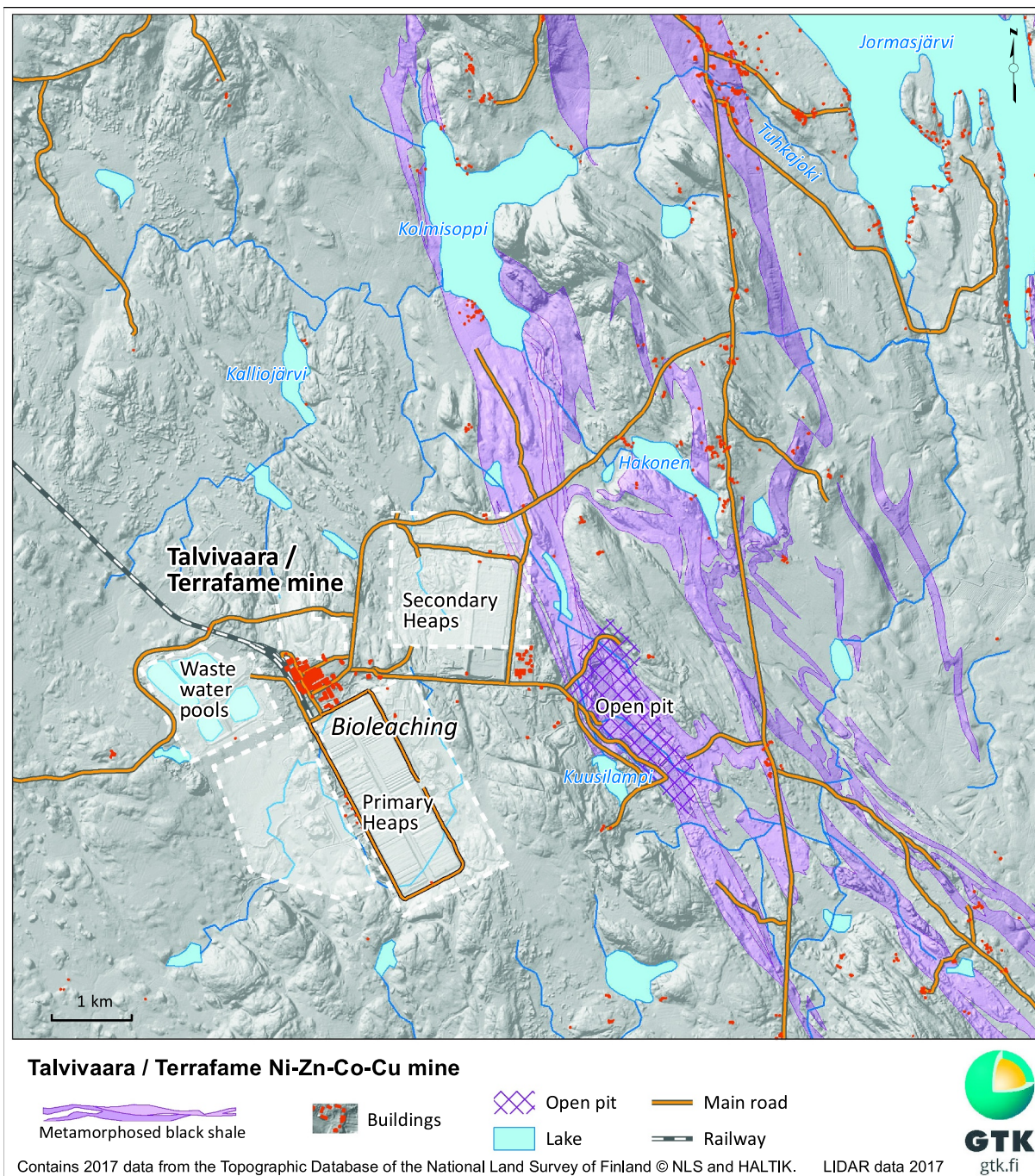


Fig. 4. The Talvivaara Ni–Zn–Co–Cu deposit has been mined since 2008 which has modified the landscape. The open pit and primary and secondary bioleaching heaps are indicated on the map. The distribution of metamorphosed black shale (black schist) is modified from the digital geological map database of Finland (DigiKP, Geological Survey of Finland, 2017).

and Zn in these stream sediment samples exhibit 2.7- to 3.5-fold higher values than in the nearby non-mineralised areas (Gustavsson et al., 2012). Lake sediment profiles of the adjacent lakes record past events, showing that acid rock drainage has been active already during the deglaciation 9000 years ago. The intense metal accumulation took place when the ice lake in front of the retreating ice sheet found a new channel to the sea and the water level suddenly dropped, exposing black shale bedrock to oxic conditions (Loukola-Ruskeeniemi et al., 1998). Lake sediments were affected, which can be seen at present at roughly 5.8 m depth, and show 7- to 11-fold higher concentrations of Cu, Ni and Zn than the recent lake sediments representing pre-mining conditions. Additionally, U, known to be very mobile in oxic conditions

show 29-fold higher concentrations in comparison to the recent sediments.

Before mining activities began in the Talvivaara area, the drainage of peatlands was the main anthropogenic activity that contributed to the mobilisation of metals from the soils. Shallow lake sediments exhibit a moderate increase in metal concentrations starting from the early 20th century and a more pronounced increase in the concentrations of Ca, Cr, Cu, K, Mg, Na and Ni in the layers corresponding to the 1970s and 1980s, when the drainage of peatlands was a common practice in forestry in Finland (Mäkinen et al., 2010). For instance, Ni exhibited twice as high concentrations in the sediments deposited in the 1980s in comparison to the ones from early 20th century. Furthermore,

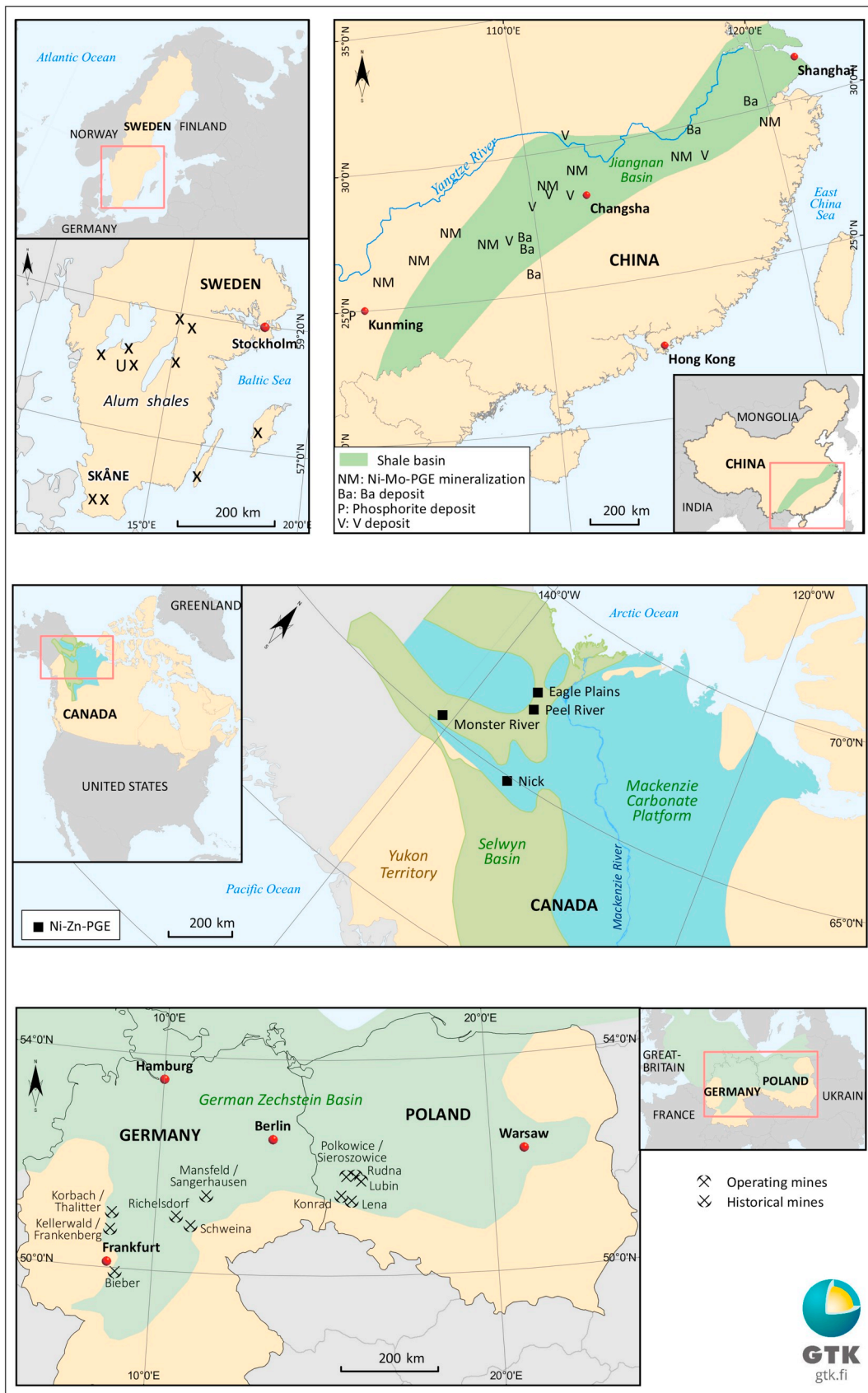


Fig. 5. Distribution of mineralised black shales in four selected regions around the world: the Cambrian alum shales in Sweden (modified from Andersson et al., 1985; Lecomte et al., 2014), the Cambrian Niutitang black shales in China (modified from Han et al., 2017), the Devonian black shales in Yukon in Canada (modified from Goodfellow et al., 2010) and the Permian Kupferschiefer in Poland and Germany (modified from Borg et al., 2012).

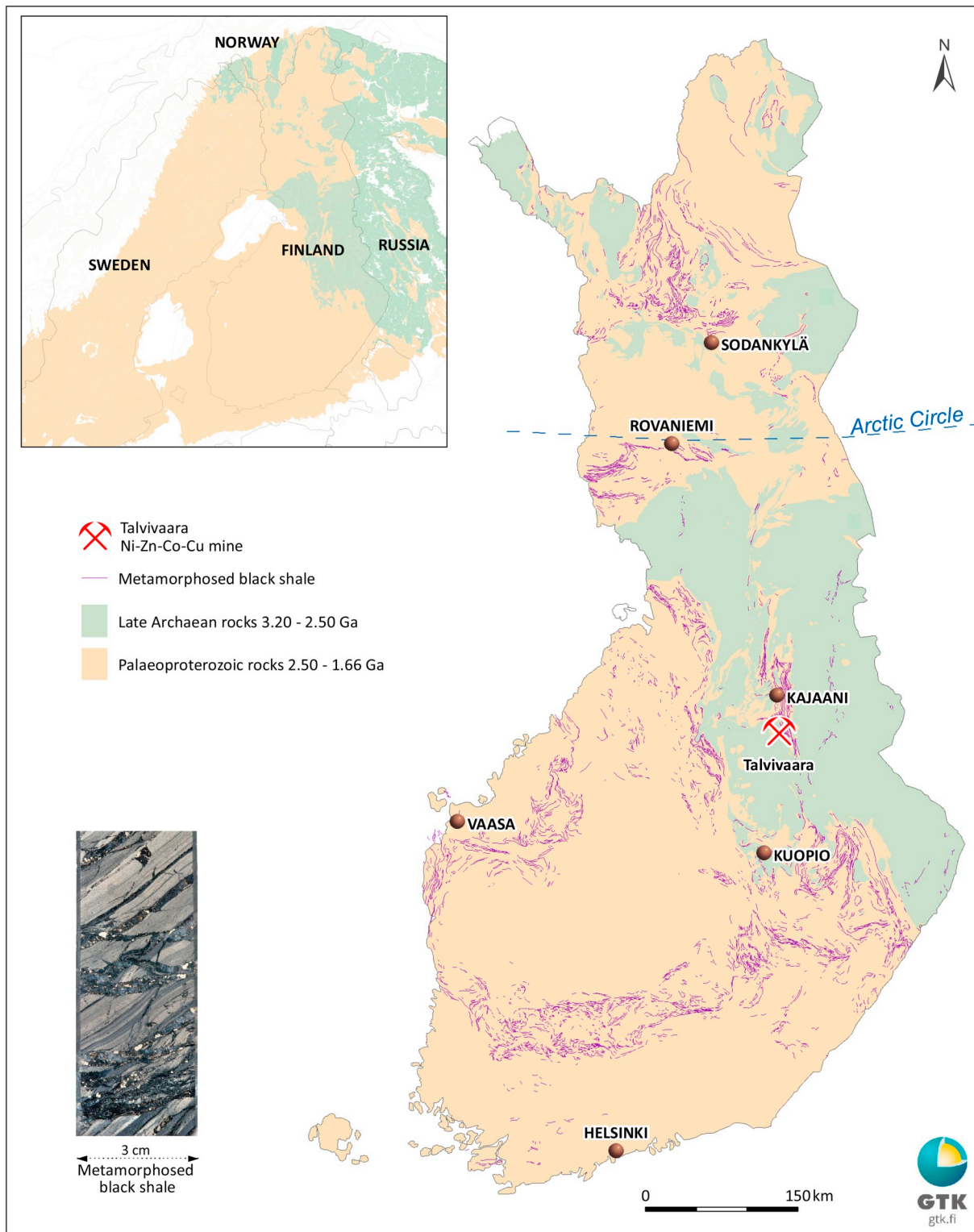


Fig. 6. Distribution of metamorphosed black shales and graphite-sulphide schists in the Palaeoproterozoic of Finland (Arkimaa et al., 1999, 2000; Loukola-Ruskeeniemi et al., 2011; Airo et al., 2009; Hyvönen et al., 2013). The map and database were compiled by correlating the aeromagnetic and aeroelectromagnetic data of the Geological Survey of Finland. The inferred black shale units were verified with geochemical and petrophysical studies of drill core samples. (Colour version of the figure is available in the web version of this article.)

northern pike in lakes with large catchment areas and bedrock rich in black shales may show elevated Hg concentrations (Loukola-Ruskeeniemi et al., 2003).

The Talvivaara mine project commenced in 2004 and the full-scale exploitation began in 2008. To recover Ni and other metals of economic

value, the enrichment process takes advantage of bio-leaching to promote sulphide dissolution (Riekkola-Vanhanen, 2010). The recovery process consists of heap bioleaching of ground black shale rock catalysed by bacteria like *Acidithiobacillus ferrooxidans*. The mining operations produce three types of solid wastes, including waste rock, leached

ore and production waste consisting of gypsum, calcium carbonate and Fe hydroxides. After the two-stage (primary and secondary) leaching, the mine wastes are permanently stored on the secondary leaching site. The mining activities are leaving a significant footprint on the landscape (Fig. 4).

Since the mining activities began, the adjacent water bodies have been regularly monitored by the mining company under the supervision of the local environmental authority, the Centre for Economic Development, Transport and the Environment (the Kainuu ELY Centre). The water quality in the adjacent rivers and lakes has experienced changes, and peaks in sulphate and metal concentrations have been observed. In 2012, a major leakage from the gypsum waste pool was reported, and the consequences of the spill can be seen in the monitoring data in the surrounding streams and lakes. Here we do not present the monitoring data directly after the spill, but data from 2015 to 2017 (Table 2). The water quality has recovered lately, although the monitoring data still reveal elevated concentrations of SO_4 , Fe, Mn and Na in some of the nearby lakes and streams, as well as elevated Ni and Zn in some sites. The impact of mining activities has also been recorded in the lake sediments of Lake Kivijärvi, about 1 km southwest from the Talvivaara mine. The S, Fe, Mn, Ni and Zn concentrations have increased since the exploitation started (Table 2; Leppänen et al., 2017). The lake sediments deposited at the time of the major spill from the gypsum waste pool record for instance 10- and 5.6 -fold higher concentrations of Ni and Zn in comparison to pre-mining values. The concentrations have decreased in the most recent sediments suggesting that the leakage was successfully blocked.

The Regional Council of Kainuu ordered a study on the water quality in privately owned dug wells and wells drilled into bedrock (Karppinen et al., 2012). The objective was to evaluate the natural impact of metal-enriched black shale on local groundwater. The water from the studied wells located away from the mine generally exhibited good quality, although the mean of Mn and Fe exceeded the threshold values for private household water: 400 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$, respectively (Table 2; Karppinen et al., 2012). Nickel concentration exceeded the threshold value (20 $\mu\text{g/L}$) in only a few of the studied wells (Table 2; Karppinen et al., 2012). However, the groundwater investigations in the vicinity of the mine performed by Terrafame Ltd. demonstrate deterioration in the quality of groundwater (Terrafame report, 2017; Terrafame report, 2018). Low pH values (3.5–6.1) and elevated metal concentrations were recorded in the groundwater (Table 2; Terrafame report, 2017), especially in the shallow groundwater. Additionally, the water samples from two shallow groundwater monitoring wells installed in the primary leaching stacks exhibited low pH values (3.4–4.3) and exceptionally high sulphate and metal concentrations (up to 79,000 mg/L SO_4^{-2} , 0.100 mg/L As , 1.3 mg/L Cd , 10 mg/L Cu , 1000 mg/L Mn , 310 mg/L Ni , 660 mg/L Zn , 1700 mg/L Fe , 2.6 mg/L U) (Terrafame report 2017; Terrafame report 2018).

The air quality of the Kainuu Region was evaluated in 2015 by analysing epiphytic lichen (*Hypogymnia physodes*). Concentrations of Cr, Cu, Fe and Ni were higher than average around the Talvivaara mine due to the emissions from the mine site (Laatikainen and Seppänen, 2017).

5.2. Niutitang black shales, China

The Lower Cambrian black shales hosting the Mo–Ni–PGE ores of the Niutitang Formation in southwestern China form an over 1600-km-long belt that outcrops discontinuously (Fig. 5). The mineralised layer corresponds to a thin accumulation (5–20 cm) of Ni, Mo, Au, Ag, Se, Cr, V, Zn, U, rare earth elements (REE) and platinum group elements (PGE) that can be traced along the same stratigraphic horizon (Table 1). Here Niutitang black shales are classified as Ni deposits as they occur in the Zunyi area, though U deposits are reported in the Hunan, Jiangxi and Guangxi Zhuang regions. The exceptional enrichment of metals from seawater is ascribed to high biological productivity in the surface oxic layer above sediment-starved euxinic basins (Mao et al., 2002;

Lehmann et al., 2007), and organic matter played an important role in mineralisation though it was not the sole control (Shi et al., 2014). The origin of the highly metal-rich layer is also related to hydrothermal processes, whereas a seawater and terrigenous origin is suggested for the thicker black shale sequence (Fan, 1983; Lott et al., 1999; Shi et al., 2014; Han et al., 2015). The chondrite-normalised patterns of PGEs indicate that PGE enrichment of the polymetallic ores is most likely originated from mafic rocks (Han et al., 2015). The black shales deposited intercalated with phosphorite, barite and sapropelic beds (Mao et al., 2002). The Cambrian facies shifts from a shallow shelf environment with phosphatic carbonate rocks in the northwest to deep basinal facies of black shale in the southeast (Zhu et al., 2003). The Niutitang Formation unconformably overlies the Ediacaran Dengying Formation (551–541 Ma) and is mainly composed of organic-rich black shales containing phosphatic beds, varying between 0.3 and 1.35 m, and tuff layers. The polymetallic Ni–Mo–PGE–Au sulphide ore is locally present in the lowermost part of the formation.

5.2.1. Natural and post-mining conditions around the Niutitang black shales

Peng et al. (2004) reported V, Cr, Co, Cu, Zn, Pb, Cd and Tl enrichment in soils and Sc, Cr, Fe, Mn, Co, Ni, Cu, Zn, Pb and Cd enrichment in surface waters near weathering profiles of Lower Cambrian black shales in Hunan, China, which are associated with a locally high incidence of endemic diseases, such as cancer. Additionally, notable enrichment of Mo, Cd, Sb, Sn, U, V, Cu and Ba was observed in soils associated with another weathering profile of black shale in Hunan (Yu et al., 2012). The mobilisation of Mn, Sr, Ba, Pb, U, V, Cr, Co, Ni, Cu, Zn and REE was observed in natural weathering profiles in northeast Chongqing, China, and their redistribution was dependent on the pH, weathering intensity and the secondary minerals formed (Ling et al., 2015). The comparison of an outcropping weathering profile of Ordovician–Silurian black shales in Guizhou Province, China, with the respective unweathered shallow borehole samples reveals mineralogical changes and the depletion of organic matter, V, Cr, Th, U, Ni and Co in the weathered samples (Tang et al., 2018).

The most significant U deposits are reportedly in Hunan, Jiangxi and Guangxi Zhuang regions, whereas Ni–Mo deposits occur in the Zunyi area. There is limited information available about the black shale mines in China. However, couple of publications describe soil and water pollution associated with black shale mining. According to Peng et al. (2009b), soils in the vicinity of the black shale U mine in the Hunan region are enriched in Mo, Cd, Sb and U. Besides the pollution of soils and local water sources, bioaccumulation has occurred also to crop. The soil pollution and subsequently observed bioaccumulation of potentially harmful metals into maize are related to the chemical concentration of the bedrock. Acid mine drainage from another U mine in Hunan is affected by Cd, Co, Ni, Zn and U (Table 2; Peng et al., 2009a). Additionally, in the surroundings of the Ni–Mo mines in the Zunyi area agricultural soils (Table 2) are polluted by drainage waters derived from the mine waste dumps and consequently bioaccumulation of potentially harmful metals occurs in local tobacco, rice, corn and turnip (Pašava et al., 2003).

5.3. Yukon black shales, Canada

The Devonian strata in the Yukon Territories includes an extensive shale sequence that hosts Ni–Zn–PGE occurrences (Fig. 5). The black shale sequence was deposited in the Selwyn epicratonic marine basin, and overlies Cambrian and Ordovician carbonate rocks. The sequence commences with Road River Group calcareous black shales and is followed by the Canol Formation in north Yukon and the Earn Group siliceous black shales in the central parts of Yukon (Fraser, 2014; Fraser and Hutchison, 2017). The Selwyn basin black shales have undergone lower greenschist facies metamorphism.

Here, we focus on the sulphide mineralisation enriched in

Ni–Zn–PGE and other metals, which occurs in the interface of the Road River Group and Canol Formation or Earn Group in between the layers of the limestone ball member (black shales containing limestone spheroids) and phosphatic chert (Butterworth and Caulfield, 1997; Goodfellow et al., 2010; Hulbert et al., 1992). The stratigraphic and sedimentological sequence is similar throughout the black shale sequence in the Nick Property, Eagle Plain and Peel River occurrences (Goodfellow et al., 2010). The mineralisation, principally consisting of vaesite [NiS₂], pyrite, marcasite [FeS₂], sphalerite and wurtzite [(Zn,Fe)S], varies in thickness from a few centimetres to 40 cm (Fig. 1), but it covers a large area where different occurrences are located up to 400 km apart. The massive sulphides were formed as rhythmically laminated layers of sulphide grains and the sulphides are of both hydrothermal and biogenic origin (Hulbert et al., 1992; Orberger et al., 2003). They contain high concentrations of Ni, Zn, PGE and Re and anomalous levels of U, Mo, Ba, Se, As, V and P (Table 1; Butterworth and Caulfield, 1997; Goodfellow et al., 2010; Hulbert et al., 1992; Orberger et al., 2003). According to Orberger et al. (2003), the trace element concentrations vary among different sulphide phases.

The thicker sequences of black shales in the Road River Group and Canol Formation are not enriched in trace metals. However, in the Canol Formation (including the Lower Earn Group), thin pyritic layers or disseminated pyrite occur within the beds, generally with low concentrations of trace metals (Hulbert et al., 1992; Fraser and Hutchison, 2017). Furthermore, there are some exceptions, such as the sedimentary exhalative massive sulphide (SEDEX) deposits, for instance the Zn–Pb–Ag occurrence of Macmillan Pass hosted within the Lower Earn Group rocks and Howards Pass hosted within the Road River Group (Goodfellow, 2004).

Two models have been developed for the genesis of the sulphide-rich layer:

- 1) Hydrothermal fluids originated from the underlying black shales, discharged in the ocean floor and expanded laterally, interacting with basinal brines. In the nutrient-rich ambient environment, the deposition of the sulphide-rich layer was promoted by bacterial activity. The mineralised layer exhibits a similar geochemical signature to the bitumen veins in the Road River Group, which represent the conduits for the hydrothermal fluids (Hulbert et al., 1992).
- 2) Meteorite debris deposited on the sea floor is the source of the mineralisation (Goodfellow et al., 2010).

5.3.1. Anthropogenic actions in the Yukon black shale occurrences

The Devonian Nick property mineralisation in Yukon Territory was initially discovered as anomalous concentrations of Ni, Zn, PGE, U, Ba and P in the adjacent stream sediments (Hulbert et al., 1992). Other outcropping black shale and SEDEX deposits hosted in black shales in Yukon Territory have produced acid rock drainage characterised by high concentrations of trace metals in surface waters (Kwong et al., 2009). The black shales in Yukon have not been exploited to date. The Ni-rich sulphide mineralisation at the base of the Canol and equivalent formations form a thin layer, though it has a vast extension and high Ni, Mo and PGE concentrations (Table 1). The black shale-hosted SEDEX massive sulphide deposits have been economically more attractive. For example, MacMillan Pass has been a target of exploitation of Zn, Pb and Ag.

Excavations, road cuts and other anthropogenic activities have caused acid rock drainage in Yukon as sulphide-rich black shales have exposed and consequently, the oxidation of sulphide minerals has occurred. For instance, along the Dempster Highway near Eagle Plains Lodge, acid rock drainage has caused damage to local vegetation. Removal of the surficial sediments for a storage area during the construction of the highway in the early 1970s exposed the underlying sedimentary rocks and disturbed the permafrost leading to the circulation of oxygenated water. The oxidation of pyrite-rich shales is

suggested to be promoted by Fe-oxidising bacteria, *A. ferrooxidans*, that converts immobile elements into their mobile state, provoking locally acid rock drainage with a pH of < 3.8 (Table 2; Lacelle et al., 2007; Lacelle and Leveillé, 2010). In periglacial regions, the seasonal freeze–thaw cycles in the near-surface environment cause the temporary storage of acidity, solutes and trace metals, whereas their abrupt release can be observed during the spring thaw (Lacelle et al., 2007). Hence, these studies emphasise that acid rock drainage may have a severe impact in periglacial areas.

5.4. Enterprise deposit, Zambia

The Proterozoic Zambian Copperbelt is part of the Central African Copperbelt, which hosts stratiform sedimentary Cu mineralisations. The Ni-rich Enterprise deposit within the Zambian Copperbelt is estimated to contain 40 Mt. of ore with 1.07% Ni on average. It is thought to originally have been hosted by organic-rich, weakly argillaceous carbonate rocks that were silicified and then replaced by kyanite during a complex metasomatic event (Capistrant et al., 2015). The highest Ni concentrations are encountered in organic-poor and quartz-rich rocks in close association with the organic-rich carbonaceous black shales. This may imply that the organic-rich sedimentary rocks acted as a reductant. As a result, Ni and Fe–Ni sulphides, including bravoite [(Fe,Ni)S₂], vaesite, millerite [NiS], pyrite, chalcopyrite, molybdenite, pyrrhotite and carrollite [Cu(Co,Ni)₂S₄], precipitated in veins and as semimassive replacements of host rocks. In places, the mineralisation exhibits high concentrations of Ni and Cu (Table 1; Capistrant et al., 2015).

5.4.1. Acid mine drainage in the future

The black shale-associated Ni Enterprise deposit is currently under development in order to open the mine in the future. Due to the current development stage of the mine, the environmental impacts cannot yet be estimated. However, it may be stated that the deposit has potential to produce acid mine drainage characterised by Co, Cu, Mo and Ni based on its ore mineral assemblage. The presence of carbonate minerals in the adjacent rock units (Capistrant et al., 2015) may provide acid neutralisation potential.

6. Copper deposits

6.1. The Kupferschiefer, Poland and Germany

The ore deposits of the European Kupferschiefer are hosted by sediments deposited on a Permian sedimentary basin (Fig. 5). Lower Zechstein beds cover the surface of about 1,000,000 km². The Kupferschiefer is organic-rich black shale, up to 1.2 m thick with an average thickness of 0.3 m (Fig. 1). The shale exhibits a sharp contact with underlying sandstone. In the boundary there is a discontinuous dolomite layer. The contact between the Kupferschiefer and the Zechstein limestone above is gradational (Pieczonka et al., 2015). The generally stratiform Kupferschiefer mineralisation occurs in the footwall sandstones, in the Kupferschiefer black shale, and in the lowermost part of the hanging-wall limestone (Kucha, 1990). The total thickness of the mineralisation, including the footwall and hanging-wall ore, can range from several decimetres to locally up to 50 m, and the vertical thickness of the mineralisation gradually increases from west to east, being thickest in Poland. The Kupferschiefer black shale has three mineralogical varieties: organic-rich pitchy shale, clayey shale and carbonate-rich shale. The Kupferschiefer is composed of organic matter, illite, glauconite, carbonate, sulphides, sulphates, quartz and feldspar (Kucha, 1990). The cut-off grade for Cu ores is 0.7% Cu. This mineralisation is composed of a variety of sulphide minerals (Table 1).

There are many theories of the genesis of the Kupferschiefer deposits which Kulick et al. (1984), Vaughan et al. (1989), Oszczepalski (1999) and Borg et al. (2012) have summarized. The original theory was a syngenetic one. Early diagenetic formation as well as multistage

ore formation have also been suggested. Another view is that the significant enrichment of Cu, Zn and Pb is related to an epigenetic process. The brines were mobilised due to tectonic compression and magmatic activity and redox reactions in the vicinity of the black shale assisted in precipitating Cu, Zn and Pb from the brines (e.g., Borg et al., 2012).

6.1.1. Environmental impacts of the Kupferschiefer deposits during and after the mining activities

Cu ores have been mined from the Central European Kupferschiefer for many centuries, but only three mines are currently active. The active mines are located in Lubin, Polkowice-Sieroszowice and Rudna in SW Poland. Stream water, stream sediments and soil are reported to suffer Cu–Ni–Pb–Zn-rich pollution due to tailings areas and smelter activity in the Lubin district (Table 2; Helios Rybicka et al., 1994; Sun, 1999; Sun et al., 2000), although no recent data are publically available. Bacteria-mediated weathering of organic matter and sulphide minerals occurs in the underground workings of the Lubin mine where microorganisms have affected the chemical composition of the Kupferschiefer black shale (Matlakowska et al., 2012; Włodarczyk et al., 2016). Physicochemical properties are changed through the bio-oxidation of sulphide minerals and fossil organic matter, including kerogen, and consequently, also the chemical characteristics of groundwater changed (Bakowska et al., 2017). As a result of the degradation of organic matter, a number of oxidised organic and inorganic compounds are formed, including alcohols, organic acids, ketones and aldehydes. Secondary inorganic compounds are formed as well like biominerals such as sulphates. A study on a weathering profile in a black shale quarry, in Poland, exhibits metal mobilisation in the superficial layer of the profile due to the alteration of organic matter and sulphides under oxic surface conditions (Marynowski et al., 2017). Organic carbon, Cu, Mo, Pb, S, and U are depleted in the weathered layers, whereas Cu, Pb, U and V are enriched in the interface between the weathered and partially weathered layer.

In Germany, the Kupferschiefer deposits have had pronounced environmental impacts. In East-Thuringia decades of U mining and in Saxony-Anhalt centuries of Cu mining have produced wastes. The weathering of mine wastes have caused soil, surface water and groundwater pollution (Table 2). In East-Thuringia, metal and U concentrations are elevated in soils. Secondary Fe and Mn oxides retain these elements and hard pan cover is formed. The groundwater is contaminated by F, Cl⁻, SO₄²⁻, Al, As, B, Cd, Cu, Fe, Mn, Ni, U and Zn (Table 2; Carlsson and Büchel, 2005; Grawunder et al., 2009; Schäffner et al., 2015). Similarly, in the Mansfeld district in Saxony-Anhalt, waste rock, slag from Cu smelting and scrubber dust, known as the Theisen sludge, were deposited on site without isolation from the soil or the atmosphere (Daus and Weiß, 2001; Schubert et al., 2003, 2005; Schreck et al., 2005). The Theisen sludge is considered as an important source of pollution, as it is enriched in Zn, Pb, S and C (> 10 wt% each) and additionally it contains elevated concentrations of As, Cd, Cu, Fe, Hg, Rh, Sb and Ag (Table 2; Daus and Weiß, 2001; Wennrich et al., 2004). The harmful elements are mobilised from the Theisen sludge through mechanical erosion, by wind and heavy rains, by chemical weathering and by leaching. The dispersion of polymetallic pollutants has been reported along a 20-km watercourse, where elevated As, Cu, Pb, U and Zn concentrations have been measured in the river sediments (Table 2; Wennrich et al., 2004). Elevated concentrations of As, Cr, Cu, Ni, Pb, V and Zn are reported in river sediments in the Mansfeld mining district (Schreck et al., 2005). Müller et al. (2008) report differences in weathering behaviour among black shale rock and historical slag heaps of different ages in Mansfeld. The slag heaps generate a more readily mobilised load of both radionuclides and chalcophile elements than the black shale rock (Müller et al., 2008). Furthermore, Baborowski and Bozau (2006) and Bozau et al. (2017) show that Zn, Cu, Pb, As and U pollution occurred in the river systems during the mining activities in the Mansfeld area (Table 2).

6.2. Black shales in the Zambian Copperbelt

The Proterozoic Zambian Copperbelt hosts stratiform Cu mineralisations. Two ore bodies occur within arcogenic units: a lower ore body is associated with overlying black shale and an upper ore body is associated with a shale sequence (McGowan et al., 2006). The mineralisation of the lower ore body originated from hydrothermal fluids entering the arenites and coarser-grained layers of black shale where the sulphides precipitated. The black shale unit may have facilitated the lateral flow of the ore-forming hydrothermal fluids and has acted as a sealing cap promoting sulphide precipitation. The lower ore body contains abundant pyrite with bornite [Cu₅FeS₄], chalcopyrite, chalcocite [Cu₂S], malachite [Cu₂(CO₃)(OH)₂], chrysocolla [(Cu,Al)₄H₄(OH)₈Si₄O₁₀·nH₂O] and cuprite [Cu₂O] (Table 1; McGowan et al., 2006).

6.2.1. Environmental impacts of mining in the Zambian Copperbelt

Large-scale mining operations in the Central African Copperbelt for almost a century have caused environmental pollution. Topsoil and water pollution attributed to Cu smelting and acid mine drainage has been described in the Kitwe (Nkana deposit) and Chambishi areas in Zambia, respectively (Table 2; Ettler et al., 2011; Ntengwe and Maseka, 2006).

7. Uranium occurrences

7.1. Alum shales, Sweden

Black shale precursor sediments were deposited in the shallow-marine environment of the Baltoscandian Platform over an extensive period of tectonic stability during the Middle and Late Cambrian and locally during the Early Ordovician (e.g., Andersson et al., 1985). They extend from Norway to Estonia, but here we focus on the black shale deposits located in Sweden (Fig. 5).

The black shales, known as alum shales, occur in the entire lithostratigraphic unit, although the name refers to particular parts of the black shale formation from which the alum salt, KAl(SO₄)₂·12 H₂O, was extracted in the 17th century. The alum shale formations are in many sites about 20 m thick, but they may reach thicknesses of up to 100 m in southern Sweden. Folded formations occur in northern Sweden, resulting in thicknesses of up to 185 m (Andersson et al., 1985). The formation is underlain by Early Cambrian sandstones and overlain by Ordovician limestones and/or grey shales, and the shale and limestone dominated sequences continue through the Ordovician into the Silurian (Anderson et al., 1985). The maturity of the alum shales varies due to the subsequent depositional history. Generally, the alum shales in central Sweden are less mature than those in the southern parts of the country. Locally, in central Sweden, magmatic heating by the intrusion of Permo-Carboniferous dolerites has matured the alum shales (Buchardt et al., 1997; Sanei et al., 2014; Schovsbo, 2002). Alum shales that have undergone low-grade metamorphism have experienced mobilisation and enrichment of V, Ni, Zn and Ba, with organic matter and pyrite acting as reductants. In central Sweden, in the more immature alum shales, the organic carbon of algal origin is mainly present as kerogen (99%) and < 1% is oily matter (Sanei et al., 2014). On the other hand, in northern Sweden, the black shales underwent greenschist metamorphism during the Caledonian orogeny, which affected their maturity and organic carbon is present as graphite.

According to Schovsbo (2002), the U was preferentially enriched in the near-shore environment, reflecting more vigorous bottom water circulation that promoted higher rates of mass transfer and diffusion of U across the sediment–water interface in comparison to the environment further offshore. The U concentrations may vary considerably. Lecomte et al. (2017) described phosphate nodules containing 100 to 3000 ppm of U. By contrast, U is especially enriched in lenses, called “kolm”, principally composed of organic matter, where the

concentrations may reach up to 1000–8000 ppm due to the resuspension of sediment in an anoxic water column enhancing diffusive exchange between suspended particles and the water column (Lecomte et al., 2017; Schovsbo, 2002). The metamorphic grade also has an impact on the mineralogy. On the one hand, the black shales of southern Sweden with lower metamorphic grade do not present individual uranium minerals, but U rather appears associated with the organic matter and in phosphate phases, such as in apatite (CaF[OH]; Lecomte et al., 2017). On the other hand, the temperature and pressure gradient of the greenschist facies metamorphism caused remobilisation of U and metals. This process led to the precipitation of uraninite and other uraniferous phases associated with Ca, P, V and Si (Lecomte et al., 2017). Different forms of pyrite have also been detected. First, framboidal pyrite precipitated, followed by the formation of more massive pyrite grains. With progressing diagenesis, pyrite crystallised in fractures and, as a consequence of metamorphism, overgrowth occurred on previously existing pyrite grains together with the precipitation of chalcopyrite and sphalerite. Concentrations of trace elements in the alum shale vary even within a deposit (Table 1).

7.1.1. Post-mining condition of the environment near the alum shale occurrences

The alum shales are a source of acidity to the environment. The oxidative dissolution of pyrite is principally responsible for acid production, contributing to the release of elements and compounds and forming secondary precipitates that are enriched in metals with respect to those of the source black shales (Chi Fru et al., 2016). Organic carbon is not trapped by the acid rock drainage precipitates; hence, it is released as a consequence of the weathering process (Chi Fru et al., 2016). Field observations and laboratory weathering experiments have demonstrated the acid generation and metal release from alum shales (Falk et al., 2006; Lavergren et al., 2009b, b; Yu et al., 2014; Chi Fru et al., 2016).

The environmental impacts are the consequence of the deposit type and the exploitation history. In Degerhamn, SE Sweden, the burning and processing of alum shales have intensified the mobility of sulphide-associated elements and U (Falk et al., 2006; Lavergren et al., 2009 a,b). Conditions on the sea shore promote the weathering of outcrops, waste rocks and burnt alum shale residue. The Cd, Ni and Zn concentrations in non-weathered alum shale are 6.9-, 2.3- and 6.8-fold higher, respectively, than the concentrations in weathered or burnt shale, indicating the liberation of metals during weathering or burning of the shale (Falk et al., 2006). The sulphide oxidation from the deposits and the subsequent mobility of the elements, controlled by pH, have an adverse influence on the quality of local groundwater (Table 2). For instance, Co, Cu, Fe, Mn, Mo, Ni, Sr, U and Zn concentrations are elevated. Further, Åström et al. (2009) report elevated U concentrations in the groundwater and stream waters in the black shale areas of Degerhamn (Table 2). Additionally, leaching tests and humidity cell tests coupled with sequential extraction procedures on processed black shale materials from Degerhamn corroborate the leaching behaviour of metals and U and decreasing pH of the leachates (Falk et al., 2006; Yu et al., 2014). Ni and U are abundantly leached into solution, whereas As is not as mobile under acidic conditions, as it is retained by secondary oxyhydroxides and sulphates such as schwertmannite and jarosite. This trend is also reflected in the local groundwater chemistry (Yu et al., 2014). Additionally, during World War II, black shales were burnt for oil production in Kvarntorp, central Sweden, leaving 28 Mt. of wastes deposited in open pits and in a waste facility. The wastes are mainly composed by ash, pyrite and kerogen, which are still burning. The ignition of the organic matter generates temperatures above 500 °C. The wastes are reported to drain acidic waters and the local groundwater contains elevated concentrations of Ni, Mo and U (Table 2). The leaching is predicted to increase when the deposits cool down (Bäckström and Sartz, 2015). The water chemistry has changed after neutralisation from pH 3 to around 7.5 in a pit lake filled with water in

Kvarntorp. Elements such as, Cd, Co, Cu, Ni, Pb and Zn have decreased approx. > 10 to 60 times lower concentrations, whereas U remains elevated and Mo has even increased from sub-microgram level to approx. 9 µg/L (Table 2; Allard et al., 2011). Furthermore, U was exploited in Ranstad (Billingen area) in south-central Sweden in the 1960s. For remediation, the U mine tailings materials were mixed with 5% limestone and covered by a sequence of bentonite, till and top soil layers (Allard et al., 1991). These measures have retarded the water and oxygen influx, but some leachates contain elevated concentrations of As, Cd, Cu, Mn, Ni, Mo, Zn and Pb (Table 2; Allard et al., 1991).

7.2. Okchon deposit, South Korea

The Okchon uraniferous black shales, also referred to as black slates in the literature, in the central part of the Korean peninsula are of Cambrian to Ordovician age and form part of the Guryongsan Formation of the Okchon Group. The black shales extend over 100 km and the uraniferous layer is several metres thick (Kim, 1989). These rocks are considered as analogues to the Cambrian black shales in China. Uranium exists in phases such as uranothorite [(Th,U)SiO₄], uraninite, brannerite [(U⁴⁺,Ca)(Ti,Fe³⁺)₂O₆], ekanite [Ca₂ThSi₈O₂₀] and thorutite [(Th,U,Ca)Ti₂(O,OH)₆] commonly disseminated in the quartz and muscovite matrix (Shin et al., 2016). Uraninite and brannerite have also been found to appear in association with pyrite and monazite in the Okchon black shales (Lee et al., 1998). The formation of uranium phases is associated with submarine hydrothermal processes. Afterwards, they suffered regional metamorphism (Shin et al., 2016). Besides of U, these rocks are enriched in As, Ba, Cu, Mo, V and Zn, and the average content of total organic carbon, now present as graphite, is as high as 21.2% (Table 1; Kim et al., 1989, 2015; Lee et al., 1998).

7.2.1. Natural weathering and the impact of mining activities in the Okchon black shales

Several small-scale mines have operated locally to extract the highly carbonaceous parts of the Okchon black shale deposit in South Korea. However, there is very limited information on the environmental impacts of these mines on the surrounding water bodies and soils. Woo et al. (2002) reported high SO₄ and slightly elevated Mn, U and Zn concentrations (Table 2) in groundwater near an abandoned U mine. Research on the environmental impacts has focused on describing the natural pollution in soils and accumulation in crop plants associated with Okchon black shales, which outcrop in many places along the 100-km formation (Table 2). Many investigations report on soil contamination by a wide range of elements including As, Cd, Cu, Mn, Mo, Ni, Pb, Se, Th, V, U and Zn (Kim and Thornton, 1993a, 1993b; Lee et al., 1998; Yi et al., 2003; Park et al., 2010).

7.3. Black shale occurrences with higher than average U concentrations in Kentucky, USA

Extensive Devonian black shale sequences occur in the eastern USA covering the Michigan basin, the Illinois basin and the Appalachian basin. The Appalachian Basin extends from northern Alabama to Newfoundland, but here the focus is on the black shales in Kentucky. The precursor mudrocks include sections rich in organic carbon and sulphur and some units contain higher than average concentrations of U (Table 2; e.g., Roen, 1984; Leventhal and Hosterman, 1982). Pyrite and marcasite are the principal sulphide mineral phases.

7.3.1. Impact of road construction on the weathering of black shale

A road cut in the New Albany Shales in eastern Kentucky has promoted weathering of the adjacent black shales. Under low pH (< 4), Cd, Co, Ni and Zn are transported to surface water, though upon pH rise they are absorbed and precipitated to the stream sediments. Mo, Pb, Sb and Se seem to be enriched in Fe-oxyhydroxide coatings in the soil layer covering the black shales, whereas Cu and U are retained by plant litter

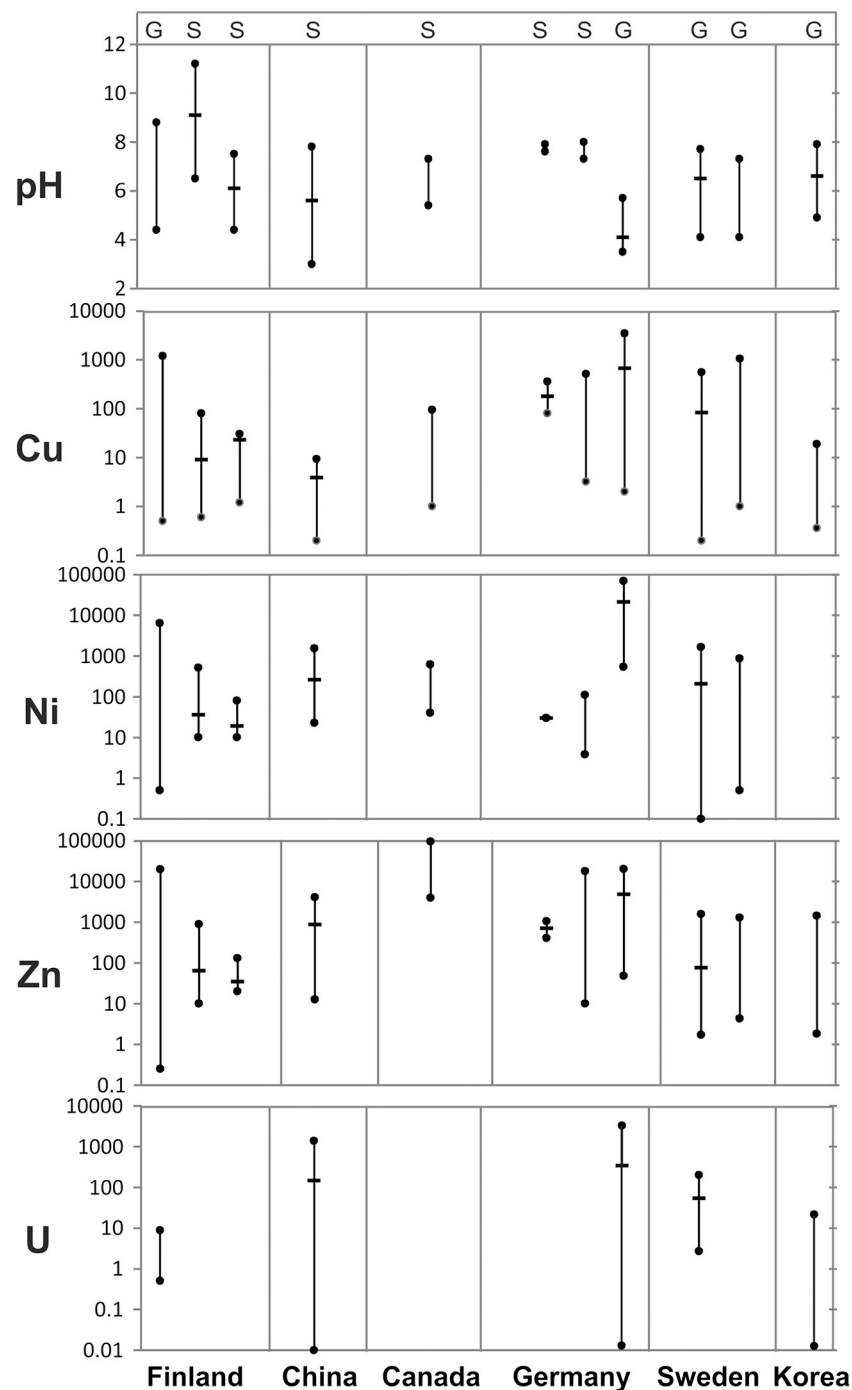


Fig. 7. Min., mean and max. values of pH and the Cu, Ni, Zn and U concentrations in groundwater (G) and surface waters (S) in selected black shale locations affected by mining or other anthropogenic activities. (Terrafame report, 2017; Terrafame, public monitoring data; Peng et al., 2009a; Kwong et al., 1997; Bozau et al., 2017; Bobarowski and Bozau, 2006; Carlsson and Büchel, 2005; Lavergren et al., 2009b; Falk et al., 2006; Woo et al., 2002).

in soil (Table 2; Tuttle et al., 2009). In another road cut in the Sunbury Shale in north-eastern Kentucky, weathering of black shale has mobilised Mn, Cd, Co, Cu, Mn, Ni, U and Zn (Perkins and Mason, 2015).

8. The country-wide black shale map and database in Finland

Black shales have been a target of extensive investigation in Finland since the 1950's (e.g., Peltola, 1960). Finland is the first country in the world which has completed the nation-wide mapping of black shales (Arkimaa et al., 1999, 2000; Airo et al., 2009; Loukola-Ruskeeniemi et al., 2011; Hyvönen et al., 2013). The map was compiled by

correlating aeromagnetic and aeroelectromagnetic data (Fig. 6) since earlier studies had shown that sulphide deposits and black shale units can be classified by airborne magnetic and gamma-ray responses (Airo and Loukola-Ruskeeniemi, 2004; Hautaniemi et al., 2005). The inferred black shale units were verified with geochemical and petrophysical studies of the samples selected from the deep drill cores. Statistical analyses and interpretation of the airborne geophysical, geochemical and rock petrophysical data were applied to characterise and classify different types of black shales. The results are compiled in the black shale database which is designed to be part of the digital geological map database of Finland (DigiKP, Geological Survey of Finland, 2017).

The black shale database provides background constraints for mineral exploration, environmental studies and regional planning. The database has been in active use since its release.

9. Discussion

9.1. Environmental concern

Wherever they occur, black shales are probable sources of acidity. At the surface environment, chemical weathering of sulphide minerals and organic matter or graphite is enhanced by bioweathering (Petsch et al., 2005; Matlakowska et al., 2012; Nordstrom et al., 2015; Włodarczyk et al., 2016; Chi Fru et al., 2016). Fig. 1 shows that the environmental impacts of black shales may vary due to the volume of sulphide-rich layers: the exceptionally metal-enriched parts may be merely few centimetres thick, as in Yukon, or the low-grade ore may exceed 300 m as in Talvivaara. However, in Yukon, even sulphide-poor, but thicker black shale sequences have been shown to be a source of acid rock drainage which may be especially harmful in periglacial regions (Lacelle et al., 2007; Lacelle and Leveillé, 2010). In addition to the chemical composition and mineralogy, the volume of the metal-rich black shale and the chemical composition of the surrounding rocks are important. Whether the adjacent rock units provide neutralisation capacity or not makes a difference. Especially, alternation of Ca-rich rocks and black shale layers in the sequence favours acid neutralisation. The Talvivaara black shale units are exceptional in thickness and Ca-rich layers are scarce (Loukola-Ruskeeniemi and Heino, 1996), which translates into a high potential for acid rock drainage. By contrast, in the Lubin Cu-Ag mine in Poland, the black shale layer is less than one metre thick and it occurs below a thick pile of limestones (Borg et al., 2012).

The varying composition of the mineralisation within a deposit results in different pollution patterns. Generally speaking, the acid drainage under natural and anthropogenic conditions is characteristically contaminated by the main metal constituents of each black shale deposit, including Fe, Ni, Zn and Cu derived from pyrite and/or pyrrhotite, pentlandite/vaesite, sphalerite and chalcopyrite, respectively (Fig. 7). Additionally, other elements such as As, Cd, Mo and U released from, for example, arsenian pyrite, sphalerite, molybdenite and thucholite/uraninite may have an adverse impact on the surrounding environment (Liu et al., 2017; Paikaray, 2012). Even the natural soils formed on black shale bedrock display elevated concentrations of associated metals and serve as a source of contamination (Tables 3; Loukola-Ruskeeniemi et al., 1998; Peng et al., 2004; Mäkinen et al., 2010; Parviainen et al., 2014; Yu et al., 2012). Translocation to plants from soil and water may consequently occur as described in China and Korea (Kim and Thornton, 1993a, 1993b; Lee et al., 1998; Fang et al., 2002; Yi et al., 2003; Park et al., 2010). In Talvivaara, the natural geochemical signature of the black shales is reflected as elevated concentrations of Cu, Mn, Ni, Pb and Zn in till, peat and stream sediments evidencing multiple dispersion routes into the environment (Table 3). The data in Table 2 illustrate the high variety of concentrations of potentially harmful elements in the recipient environment, and also in some cases show elevated concentrations as a consequence of mining activities.

The impact of active mining at Talvivaara can be seen as elevated concentrations of Cu, Ni, Zn and U in groundwater and elevated Ni and Zn in surface water (Table 2; Fig. 7). In Hunan, U mining impacts the surface waters where Cd, Co, Ni, Zn and U are recognised as major pollutants (Peng et al., 2009a). On the one hand, in the Mansfeld district in Germany, mining and processing of the Kupferschiefer ores have produced waste with Cu, Pb and Zn as the main contaminants together with As, Ni and U (Table 2; Daus and Weiß, 2001; Wennrich et al., 2004; Schreck et al., 2005). Co, Mn, Ni, Zn and U exhibit high concentrations in river water and river sediments (Table 2; Carlsson and Büchel, 2005; Grawunder et al., 2009; Schäffner et al., 2015).

Additionally, the mining of the Kupferschiefer ores in Poland release Cu, Mo, Ni, Pb, U and Zn (Sun, 1999; Sun et al., 2000; Marynowski et al., 2017). In Sweden, in Degerhamn, up to 200 µg/L of U is observed in groundwater and up to 80 µg/L in surface water due to the burning and processing of black shale (Åström et al., 2009).

Despite some tendencies in the pollution patterns, it is necessary to highlight the polymetallic character and the heterogeneity of the black shale occurrences (Tables 1 and 2). Consequently, the environmental impacts vary even within a deposit which impedes generalisation of the impact assessment. Hence, the potential for acid rock drainage and soil pollution should be evaluated in each case.

Finally, a number of environmental factors affecting the behaviour of elements in nature should be kept in mind when evaluating the contamination risks. The geochemistry of the receiving water bodies is controlled by pH as was observed in the closed mine sites of the alum shale in Sweden (Falk et al., 2006; Allard et al., 2011). The divalent cations are mobilised at low pH range whereas As, Mo and U tend to be more mobile at pH > 7 although the behaviour of these elements is complex. For example, the behaviour of U is related to pH, Eh, the oxidation state of U and the abundance of CO₃²⁻ ions (Cumberland et al., 2016). In addition, microbial metabolism has the capability to alter the solubility of U (Newsome et al., 2014).

9.2. Mining

Mining of black shales is without a doubt a major cause of pollution, even though other anthropogenic activities are known to cause acid rock drainage as well. The permitting procedures for mining projects in most countries require the environmental impact assessment (e.g., Jantunen and Kauppila, 2015). In the active mining phase, a mining company is obligated to monitor the quality of surface water, groundwater, lake sediments, air and biosphere. For example, at Talvivaara, attention has been paid into the water quality of the wells used for drinking water (Karppinen et al., 2012; Terrafame report, 2017; Terrafame report, 2018). In the Talvivaara black shale area, bioaccumulation into crop is not the issue due to the scarcity of agricultural activities, but the bioaccumulation studies have focused on fish, wild mushrooms and berries that are habitually consumed by local residents. The naturally elevated geochemical background levels for Ni and Zn and low Ca values in glacial till seem to have been reflected in the low Ca concentrations in the blood serum of local residents already well before the large-scale mining activities began in the area (Kantola et al., 2008; Kousa et al., 2011).

In historical black shale mining areas, such as the Kupferschiefer in Germany, extensive research has revealed the major sources of pollution, the weathering mechanisms and the characterisation of the mobilised harmful elements (Daus and Weiß, 2001; Schubert et al., 2003, 2005; Schreck et al., 2005). This allows the evaluation of the need for remediation measures. In the Freiberg area in Saxony with a history of 800 years of mining activities, recommendations are updated annually for the treatment of soils contaminated with As and Cd if they are used for agriculture or gardening (Hertwig et al., 2010). These lessons learnt may be useful for the other mining areas to manage the impacts of acid mine drainage.

An important issue to consider in the prevention of harmful environmental impacts is the handling of wastes after mine closure. Effective mine closure plans are crucial in order to prevent the release of harmful elements and compounds from residual sulphides and secondary phases to the environment (e.g., Heikkinen et al., 2008).

9.3. Land use planning for anthropogenic actions in black shale areas

The potential for acid rock drainage should be taken into consideration in any anthropogenic actions causing disturbance to the soils or bedrock and consequently causing acceleration of chemical weathering. In the past, road cuts in black shale areas have caused

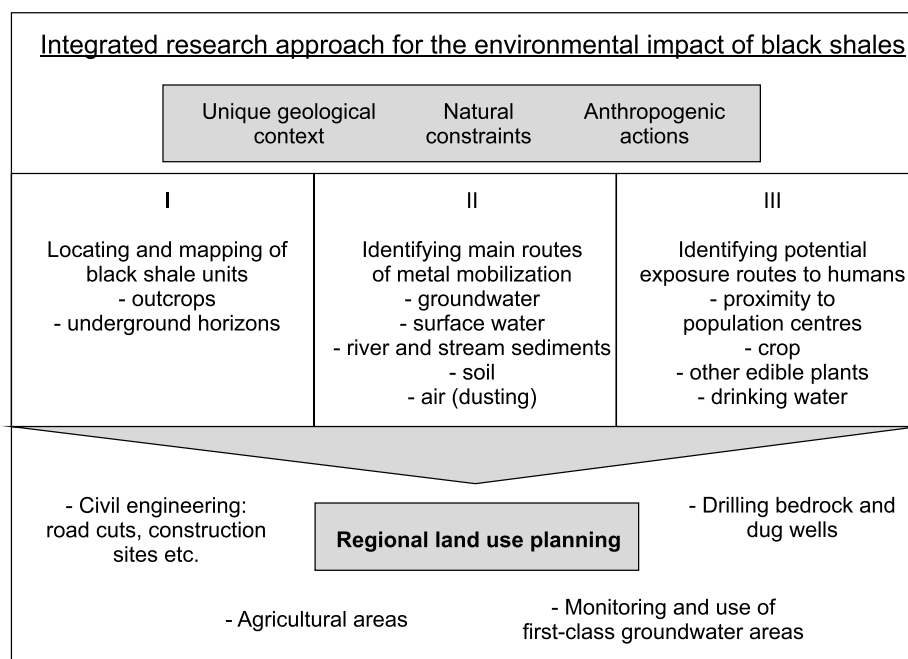


Fig. 8. A scheme for an integrated research approach for the evaluation of the environmental impacts of black shales.

mobilisation of metals into groundwater, stream water and soil (Lacelle et al., 2007; Tuttle et al., 2009; Lacelle and Leveillé, 2010; Perkins and Mason, 2015). Disturbance of the black shale bedrock during the construction of the Halifax airport in Nova Scotia, Canada, contaminated local surface water causing fish deaths (Lund et al., 1987; King and Hart, 1990). In China and Korea, investigations have mainly focused on the natural weathering profiles and the bioaccumulation of metals into plants. Bioaccumulation by agricultural plants may pose a risk to humans and therefore land use planning is recommended in the agricultural areas located in black shale areas.

In Finland, the authorities use the nation-wide black shale database in regional planning. The information is used during road construction, excavation and peat production activities as well. As black shales cause acid rock drainage in Finland (e.g., Loukola-Ruskeeniemi et al., 1998) and drilling a well into black shale bedrock may provide drinking water with poor quality, the database is also used in planning drinking water supplies. For example, a map has been developed to show black shale areas located in the areas with important groundwater resources (Tarvainen et al., 2013). In addition, comparison of the chemical concentration of peat with the occurrence of black shales reveals that in average the Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, S, Ti, V, Zn and ash contents of peat are elevated in black shale areas (Herranen, 2009; Herranen and Toivonen, 2018).

An integrated approach is recommended for the evaluation of the environmental impacts of black shale taking into account the geological context, the natural constraints and the anthropogenic actions in each site (Fig. 8). First, mapping of the outcropping black shales, and, if possible, also the underground horizons at regional or national level is recommended. This helps to locate the risk areas and allows a more advanced land use planning to avoid exposing the sulphide-rich rocks. Secondly, the main routes of metal mobilisation should be identified. We highlight groundwater, surface water, river and stream sediments and soil as the main recipients of the contamination derived from chemical, biological and mechanical weathering of black shale. Soils and biosphere in the proximity of mines may also be impacted by dusting of mine residues. Furthermore, when evaluating the risk to humans, the proximity of black shale deposits to the population centres and to the wells for household use should be investigated, as well as the bioaccumulation into edible plants and subsequent human intake. The

area affected by metal mobilisation is relatively local in most sites, for instance concentrations of harmful elements in surface waters decrease considerably after roughly one kilometre. Yet, the precipitated metals in stream bed may become remobilized upon changes in the pH and Eh conditions.

If prior information of the environmental impacts of a black shale deposit is not available, examining the mineralogical and geochemical data of the deposit itself is recommended to evaluate the metal distribution, *i.e.*, where the potentially harmful elements sit to appraise their potential mobilisation. Risk assessment and risk management may control the environmental impact of black shale both under natural conditions and during anthropogenic actions. For the black shale areas, it is recommended to follow the risk management procedures developed for example for the naturally As-rich bedrock and soil (e.g., Lehtinen et al., 2007; Loukola-Ruskeeniemi et al., 2007; Parviainen et al., 2015).

Future research would benefit of joint projects between different scientific disciplines. Comparing the microbial processes and organic geochemistry during the genesis of black shale with the low-temperature processes during weathering or during the bioleaching of black shale ores, could bring novel ideas for the remediation actions and for the prevention of pollution during and after mining activities.

10. Conclusions

Black shales are common in sedimentary sequences world-wide. They are a noteworthy source of metal contamination if exposed, even under natural conditions, due to their high sulphur, metal and organic matter contents. As black shale forms a heterogeneous group of rocks, *i.e.*, the sulphide mineralogy, associated metal assemblages, host rocks, thickness and extension vary, pollution risks have to be evaluated in each case. Groundwater, surface water and soil are the main environmental recipients. Additionally, human exposure may occur through the bioaccumulation of metals into crop from contaminated agricultural soil or water and through metal-rich groundwater. Anthropogenic activities enhance the environmental impacts of black shale. The contaminated waters are characteristically polymetallic: elevated concentrations of Cu, Ni, Pb, U, Zn, As, Cd, Co, Mn and Mo may occur depending on the deposit type. Hence, mining activities should be

carried out under regulated monitoring. In regional planning, it is recommended to map the distribution of sulphide-rich black shale to avoid acid rock drainage during civil engineering actions. Further, it is not the best alternative to drill wells into the black shale bedrock or the overlying soil.

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