

Secondary resources directive

Sampling and characterisation of burnt shale waste (*rödfyr*) in southern Sweden

Anna Ladenberger, Lisa Blomskog, George Morris,
Johan Camitz & Iain Pitcairn

September 2024

SGU-rapport 2024:08



Cover photo: Waste piles behind a little cottage in Västergötland.
Photographer: Anna Ladenberger

Authors: Anna Ladenberger, Lisa Blomskog (Stockholm University),
George Morris, Johan Camitz, and Iain Pitcairn (Stockholm University)

Reviewed by: Dick Claeson

Head of unit: Ildiko Antal Lundin

Editor: Lina Rönnåsen

Geological Survey of Sweden

Box 670, 751 28 Uppsala

phone: 018-17 90 00

e-mail: sgu@sgu.se

www.sgu.se

CONTENTS

Abstract.....	5
Sammanfattning.....	5
Introduction	7
Regional geology.....	8
Industrial exploitation of black shale.....	10
Alum production.....	10
Lime production	11
Oil production.....	11
Uranium production.....	11
Methods.....	12
Sample preparation.....	12
Chemical analyses	12
Quality control of ALS data.....	13
Results	14
Hunneberg.....	14
Geology and history of exploitation.....	14
Sampling.....	16
Results.....	17
Kinnekulle.....	18
Geology and history of exploitation.....	18
Sampling	19
Results.....	21
Billingen & Falbygden.....	22
Geology and history of exploitation.....	22
Sampling	24
Results.....	26
Närke	27
Geology and history of exploitation.....	27
Sampling	30
Results.....	31
Scania (Skåne).....	32
Geology and history of exploitation.....	32
Sampling	33
Results.....	35

Kalmar and Öland	36
Geology and history of exploitation.....	36
Sampling	39
Results.....	40
Discussion	41
Geochemical characteristics of burnt shale waste.....	41
Major elements and volatile components.....	41
Trace elements and metals.....	44
REEs	49
Geographical variation in chemical composition of burnt shale waste.....	50
Secondary resource potential	54
Conclusions	54
Acknowledgements	54
References	55

ABSTRACT

In 2021, the Geological Survey of Sweden (Sveriges geologiska undersökning, SGU) together with the Swedish Environmental Protection Agency received a governmental directive to work to increase the possibilities for sustainable extraction of metals and minerals from secondary resources (N2021/01038).

As part of the directive, SGU has documented, sampled, and characterised mining waste (waste rock and tailings) at closed Swedish mines to estimate the quantities of metals and minerals. Metallurgical slag and burnt alum shale were also investigated.

A total of 70 locations was sampled by SGU during 2021 and 2022, with altogether 1,067 samples. A series of reports present background information and available data for each of these locations, as well as the results from the new investigations.

This report presents the geochemical characteristics of burnt shale waste (swe. *rödifyr*) collected in southern Sweden. Sampling was conducted in Västergötland, Närke, Scania (swe. *Skåne*), south of Kalmar and on Öland island.

The burnt black shale waste heaps in southern Sweden originate from the alum, lime, and oil industries which utilised Palaeozoic black shale (so called alum shale) either as a primary resource or a fuel. The burnt black shale waste heaps can be found in many places and in variable volumes; in urban, agricultural, recreational, and forested areas in Västergötland, Närke, Scania (Skåne), south of Kalmar and on Öland island.

During the 2021 and 2022 field campaigns 68 locations with burnt shale waste were visited and representative samples were collected. By analysing the whole rock chemistry, the mineral potential of the waste as secondary raw material as well as its impact on the local environment could be evaluated. The results show that some elements and compounds, such as carbon and sulphur, have undergone mass loss while many others e.g., Fe_2O_3 , P_2O_5 , CaO and metals such as Cd, Co, Cu, Ni, Zn as well as rare earth elements (REEs) are enriched in the burnt shale when compared with the source black shale. At some locations, the contents of metals are high and can be considered for extraction, e.g. vanadium in Scania and uranium in Falbygden (near Falköping) region.

The relative enrichment in economically interesting raw materials may facilitate efforts to recycle the mining waste in order to obtain valuable metals for the green transition technologies and at the same time remediate local sites with potentially hazardous waste.

SAMMANFATTNING

År 2021 fick Sveriges geologiska undersökning (SGU) tillsammans med Naturvårdsverket i regeringsuppdrag att arbeta för ökade möjligheter till hållbar utvinning av metaller och mineral ur sekundära resurser (N2021/01038). Arbetet är tänkt att bidra till omställningen till en mer cirkulär och resurseffektiv ekonomi. Uppdraget i sin helhet redovisades till regeringen i februari 2023 (SGU RR 2023:01).

Som en del av uppdraget har SGU dokumenterat, provtagit och karakteriserat gruvavfall (varphögar och sandmagasin) vid nedlagda svenska gruvor för att bedöma mängden metaller och mineral. Även metallurgiskt slagg samt rödfyr, som är en rest av bränd alunskiffer, har undersökts. Sekundära resurser från gruvavfall kan möjligen bidra till försörjningen av de kritiska råvaror som behövs i den pågående energiomställningen.

Inom uppdraget har totalt 70 platser provtagits under 2021 och 2022, med sammanlagt 1 067 prover. I en serie rapporter presenteras förutom resultaten från de nya undersökningarna även bakgrundsinformation och tillgängliga data för respektive undersökt plats.

Denna rapport tar upp en delmängd av de undersökta platserna inom uppdraget och omfattar provtagning av rödfyr från bränd alunskiffer i södra Sverige. Inom projektet togs prover på 68 platser i områdena Kinnekulle, Hunneberg, Billingen, Falbygden (Falköping), Närke, Andrarum (Skåne), Lovers bruk (Kalmar) och Degerhamn (Öland). Provtagningen skedde från avfallshögar i direkt anslutning till historiska industriverksamheter där kalk, alun och olja använts. Ett syfte med projektet var att utvärdera rödfyrs potentiella värde för utvinning av kritiska och strategiska metaller och mineral, framför allt vanadin, molybden och nickel men även uran.

Rödfyr är en restprodukt efter förbränning och bearbetning av alunskiffer och kan innehålla höga halter av metaller med ursprung i skiffern. Genom Sveriges industriella historia har alunskiffer varit en viktig råvara. Skiffern användes som bränsle i fältugnar för kalkbränning, som råvara till alunframställning, till skifferoljetillverkning, till lättbetong, för utvinning av svavel och kväve, och för utvinning av uran. Utvinningen pågick från mitten av 1600-talet till slutet av 1960-talet. Efter såväl aluntillverkning som kalkbränning och oljeutvinning kvarstår skifferaska och rödfyr. Ibland innehåller rödfyr rester av kalk, orsten och obränd skiffer.

De huvudsakliga områdena för utvinning av alunskiffer var Andrarum i Skåne, Degerhamn på Öland med Lovers bruk söder om Kalmar, Latorp i Närke, Kinnekulle i Västergötland, Kvarntorp i Närke och Ranstad i Västergötland. Alunskiffern bröts oftast i dagbrott men på några platser även i underjordiska gruvor, till exempel vid Kinnekulle. Rödfyr deponerades i stora högar, ofta i anslutning till skifferbrotten och bruken. Många av dessa rödfyrshögar har inventerats och riskklassats efter Naturvårdsverkets metodik för inventering av förorenade områden, men sällan har dessa områden sanerats. Rödfyr har också använts bland annat som utfyllnadsmaterial, underlag till tennis- och löparbanor samt som vägbeläggning.

De kemiska analyserna av den rödfyr som provtagits inom uppdraget visar höga och förhöjda halter av flera grundämnen, där halterna också är högre än i den ursprungliga alunskiffern. Vid förbränning förlorar alunskiffer sina lättflyktiga komponenter som kol, svavel och vatten/vätska. Grundämnena som sitter i organiska föroreningar i skiffern omfördelas till andra, nybildade faser, som är amorfa eller till delar kristallina. Den nya avfallsbergarten eller askan blir mer kiselrik och järnrik. Eftersom järn oxideras kraftig under uppvärmning får hela avfallet en orange till röd färg. Anrikningen av spårgrundämnena och metaller är tydlig i restprodukterna, framför allt för Cu, Zn, Ni, V, U och REE. På vissa ställen innehåller avfallet kalk vilket märks i form av högre halter av Ca, Ba och Sr.

Genom att analyserna av rödfyr kommer från flera platser i södra Sverige kan man observera att det finns variation i den kemiska sammansättningen som avspeglar variationen hos den ursprungliga alunskiffern. På vissa platser är halterna så pass höga att de kan väcka intresse från gruv- och återvinningsindustrier och på andra platser kan rödfyr utgöra en viss miljörisk och påverka kvaliteten hos jord och vatten. Lakbarheten hos avfallet varierar och beror på hur stora fragmenten är, på dess vittringsgrad och om de ligger i vatten eller på ytan, till exempel i en hög. Vidare studier behövs för att bedöma avfallets miljörisker och dess praktiska möjligheter för utvinning.

INTRODUCTION

In 2021, the Geological Survey of Sweden (Sveriges geologiska undersökning, SGU) together with the Swedish Environmental Protection Agency received a governmental directive to work to increase the possibilities for sustainable extraction of metals and minerals from secondary resources (N2021/01038). The work is intended to contribute to the transition to a more circular and resource-efficient economy. The directive in its entirety was reported to the government in February 2023 (SGU RR 2023:01).

As part of the directive, SGU has documented, sampled, and characterised mining waste (waste rock and tailings) at closed Swedish mines to estimate the quantities of metals and minerals. Metallurgical slag and burnt alum shale were also investigated. Secondary resources from mining waste can possibly contribute to the supply of the critical raw materials needed in the ongoing energy transition.

A total of 70 locations was sampled by SGU during 2021 and 2022, with altogether 1,067 samples. A series of reports present background information and available data for each of these locations, as well as the results from the new investigations. The goal of the sampling and geochemical investigations was to provide a general estimate of potential CRM (i.e. Critical Raw Materials) in the mining waste.

One component of the study was to investigate the mineral potential of burnt alum shale waste (swe. *rödgyr*). Sampling of *rödgyr* was carried out during the 2021 and 2022 field campaigns (Fig. 1). In September 2021, 58 samples of burnt shale were collected from waste piles in the areas of Kinnekulle, Hunneberg, Billingen (Skövde), Falbygden (Falköping) and Närke, in south-western Sweden. In June 2022, an additional 10 samples of burnt shale were collected in Andrarum (Scania), Lovers bruk (Kalmar) and Degerhamn (Öland).

The Alum Shale Formation of Scandinavia has been of economic interest for more than 300 years. The Cambrian to Early Ordovician black shale deposits have been mined for alum salt, oil and uranium, as well as used as fuel source in lime production. The black shale has been recognised as a primary source for selection of critical raw materials (CRM), including REE's and vanadium.

During industrial processing, the black alum shale was heated to a temperature between 500 and 1000° C for a period of weeks to months. High-temperature processing modified the original composition of the black shale leaving a waste product, burnt alum shale, known as *rödgyr* in Swedish.

Today burnt alum shale waste heaps can be found in small to large volumes in urban, recreational, forested, and agricultural environments of central (Västergötland, Närke, Östergötland) and southern Sweden (Scania, Kalmar, Öland). The largest of these waste heaps, Kvarntorpshögen in Närke is ca 100 metre high and covers an area of 450,000 m². In 2014 the County Administrative Board of Västra Götalands Län reported 65 burnt shale waste heaps in the county which are now registered in the national database of contaminated sites (Länsstyrelsen Västra Götalands län, 2014).

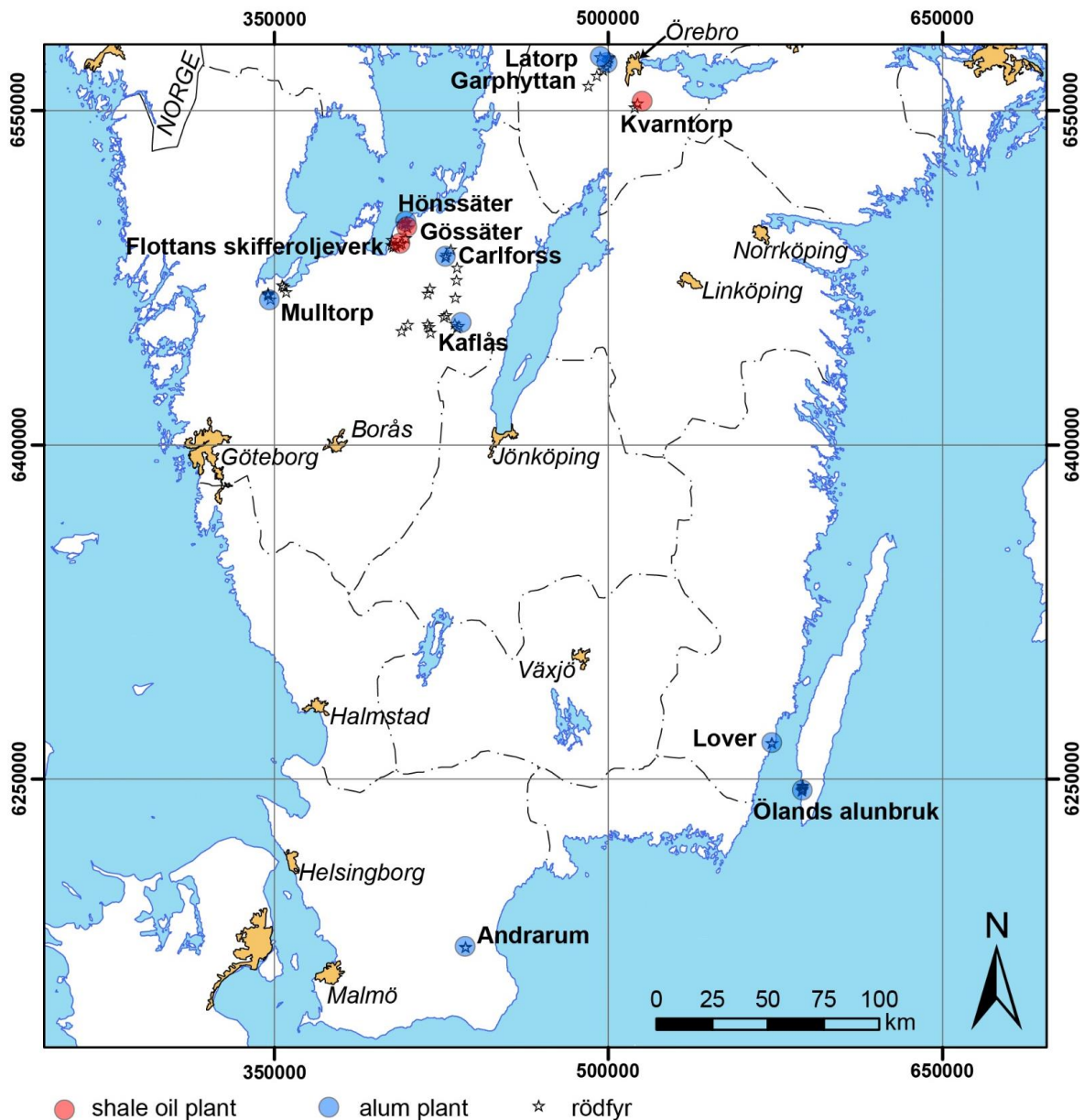


Figure 1. Sampling sites of burnt shale waste (swe. rödfyr) in central-southern Sweden.

REGIONAL GEOLOGY

The Proterozoic crystalline basement of the Fennoscandian Shield is locally unconformably overlain by tillites and other Late Proterozoic sediments, which in turn is locally overlain by an Early Cambrian quartz sandstone (Andersson et al., 1985). In the Mid-Cambrian, the sandstone deposition transitioned into a mudstone which directly underlies the Alum Shale Formation (Andersson et al., 1985). The Alum Shale Formation itself was deposited in a shallow epicontinental sea (Snäll, 1988) in the Middle Cambrian to the Early Ordovician. The Alum Shale Formation of Scandinavia (sensu stricto) refers to specific parts of a black shale formation rich in alum salt, $KAl(SO_4)_2 \times 12 H_2O$. The name Alum Shale Formation was then applied to the entire black shale unit throughout Scandinavia (Andersson et al., 1985). It extends from Finnmark in Northern Norway to Scania in southern Sweden (Fig. 2).

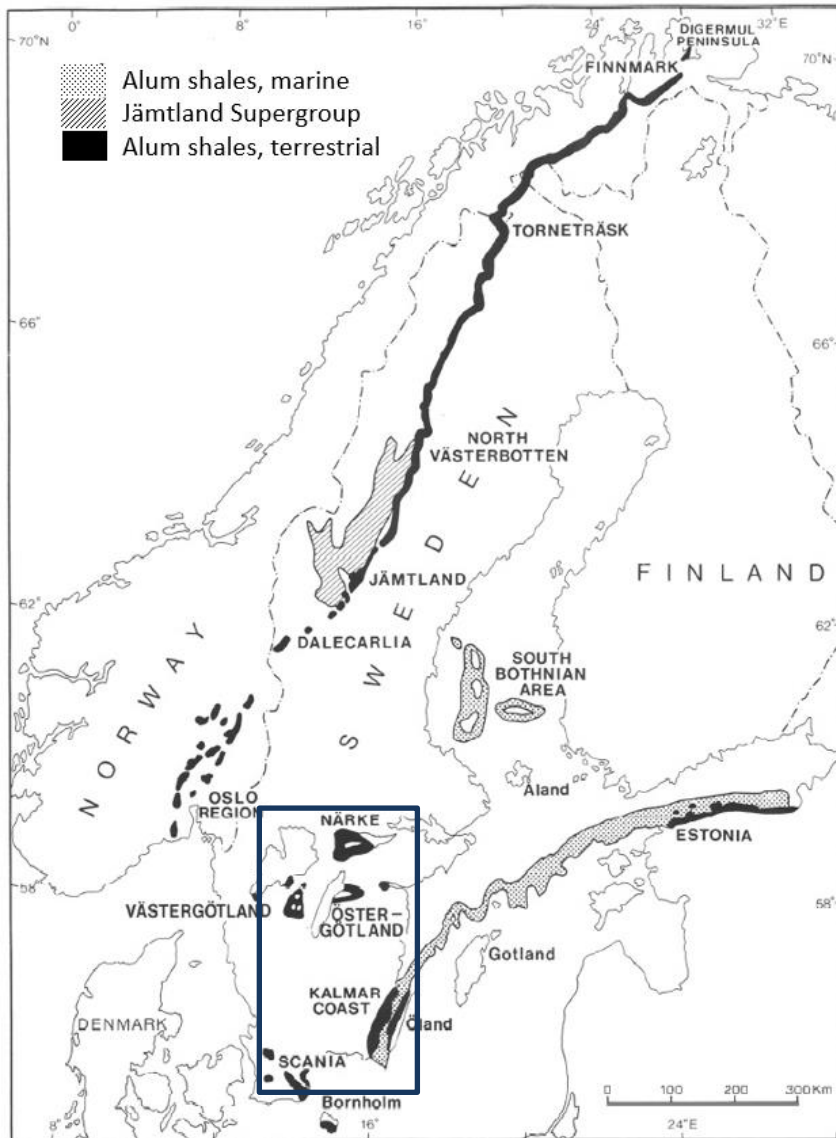


Figure 2. Occurrence of alum shale in Scandinavia and the Baltic region (from Thickpenney 1984). The rectangle shows the study region.

The formation displays lateral variation in thickness ranging from ~20 m to ~100 m. The thickest parts can be found in southern Scania (Sweden), around the Oslo area (Norway), and in both the Swedish and Norwegian Caledonides (Andersson et al., 1985). Bituminous limestone (swe. *orsten*), also known as stinkstone, occurs in lenses and pinches out locally throughout the formation. These lenses commonly contain a high abundance of fossils, which allow for more accurate biostratigraphic correlation across the formation. Nodules and thin bands of iron sulphides are common throughout the formation. An Early Ordovician (Late Tremadoc) glauconitic phosphatic limestone overlays the Alum Shale Formation, followed by an alternating succession of grey shales and limestones continuing from the Ordovician into Silurian. In the western areas of the Caledonides, thick greywackes can be found interbedded in the Ordovician carbonates (Andersson et al., 1985). In areas such as Hunneberg and Kinnekulle, Permo-Carboniferous diabase intrusions overlay late Ordovician limestone and Silurian shale successions. These intrusions form a cap rock that has protected the underlying layers from being eroded away and created the distinctive table-mountain topography seen today.

The alum shale shows little evidence of bioturbation and is thought to be formed under poorly oxidised and stable tectonic conditions. Parallel laminations and the lack of sedimentary structures are characteristic of shallow marine tidal environments with deposition below the storm wave base and very low rate of sedimentation (ca 1–10 mm/1000 years). The lithological homogeneity and the large areal extent of the alum shale facies indicate a uniform depositional environment in a large epicontinental sea that covered much of the present western part of Baltica (Thickpenny 1984; Ahlberg et al., 2009).

The black shale of the Alum Shale Formation is characterised by a high organic carbon content of up to ca 20% and high concentrations of sulphur (S), calcium (Ca), nitrogen (N), phosphorus (P), potassium (K) and trace elements such as molybdenum (Mo), nickel (Ni), uranium (U), vanadium (V) and rare earth elements (REE) (Armands 1972, Hessland and Armands, 1978).

INDUSTRIAL EXPLOITATION OF BLACK SHALE

The alum shale has been of economic interest for more than 300 years. The shale has been mined for alum salt, oil, and uranium, as well as used as fuel source in lime production. In the last decade, a demand for critical raw materials (CRM) brought attention to the black shale as a primary source for vanadium, molybdenum, and nickel.

In each of the industries: alum, lime, oil, and uranium, the black alum shale was heated to a temperature between 500 and 1000° C for a period of weeks to months. High-temperature processing modified the original mineralogy and chemical composition of the black shale leaving a distinctive red waste product known as burnt alum shale or *rödifyr* in Swedish.

Alum production

Alum produced from alum shale is a hydrated double salt of potassium and aluminium sulphate ($KAl(SO_4)_2$) which has numerous applications, for example in leather tanning, as a pharmaceutical astringent, a flocculant in water purification, for setting dyes on textiles, in cosmetics (deodorants, depilatory waxes), as a pickling agent, in baking powder and many others.

The mining of alum shale began at Andrarum in Scania in 1637 and continued until 1912 (Stoltz, 1932). Alum was also produced in Latorp, Närke from 1773 to 1878 (Stoltz, 1934) and in Degerhamn, Öland where the remains of 2,700,000 m³ of burnt shale from alum production can be found (Yu et al., 2014).

The historical process to extract alum salts from the black shale was laborious and time consuming. The black shale was mined in quarries or small shafts, often near the kilns. The shale was stacked and burned with wood at temperatures around 700° C until the organic matter was burned away, which could last weeks or even months (Falk et al., 2006). The high temperatures during burning produced iron oxide and sulphuric acid whereby the acid would react with the silicate minerals in the black shale to form alum salt (Falk et al., 2006). The burned shale material was then transferred into leaching pools where the alum salt was dissolved and leached out with warm water, then subsequently evaporated to precipitate the salt.

At the end of the 18th century, it was found that the shale had a high enough kerogen content to burn on its own. Kilns were then constructed for this purpose and the alum salt extraction continued in southern Sweden until the early to mid- 1900's. At its peak, alum production reached up to 250 tonnes (Andersson et al., 1985). By-products of the alum industry included iron sulphate, gypsum, and red pigment from iron oxide.

Lime production

Calcium oxide (CaO), known as quicklime or burnt lime, forms when limestone (calcium carbonate) is heated to above 900° C (calcination) in a lime kiln. The first application of lime was to improve soil nutritional status in agriculture. Calcium oxide can be used to stabilise pH, soften water, and precipitate nutrients. It is commonly used in agriculture, the cement industry, steel production, water treatment, the paper industry etc. Quicklime is unstable unless slacked with water to form solid calcium hydroxide Ca(OH)₂, which is a hydrated lime known as slacked lime. The reaction is exothermic, and the heat produced can reach up to 50° C.

Kerogen-rich black shale has been used as fuel in lime production. At the end of the 18th century, it was found that the alum shale would burn on its own, and the shale slowly began to replace wood in lime burning process and was used until 1956 (Armands, 1972). Shale and limestone were stacked in alternating layers in a semi-circle shape and fired at the bottom. Most early field kilns were built next to the quarries where both the shale and the limestone were quarried. The kiln walls were often constructed from the local black shale blocks which were easy to work with.

Oil production

The interest in oil extraction from alum shale began as early as 1873, with production starting in Kinnekulle in 1923 (Armands, 1972). In most locations in Sweden, the oil content in bituminous limestone and shale is too low to be of economic interest. There are only three areas that are economically viable (with at least 4% oil content): Kinnekulle, Närke (Kvarntorp with 5.5–6.5%, and Kumla with ca 5%), and Östergötland. From 1934–1939 approximately 48,650 tonnes of alum shale were mined for oil production (Bergh, 1942).

In 1941, the demand for oil in Sweden during the Second World War drove the start of oil production in Kvarntorp in Närke by the Svenska Skifferolje AB (Schwartz, 1945, Casserstedt 2014). Production decreased significantly in the 1960's and ceased by 1969. By this time approximately 50 million tonnes of alum shale had been mined for oil production (Andersson et al., 1985). The shale used for oil production was mined in open pits (now filled with water and called 'pit lakes'), crushed, and then pyrolysed in Channel or Hultman-Gustafson ovens as well as in Bergh ovens. To obtain oil, shale was heated to produce a gas, which was then cooled down and heavy hydrocarbons were separated from the light hydrocarbons. The heavy hydrocarbons were extracted as oil while the light hydrocarbons remained a gas.

Crushed shale fraction less than 5 mm and shale which was partially to completely burned was discarded as waste material (Schwartz, 1945). The waste products were deposited near an extraction plant and the large 100 m high pile-mountain of waste (mainly ash) after burning shale was formed and called Kvarntorpshögen. Apart from containing high amounts of potentially toxic metals, Kvarntorpshögen is also very hot. Within the burned ash, together with unburned alum shale, pyrite and kerogen still undergo exothermic chemical reactions, which even today generate heat with temperatures of up to 700°C measured just 15 m below the surface.

Uranium production

The Alum Shale Formation has long been known to be enriched in uranium. Nordenskiöld (1893) was the first to report uranium concentrations of 5,000 ppm within the kolm lenses and it was later estimated that the kolm lenses in the Kvarntorp area alone contained 100 tonnes (Ljunggren, 1949). The company AB Kolm operated from 1909 to 1915 but had little success with extracting uranium (Hultgren et al., 1993).

In 1945 the Atomic Energy Committee was formed to develop a national nuclear energy program. With the intention of decreasing fuel imports and making Sweden more energy

independent it was decided that Sweden should use their own indigenous uranium. In 1947 AB Atomenergi was established by the Research Institute of National Defence (FOA) and owned by the state (more than 50%), oil companies, refineries, and mining companies. Universities (e.g. KTH and Lund) and the Geological Survey of Sweden (SGU) were included in the research and development. Early years were spent researching both nuclear technology and the extraction of uranium from indigenous sources. Multiple sources of uranium were explored and investigated, including extraction from untreated alum shale kolm, and from the burnt alum shale (referred to in the literature as *shale ash*) produced from the shale oil industry during the Second World War.

In 1950, AB Atomenergi started a pilot program at the Swedish Shale Oil Company's plant in Kvarntorp which was later moved in full scale to Ranstad, a small village on the southern slope of Billingen (Hultgren et al., 1993). Planning for Ranstad started as early as 1957 and included an open pit mine, a uranium processing plant, and a waste disposal area situated on an area of 7.5 km². The processing plant had the capacity to produce 120 tonnes of uranium from 800,000 tonnes of shale per year. Poor market conditions were a key factor in the decision to keep the plant running at half capacity until 1969 (Hultgren et al., 1993). Between 1965 and 1969 Ranstadsverket processed 1.5 million tonnes of shale containing 0.03% uranium, and 215 tonnes of uranium oxide was produced (Sjöblom, 2014). During these years, the average production of uranium was 54 tonnes per year (Hultgren et al., 1993). The mining of alum shale at Ranstad ceased in 1969, but processing of the shale continued at a reduced capacity. In 1973 the Swedish mining company LKAB became a partner and took over the mine. LKAB submitted an application called 'Project Ranstad 75' (swe. *Projekt Ranstad 75*) to resume mining, but they later withdrew this proposal. A second application was submitted in 1977 called 'Mineral Project Ranstad' (swe. *Mineralprojekt Ranstad*) which included other minerals in addition to uranium, but due to falling uranium prices mining never resumed. Between 1990 and 1993 remediation and restoration of the Ranstad area was completed by the Swedish government and AB Atomenergi (later called Studvik AB, Hultgren et al., 1993).

METHODS

Sample preparation

Samples collected from the waste piles were air-dried for ca one week. Plant remnants, fine-grained material and soil were removed before packing of ca 300–400 grams of clean 'rödfyr' fragments into sealed plastic bags for submission to the ALS preparation lab for milling and weighing (Fig. 3).

Chemical analyses

The samples of burnt shale and alum shale were sent to the ALS Scandinavia laboratory for chemical analysis. At the ALS lab samples were crushed and milled to a powder of size <75 µm. Major element oxides were determined with ALS method ME-ICP06 whole rock analysis with ICP-AES (inductively coupled plasma atomic emission spectroscopy). Trace elements Ba, Ce, Cr, Cs, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Nb, Nd, Pr, Rb, Sm, Sn, Sr, Ta, Tb, Th, Tm, U, V, W, Y, Yb, and Zr were determined with ALS method ME-MS81 Lithium Borate Fusion ICP-MS. Trace elements Ag, Cd, Co, Cu, Li, Mo, Ni, Pb, Sc, and Zn were determined with ALS method ME-MS61 4-acid digestion ICP-MS. Loss on Ignition (LOI) was determined with ALS method OA-GRA05 at 1000° C. C-IR07 total carbon (IR Spectroscopy) and S-IR08 total sulphur (IR Spectroscopy) were also included in the analysis. The data tables for the whole rock analysis can be found in Appendix 1.

Quality control of ALS data

The ALS laboratory validated analytical results using certified reference materials (CRMs), duplicate samples, and lab-blind repeat samples. (Table 1). Three in-house SGU standards (NOT050082, ARG050109 and BAG050062) representing a range of chemical compositions were sent as blind samples together with collected samples to monitor the analytical performance. All three standards gave satisfactory results.



Figure 3. Sample preparation: drying and storage.

Table 1. Reference materials and duplicates used for each method at ALS laboratory (ALS Scandinavia 2015).

Method	Reference material	Duplicate samples
ME-ICP06	AMIS0304, MRGeo08, REE-1	001, 10B, 031, 032, 043B,
ME-MS81	AMIS0304, MRGeo08, OREAS 102a, REE-1	001, 10B, 032, 043B
ME-MS61	EMOG-17, MRGeo08, OGGeo08, OREAS 922	008, 022, 042
OA-GRA05	LRLOI2, LRLOI4	001, 022, 040, 054
C-IR07	GGC-09, GS910-4, GS914-5	009, 019, 043, 053
S-IR08	GGC-09, GGC-11, GS910-4, GS914-5	009, 020, 043, 053

RESULTS

Sampling of rödfyr was carried out during 2021 and 2022 field campaigns. In total, 68 samples of burnt shale were collected from waste piles in the areas of Kinnekulle, Hunneberg, Billingen (near Skövde), Falköping (Falbygden), Närke (eastern and western part), Andrarum (Scania), Lovers bruk (Kalmar), and Degerhamn (Öland). The summary of sampled regions with number of samples collected is shown in Fig. 4.

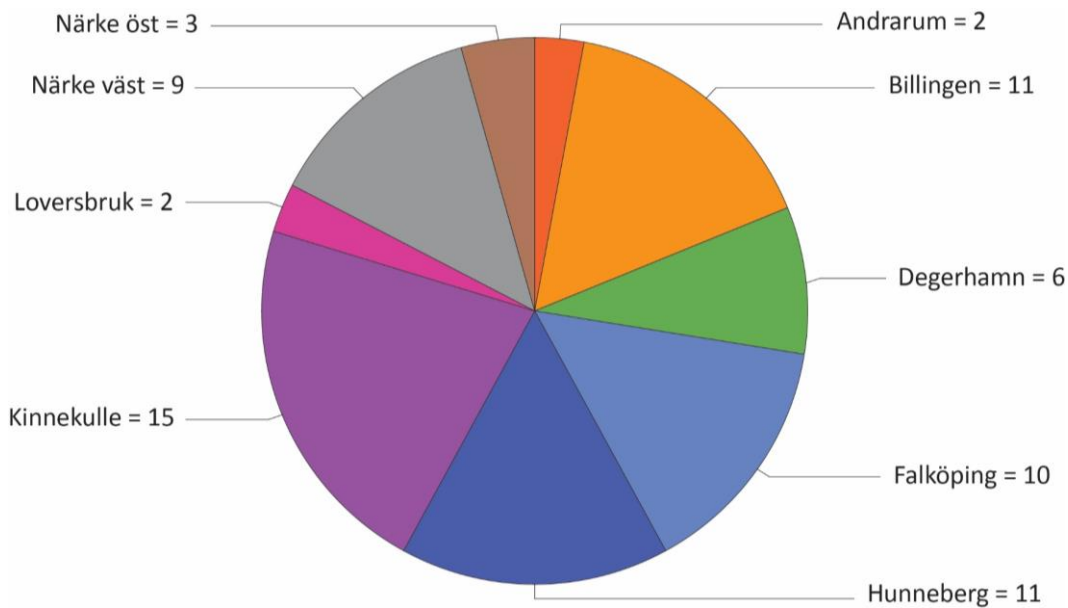


Figure 4. Overview of waste samples collected for this study.

Hunneberg

Geology and history of exploitation

The local geological units at Hunneberg comprise a flat lying basal sandstone (ca 25 m), black shale (ca 25 m), locally with thin layers of Ordovician limestone and shale, overlain by a thick, up to 60 m unit of Permian diabase. Evidence of thermal metamorphism from the overlying diabase can be seen throughout the sedimentary sequence. The entire Palaeozoic sequence rests on Fennoscandian Shield gneisses (Bergström et al., 2004, Egenhoff & Maletz, 2012).

In the 18th century the local soils needed to be limed and the local industry of lime production was established in 1754. Numerous excavations of limestone and black shale to produce lime occurred around the Hunneberg table mountain. Limestone was mainly sourced from stinkstone nodules within the alum shale. In 1790 it was discovered that due to high kerogen content alum shale could be used as fuel, even without using wood, to produce the lime. It took approximately two weeks to reduce the limestone in a lime kiln (Fig. 5 & 6). At the end of 19th century, lime production at Hunneberg reached over 100 000 barrels a year and the last kiln operated until 1950 (Fig. 5). Workers excavated the stone using simple tools like hand drills and black powder. Shafts were driven ca 30 m sideways into the Hunneberg mountain (Fig. 7).



Figure 5. The lime kiln at Västra Tunhem, Hunneberg 1950.
Photo: <https://digitalmuseum.se>.



Figure 6. The ruin of the lime kiln at Västra Tunhem (Mulltorp).
Photo: Anna Ladenberger.



Figure 7. Typical level in alum shale at southwestern side of the Hunneberg table mountain.
Photo: Anna Ladenberger.

Sampling

Eleven samples of burnt shale waste were collected at nine sites around Hunneberg table mountain (Fig. 8). Samples were collected from small to medium size waste heaps located by southwestern and northeastern slopes of Hunneberg. Most of the sites are located close to the original small black shale mines. Samples are orange to red in colour and some are contaminated by lime products.

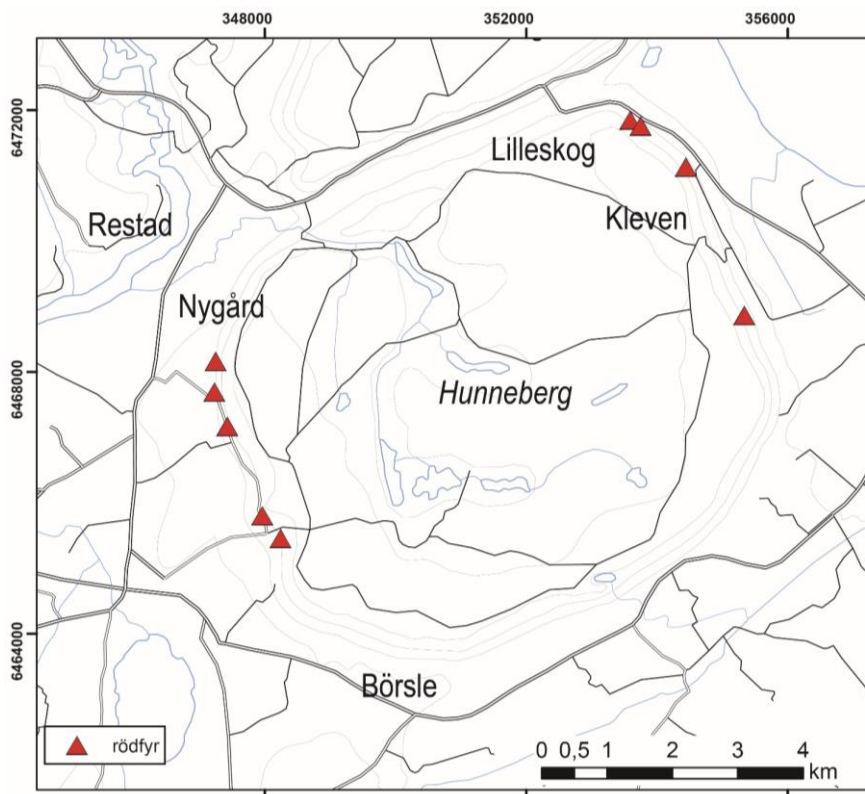


Figure 8. Sampling sites of burnt shale waste (swe. *rödfyr*) at Hunneberg.

Results

Collected waste samples from Hunneberg have high concentrations of CRMs such as V (mean = 599 ppm), Mo (mean = 140 ppm), and Ni (mean = 147 ppm), and elevated contents of REEs (mean = 233 ppm), copper (mean = 147 ppm), cobalt (mean = 33 ppm) and gallium (mean = 23 ppm). Ba, Ti and P also have high concentrations. Locally, As content in rödfyr is up to 121 ppm (Table 2).

Table 2. Basic statistics for selected elements in burnt shale waste from Hunneberg (n = 11). Reported as ppm.

Element	Mean	Max	Min
Ag	0.6	0.6	0.5
As	48	121	6
Au	0.007	0.021	0.001
Ba	3363	8360	507
Be	3.2	4.1	0.9
Bi	0.2	0.7	0.1
Co	33	44	21
Cu	147	193	27
Fe	67834	108065	55256
Ga	22.6	24.5	18.9
Hf	3.6	4.7	3.0
In	0.04	0.07	0.01
Li	42	60	10
Mo	140	188	14
Nb	16	18	13
Ni	147	201	60
P	1222	2138	785
Pb	53	87	8
REE + Y	233	288	129
Sb	2.3	3.6	0.2
Sc	14	27	10
Sr	176	452	90
Ta	0.9	1.2	0.7
Ti	5532	13189	4136
U	88	106	9
V	599	871	360
W	2.4	4.0	2.0
Zn	76	121	43

Kinneulle

Geology and history of exploitation

The geology of Kinneulle table mountain comprises a Cambro-Ordovician to Lower Silurian sedimentary sequence composed of Cambrian sandstone and Upper Cambrian to Lower Ordovician alum shale overlain by thick Ordovician limestone and younger shale. The number of stinkstones is relatively high in the alum shale at Kinneulle. Permian diabase caps the sequence. The alum shale shows no evidence of thermal alteration by the overlying intrusion and is therefore rich in hydrocarbons. The content of both kerogen and uranium increases upwards within the formation (Andersson et al., 1985).

As early as in the middle 16th century up to beginning of the 19th century alum shale was mined here for alum salts. Shale was also used as fuel for burning limestone in kilns to produce agricultural lime. Alum production at Hönsäter started in 1768 but it ceased in 1873 and instead lime and cement production were established. The cement factory finally closed in the late 1970's (Fig. 9 & 10).

The kerogen-rich shale has been used for crude oil extraction since the 1920's. The oil extraction plant opened in 1924 near Kinne-Kleva and, after few years, was bought by the state and named 'Flottans Skifferoljeverk' (Bergh 1942). From 1930 to 1966 fuel oil, gasoline, aviation fuel and gasol, as well as sulphur and nitrogen as biproducts, were produced at Kinneulle (SOU 2020:71). A pilot plant at Kinneulle operated during World War II producing up to 500 tonnes of petroleum per year, mainly for military purposes (Andersson et al., 1985). At Kinneulle, alum shale was excavated both in quarries and underground. Exploited black shale contained ca 18% bitumen and 12% pyrite. After burning ca 76% ash was produced (Bergh 1942).



Figure 9. Limestone quarry at Hönsäter, Kinneulle in 1901. The previous alum factory was closed in 1873 and turned to lime and cement production. Photo: Werner Lindhe (Tekniska museet).



Figure 10. Lime kilns at Hönsäters kalkbruk, Kinnekulle in 1902. Photo Werner Lindhe (Tekniska Museet).

Sampling

Fifteen samples of burnt shale waste were collected at Kinnekulle (Fig. 11). Waste heaps of rödfyr of varying sizes are found at several locations around Kinnekulle. Waste heaps are usually closely associated with black shale quarries where reference samples were also collected for the SGU lithological database. One of the biggest heaps is at Kinne-Kleva in the southern part of the area where the waste has been used as crushed road material for a rally racing circuit (Fig. 12). In the northern part of Kinnekulle, waste material is present in Hönsäter village and by the lake shore. The old industrial area at Råbäck and Gössäter contains larger burnt shale heaps but they are very overgrown.

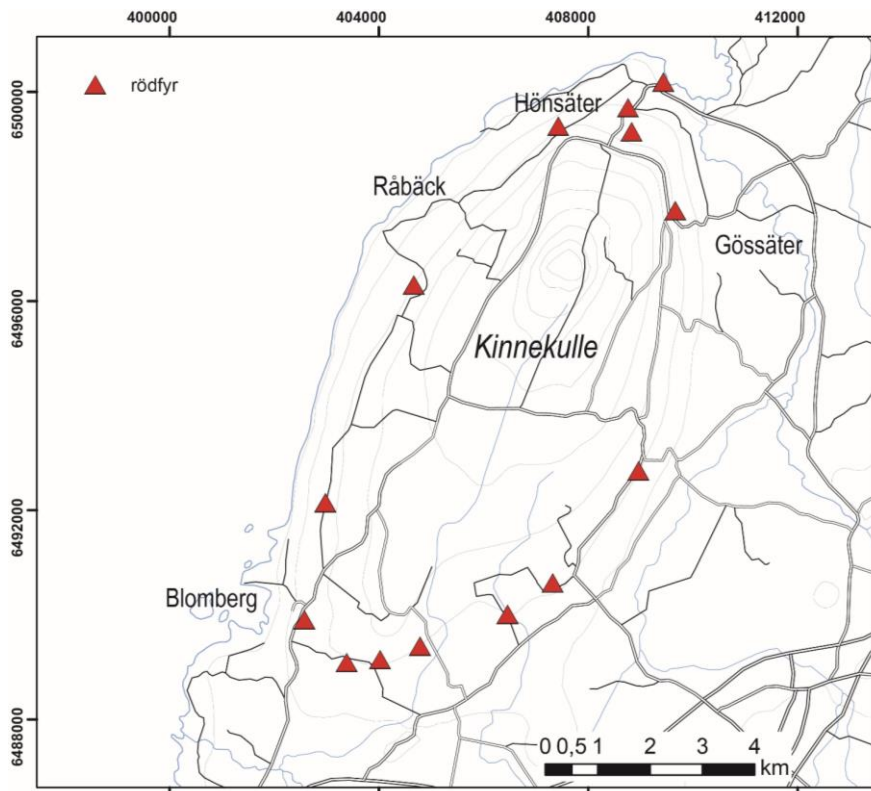


Figure 11. Sampling sites of burnt shale waste (swe. *rödfyr*) at Kinnekulle.



Figure 12. "Rödfyr" sampling at southern Kinnekulle. Photo Anna Ladenberger.

Results

Fifteen samples of burnt shale waste were collected at Kinnekulle. Ca, Ba, and P concentrations in waste from Kinnekulle are higher than in other studied regions. REEs also show the highest concentration of all studied regions with a mean of 323 ppm. Average As concentrations are 53 ppm, with maximum of 114 ppm noted in north-western part of Kinnekulle at Hällekis. Relatively high concentrations of Cu (mean = 186 ppm), Mo (mean = 175 ppm), Ni (mean = 209 ppm) are also observed (Table 3). Elevated concentrations of Zn (mean = 104 ppm) and U (mean = 132 ppm) are noted.

Table 3. Basic statistics for selected elements in burnt shale waste from Kinnekulle (n = 15). Reported as ppm.

Element	Mean	Max	Min
Ag	0.7	1.0	0.5
As	53	114	21
Au	0.006	0.009	0.004
Ba	1045	1565	585
Be	4.9	6.3	4.1
Bi	0.2	0.5	0.1
Co	37	47	6
Cu	185	212	140
Fe	76916	87781	56795
Ga	25.7	29.0	20.9
Hf	4.0	5.0	2.9
In	0.04	0.06	0.03
Li	47	60	20
Mo	175	337	115
Nb	18	22	14
Ni	209	296	63
P	1265	2051	436
Pb	34	46	22
REE + Y	323	528	220
Sb	3.1	5.6	2.3
Sc	13	17	11
Sr	146	195	78
Ta	1.1	1.4	0.8
Ti	4960	6175	3657
U	132	225	46
V	853	1120	602
W	3.1	4.0	2.0
Zn	104	161	56

Billingen & Falbygden

Geology and history of exploitation

The geology in the Billingen–Falbygden area is similar to that at Kinnekulle. The Cambrian basal sandstone (ca 35 m) is overlain by alum shale (ca 25 m), Ordovician limestone (ca 50 m), minor Silurian shale with Permian diabase forming a caprock. The volume of preserved diabase is higher at Billingen than at Kinnekulle, but varies between several smaller table mountains (Mösseberg, Ålleberg, Varvsberget and Gerumsberget) which occur in the area (Fig. 13 & 14). The number of stinkstones and kolm lenses varies within the alum shale. The highest content of kerogen and uranium was found in the upper part of the Upper Cambrian shale unit. At the end of 19th century, high uranium content in the kolm lenses in shale was discovered at Stolan in northern Billingen. As a result of investigations carried out by SGU and Atomic Energy Company, uranium-rich layers were identified within the alum shale. In the early 1960's the Ranstad uranium plant was built at Ranstad, where the excavated alum shale (so called the Ranstad member) was leached in place and uranium was extracted using various methods. The deposit was not economical, and the plant closed in 1969. The alum shale contains ca 300 ppm uranium.

Other industries related to alum shale were lime and alum production. Alum was produced at Karlsfors in Lerdala and at Kaflås near Tidaholm. During the early 18th century, Karlsfors was the largest alum mill in Skaraborg county, but it closed in 1856 and shifted to small-scale lime production until 1920. Alum production at Kaflås and Övertorp started in 1746 and was in operation until 1855, later focussing only on lime production but using alum shale as a fuel. In early 20th century the Kaflås/Övertorp was the largest lime mill in the Billingen–Falbygden region. Production ceased in 1954. In the vicinity, in Ekedalen near Tidaholm, the remnants of the Ödegårdens lime mill, where alum shale was also used as fuel for burning limestone, can be found. The mill was active until 1927.

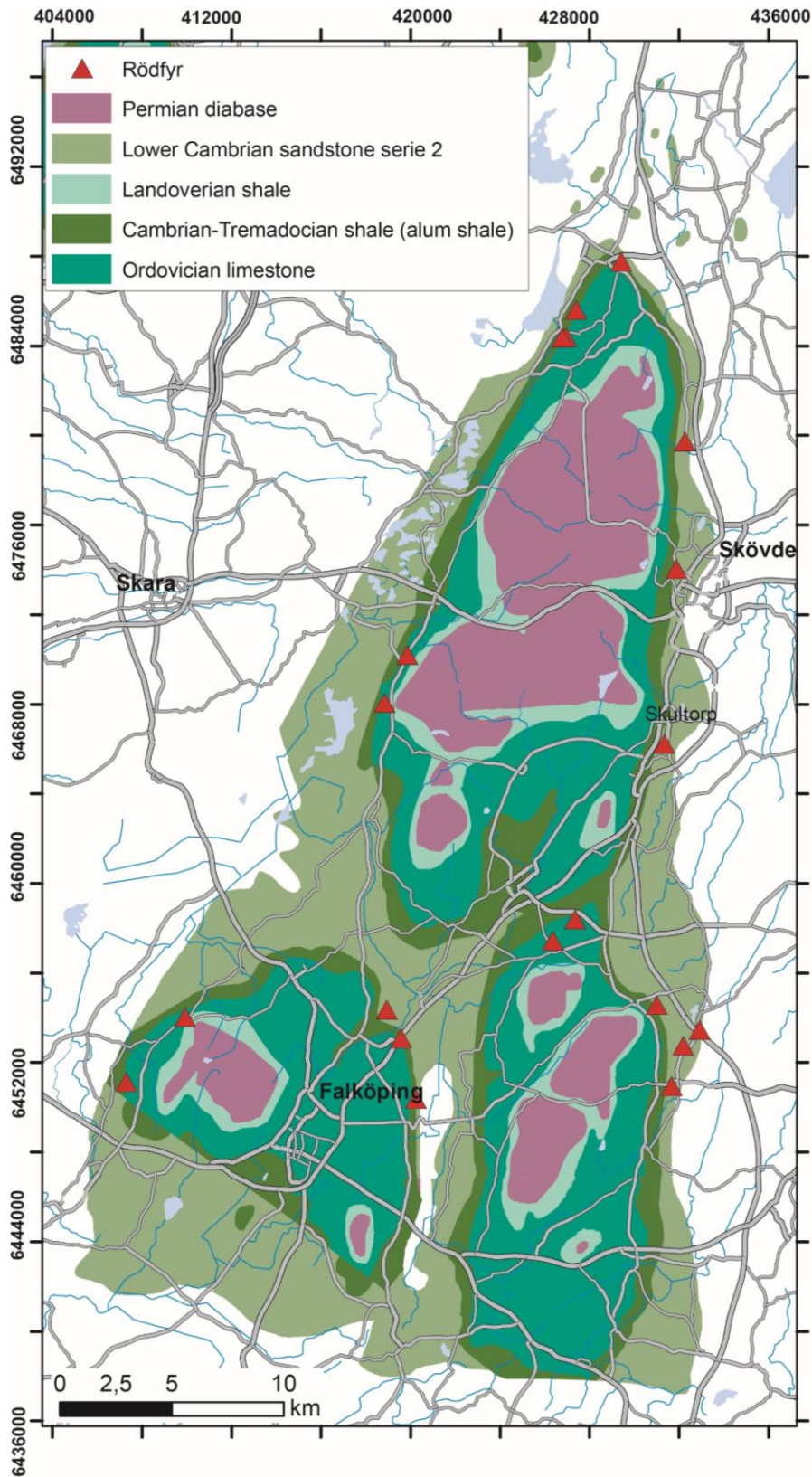


Figure 13. Geological map of the Billingen–Falbygden area with sample locations marked by red triangles (from SGU digital database Bedrock Map 1:50 000–1:250 000).

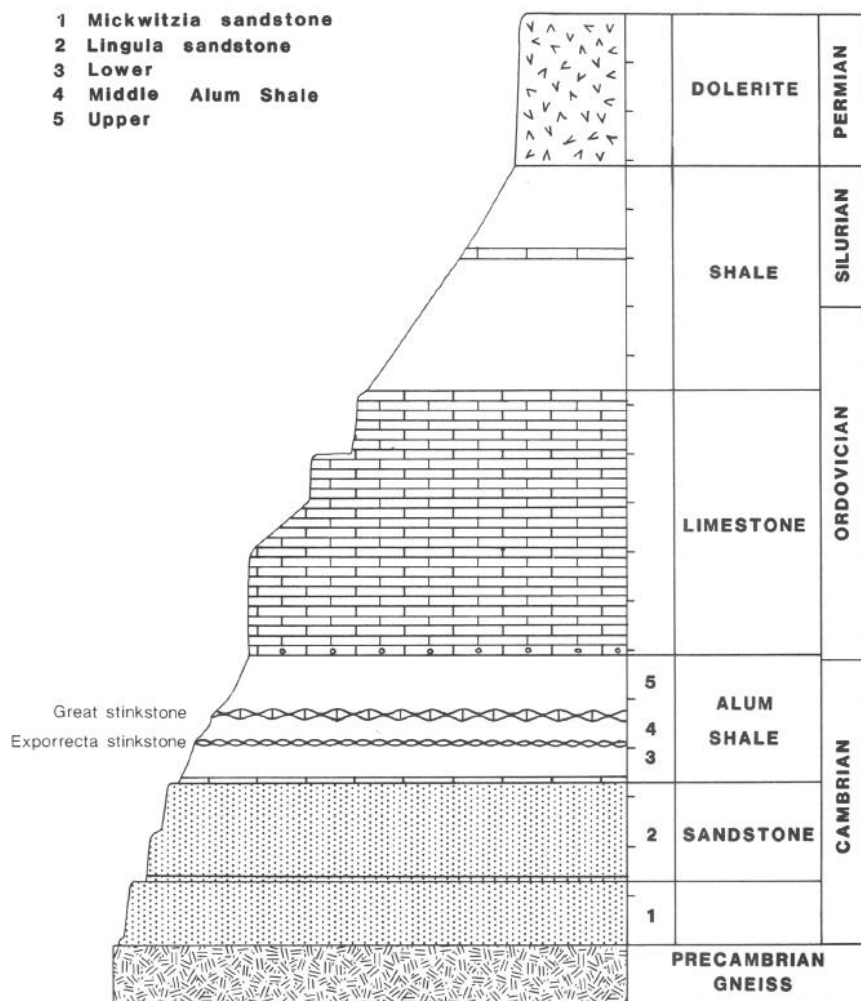


Figure 14. Simplified stratigraphy of the Billingen area (from Dahlman & Gee 1977).

Sampling

Eleven samples of waste were collected at Billingen (Fig. 15). Locally, rödfyr heaps are very large, for example at Stolan quarry north of Skövde and near Dala limestone quarry. In the Falbygden region (south of Billingen, near Falköping) 10 samples were collected. The locations vary in size, from small occurrences to large heaps, often in the vicinity of old limestone and shale quarries (Fig. 16).

Waste can be found within the town of Skövde (recreational area), within industrial areas and even adjacent to protected natural reserves. Most of the waste heaps are overgrown by forest.

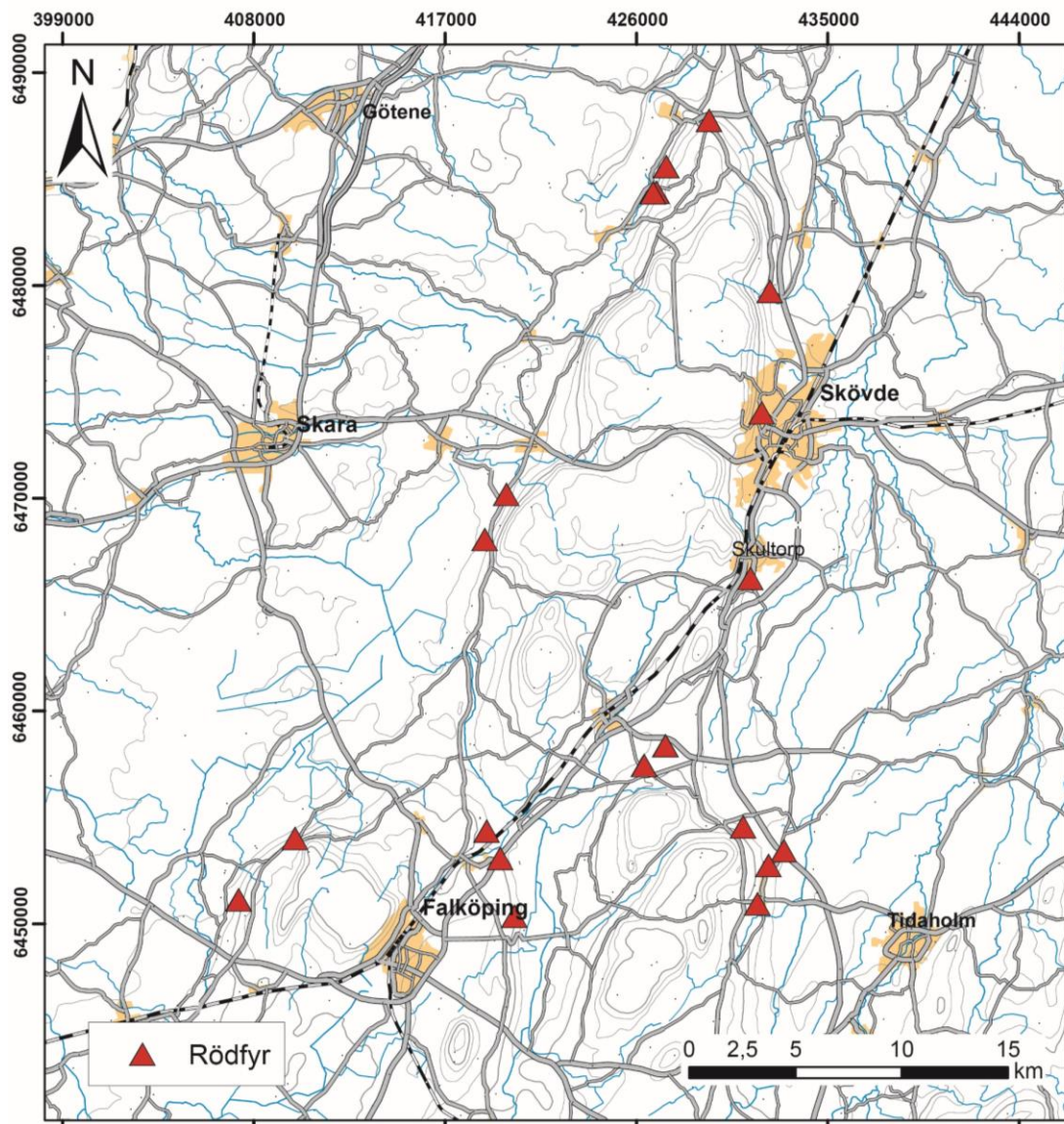


Figure 15. Sampling sites of burnt shale waste (swe. *rödfyr*) at Billingen and Falbygden.



Figure 16. Waste heap near Kungslena in the northern part of Varvsberget, East Falbygden. Photo: Anna Ladenberger.

Results

Burnt shale waste from Billingen and Falbygden has a similar chemical composition with high concentrations of Mo, U and V (Table 4). Billingen has the highest Mo contents in waste among all the studied regions, while Falbygden shows the highest concentrations of U and Ni. At Billingen the highest Mo concentrations in waste rock occurs in Skövde, on the western side of Billingen, and near Dala. At Falbygden, high Mo is noted at Ekedalen and near Baltorp. The highest U contents (>340 ppm) were obtained from waste near Dala quarries, at Baltorp and south of Kungslena. Vanadium contents in burnt shale are highest (>1000 ppm) in western Billingen, near Dala and at Baltorp.

Mean Pb contents are 54 ppm at Billingen, and the total REEs is approx. 300 ppm. Relatively high concentrations of Cu (mean = 185 ppm) are also observed.

Table 4. Basic statistics for selected elements in burnt shale waste from Billingen (n = 11) and Falbygden (n = 10). Reported as ppm.

Element	Bilingen			Falbygden		
	Mean	Max	Min	Mean	Max	Min
Ag	0.6	0.8	0.5	0.6	0.7	0.5
As	29	60	9	23	80	9
Au	0.005	0.008	0.004	0.005	0.007	0.004
Ba	680	730	589	737	835	544
Be	5.8	6.9	4.3	6.5	7.3	5.5
Bi	0.2	0.5	0.0	0.1	0.2	0.0
Co	35	40	29	34	38	31
Cu	185	202	142	185	201	170
Fe	76043	94775	62181	74260	80786	69035
Ga	27.9	30.4	24.5	28.3	30.7	23.0
Hf	4.2	4.8	3.7	4.4	5.1	3.7
In	0.03	0.04	0.02	0.02	0.04	0.02
Li	36	60	20	40	50	30
Mo	224	255	152	223	266	170
Nb	17	19	15	17	19	14
Ni	230	274	167	233	291	190
P	980	1222	873	1025	1353	829
Pb	54	84	30	41	54	23
REE + Y	287	350	218	301	329	266
Sb	1.7	2.7	1.3	1.5	3.0	1.0
Sc	14	15	11	14	15	13
Sr	77	124	58	83	205	54
Ta	1.2	1.3	1.0	1.2	1.4	1.0
Ti	4916	5335	4256	5054	5515	4436
U	244	378	141	280	363	166
V	878	1040	733	916	1120	803
W	3.9	5.0	3.0	3.7	4.0	3.0
Zn	112	171	88	112	166	81

Närke

Geology and history of exploitation

The Alum Shale Formation in Närke occurs in two main regions, called West (Garphyttan–Latorp–Fjugesta) and East Närke (south of Örebro). A number of other small outcrops also occur in the area (Fig. 17). In West Närke the thickness of the unit increases from 13 m in the north (Garphyttan) to 20 m in Fjugesta to the south. In East Närke, the thickness of the formation varies from 15 to 19 m by Kvarntorp. Shale units contain subordinate lenses of stinkstone and kolm and are overlain by Ordovician limestone. The chemical composition of the shale from Närke is similar to that from Billingen–Falbygden (Andersson et al. 1983). The kerogen content in shale is high (locally up to ca 20%), therefore the shale from this area was previously considered as an important reserve of fossil fuel (shale oil).

In West Närke the biggest alum production took place at Latorp (swe. *Latorpsbruk*, Fig. 18). Alum production moved from Garphyttan to Latorp in 1773 where a large shale quarry was in operation. In the mid 19th century it was the country’s largest alum factory, finally closing in 1878 (Stolz 1934).

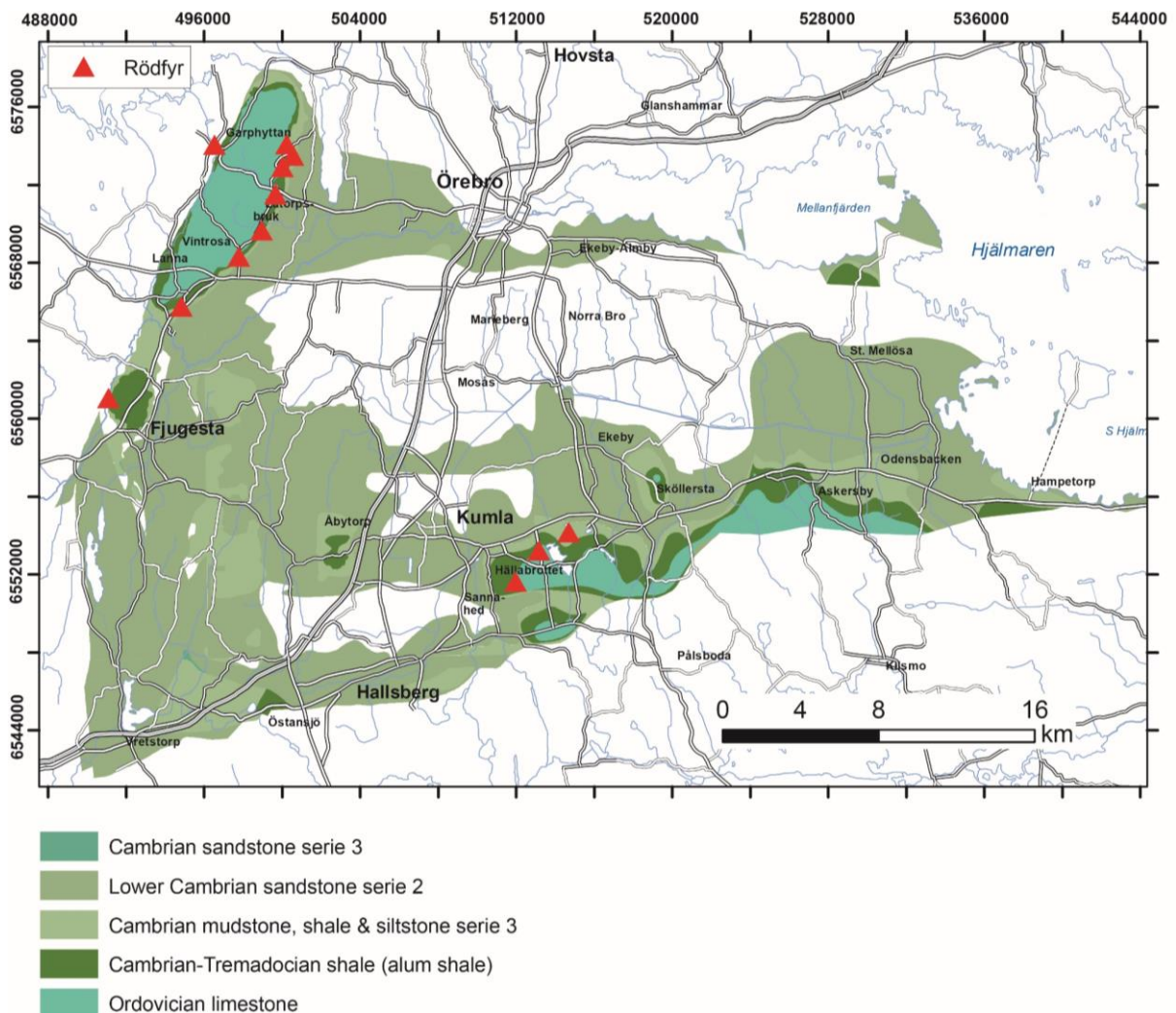


Figure 17. Simplified geology of the Närke area with Palaeozoic sedimentary rocks and sampling sites indicated by red triangles (from SGU digital database Bedrock Map 1:50 000–1:250 000).

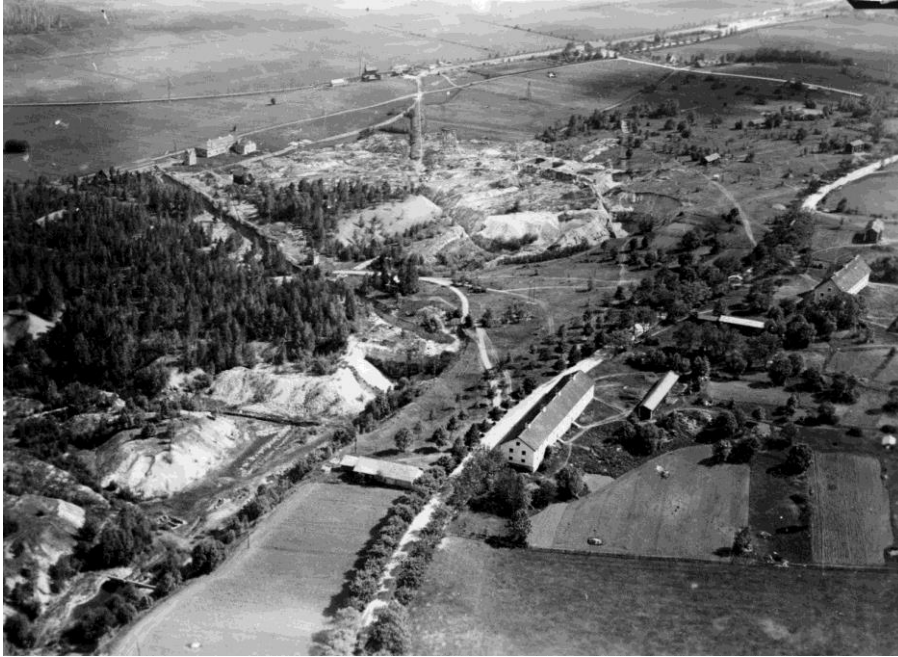


Figure 18. Alum factory (swe. *alunbruk*) at Latorp. Photo: Oscar Bladh (Tekniska museet).

During World War II, the kerogen-rich alum shale in East Närke became a promising source of crude oil and Svenska Skifferolje AB was constituted to start extracting oil from the alum shale. This shale contains 15–18% kerogen and 6–9% sulphur and is rich in vanadium, molybdenum, uranium (up to 0.030%), and rare earth elements (Andersson et al., 1985; Swanson, 1960).

Oil production started in 1941 at Kvarntorp east of Kumla and continued until 1966. (Schwartz 1945). The alum shale was mined in open pit quarries and the oil was extracted from shale through pyrolysis (Fig. 19). The shale was heated to release volatile organic compounds in gas state, which then via condensation and distillation, were turned into liquid oil. Gasoline, fuel oil, sulphur, lime, gasol, impregnation oil, and ammonium sulphate were produced. During 1950–1961 a small amount of uranium was also extracted as a byproduct (Grandin et al. 2015). The waste products from the oil production were crushed un-processed alum shale (“fines”), processed burned alum shale (“coke”) and processed alum shale burned to ash (“shale ash”). The waste was deposited back into open pits as well as a waste heap which grew over the years into a 100 m high by 700 m wide hill with ca 40 million m³ of mixed waste (Casserstedt 2014).

After the mine’s closure most of the open pits filled with water. The waste material deposited onto Kvarntorpshögen was still very hot. A combination of hot ash, pyrite, and organic matter (kerogen) led to high temperatures (>500 °C) in the waste pile and these exogenic processes are still ongoing. Oxidation of pyrite can increase the temperature up to 100 °C, followed by ignition of kerogen giving rise to temperatures close to 1 000 °C (Puura 1998, Bäckström 2010). Even though extensive covering has been carried out by Kumla municipality in recent years, locally, temperatures of up to 70°C have been measured close to the surface and a maximum of 700°C was obtained at a depth of ca 15 m below the surface in 2004 (Holm, 2005). The burning waste is continuously monitored, and warning signs mark the hotspots (Fig. 20).

Kvarntorpshögen is a protected industrial heritage site and even used as a recreational area with golf courses, ski slopes and hiking trails. It is also considered as one of Sweden’s most contaminated sites.

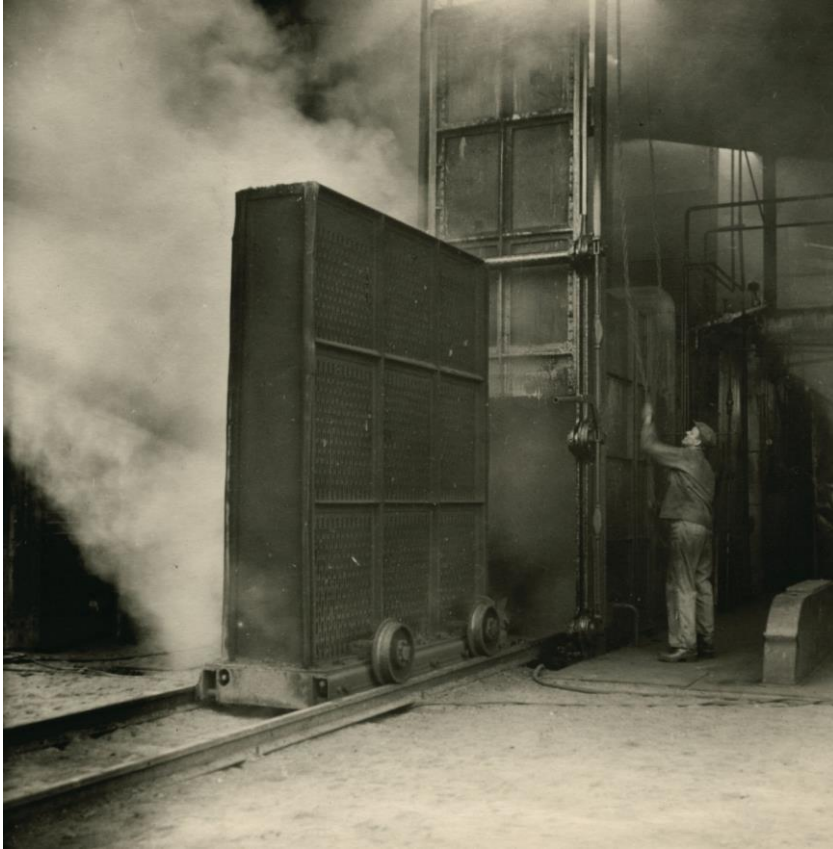


Figure 19. Shale oil production in distillation ovens at Kvarntorp in 1944. Photo: Svenska Skifferolje AB (Tekniska Museet).



Figure 20. Anthropogenic 'fumaroles' at Kvarntorp. Photo: Anna Ladenberger.

Sampling

The samples of waste were collected in West (nine samples) and East Närke (three samples) (Fig. 21). The burnt shale waste is spread out in a large area west of Örebro, between Garphyttan and Vintrosa, with the largest piles at Latorp. The waste can often be found in small groves within agricultural land and along the road from Garphyttan to Fjugesta. In the East Närke three samples were taken on the eastern slopes of Kvarntorpshögen, ca 10–20 m under the hotspot area (Fig. 22), by the Janssonska quarry and at Hynneberg, south of Hällabrottet.

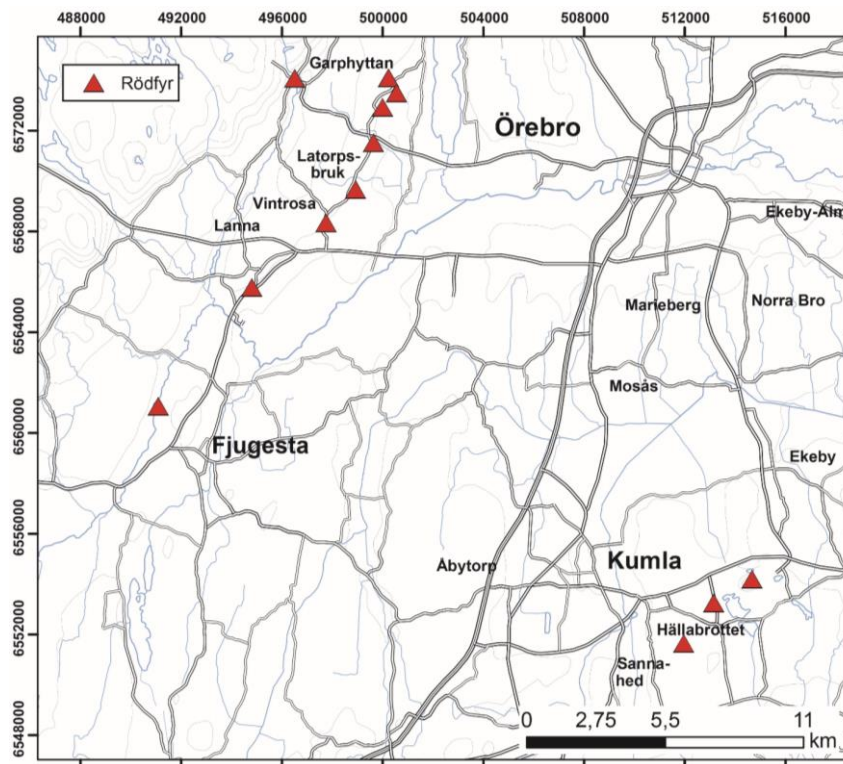


Figure 21. Sampling sites in the West and East Närke.



Figure 22. Sampling sites of burnt shale waste (swe. rödfyr) at Kvarntorp. Photo: Anna Ladenberger.

Results

Burnt shale waste from Närke shows high concentrations of V (mean = 761 ppm), Mo (mean = 194 ppm), Ni (mean = 186 ppm) and U (mean = 2018 ppm), as well as medium-high contents of REEs (mean = 269 ppm), Cu (mean = 199 ppm), P (mean = 916 ppm), Tl (mean = 18 ppm), and Ga (mean = 28 ppm).

The highest Mo contents in waste were found at Vintrosa and Garphyttan, while high concentrations of U were obtained north of Latorp, in Vintrosa and by Kvarntorp. Vanadium content in waste is quite uniform in Närke.

The highest As content was measured in waste from Kvarntorp (56 ppm) and, for Pb, in Garphyttan (76 ppm). Relatively high concentrations of Cu (mean = 199 ppm) have also been observed (Table 5).

Table 5. Basic statistics for selected elements in burnt shale waste from Närke (n = 12). Reported as ppm.

Element	Mean	Max	Min
Ag	0.7	0.7	0.5
As	18	56	5
Au	0.006	0.008	0.004
Ba	634	791	519
Be	5.6	6.0	4.6
Bi	0.1	0.2	0.0
Co	35	42	19
Cu	199	227	150
Fe	80011	91278	67986
Ga	28.3	31.6	24.6
Hf	4.6	4.9	4.3
In	0.02	0.04	0.01
Li	56	80	40
Mo	194	241	130
Nb	18	19	16
Ni	186	213	118
P	916	1353	698
Pb	37	76	16
REE + Y	269	324	171
Sb	1.2	2.8	0.3
Sc	15	16	13
Sr	80	106	57
Ta	1.2	1.3	1.2
Ti	5410	5875	4676
U	218	279	171
V	761	853	648
W	3.8	5.0	3.0
Zn	104	203	59

Scania (Skåne)

Geology and history of exploitation

The Lower Palaeozoic rocks in Scania form a belt trending northwest to southeast, with Cambrian and Ordovician sediments only occurring locally at the surface, predominantly in the southeast. The thickness of alum shale reaches ca 95 m at Tosterup (Andersson et al. 1985). The Alum Shale Formation is the most complete and the thickest in Scania. The alum shale was intensively studied from the drill core and recorded as deep as 2000 m at Haslöv near Malmö (Andersson et al. 1985). The classic locality in Andrarum consists of undeformed and continuous Middle Cambrian to Furongian successions dipping gently to the southeast (Ahlberg et al., 2009). The shale in Scania seems to have lower organic and U concentration but high V, with anomalous levels >3500 ppm in the so called Dictyonema zones (Andersson et al., 1985).

Shale was processed to produce lime and alum salts at Andrarum since the early 17th century. The Andrarum Alum Works was established in 1637 by the Danish nobleman Jochum Beck and then bought by Christina Piper who increased the alum production and made Andrarum into Scania's largest factory at that time (Fig. 23). Black shale was mined in quarries in the direct vicinity to the works where it was used both as fuel and an alum source (Fig. 24). The total production between 1682–1912 was ca 77 500 tonnes of alum. Alum production ceased in 1912 and the works closed at the end of the 1920's. (Stolz 1934).

Nowadays Andrarum is a protected industrial heritage site and a nature reserve.



Figure 23. Old warehouse at Andrarum. Photo: Anna Ladenberger.



Figure 24. Leaching pools in the alum factory at Andrarum, 1910. Waste heaps with burnt shale can be seen behind the workers. Photo: Alfred B. Nilsson (Tekniska Museet).

Sampling

Two samples of burnt shale waste were collected at Andrarum, one in the northwestern part of the waste pile and one at the southeastern end (Fig. 25). The waste heaps are used as grazing land for sheep and cows (Fig. 26).

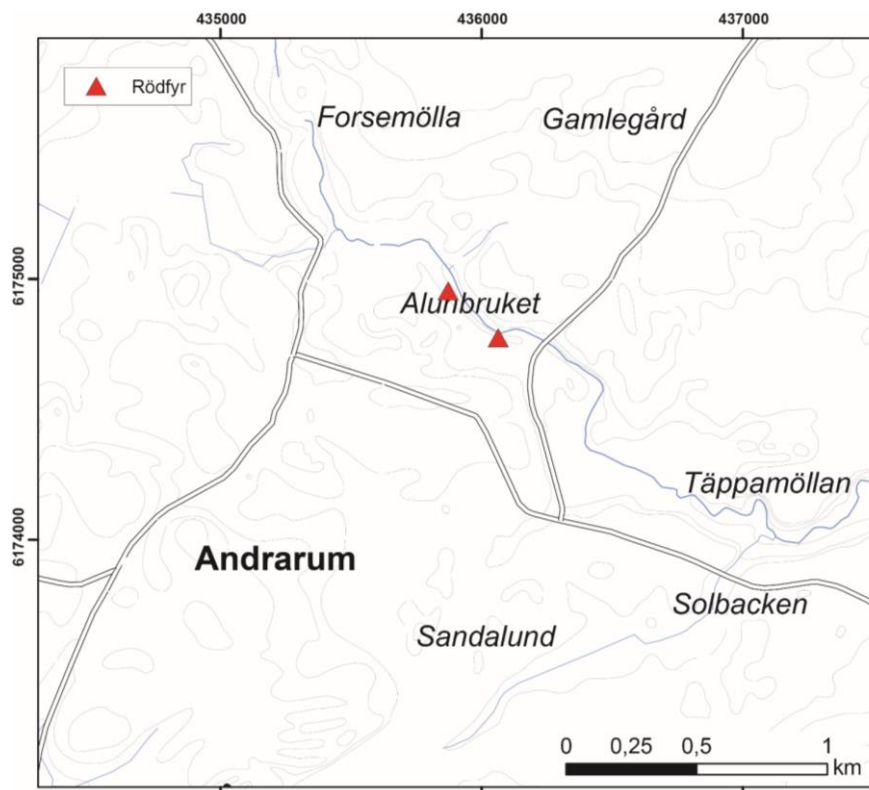


Figure 25. Sampling sites at Andrarum.



Figure 26. Waste sampling at Andrarum. Photo: Anna Ladenberger.

Results

Burnt shale waste from Andrarum shows high concentrations of V (mean = 1355 ppm), Mo (mean = 130 ppm), Ni (mean = 215 ppm), and Ba (mean = 5188 ppm) as well as medium-high contents of REEs (mean = 269 ppm), Cu (mean = 200 ppm), and gallium (mean = 31 ppm) (Table 6).

Table 6. Basic statistics for selected elements in burnt shale waste from Andrarum (n = 2). Reported as ppm.

Element	Mean	Max	Min
Ag	0.8	0.8	0.7
As	20	24	15
Au	0.003	0.003	0.003
Ba	5188	9180	1195
Be	5.7	6.0	5.4
Bi	0.1	0.1	0.1
Co	33	36	30
Cu	200	223	177
Fe	71414	77289	65538
Ga	31.3	31.8	30.8
Hf	4.8	4.9	4.7
In	0.03	0.03	0.03
Li	15	20	10
Mo	130	153	107
Nb	19	20	19
Ni	215	274	156
P	633	742	524
Pb	26	27	24
REE + Y	269	280	258
Sb	1.6	1.8	1.4
Sc	17	18	15
Sr	61	85	38
Ta	1.4	1.4	1.4
Ti	6055	6235	5875
U	93	94	92
V	1355	1545	1165
W	3.3	3.3	3.2
Zn	126	130	121

Kalmar and Öland

Geology and history of exploitation

Alum shale on Öland occurs along the western coast and its thickness increases southwards where it reaches ca 24 m. The formation dips gently (ca 1°) south-eastwards and underlies the Ordovician limestone. The Upper Cambrian black shale facies on Öland progress into Ordovician units and they are the youngest of this rock type in Sweden. The formation can be divided into two units: an upper unit (ca 10 m) with black shales and subordinate stinkstones, and a pyrite rich lower unit (ca 14 m) with a greater quantity of stinkstones (up to 35%). The stratigraphy is constrained based on trilobite populations (Andersson et al. 1985; Erlström 2016). Black shale from Öland contains ca 10% organic matter and ca 2% crude oil while sulphur content is ca 10–14% in the lower part and 2–3% in the upper part of the unit. It has high vanadium and medium high uranium content, locally high arsenic, cadmium, and zinc content (Andersson et al., 1985; Erlström 2016).

From the early 18th century, the shale was mined on Öland and burnt on site for production of alum and lime (Eklund et al., 1995). Two major alum works existed: Lovers works, south of Kalmar and Ölands alum works at Degerhamn on southwestern coast of Öland island. Both works used the same black shale, quarried at the Lovers shale quarry near Degerhamn. Lovers works was established in 1724 where it was moved from Degerhamn due to lack of wood on Öland used for burning shale. The black shale was transported to Lovers by boat across Kalmar Bay. Alum production at Lovers was operational between 1726 and 1840. At this works, large quantities of alum were produced by leaching burnt shale (Bergbäck et al., 1997). Lovers works closed in the late 1830's and all equipment was moved to Degerhamn where alum production continued until 1877 (Stolz 1934). At Lovers, the remnants of burnt shale cover ca 5.5 ha.

Alum works at Degerhamn on Öland (swe. *Ölands alunbruk*) was established at the beginning of the 18th century (Fig. 27). The staff was moved from alum works at Garphyttan and Latorp in Närke. Production started in 1806 and one year later the Öland works was the largest in Scandinavia with ca 168 tonnes alum produced (Lamke & Nilsson 2004). The black shale was used both as fuel and an alum source. Apart from alum, quick lime and cement were also produced using local limestone and black shale mined from nearby quarries. After alum productions ceased the works were sold in 1886 and the cement factory Ölands Cement AB was established in Degerhamn. The industry had a significant influence on the current landscape with large open pit quarries and waste heaps of burnt shale being readily apparent (Fig. 28). At Degerhamn, ca 2,700,000 m³ of burnt shale deposits cover ca 1.2 km² from quarry walls towards the shoreline (Fig. 29). The deposits are to some extent mixed with lime residues, and occasionally with non-burnt shale. Ca 60,000 m² mined black shale is exposed along the walls and floor of the old opencast mine (Eklund et al., 1995). Degerhamn is a protected industry heritage site.



Figure 27. Remnants of Ölands alum works. Photo: Anna Ladenberger.



Figure 28. Black shale blocks used to build kilns. Photo: Anna Ladenberger.



Figure 29. Burnt shale waste by the shoreline south of Degerhamn. Photo: Anna Ladenberger.

Sampling

Two samples of burnt shale waste were collected at the old Lovers processing plant (swe. *Loversbruk*) located by the coast south of Kalmar and six samples in the old industrial site at Degerhamn (swe. *Degerhamnsbruk* or *Ölandsbruk*) on the southwestern coast of Öland island (Fig. 30). Burnt shale samples avoiding lime-residues were collected at six sites from vast waste deposits remaining after previous alum and lime production (Fig. 31).

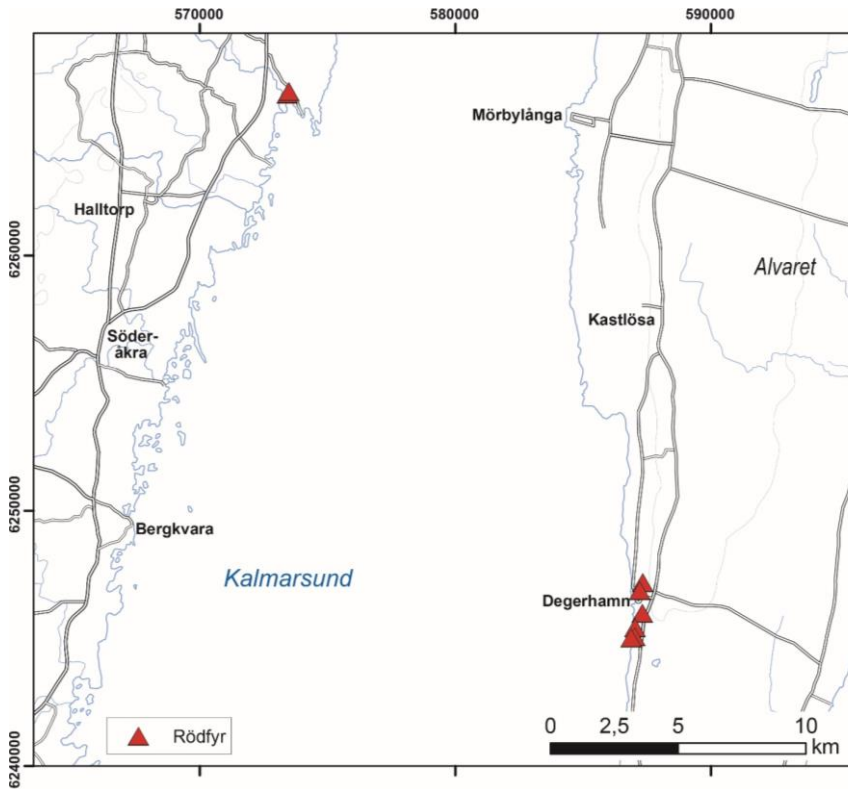


Figure 30. Sampling sites at Lovers and Degerhamn.



Figure 31. Burnt shale waste heaps at Degerhamn, Öland. Photo: Anna Ladenberger.

Results

Collected waste samples from Lovers bruk (2 samples) and from Degerhamn (6 samples) have high concentrations of V (mean = 641 ppm), Mo (mean = 189 ppm), Ni (mean = 160 ppm), and elevated contents of REEs (mean = 232 ppm), copper (mean = 224 ppm), and gallium (mean = 30 ppm). High concentrations of Co, Zn and As are also observed (Table 7).

Table 7. Basic statistics for selected elements in burnt shale waste from Lovers bruk and Degerhamn (n = 8). Reported as ppm.

Element	Mean	Max	Min
Ag	0.8	1.2	0.7
As	33	111	15
Au	0.012	0.013	0.009
Ba	930	1500	775
Be	5.0	5.8	4.3
Bi	0.1	0.2	0.1
Co	51	64	39
Cu	224	254	205
Fe	121922	132545	102819
Ga	29.9	32.2	27.9
Hf	4.4	4.8	4.1
In	0.03	0.08	0.02
Li	44	60	30
Mo	141	171	107
Nb	17	18	16
Ni	160	239	117
P	611	1004	393
Pb	33	53	25
REE + Y	232	284	177
Sb	3.4	5.2	2.2
Sc	15	17	14
Sr	61	88	47
Ta	1.3	1.3	1.2
Ti	5583	5815	5216
U	80	150	47
V	641	923	484
W	2.9	3.5	2.5
Zn	192	247	121

DISCUSSION

Geochemical characteristics of burnt shale waste

The most prominent change in chemical composition in the waste rock after the black shale is burnt is the removal of organic compounds (expressed as loss of carbon), decomposition of sulphides (loss of sulphur) and loss of water (drop in loss on ignition values). The loss of other volatile elements such as mercury, selenium, rubidium, caesium, noble gases, and halogens can also occur. This process is followed by passive enrichment in other metals and elements as a result of element redistribution from decomposed minerals and formation of new phases.

Major elements and volatile components

Major element chemistry mainly changes due to partial melting of the shale components and formation of partly amorphous silica and aluminium rich phases, as well as oxidation of iron resulting in formation of hematite.

The parent rock of the waste is black shale and plotting waste composition together with reference black shale collected in the study area on the classification diagram for sedimentary rocks by Herron (1988) gives an overview how the remaining product is modified in major element composition but can still be identified as shale (Fig. 32). On this classification using $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio versus $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ ratio, it can be observed that the burnt shale samples (denoted by orange dots) have significantly higher iron content with weak enrichment in aluminium in comparison with the source rock but remain within the classification field for shale.

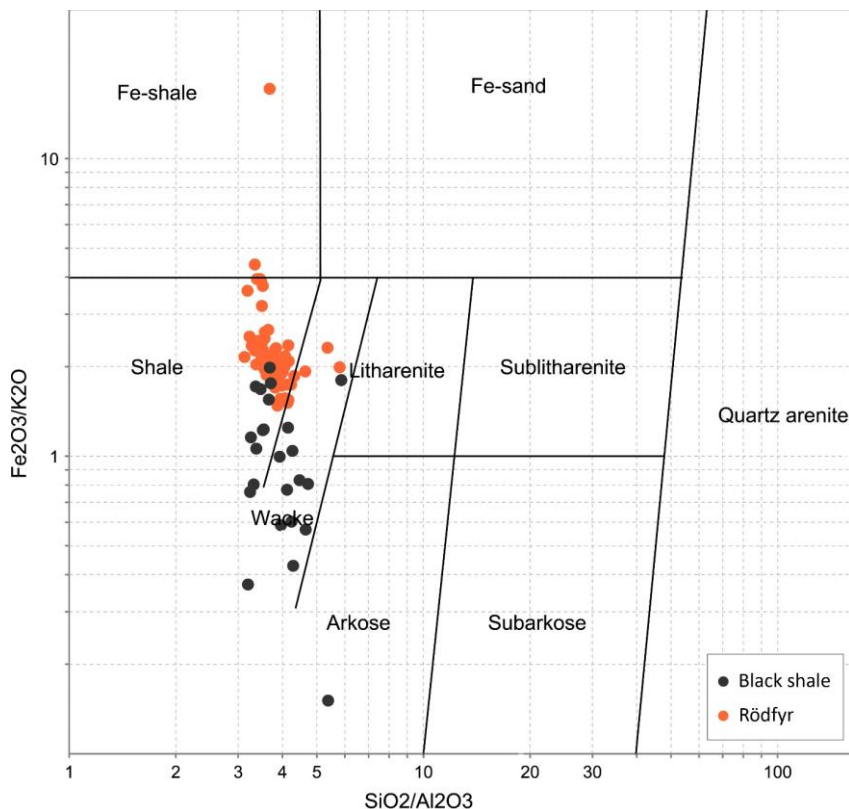


Figure 32. Classification diagram for shale and sandstone (Herron 1988) with plotted waste and reference black shale.

To investigate the change in composition of the burnt shale during the industrial process of burning, the loss on ignition (LOI) can be used as a proxy and compared to other major and trace elements. The loss on ignition (LOI) is a measure of the volatile content of the sample when heated at 1000 °C. The LOI value can also include mass gain caused by the oxidation of Fe but during this process, the loss of carbon and H₂O will dominate. Strong positive correlation between LOI and carbon content indicates that the majority of organic matter is lost during the burning process (Fig. 33a). The correlation with sulphur (Fig. 33b) is less linear but around one third of sulphur remains in the waste.

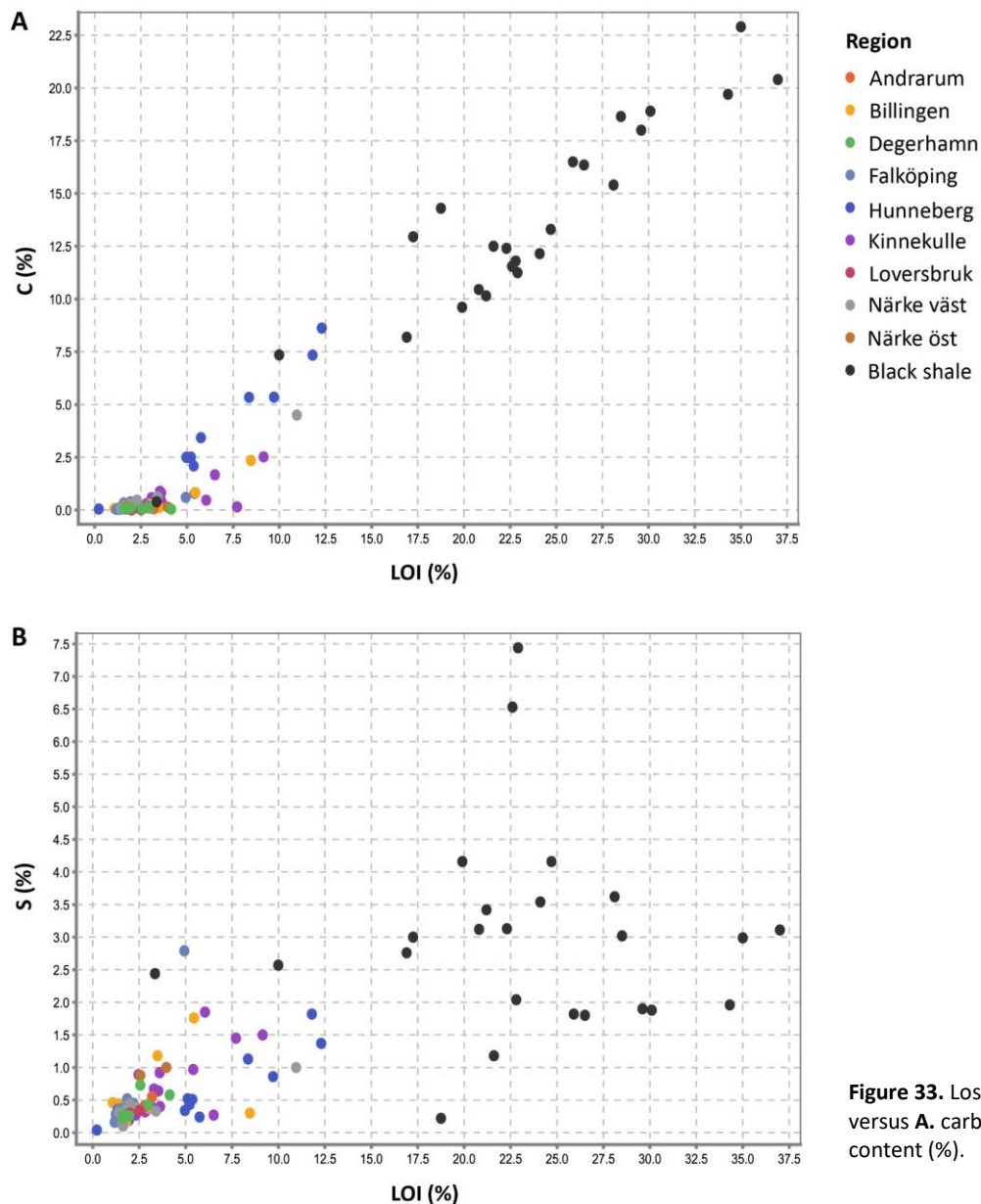


Figure 33. Loss on ignition (LOI) versus **A.** carbon and **B.** sulphur content (%).

By plotting the major oxides against LOI it can be seen how dehydration during burning contributes to the element redistribution. Figure 34 shows that, relative to black shale, the burnt shale has higher concentrations of the major oxides SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO . Additionally, CaO can be used as an indicator of lime and carbonate contamination during the processing, since the original black shale has low CaO content, and the large increase has to be caused by active addition of calcium during burning limestone to produce lime.

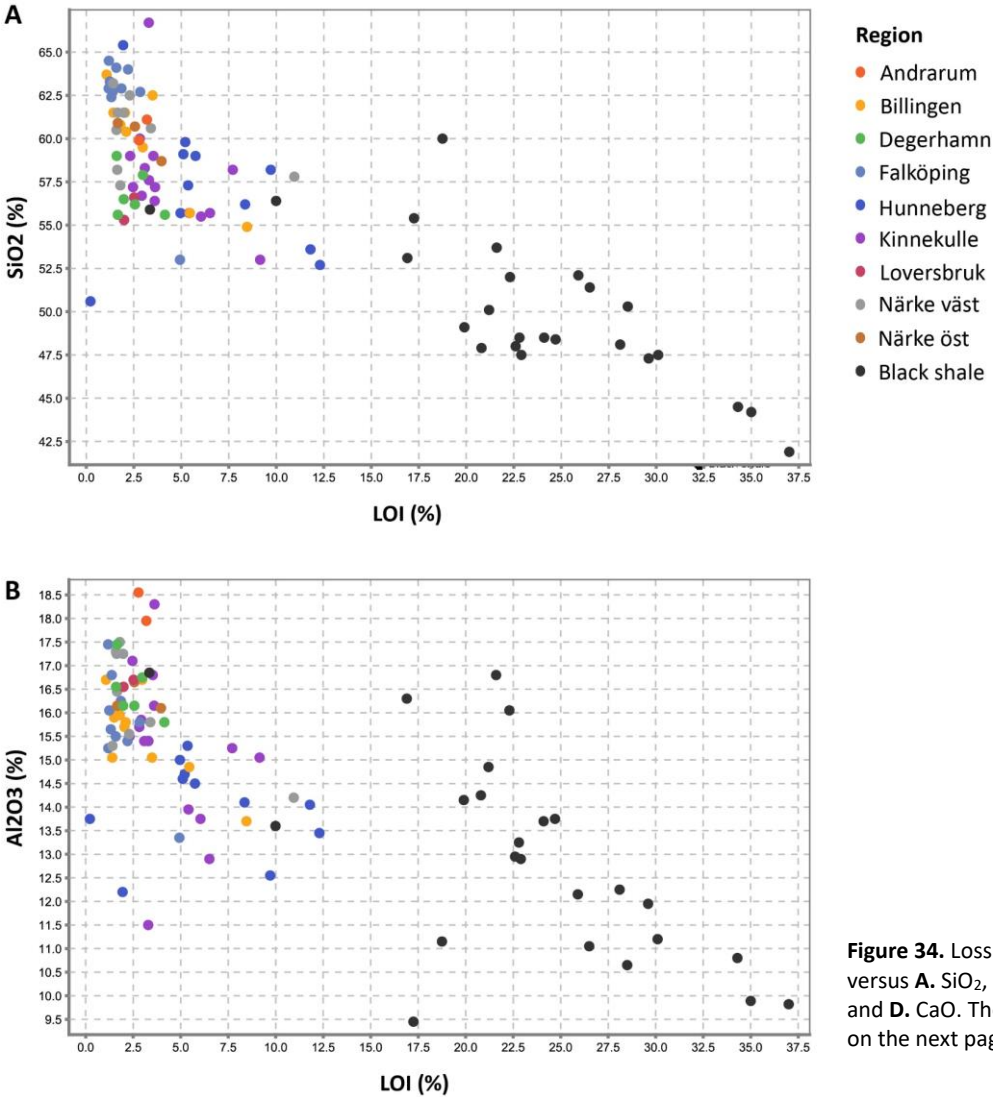


Figure 34. Loss on ignition (LOI) versus **A.** SiO_2 , **B.** Al_2O_3 , **C.** Fe_2O_3 and **D.** CaO . The figure continues on the next page.

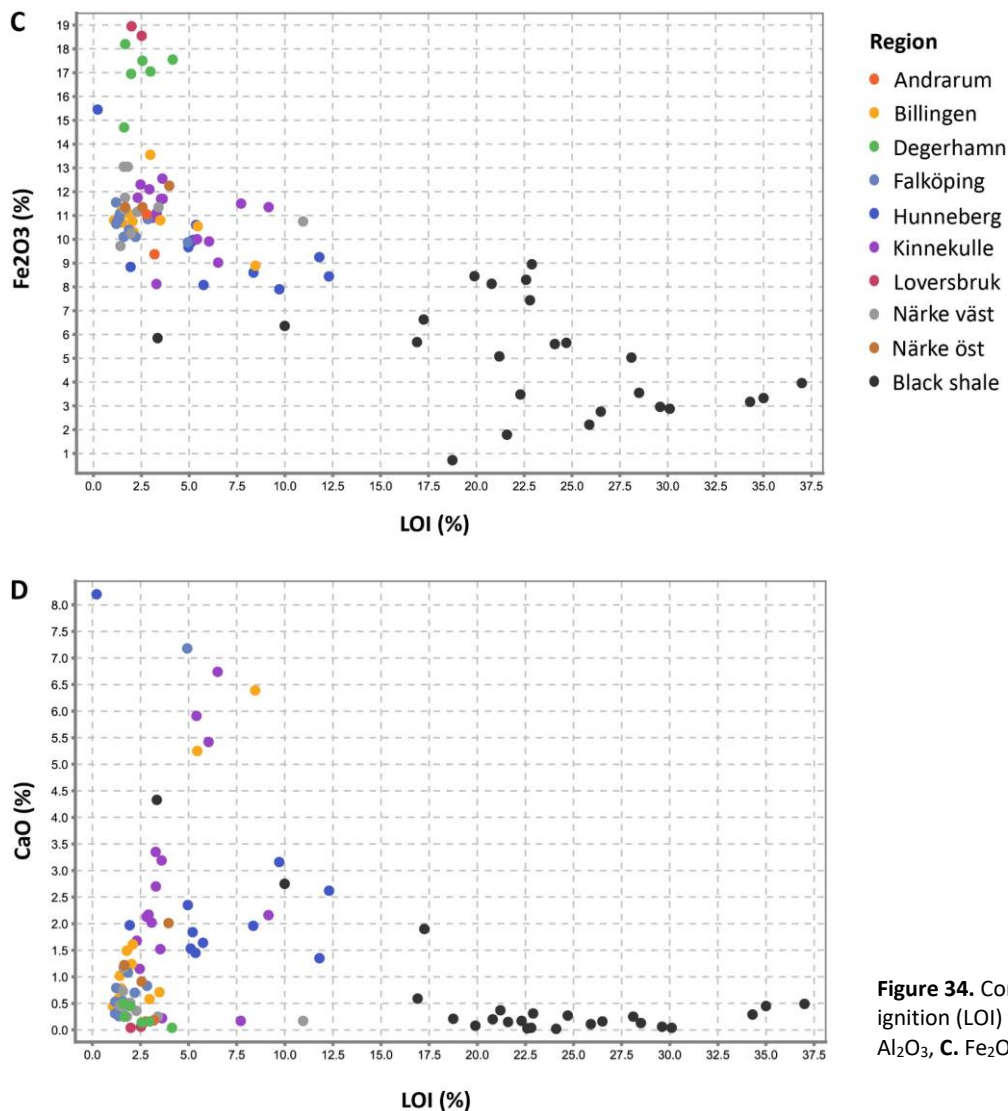


Figure 34. Continuation. Loss on ignition (LOI) versus **A.** SiO_2 , **B.** Al_2O_3 , **C.** Fe_2O_3 and **D.** CaO .

Trace elements and metals

Multi-element plot (Fig. 35) shows that many elements in black shale and its waste product are enriched in comparison to average shale composition (a reference compilation after Levinson 1974). Comparison to average upper crust composition ((Taylor and McLennan 1981; Fig. 36) show a strong enrichment in Ba, U, and lanthanides both in the source black shale and in the burnt shale. Trace elements behave in three major ways. First, they became enriched in the waste; second, their overall content does not significantly change in comparison to the source rock; and finally, their concentration decreases in the waste as a result of volatilisation (Fig. 35).

The elements which appear relatively inert after burning are As, Ba, Bi, Cs, Sr, Rb, Li, Mo, Sb, Sn, Hf, Nb, and Zr. Both Ba and Sr can however be added to the waste from the limestone, for example shale waste from Andrarum, Kinnekulle and Hunneberg where black shale, which was used for lime and alum production and burned together with limestone, shows the highest Ba concentrations.

Volatile elements such as Hg and Se decrease in the waste since they are variably lost during the burning process. Bi and Sb, which share some geochemical features, also show a tendency to be depleted in the waste. Bismuth can be volatile at high temperature and high vapor pressure, especially in the presence of halogens and organic matter, although it is more likely to remain in other phases (e.g., with Cu and Pb phases) after burning (Feldman and Hirner 1994).

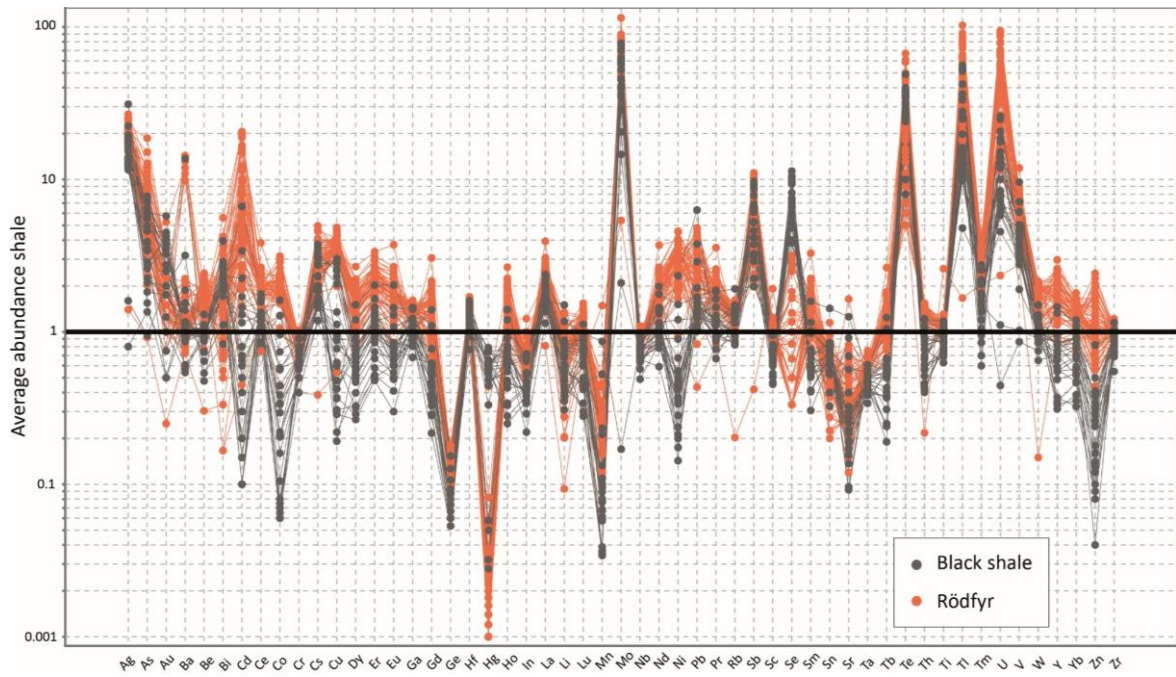


Figure 35. Spider diagram for trace elements normalised to average shale composition (after Levinson 1974). Orange: burnt shale, grey: reference black shale.

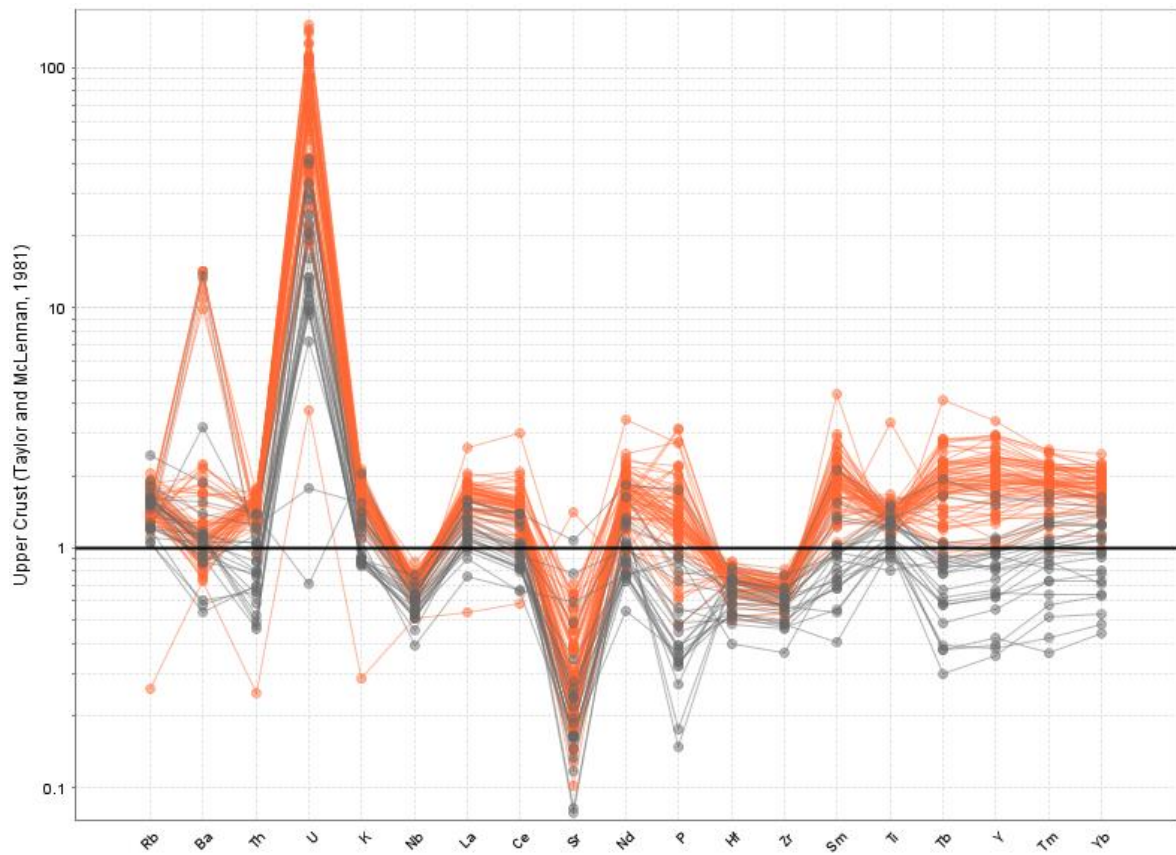


Figure 36. Spider diagram for trace elements normalised to upper crust composition (Taylor and McLennan 1981). Orange: burnt shale, grey: black shale.

Among chalcophile elements, the majority are enriched in the burnt shale waste, for example, Cd, Cu, Pb, Zn, Ga and Tl while Bi and Sb is mildly depleted. Siderophile elements, Co and Ni are enriched in waste as well as the lithophiles U and V (Fig. 37 & 38).

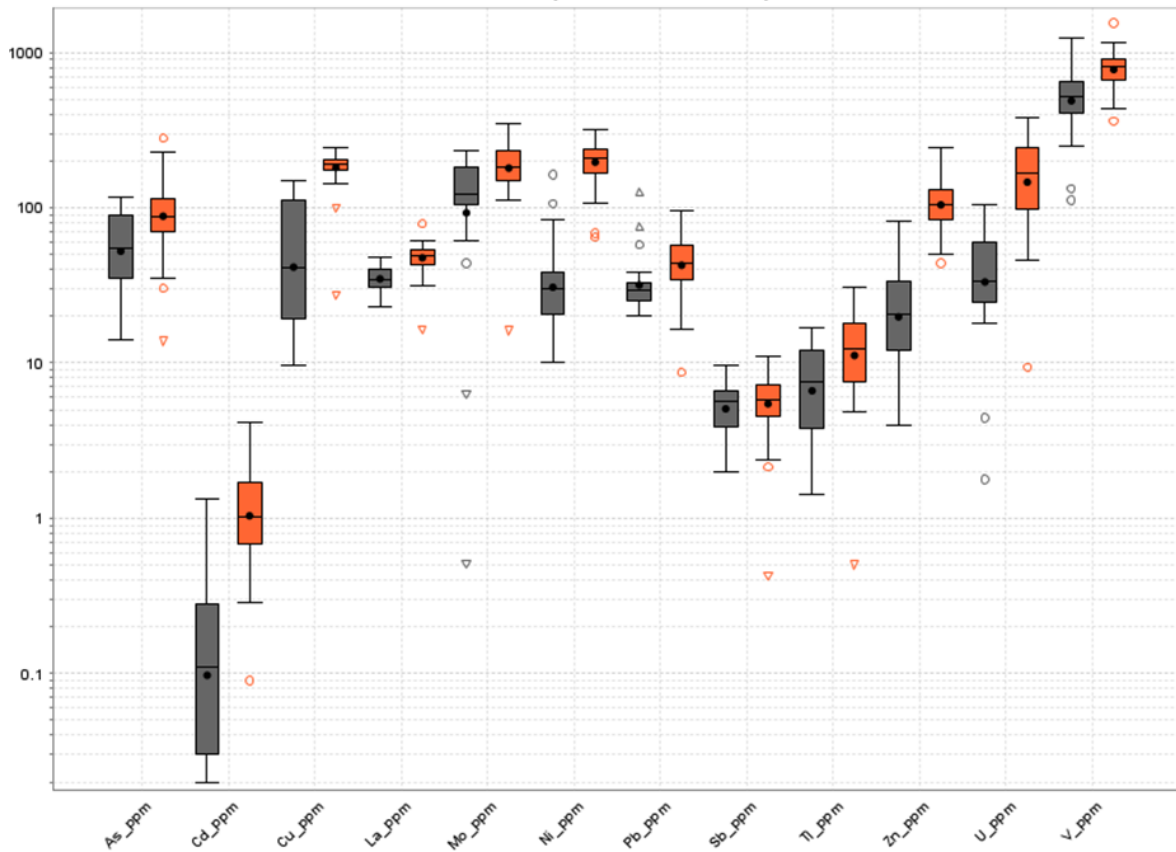


Figure 37. Comparison of element concentrations in the waste and source rock for selected elements. Orange: burnt shale, grey: black shale.

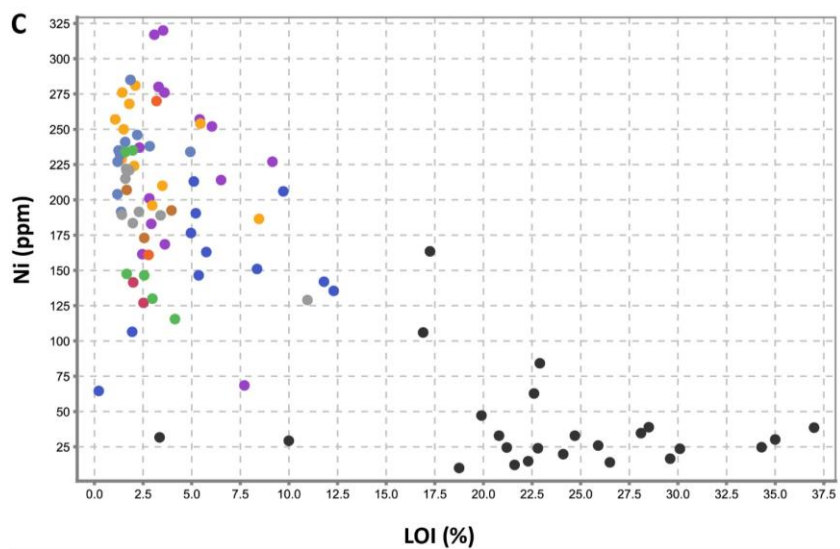
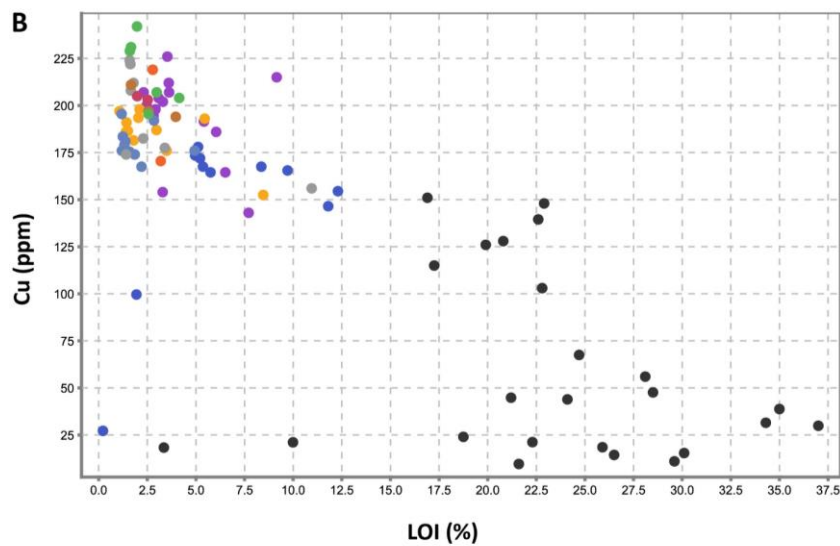
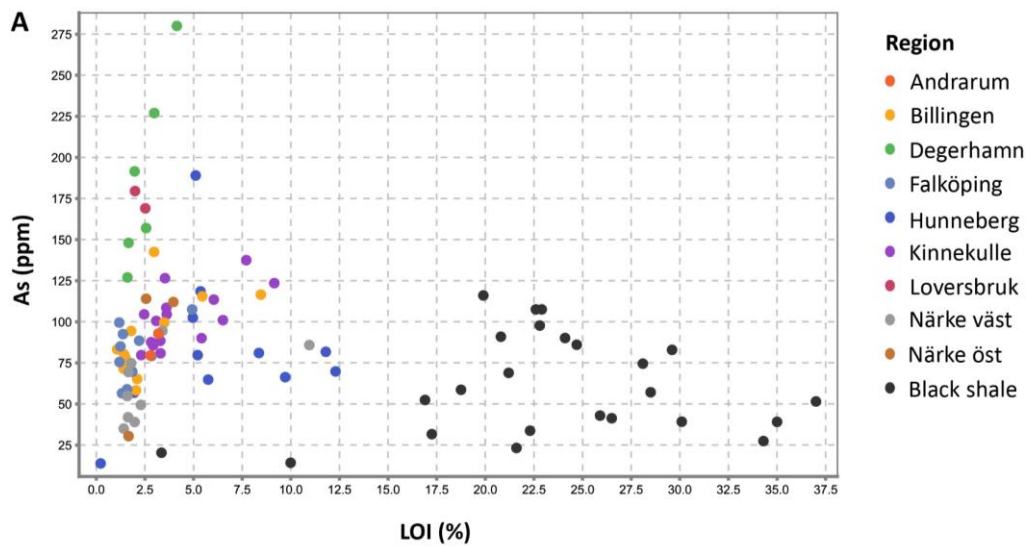


Figure 38. Loss on ignition (LOI) versus **A.** As, **B.** Cu, **C.** Ni, **D.** Zn, **E.** V and **F.** U. The figure continues on the next page.

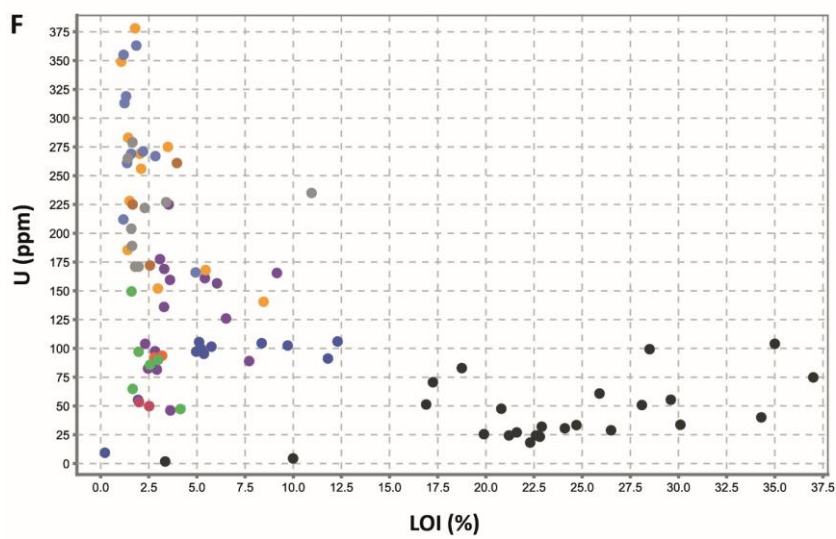
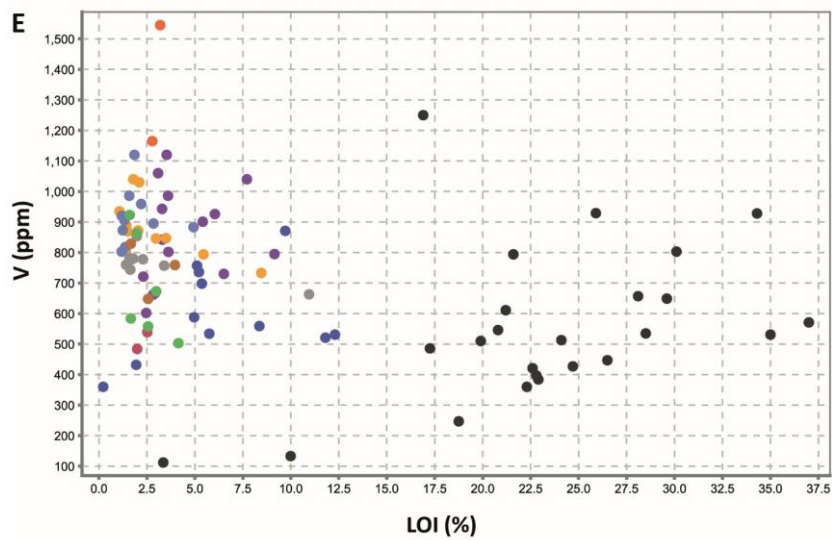
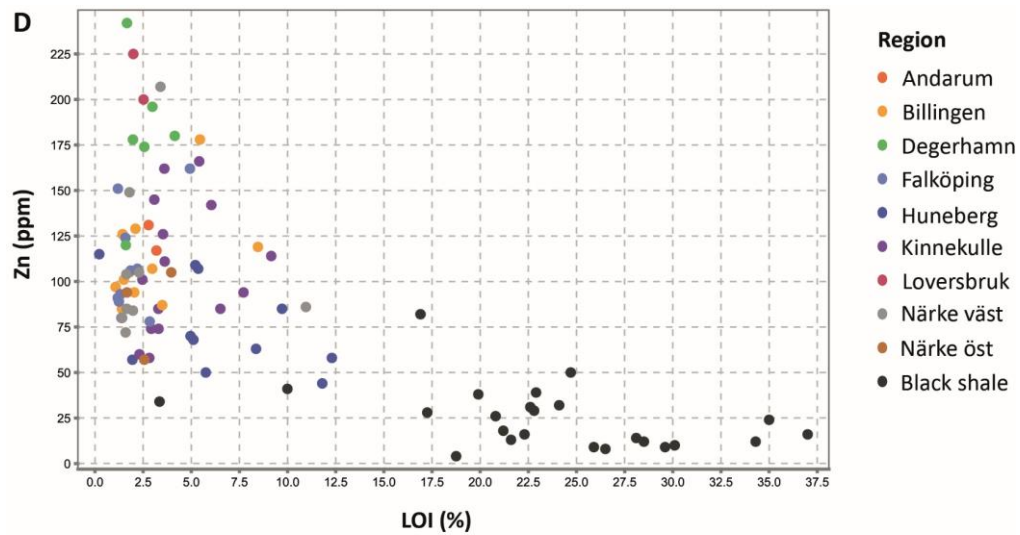


Figure 38. Continuation.
Loss on ignition (LOI) versus
A. As, B. Cu, C. Ni, D. Zn, E. V
and F. U.

REEs

The Rare Earth Elements (REE) encompass a group of elements known as the lanthanides and often include Y and Sc due to similar chemical behaviour. REEs concentrations increase with higher SiO_2 content in the burnt shale (figure 39). Silica content can be used here as an indicator of the burning grade/industrial fractional crystallisation. The box plots to the right of the diagrams in figure 39 show a clear median difference with minimal overlap of the whiskers.

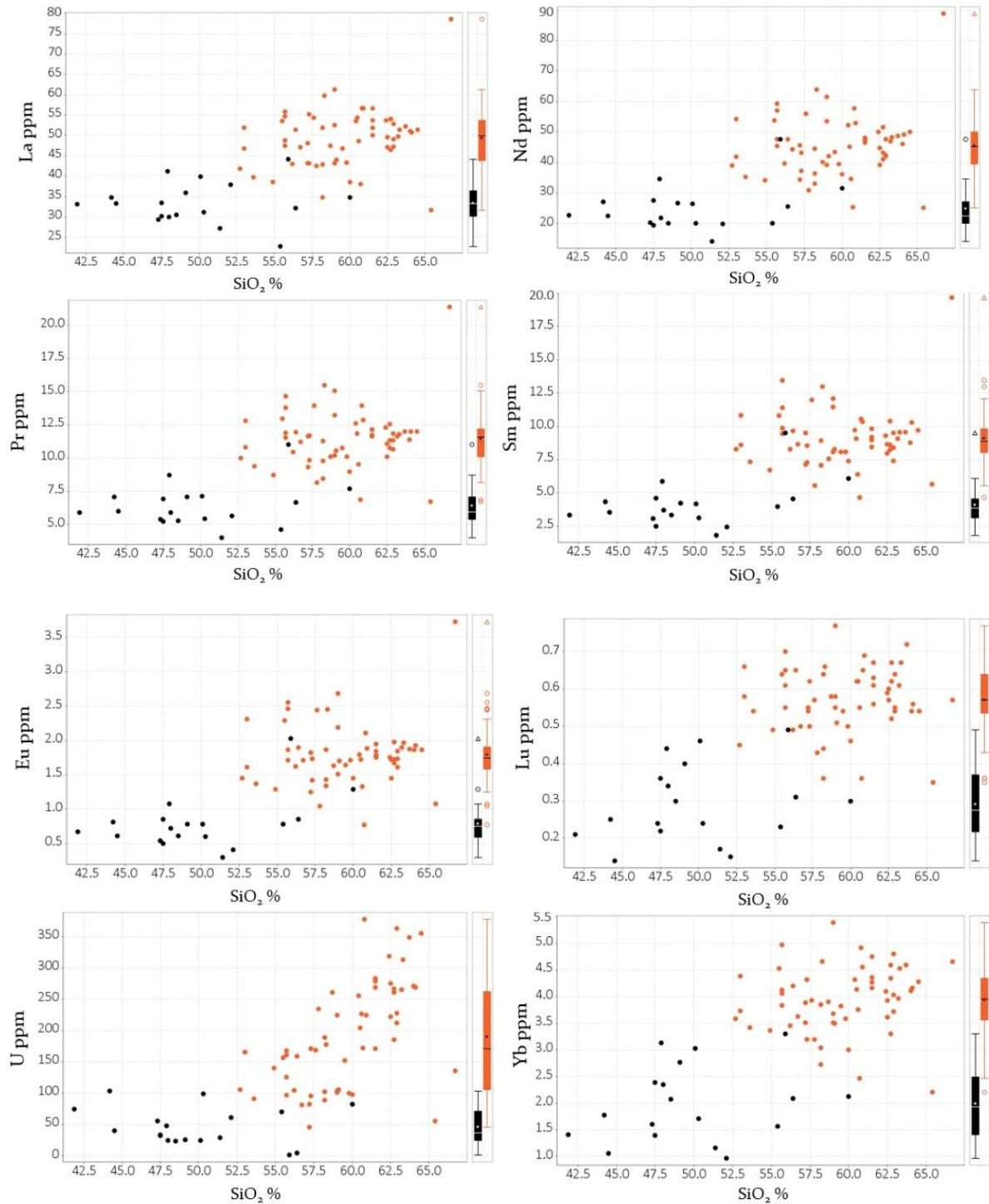


Figure 39. Binary diagrams with corresponding boxplots for SiO_2 vs selected REEs + U in waste (orange dots) and reference black shale (black dots).

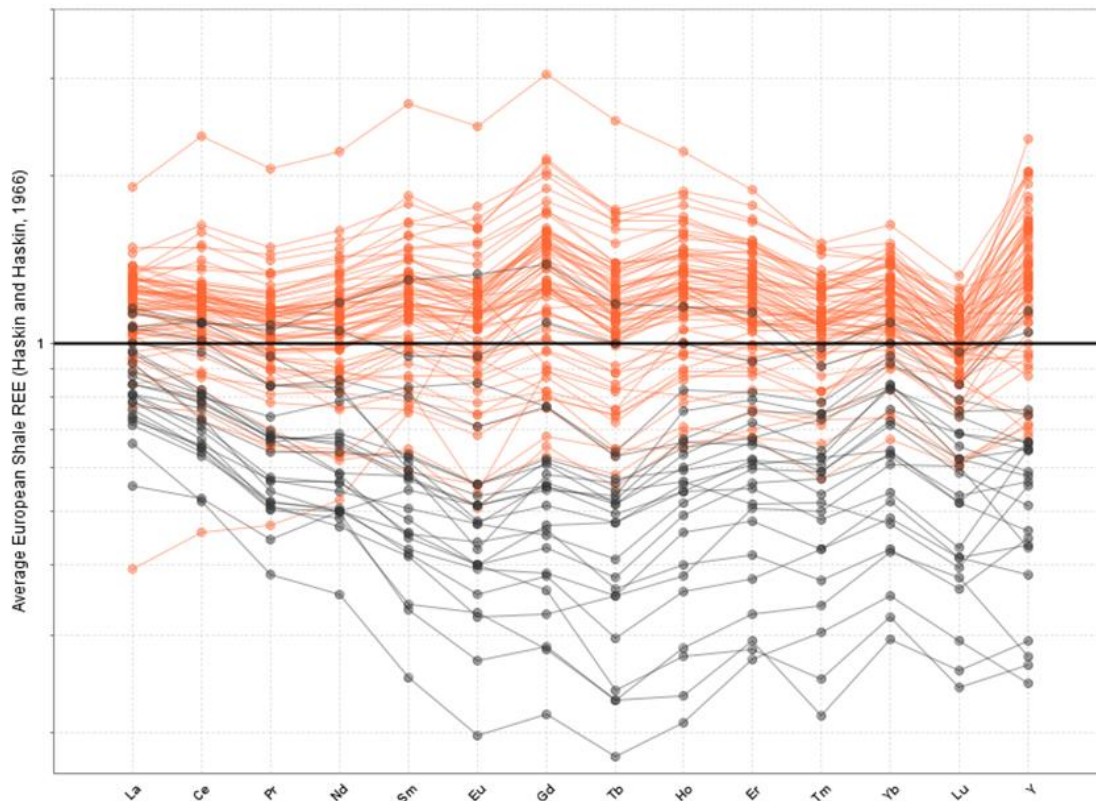


Figure 40. Spider diagram for REEs and Y normalised to Average European Shale composition by Haskin and Haskin (1966) for burnt shale waste (orange) and reference black shale (gray).

The spider diagram of REEs+Y normalised to Average European Shale by Haskin and Haskin, (1966) in Figure 40 shows the clear reverse pattern. Burnt shales (in orange) show higher element concentrations than the black shales (in black) indicating a strong enrichment in REEs during the burning process. This pattern can also be explained by the remobilization of the primary REE's resident in organic matter into silica-rich partly amorphous phases formed at high temperatures. The middle and heavy REEs (MREEs, HREEs) such as Eu, Gd and Tb are clearly more influenced than light REEs (LREE), e.g., La and Ce.

Geographical variation in chemical composition of burnt shale waste

The waste after burning black shale in south-central Sweden is spread over a large area. However, few clusters can be recognised: Närke in the north, Billingen-Falbygden in centre, Kinnekulle and Hunneberg in the west and two locations in southern Sweden: Andrarum in Scania and Degerhamn (including Loversbruk) on Öland. Although the waste is produced from Upper Cambrian-Lower Ordovician black shale from various stratigraphic levels, certain general geographical features can be observed in waste chemistry. It can be assumed that the chemical composition of the waste reflects the original chemistry of the source black shale, apart from the volatiles that were lost. Boxplots and geochemical maps generated for the defined regions and selected elements clearly show the spatial variability in waste composition (Fig. 41 & 42). Strong enrichment can be seen together with well confined compositional variation in the waste products for most metals. Cu, Co, Zn, and As have the highest concentrations in waste from Degerhamn and Loversbruk (both sites used black shale from the same quarry). Billingen and Kinnekulle have the highest Ni content. Molybdenum and uranium are enriched in waste from Billingen and Falköping, and the highest vanadium contents are found in Andrarum in Scania. REEs show the highest concentrations in burnt shale from Kinnekulle.

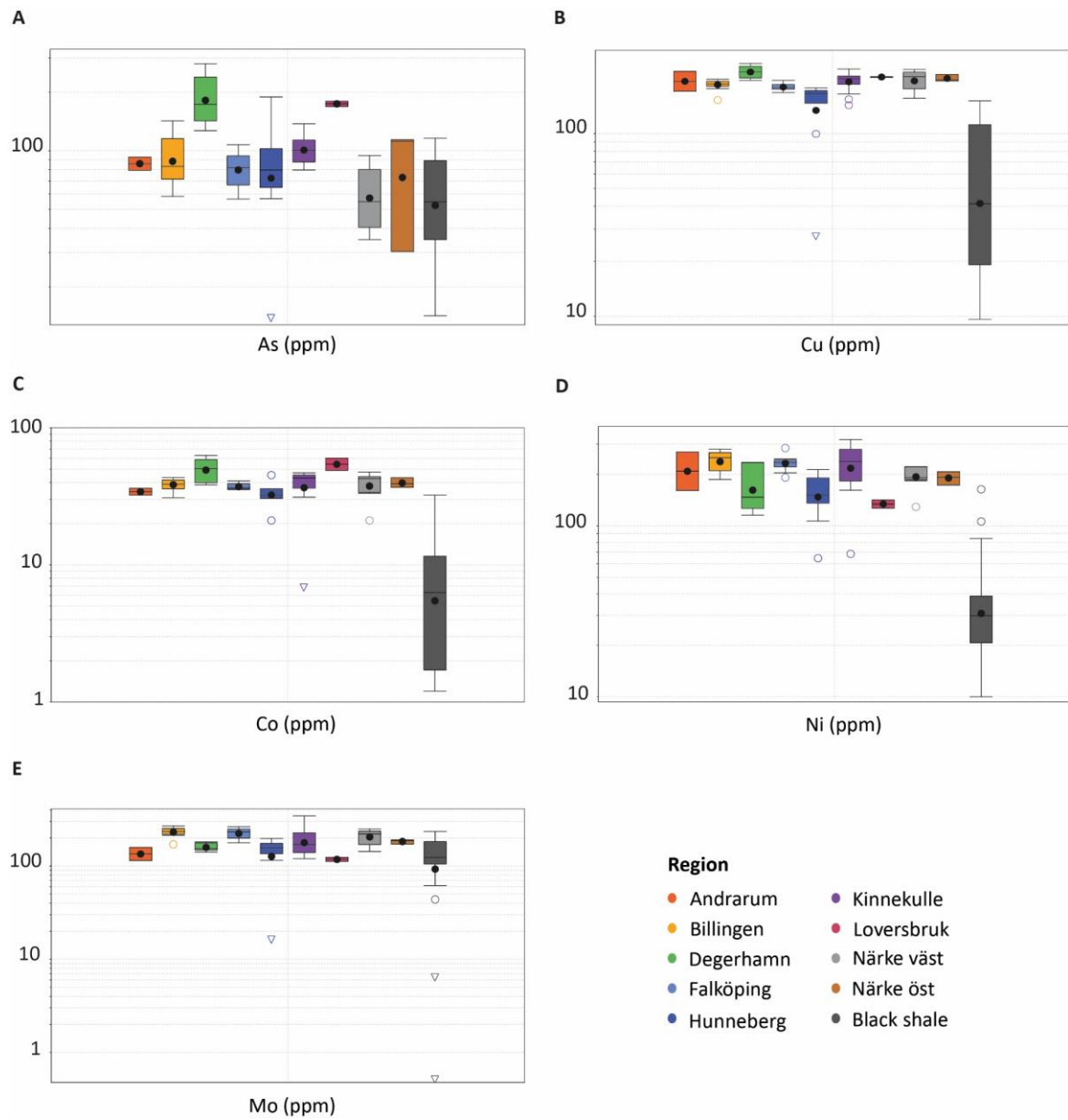


Figure 41. Boxplots for selected elements grouped according to the sampled region. The figure continues on the next page.

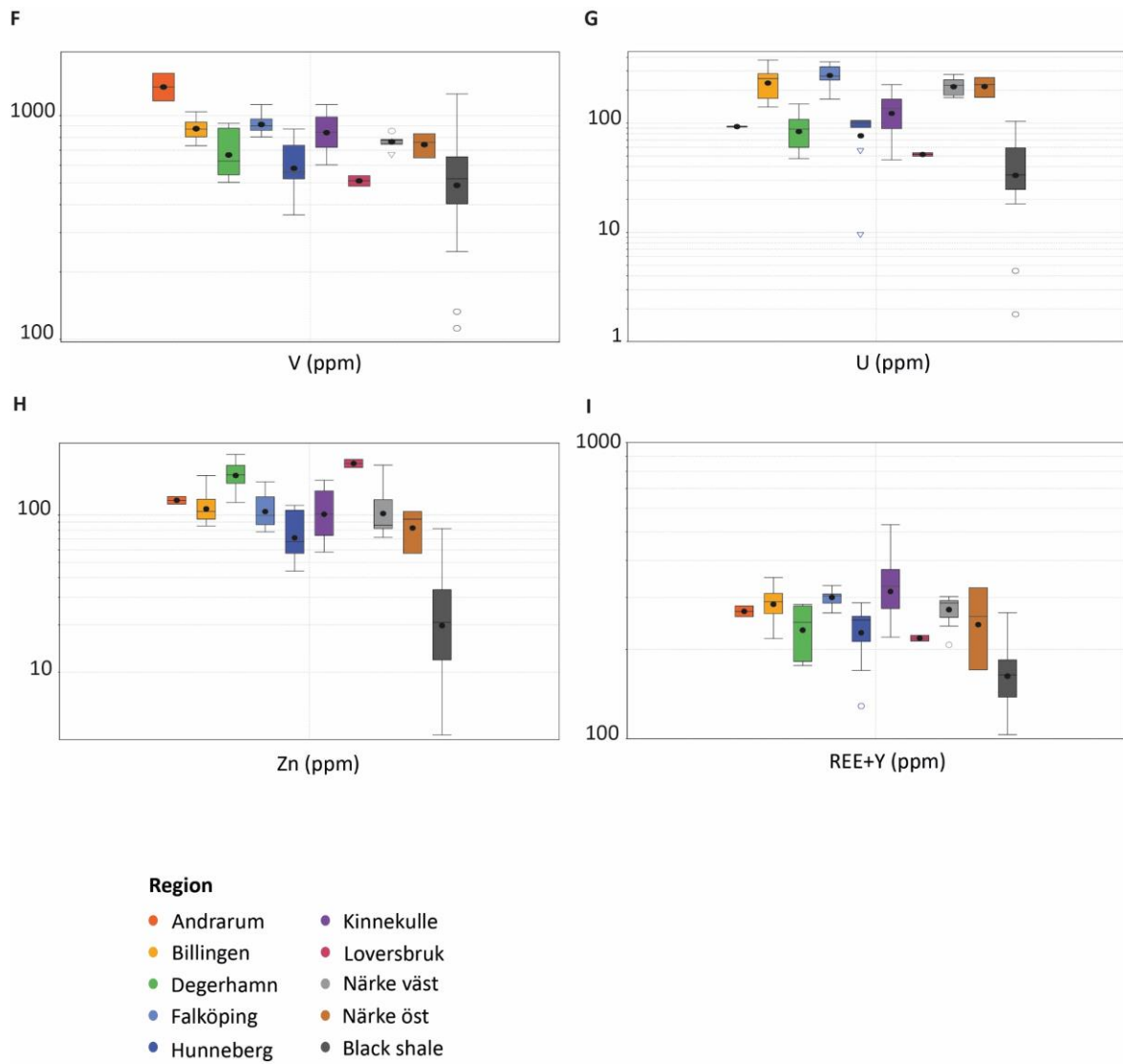


Figure 41. Continuation. Boxplots for selected elements grouped according to the sampled region.

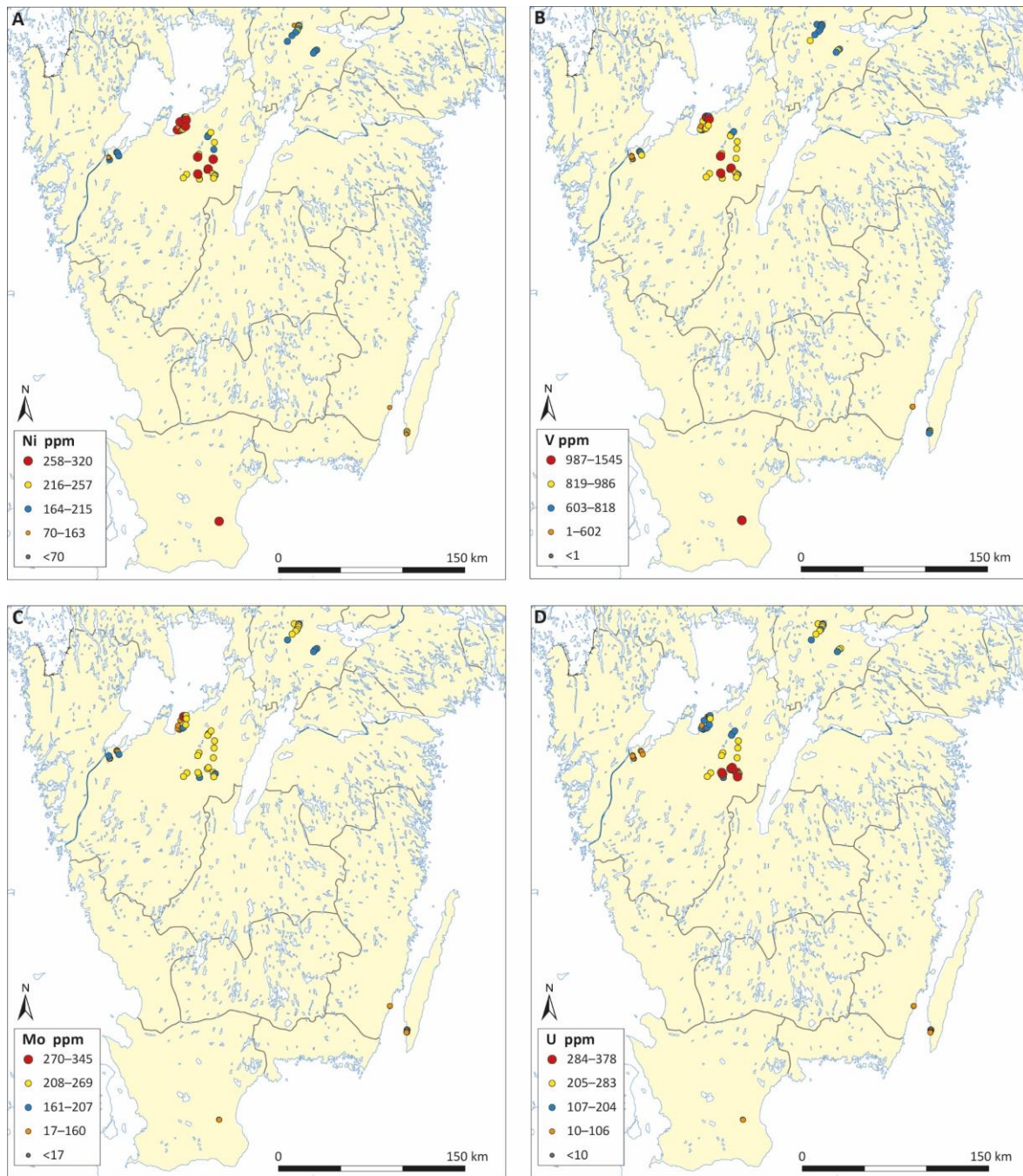


Figure 42. Geochemical maps of Ni, V, Mo, and U in burnt shale waste in southern Sweden. The map has been produced in ArcMap with class division according to natural breaks (jenks), a method which groups similar values together and maximizes the differences between classes.

Secondary resource potential

Burning of the black shale results in rather unreactive waste, which due to passive enrichment has higher concentrations of metals and critical raw elements than the original black shale. Although some of the metals are promising for secondary extraction, for example, vanadium, molybdenum, nickel as well as uranium, the difficulties with extraction processes must be evaluated.

This historical waste usually occurs in small quantities in many locations, and it is heavily overgrown by tree and bushy vegetation, which may make these places economically unimportant and of artisanal scale. Bigger waste piles may however be of interest, particularly because some of the waste products present an environmental risk, therefore their removal, in addition to CRM's extraction, could improve the chemical status of the local soil and groundwater.

CONCLUSIONS

As a result of high-temperature and long-lasting burning of the so-called alum shale, the waste has undergone considerable mass loss, and its chemical composition has been modified. C, S and H₂O are the main elements/compounds removed during burning. This mass loss has caused a remobilization and passive enrichment in most elements. However, some major elements Fe₂O₃, P₂O₅, CaO, and BaO and trace metals Cd, Co, Cu, Ni, Zn, as well as the REEs are enriched in the burnt shale above the passive concentration levels. Potential explanations for this enrichment are contamination during or after burning by limestone and lime, burning of preferentially sulphide rich layers (meaning the burnt black shales may have had higher primary Fe and metal contents), and contamination of burnt shale with fly ash.

At some locations, metals and critical elements show high enough concentrations to be of potential economic interest. There may also be an interest in removing the waste from urban areas where it can present a risk for contaminating soil and water. The leachability of the waste can vary, depending on the size of the waste fragments and the degree of its disintegration and weathering. The reactivity of this waste and extraction possibilities requires more detailed studies.

ACKNOWLEDGEMENTS

The sampling and analyses were financed by the governmental directive No. N2021/01038. The major outcomes from Lisa Blomskog's master thesis (Blomskog 2022), supervised by Anna Ladenberger and Iain Pitcairn and co-financed by the directive, were partly used in this technical report.

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