

Identification of major point sources in the severely contaminated alum shale area in Kvarntorp, Sweden

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Abstract

Scarcity of imported fuel led to oil production from alum shale in the Kvarntorp area, 200 km west of Stockholm, during 1941-1966. Remains from this are a 100 meter high waste deposit, Kvarntorpshögen, consisting mostly of shale ash and water filled open pits. As this shale is rich in sulphur and trace metals such as U, Ni and Mo, leaching from the waste deposit is feared. To elucidate the important question whether Kvarntorpshögen is the most important concern, or to what extent other sources might contribute with contamination, water sampling was extended to contain more localities than the ordinary control program. A new approach was the sulphur isotope analysis. The results point towards an area too complex for using sulphur isotopes for mixing calculations. Isotope fractionation during oil production is shown by the δ^{34} difference between shale and shale ash. Current isotope fractionation indicates sulphate reduction. Some localities indicate pyrite weathering and others rather show buffer capacities due to the presence of lime. Sr concentrations also suggest weathering. It is indicated that Kvarntorpshögen has an impact on the surroundings, but also that the water filled open pits as well as an industrial area affect the water quality. It is concluded that Kvarntorpshögen is one of the most important contributors of metal dispersion, but other point sources cannot be discarded as environmental risks.

Key words: Alum shale, Kvarntorp, Shale oil, Sulphur isotopes

Introduction

Faulting has enabled sedimentary rocks from the Cambrian and Ordovician periods to be preserved in the Kvarntorp area, some 200 km west of Stockholm. The gneissose and granitic basement is superimposed by sandstone, which higher up in the strata is followed by alum shale and limestone covered by till.

During World War II, shortage of imported fuel led to the search for alternative resources. Alum shale exists in several places in Sweden, but in most cases the oil content is too low for extraction. Svenska Skifferolje AB was formed in 1941, and Kvarntorp, where the shale contains 4.8% oil, was chosen for production (Schwartz 1945). Several methods were tested, for example an in-situ method, called the Ljungström method, which consisted in heating of holes drilled into the alum shale. Nevertheless, most of the oil was obtained by pyrolysis. This production lasted until 1966 and severely affected the area. The alum shale is from late Cambrian and is rich in for example sulphur, uranium, vanadium, nickel and molybdenum (Dyni 2006). Sulphur dioxide rich flue gas emissions (550 000 m³/hour) damaged the forest, some 13 metric tonnes of dust were spread on a daily basis and polluted water reached the water courses (Kumla municipality 1979). Remains today are water filled open pits and a 100 m high waste deposit, Kvarntorpshögen, mostly consisting of shale waste in the form of shale ash (crushed and totally combusted shale) and fines (crushed but not further processed shale). There is also lime waste. The deposit still has a hot interior and increased metal leaching has been feared when it cools and more precipitation penetrates. Elevated temperatures are believed to be generated by pyrite oxidation (<100°C) and kerogen oxidation (>100°C) (Bäckström 2010). An important question is whether Kvarntorpshögen is the most important concern, or to what extent other sources might contribute with contamination.

In this study water sampling was extended to contain more localities than the ordinary control program run by the municipality of Kumla. A new approach was the analysis of sulphur isotopes.

Methods

Surface and ground waters sampled in March 2015 were analyzed with ICP-OES for metal and sulphur concentrations at Stockholm University (analytical precision within $\pm 5\%$) and for uranium with ICP-MS at Örebro University. Sulphur isotope ratios were determined with IRMS, also at Stockholm University, after a precipitation of BaSO_4 was mixed with V_2O_5 . The sulphur isotopes are calibrated against CDT and the standard deviation is $\pm 0.2\%$. Surface waters were sampled again in November and December 2015 as well as in January and February 2016. These samples were analysed with ICP-MS at Örebro University. Solid samples consisting of alum shale, shale ash, fines and limestone were also analysed for sulphur isotopes. The map in figure 1 shows the location of the area.

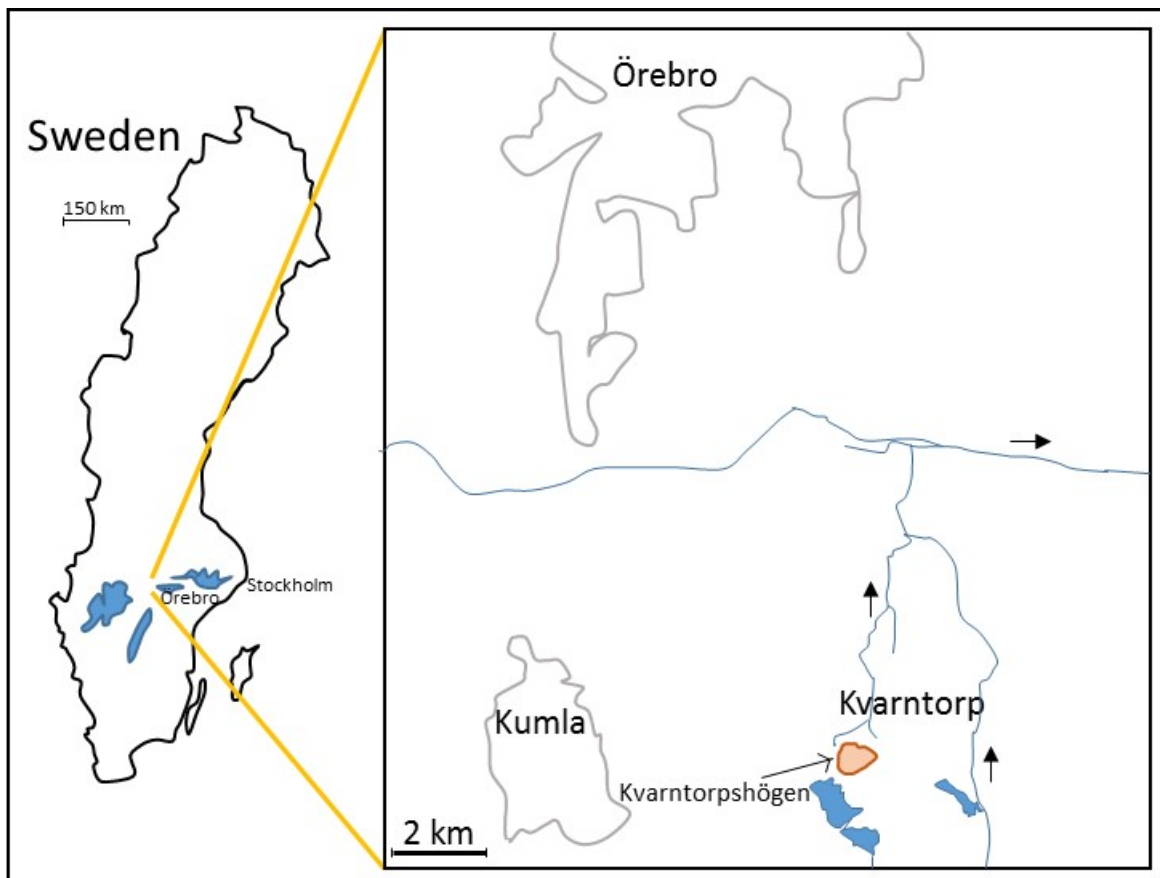


Figure 1 Map showing the location of the Kvarntorp area and the waste deposit, Kvarntorpshögen.

Results and discussion

Sulphur isotopes

A linear relationship between $\delta^{34}\text{S}$ values and $1/\text{S}$ would indicate mixing and enable sulphur isotopes to be used to calculate percentage of sulphur originating from a specific source, for example a mine or a waste deposit. No such linear relationship was found in this case.

During Cambrian the oceanic $\delta^{34}\text{S}$ was about $+30\%$ (Nielsen et al. 1991). Isotope analysis of solid samples from the area gave results as shown in table 1, with a range from $+3.18\%$ to $+6.25\%$. As the values are much lower for these samples than for the ocean at that time, this is an indication that the shale and the limestone do not show the isotopic composition of the ocean at their formation time, but an isotopic composition affected by biology and isotope fractionation. For surface water from the Kvarntorp area, the range in $\delta^{34}\text{S}$ values is between -3.42% and $+9.28$ (see map in figure 2) and for

groundwater the range is +2.83‰ to +15.77‰ (see table 2). The variety of δ -values in the different water samples is not explained by the sedimentary rocks examined in this study since they have a much narrower span. The $\delta^{34}\text{S}$ value for rainwater was +4.74, but as the sulphur concentration in this water was low compared to the surface waters, this is not an important contribution to the isotope signal in the area. All this suggests that there are several sources for sulphur. Furthermore, processes like pyrolysis and weathering might have had impact. The $\delta^{34}\text{S}$ difference between shale and shale ash indicates fractionation caused by pyrolysis. Negative values indicate oxidation of some kind.

The highest $\delta^{34}\text{S}$ values were found in some of the groundwater, indicating microbial activity where sulphate reduction has left the residual enriched in isotopic heavy ^{34}S . The result is that isotope values are too diverse in the Kvarntorp area to enable mixing calculations if solely sulphur concentrations and sulphur isotopes are used.

Table 1 $\delta^{34}\text{S}$ values for solid samples.

Solid sample	$\delta^{34}\text{S}$ vs CDT, ‰
Shale	+3.18
Shale	+4.47
Shale ash	+6.25
Fines	+4.39
Limestone	+4.08

Table 2 $\delta^{34}\text{S}$ values for groundwater

Groundwater	$\delta^{34}\text{S}$ vs CDT, ‰
G1	+2.83
G2	+3.42
G3	+5.52
G4	+15.77
G5	+6.12
G6	+3.68
G7	+9.00
G8	+10.47
G9	+9.75
G10 (deep)	+9.90
G11 (deep)	+10.63

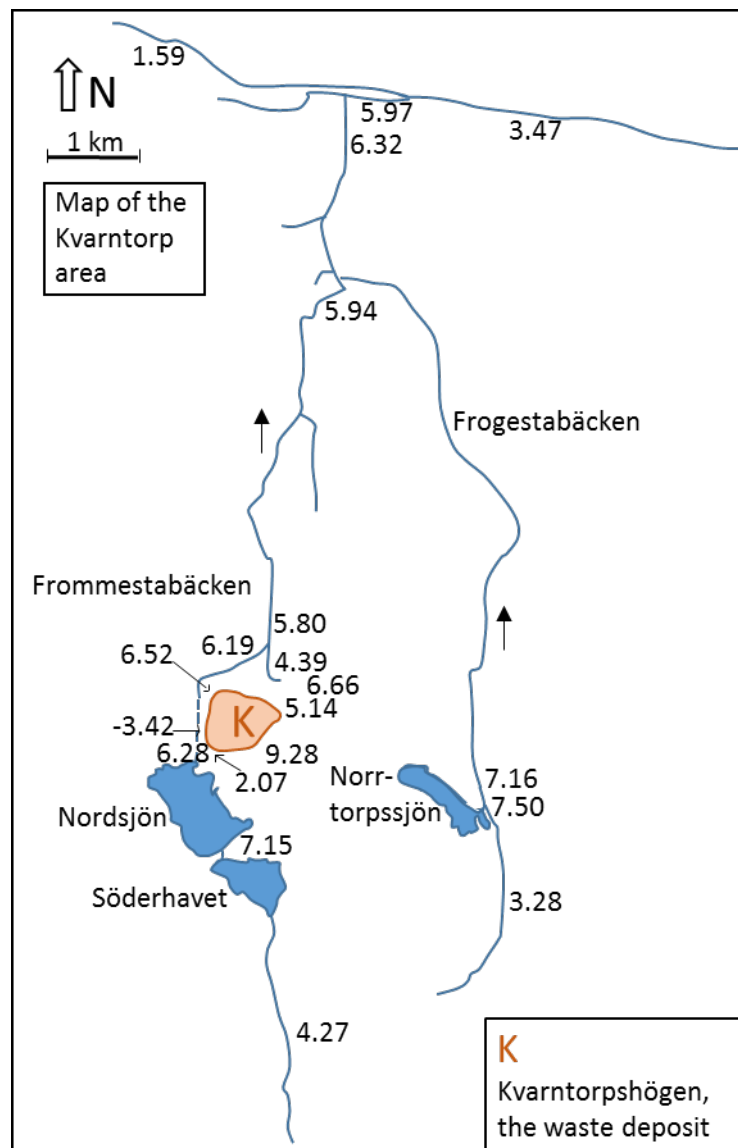


Figure 2 $\delta^{34}\text{S}$ values for surface waters. The three lakes are water filled open pits.

Metal analysis

Some of the localities for surface water sampling are shown in figure 3. A study of the western water course with a comparison between concentrations upstream (locality *a*) and downstream the waste deposit (locality *f*) shows an increase of metals and sulphur (see table 3) downstream the area, suggesting that the area affects the water.

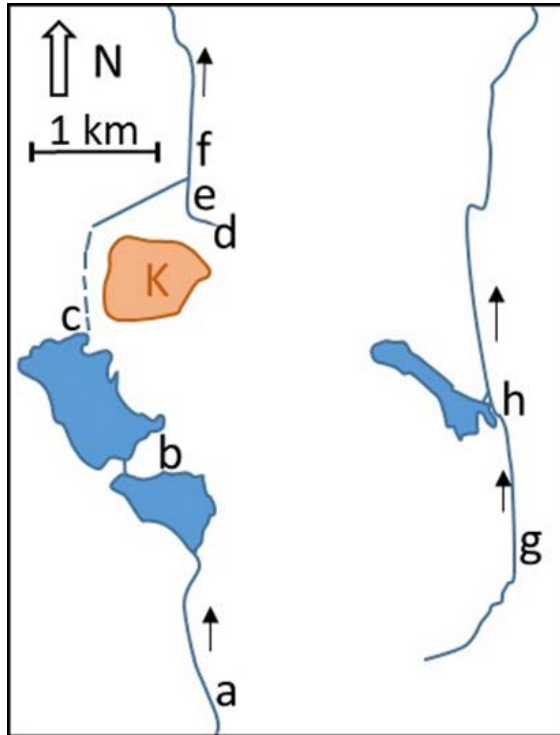


Table 3 Concentrations for some of the surface water localities sampled in March 2015

Locality	S, mg/L	Sr, µg/L	Ni, µg/L	Mo, µg/L	U, µg/L	pH
a	6.98	39.1	bdl	2.4	4.3	7.4
b	40	195	7.2	8.3	13.2	7.5
c	81	224	12.2	8.4	16.4	7.4
d	247	247	116	8.7	24.4	6.4
e	387	260	137	1.3	1.8	6.2
f	79.8	206	13.8	6.6	13.5	7.4
g	14	70.2	bdl	2.5	8.6	7.8
h	315	1280	5.4	4.9	24.0	7.1

Figure 3 The Kvarntorp area with Kvarntorpshögen labelled K and six of the localities for surface water sampling a-f. The three lakes are water filled open pits.

A plausible candidate for this influence is the waste deposit itself, but there might be other sources as well. The water passes two lakes which are now water filled former open pits. Water at locality *b*, the outlet of the southern lake, might contain weathering products from the exposed bedrock in the lake, but also water from a nearby waste treatment company, Ekokem.

Further downstream, the water enters a culvert at the outlet of the northern lake (locality *c*). Locality *d* consists of water from an industrial area whereas *e* is composed of surface water from the deposit after it has passed through a pond system, retaining some particles. In locality *f* water from *c*, *d* and *e* are already joined.

The diagrams in figure 4 show the concentrations of nickel, uranium, strontium and molybdenum in localities *a-h* for all four sampling occasions. For the western water course, nickel has its highest concentration in locality *e*, making the waste deposit the most important contributor of nickel. For uranium, on the contrary, locality *e* shows lower concentrations than the outlets of the lakes (*c*) and the water from the industrial area (*d*). For strontium locality *e* displays higher concentrations than the outlets of the lakes (*c*) and the industrial area. These concentrations, though, are much lower than for the highest concentration of strontium at the eastern water course (*h*).

Also the eastern water course passes through a water filled open pit, lake Norrtorpssjön, with locality *g* upstream and locality *h* at the outlet of the lake. There are higher concentrations of Ni, Sr, Mo and U at locality *h* compared to *g* for all sampling occasions. This is an indication of weathering of bedrock in the lake, but there might also be influence from the bedrock at the site where oil was obtained in situ. Water from this site is drained into the water filled pit and could affect its water. Also another open pit, now filled with industrial waste, is drained into Norrtorpssjön. The high Sr concentrations at the outlet

of the eastern lake point towards weathering. A study by Lavergren et al. (2009) showed that neutral groundwater from both unprocessed shale and processed shale materials contained in excess uranium, molybdenum and some cadmium, nickel and zinc. Weathering of alum shale is a plausible source for the higher concentrations at the outlet of the lake, compared to upstream.

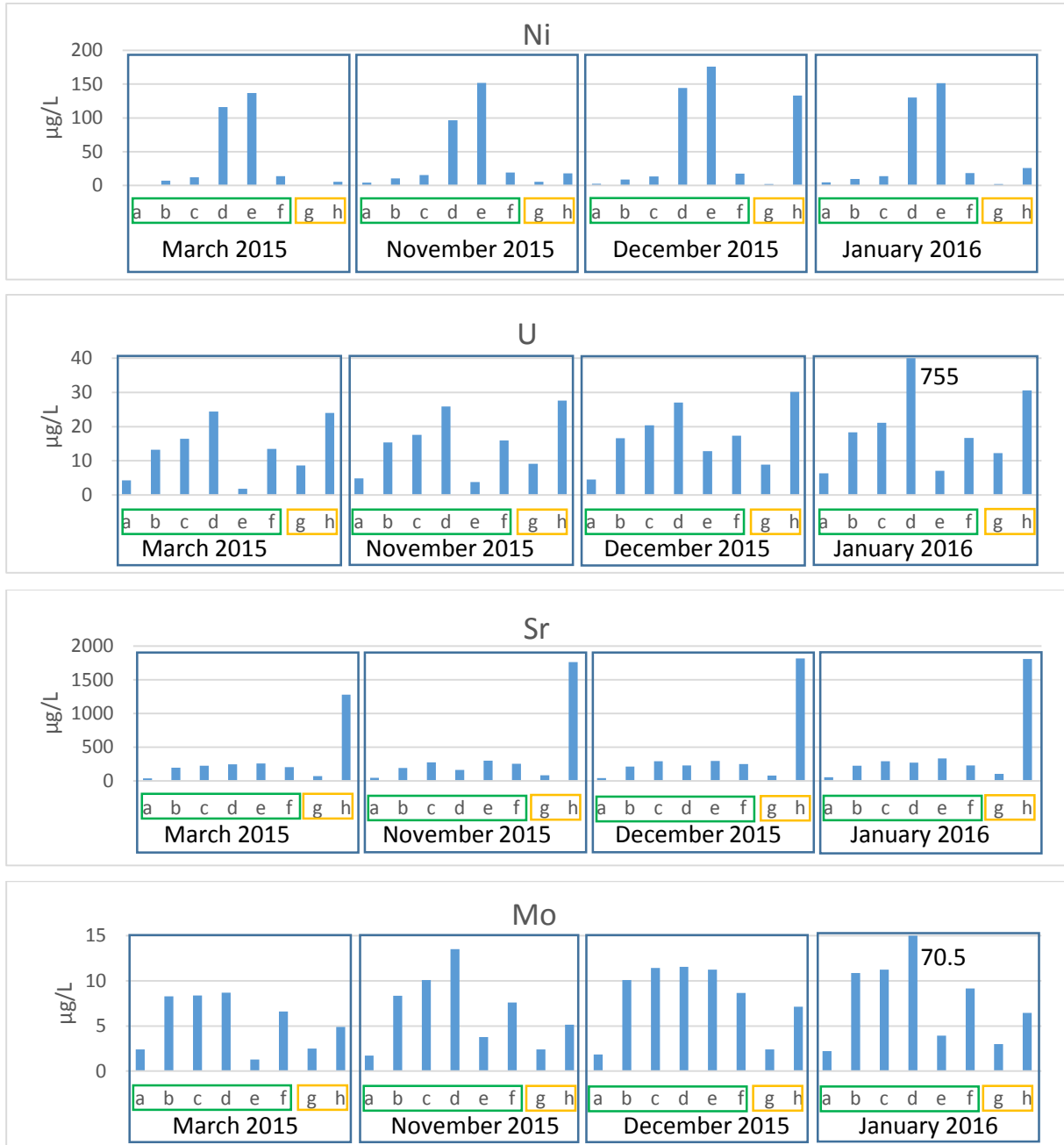


Figure 4 Diagrams illustrating the concentrations of nickel, uranium, strontium and molybdenum in localities a-h for four sampling occasions. Localities a-f represent the western water course, and g-h the eastern.

For some elements (e.g. uranium) the highest concentrations are not found in water originating from Kvarntorpshögen, while others (e.g. nickel) display their highest concentrations in water from the deposit. This implies that there are other several important point sources in the area, but also that Kvarntorpshögen is one of the most important contributors, even when water passes the pond system.

Analyses of groundwater and surface water around Kvarntorpshögen indicate that some localities are dominated by pyrite weathering, whereas at others, calcite is working as a buffer.

Conclusions

Sulphur isotopes have been subject to isotope fractionation in processes such as pyrolysis, making the isotope values too diverse to enable mixing calculations and estimations of percentage of sulphur originating from a specific source. Furthermore, current isotope fractionation processes are taking place in the area, indicating sulphate reduction.

Concentrations of elements such as nickel have shown that Kvarntorpshögen is one of the most important contributors of metal dispersion in the area. Elements such as uranium and molybdenum indicate that other point sources also affect the water quality. This statement is strengthened by the strontium concentrations in the eastern water course, indicating high weathering rates.



Figure 5 Kvarntorpshögen seen from the south with the lake (open pit) Nordsjön in the foreground.

Acknowledgements

Carl-Magnus Mörth and Heike Siegmund at Stockholm University are greatly acknowledged for the ICP-OES and IRMS analyses. Viktor Sjöberg, Örebro University, is greatly acknowledged for running the ICP-MS.

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