Evaluating a method using pXRF for measuring sulphur along Ostlänken

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Acknowledgements

Abstract

Ostlänken (The Eastern link) is going to be a new main railway in Sweden, between Södertälje and Linköping. The railroad will go through areas where there could be high sulphide concentration in the rocks, and during the construction, large amounts of rock is going to be excavated. Since sulphides reacts with water and oxygen, and causes acidification and leaching of metals, exposed sulphides in the excavated rocks can be very harmful to the local ecosystems. Trafikverket (The Swedish Transport Administration) has been working with SGU (Geological Survey of Sweden) to map the area and take samples of rocks with potentially high sulphur concentrations. However, current methods for analysing the samples are time consuming. The aim of this project is therefore to evaluate a new, quicker, method using an pXRF (Portable X-Ray Fluorescence).

A pXRF sends out X-rays that excites electrons in the rock that then emits a characteristic X-ray which the instrument detects. The instrument has been used for detecting other elements, however measuring sulphur is challenging since it is a lightweight element with low characteristic energy. This means that the X-ray can't penetrate very deep, and the sample size of the pXRF becomes quite small. The new method using a pXRF for sulphur concentration therefore needs to take this into consideration.

Furthermore, the pXRF requires a calibration specific to each rock type to work. Therefore SGU samples sent to the laboratory for testing were also used for calibration of the instrument. During the calibration, different beam times of the pXRF was also tested in the laboratory figure out what would be optimal to gain most accurate results. Finally, during field work, the sites that SGU had sampled were revisited and measured using the pXRF to be able to compare the pXRF measurements with the results from the original laboratory work. Some additional measurements were made nearby the original sample sites to see how the results were affected by measuring on weathered rock surfaces.

The results showed that the averages of the field measurements were close to the results of the powdered samples that had been analysed in a laboratory. This means that for the sites that were investigated in this paper the method is working. Each measurement series consisted of 30 pXRF measurements and results show large differences within the measurement series' due to the heterogenous distribution of sulphides. Therefore, it is important to make many measurements. The method could be a useful tool for initial screening in an area that could have high sulphur concentrations to be able to focus other more time-consuming methods to areas that are of interest.

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1. Motivation

Ostlänken (Ostlänken) is the first part of Sweden's new main railway system that eventually will link Sweden´s three largest cities together. The new main line will run from Stockholm to Malmö and Gothenburg with interconnection in Jönköping. Starting in Gerstaberg, just south of the city of Södertälje, Ostlänken will run approximately 160 km through the towns of Trosa, Nyköping, Norrköping and with a final destination in Linköping (Fig. 1 and 2). Along the new stretch of mainline, the railway will cut through approximately 170 larger cuttings and 7 tunnels. A large amount of bedrock, approximately 13.7 million cubic meters, will be excavated during the construction, which is aimed to be re-used in the project.
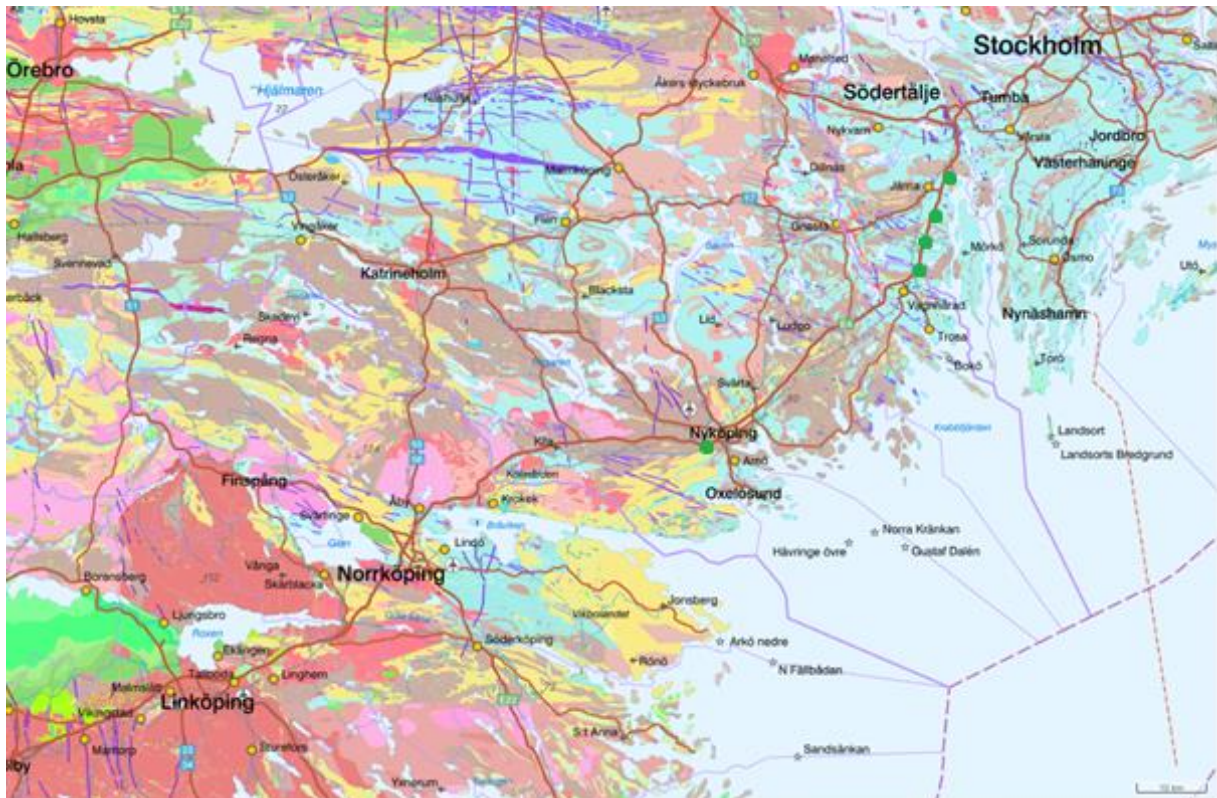
Figure 1 Shows a map of the bedrock of the area between Linköping and Södertälje where Ostlänken will go through. The field sites are marked in green and the sulphides can be found in the metasedimentary rock which is blue on the map.

In infrastructure projects, excavated material is often reused for construction later on, and there is therefore a need for intermediate storage in heaps on the construction site until the material is used elsewhere. For a project such as Ostlänken, heaps will hold large volumes and the need for intermediate storage could last for years. As the bedrock in some parts of the area can contain a significant percentage of sulphide, there are a potential risk of acidification and leaching of metals to water recipients in the proximity of the construction sites with prolonged exposure to the elements. The most common sulphides in the area is pyrite which can react according to the following example.

$FeS_{2(s)} + 7/2O_{2(g)} + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

$Fe^{2+} + 1/4O_{2(g)} + H^+ \rightarrow Fe^{3+} + 1/2H_2O$

$Fe^{3+} + 2H_2O \leftrightarrow FeOOH_{(s)} + 3H^+$

$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 1 H^+$
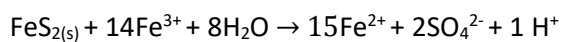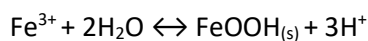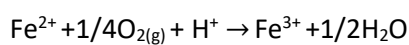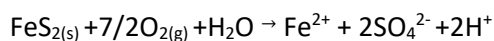
The Bergslagen region, where Ostlänken will run through, hosts a complicated and multistaged evolution. Several episodes of volcanic activity and deep burial has created a complex and variable bedrock. The area has produced several sulphide bound mineralisations, of which some are even ore-grade. The occurrence of high concentrations of sulphides in bedrock can cause problems with leaching and acidification when exposed to oxygen and humidity. There is no exact limit of when the concentrations of sulphides are *too high* since it depends on variables such as how much of the material is exposed to water, and oxygen and how sensitive the ecosystem is.

Current methods for determining sulphur content in rocks usually involve leaching tests performed in laboratories. The tests normally take weeks and require that excavated material is stored in separate piles until results are in, which isn't practically possible to do in a project of Ostlänken's magnitude. A different method is needed that allows quick screening of excavated material, so that it can be sorted into piles that can either go into production immediately or into piles that require further testing to be able to design countermeasures to acidification

1.1. Aim

The main goal of the project is to investigate a method for measuring sulphur using a *potable X-Ray Fluorescence* (pXRF). During a joint-venture project between Trafikverket and the Geological Survey of Sweden (SGU), several localities were tested regarding geochemical- and petrographic composition. This data will be compared with data obtained by a pXRF which is a much faster method since the devise is aimed directly at the rock surface and each measurement takes between 30 seconds and a couple of minutes. An important aspect of this project is to see if the pXRF results can be reliable enough to exclude some of the more time-consuming analysis, and how many measurements are required to provide those results. The pXRF could potentially be used as a tool lfor screening before doing further testing.

If the results are considered sufficient, suggestions for a testing protocol for measuring sulphur with pXRF should be made. These measurements could then also be combined with other types of analysis to make the results stronger.

The proposed method needs to take several variables into consideration. For example, one disadvantage with the pXRF is the small volume ansalysed, the XRF can measure light elements such as sulphur less than one millimetre into the material. Another factor is the fact that the sulphides are not homogenously distributed in the rock. This means that there is a possibility to hit larger nuggets with high sulphur concentration or to miss them entirely and get to low concentrations when measuring. Another important factor is the calibration of the pXRF, which needs to be done for each instrument and each rock type used.

1.2. Research questions

The following research questions will be investigated:

1. How does the pXRF-results for S compare to established laboratory measurements and could the pXRF be used to benefit already existing methods?
2. What could a test protocol for pXRF look like, how many measurements are needed?

1.3. Delimitations

The idea to use pXRF to measure sulphur in infrastructure projects is new. The only literature on the topic that has been used for this paper is a report from the Norwegian Public Roads Administration (Hagelia & Fjermestad, 2016).

The area where the railroad is going to be built is very large and elongated, so a complete mapping within the full area is not within the scope of this project. Focus is instead placed on current SGU sample sites. Those field sites were prioritised due to their high concentrations of sulphur and the fact that they had been previously studied by the SGU and therefore provide ground truth data to compare the pXRF measurement with.

The pXRF measurements were taken using an Olympus InnovX Delta Premium Handheld XRF Analyzer that was available at the Department of Earth Sciences at Gothenburg University. No other devices were tested or compared in this project. Other devises might work slightly different. However, the largest errors are related to the sampling so this should not significantly affect the study.

2. Related work

The following chapter will highlight the problem of acidification from sulphides and how this must be taken into consideration at construction sites. Furthermore, the pXRF and other methods for measuring sulphides will be introduced. Lastly, some challenges regarding sampling as well as comparing field data with laboratory data will be presented.
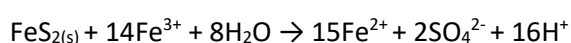
2.1. Regional geology

The rocks in Bergslagen, where Ostlänken is going to be located, are mostly Paleoproterozoic rocks formed between 1.9 and 1.8 Ga. They are metasedimentary rocks that go into metavolcanic rocks that are mostly rhyolitic or dacitic (Stephens et al., 2009). The sedimentary gneisses that are common in the area quartz and feldspar veined with biotite. They often contain aluminium rich minerals, such as, garnet, cordierite, sillimanite and andalusite which indicates that the initial material was rich in clay (Stålhös, 1975).

The metasedimentary rock was formed by sedimentation that was interrupted by a volcanic period 1.9 Ga in shallow water or just above the water surface which created volcanoclastic lithologies. After that there was a transgression and further deep-water sedimentation Furthermore, there are several suites of igneous rocks that have been intruded in the sedimentary and volcanic rock. It has been proposed that this could have been formed in a continental back-arc setting which would explain the mix of volcanic and sedimentary rocks, and the composition of the intrusive rocks matches models with incorporation of juvenile mantle materials rather than subduction of Archean crust (Stephens et al., 2009).

The main metamorphic event in the area is the Svecokarelian orogeny, 1.9-1.8 Ga. The southernmost area of Bergslagen in which Ostlänken is located is part of the southern magmatic metamorphic domain. High grade metamorphism at low pressure in the amphibolite and granulite facies due to mafic under plating created these migmatites (Stephens et al., 2009).

2.2. Acidification from sulphides

Acidification due to the weathering of sulphides has for a long time been considered an environmental hazard. The weathering leads to acidification and leaching of different metals which is harmful to most ecosystems (Qvarfort, 2003). Placed in environment with water and oxygen, minerals such as pyrite (FeS_2) and other sulphides are weathered mostly through oxidation. The product of the weathering is sulphuric acid and free metals (see equation below). The amount of acidification is determined by several factors such as access to oxygen and water, the amount of rock surface where reactions can take place, and access of buffering materials such as calcium carbonate. When rocks are excavated, for example in processes of mining or construction work, there are large increases in surface area of the rocks. This can therefore cause an increase in acidification. Thus, there are other factors to take into consideration than sulphur concentration to determine possible environmental effects (Qvarfort, 2003).

$FeS_{2(s)} + 7/2O_{2(g)} + 2H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

$Fe^{2+} + 1/4O_{2(g)} + H^+ \rightarrow Fe^{3+} + 1/2H_2O$

$Fe^{3+} + 2H_2O \leftrightarrow FEOOH_{(s)} + 3H^+$

$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$
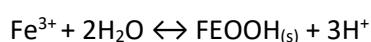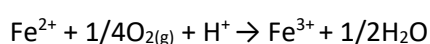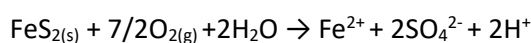
Mines in the Dalälven river catchment area which is also in Bergslagen (same as Ostlänken) has affected the river through acidification and leaching of metals that have ended up in the Baltic Sea. While problems with acidification are more commonly addressed in mines there are also various examples of acidification due to construction (Lundgren, 1990). In the United States there are examples of sulphidic shale that has caused acidification due to road construction and the construction of an airport in Virginia (Daniels, 2003). Another example is the construction of the motorway E18 in Norway which lead to acidification and leaching of metals such as Ni, Mo, Mn ,Cd, Zn and, Cu (Hindar & Nordstrom, 2015).

Acidification from construction has also occurred in Sweden during the development of the highway E6 north of Uddevalla. In that case, pH values of (3-4), high concentrations of sulphides, Co, Cu, Zn, and Ni were measured near a pile of excavated materials. The rock in the area were metasedimentary gneisses and the most common sulphides was pyrite. This might suggest that sulphides have been mobile at some point and that most of the pyrite probably was secondary. The sulphur concentrations were higher in shear zones that were very mica rich as well as in metabasites that were within the metasedimentary rocks. It was therefore recommended that special attention would be given to those areas during the continuation of the construction (Tullborg, 2001).

2.3.   Portable X-Ray Fluorescence (pXRF)

Portable XRFs (pXRF) or handheld XRFs (hXRF) have been used since the 1970s (Young et al., 2016) It is operated by sending X-rays to the sample that should be analysed. Those X-rays excite electrons in the atoms of the sample. Other electrons then fall back in to take the place of the excited electron which creates secondary X-ray beams with different characteristic X-ray peaks for different elements that the instrument can detect (Gill et al., 2014).

 In the geochemical field, the handheld devices are used for exploration, mining (Hall et al., 2014) (Gazley et al., 2011) (Simandl et al., 2013), site remediation, and waste management (Rouillon & Taylor, 2016). The method is quick (30 seconds- a couple of minutes) which leads to a fast analysis and decision making. Nonetheless, it is not as robust as other laboratory methods such as ICP-MS and quality control of selected samples is important to make sure that the results are sufficient (Lemière, 2018). The beam energies from the X-ray tube in the pXRF are lower than those of a laboratory XRF which makes the results less robust, especially for light elements (Young et al., 2016). The pXRF is also a tool for environmental applications on soils. However, in situ measurements can have a large uncertainty due to the lack of homogeneity in the material tested (Ravansari et al., 2020).

PXRF is a semi-quantitative method and the properties of the surrounding rock will affect the measurements, which means that calibration is required (Hagelia & Fjermestad, 2016). For example (P. S. Ross et al., 2014) noticed that different calibrations were required to achieve accuracy measurements of a basaltic core compared to a series of other volcanic and intrusive rock cores, and (Fisher et al., 2014) made different calibrations for "all rock" measurements and ultramafic measurements. There are multiple factors that need to be considered to achieve reliable pXRF results such as mineralogy, water content, grain size and interference of elements that have an overlap in their characteristic energy (Hagelia & Fjermestad, 2016). The "information depth" of the pXRF depends on the weight of the element measured. For example, 99 % of the response for calcium, which is a light element, is found in the first 100 μm of a soil sample. Whereas for Barium 99 % of the response is in the first 2 cm (Laperche & Lemière, 2020).

(Bourke & Ross, 2016) have compared measurements directly on unprepared drill cores with measurements on powder to obtain geochemical data faster. They found that the sample preparation does not affect the precision or accuracy of the pXRF (portable XRF) measurements, but the heterogeneity of the mineralogy makes it more difficult to get representative results. The error can be limited by making multiple measurements close to each other and average the results (Hall et al., 2013) or making measurements with a high spatial resolution along the core and smooth the data (Ross et al., 2014).

2.4.   Established Laboratory methods for evaluating sulphides

When evaluating the risk of acidification, one method is measuring sulphur concentrations of a sample in a laboratory. The analysis can for example be conducted using *ICP-MS (Inductively coupled plasma- mass spectrometry)* which is a method that can detect very low concentrations of ions utilizing the relationship between charge and size while sending the sample through the spectrometer *(Gill et al., 2014).* Another method is *IR (Infrared spectroscopy)* works by sending infrared to a material and the energy is absorbed by the bindings between different atoms. This is good for analysis of molecules and characteristic groups. The method can detect low concentrations in small samples (Larkin, 2011). In both methods, the rocks are sampled in the field and sent to a lab where they are analysed. The process takes about one or two weeks.

However, since there are other factors apart from sulphur content that determine weathering, methods that measure the weathering potential, so called "humidity cell test", can also be useful (Qvarfort, 2003). During a humidity cell test, leaching is done in a laboratory by adding water to the excavated material while measuring pH, conductivity, and metal concentration. One cycle of that test takes about a week, but the results are better if the tests go on for several cycles. For example, testing of the weathering potential in material from Fäboliden was done for 230 days. That test gave sufficient results but could have been further improved if it would be given more cycles (Qvarfort, 2003).

2.5.   Earlier studies using an pXRF by the Norwegian Public Roads Administration

Hagelia & Fjermestad (2016) tested the use of a pXRF as a tool for investigating sulphur content for the Norwegian Public Roads Administration (NPRA). For calibration they suggest studying the area of interest and taking samples that represent the variability of the area. If there is a large variation in the types of rock, either in minerology or grain size, separate calibrations should be made. The samples are made into a fine-grained powder < 50 μm and analysed with a quantitative method, for example ICP-MS, at an accredited laboratory. These results are then compared to measurements with the pXRF.

For measurement on rock surfaces, they suggest doing multiple measurements and measuring across layers of alum shale due to its large variation in concentration over thin layers. They also point out that it is necessary to make measurements on both weathered surfaces and unweathered rock to get the best results.

2.6.   Comparing field and laboratory work

When comparing field methods and laboratory methods there are multiple factors to consider. The main problem is the fact that it is difficult to access the ground truth of the analysis without costly laboratory work. Laboratories are often limited by the cost of a measurement and the amount of time it takes to get the results. This means that even if the field results vary slightly from the laboratory work, this does not necessary mean that the field results are false since the lab results

also can vary in their accuracy. Furthermore, the quality of a field method could be lower than that of a laboratory method and still be good enough for decision making, it just needs to be *fit-for-purpose* (FFP) (Ramsey & Boon, 2012) ,(Boon & Ramsey, 2012). The FFP can be described as "the property of data provided by a measurement process that enables a user of the data to make technically correct decisions for a stated purpose" (Thompson & Ramsey, 1995).

An advantage with a field method is the possibility of making more measurements and adapting what measurements are made depending on the results. Whether a method is done in the field or in a laboratory, the total error consists of error of the analysis and the error of the sampling. If the precision from a method needs to be improved, that can be achieved by making more measurements (Thompson & Fearn, 1996). In many cases it is hard to determine the sampling error, yet the sampling is often the biggest source of error. In a case study where measurements of arsenic with pXRF and laboratory methods were compared the analysis variance was higher for the field method, but the sample variance was still > 99% of the total variance for both methods, due to the heterogeneity of the arsenic distribution (Parsons et al., 2013). Traditionally, laboratory data is considered to be more reliable for environmental applications. However, the total uncertainty could potentially be smaller for field methods if the increase in measurement error is smaller than the decrease in sampling error(Crumbling et al., 2001).

3. Method

The method can be divided into three phases: lab work, field work, and data analysis. The materials accessible for the project were the samples that SGU had collected along the line of the new railroad (Fig 1). Samples of 300 kg were taken with a hydraulic drill. The sites that were chosen were accessible with the drill and represented different rock types along the proposed railway. After initial crushing of the rock sample about 2-4 kg of rock that are considered representative of the sample was chosen for geochemical analysis. The samples were powdered and then analysed at an authorised laboratory (ALS) with ICP-MS and IR. Some of the sample sites also had corresponding rock samples that were made into thin sections analysed by SGU. The rocks left over after making the thin sections were used to make some initial tests of measuring directly on the rock in the lab. When using the pXRF it was important to give it time to warm up, especially after not using the instrument for a while, otherwise the results would be inaccurate (too low). This can be tested by doing a series of measurements and making sure the results are not increasing for every measurement.

Figure 1 Map of the area between Södertälje and Norrköping. The sites where the calibration powders were sampled and field measurements were made are shown.

3.1. Sample preparation, and XRF setup

The samples from SGU consisted of a fine-grained powder. These samples were used to make calibrations for the pXRF and other necessary evaluations of the method.

The instrument used was an Olympus InnovX Delta Premium. The XRF uses two beam settings, the second beam can best detect sulphur according to the user manual of the instrument, thus the time for beam 2 was the only setting that needed to be evaluated. Each sample was measured with three different settings (Tab.1).

Table 1 The settings of the pXRF in the lab

	Beam 1	**Beam 2**
Setting 1	5 seconds	30 seconds
Setting 2	5 seconds	60 seconds
Setting 3	5 seconds	120 seconds

Out of all the samples SGU provided every sample with detectable sulphur concentrations as well as three samples with no detected sulphur were used. The powder was placed in small containers 25 mm in diameter and 5 mm in height and compacted as much as possible. That was done by putting a plastic test tube without the bottom over the container and fill with powder (Fig 3a) and thereafter compact with a smaller test tube (Fig 3b). The setup for the pXRF is shown in figure 3c.
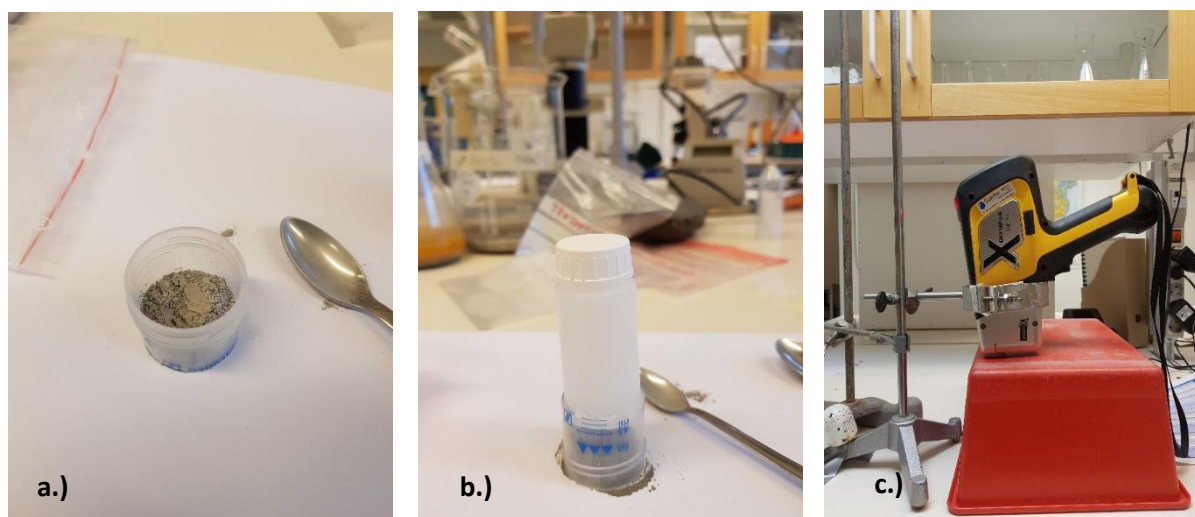

a.)   **b.)**   **c.)**

Figure 3 Preparing the powder for analysis and setup for the pXRF. 3a shows how the container was filled with an overflow of powder with a cutoff plastic test tube over it to keep the powder from leaving. 3b shows how the powder was compacted with a differen plastic test tube and 3c show the setup of the pXRF.

3.2.   Calibrating the pXRF for different beam times

The laboratory data from SGU contained results from both ICP-MS and IR analysis. By plotting them against each other as well as calculating the relative errors the quality of that data could be evaluated. After that it was decided that the IR data would be used for the calibration of the instrument.

The calibrations were made by taking the average of the 5 measurements done with each different beam time and plotting that against the IR data. A linear regression that went through (0,0) was made which became the calibration curve. The y-value of that curve corresponds to the factor between the IR measurements (ground truth) and the pXRF measurements.

3.3.   Tests of containers, rock samples, repeatability, and standards

Some further tests of the method were made in the lab: Different containers, standards and rock samples were tested.

The containers were tested to see if the depth of the container affected the results since the containers used were smaller than the standard XRF containers. Due to not having enough powder with high sulphur concentrations these tests were done with silica for three as well as one sample with a low concentration of sulphur. Silica is also a light element and behaves similar to sulphur. The tests were made during 30, 60 and 120 seconds and each measurement was made five times.

Table 2 Parameters of the containers that were tested

	Diameter	Height
Container 1	25 mm	4 mm
Container 2	25 mm	5 mm
Container 3	25 mm	10 mm

Apart from the samples from Ostlänken project, five powdered standards were analysed (Tab. 3) There were two certified reference materials (CRMs) (Ring, 1989) and samples from SGU that work as standards as they always send them for analysis when they send samples to a lab. These measurements were also made in *settings 1, 2* and *3* five times.

Table 3 Standards that were measured along with the Ostlänken samples

Sample name	Original material	Type of standard	S concentration
SARM46	Stream sediment	CRM	0.17%
SARM51	Stream sediment	CRM	0.24%
NOT050003	Tonalite	SGU	0.03%
BAG050012	Gabbro	SGU	0.03%
ARG050014	Granite	SGU	0%

To further compare beam times the shortest beam time (*Setting* 1) was plotted against the longest beam time (*Setting* 3). In addition to that the repeatability of the XRF measurements were studied by picking three samples with high, low, and medium concentrations of sulphur and making 25 measurements on them with each setting. The average concentration, standard deviation, and variance of each set of 25 measurements were calculated.

The rock samples that contained sulphur were used as an initial test for the final method. Based on earlier tests it was decided that *setting 1* would be used for these measurements. The rock samples were left from making thin sections and were a couple of cm in width and length and about 1 cm thick and 25 measurements were made on each rock sample. After the average, standard deviation and variance was calculated and compared to the IR data of the corresponding powder samples.

3.4.   Field work

The final test of the method was carried out during a weeklong field trip to Ostlänken area. The focus was on the SGU sites with metasedimentary rock where high concentrations of sulphur had been measured (Fig 1.) For all measurements in the field *Setting 1* was used (Tab 1.). Measurements were made where there were fresh surfaces from the sampling, and they were made across the sedimentary layers. Each measurement was made three times and between every measurement the XRF was slightly moved to see if the results were consistent. This was done 10 times at every site.

(Hagelia & Fjermestad, 2016) suggested that unweathered surfaces should be measured along with the fresh surfaces. Thus, some additional XRF measurements were also made at each site on

weathered surfaces, the measurements were made the same as the unweathered surfaces, three measurements close to each other ten times.

All the results were quantified using the calibration curve. Three measurements in each series that were made at the same spot, an average was calculated as well as the standard deviation. The average of all ten sets of measurements from each site were plotted in a diagram with error bars that had the value of the standard deviation and the measurement error given by the pXRF.

At one site (TEN200165A) measurements were also made along a profile similar to what (Ross et al., 2014) described with rock cores. Those measurements were plotted in a diagram and the results smoothed to counteract local heterogeneity.

4. Results

The first part of the chapter is a brief evaluation of the data provided by SGU. After that are the results from calibration, and thereafter the rest of the work in the laboratory, and finally the results from the field work.

4.1. Analysing ICP-MS and IR data

There were two types of data from the laboratory where SGU sent their samples, results from an IR analysis and ICP-MS. To figure out which results should be used to compare with the pXRF analysis the IR and ICP-MS data were compared.

Figure 4a shows that both methods are showing similar results. The linear regression is y=0.9922 which is very close to one. However, figure 4b that shows the relative error between IR and ICP-MS, shows that when sulphur concentrations are low, the IR was showing higher concentrations then the ICP-MS. For this project it was decided that the IR would be used as a ground truth for calibration and comparing the results since it´s preferrable to have higher results in applications for environmental purposes.
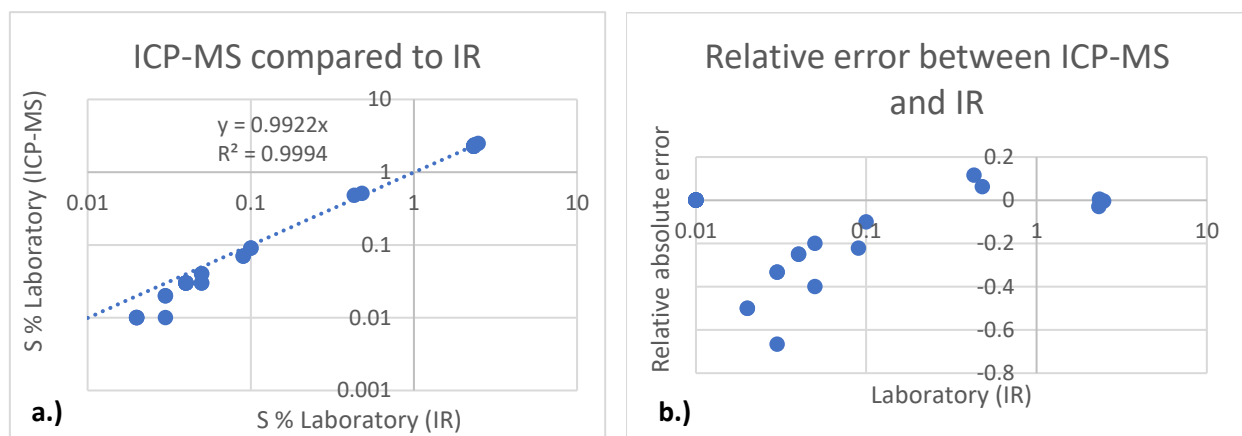

Figure 4 a.) The two laboratory measurements - IR and ICP-MS plotted against each other. The linear regression has a good fit and is close to one. b.) The relative error of the IR and ICP-MS plotted against the IR measurements, the error is larger for low concentrations.

4.2. Laboratory work

The pXRF was calibrated in the laboratory. Most of the laboratory tests were done with all the different settings (tab.1) to see which ones should be used in the field. There was also a test with different containers for the powder to confirm there were no errors caused by the thinness of the samples.

4.2.1. Different container sizes

There were three types of containers (tab.2) 4 mm, 5 mm, and 10 mm thick. The results from the pXRF are similar but results from the 4 mm one show lower concentrations (Fig. 5). The largest difference is 0.008 % between container 2 and container 3 from the 60 s measurements. For the rest of the measurements container 1 was used since it required a small amount of material while giving good results.
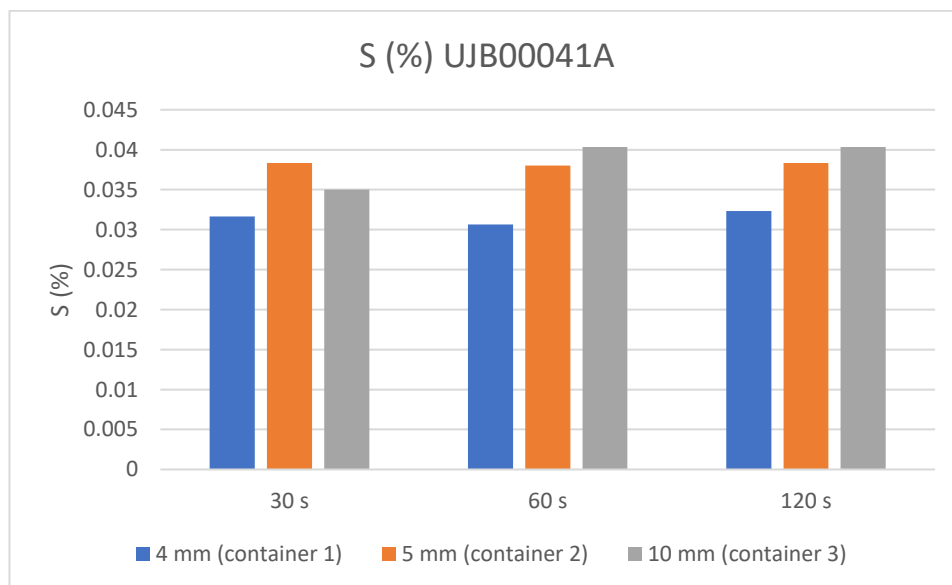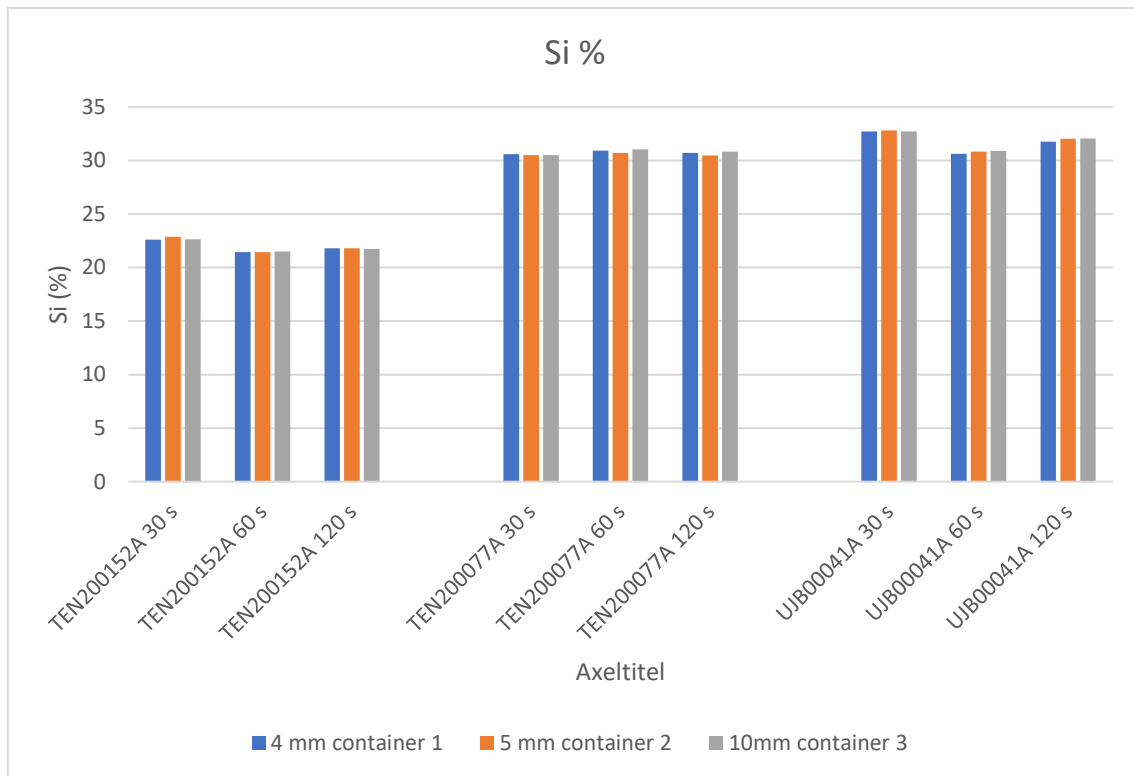
Figure 5 Comparing the effect of different containers on Si and S concentration measured with pXRF

4.2.2. Calibrating the pXRF for different beam times

The calibrations of the pXRF were done with IR results from the accredited laboratory and the average of the 5 measurements done for each beam time (tab. 1). The measurements from the pXRF suggests lower concentrations compared to the IR, but the results fit well with on a linear regression curve (fig. 6). Thus, the calibration factors are linear. The results displayed in figure 6 suggests that they are:

Beamtime 30 s – 0.7643
Beamtime 60 s – 0.7658
Beamtime 120 s – 0.7682

Figure 6 Calibration curves for S made with an average of five measurements during 30, 60 and 120 seconds. The pXRF measurements are plotted against the laboratory IR measurements. The linear correlation represents the calibration factor that should be used for further measurements. Reported errors for the sulphur measurements are between 0.004 and 0.01 for 30 s, between 0.003 and 0.008 for 60 s and between 0.002 and 0.006 for 120 s.

4.2.3. Analysis of standards

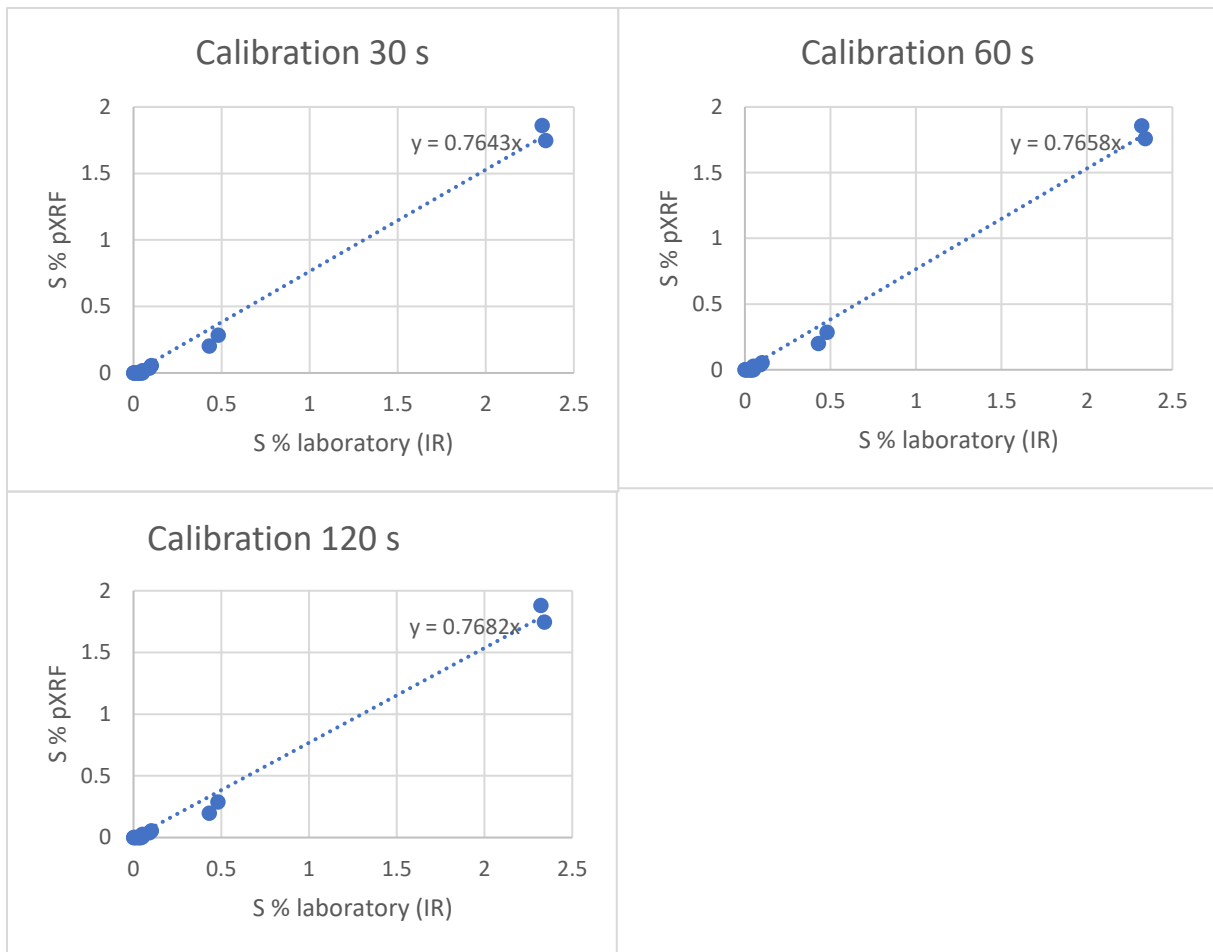The results from the analysis of the CRMs (Jochum et al., 2007) and SGU standards (tab. 3) are shown in table 4. The pXRF consistently gave higher concentrations compared to the already known values. Since this could be caused by difference in composition, these measurements were therefore not included in the calibration used for the field work.

Table 4 Average of 5 pXRF measurements on known standards, the pXRF is measuring higher sulphur concentrations compared to the known values.

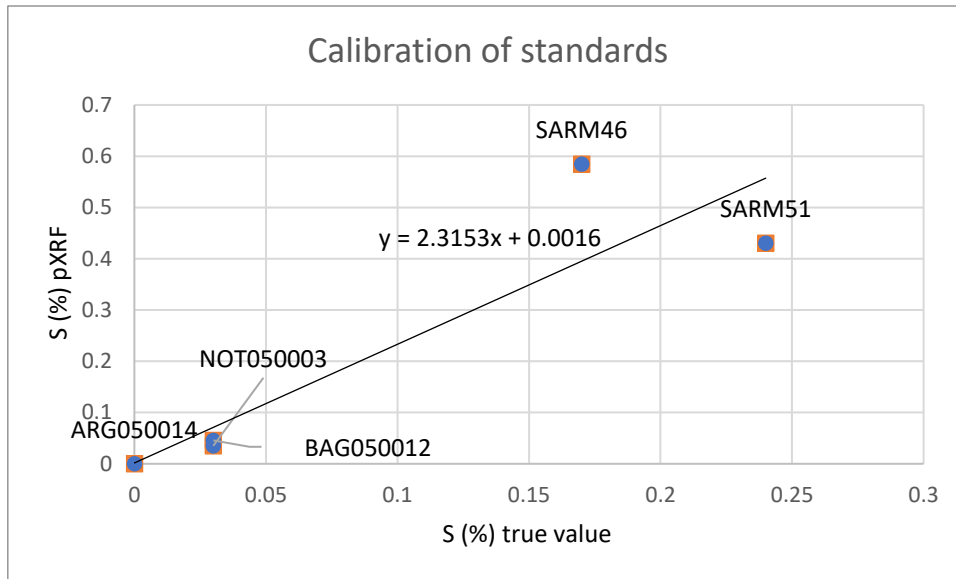|	S (%) pXRF 30 s	S (%) pXRF 60 s	S (%) pXRF 120 s	S (%) reported value
NOT050003	0.035	0.0372	0.0374	0.03
BAG050012	0.0456	0.0366	0.0322	0.03
ARG050014	0	0	0	0
SARM51	0.4306	0.402	0.4244	0.24
SARM46	0.58475	0.5696	0.5265	0.17

Figure 7 The pXRF measurements of the powdered standards plotted against the true sulphur concentrations. The linear regression shows that the concentrations from the pXRF measurements are more than twice as lareg as the true concentrations.

4.2.4. Choosing beam time for the pXRF

To choose the beam time for the analysis the shortest beam time, 30 s, was compared to the longest beam time, 120 s. When plotted against each other (Fig. 8) the linear regression is close to one which suggests that increasing the beam time more than 30 s does not improve the results.
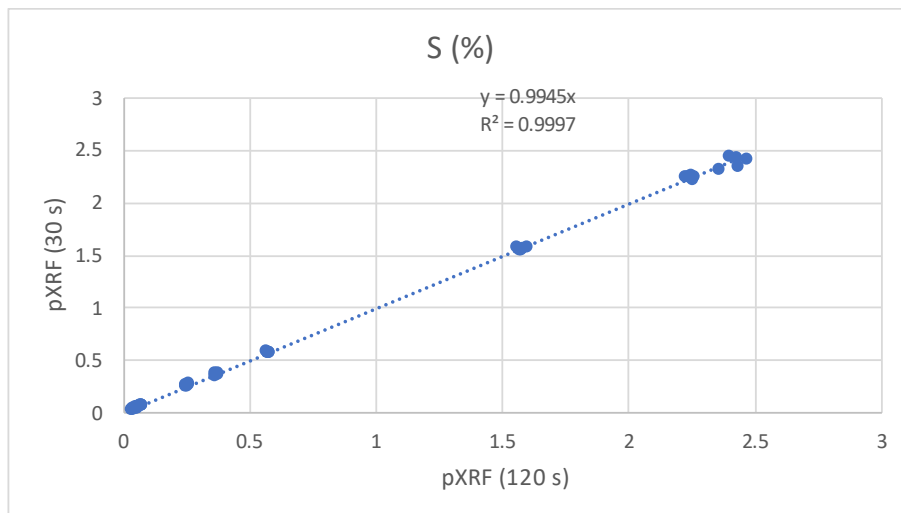
Figure 8 Average of five measurements with XRF. 30 seconds beam time against 120 seconds beamtime. The linear regression is almost 1 which shows that the results are similar for both settings

To test the repeatability of the settings, 25 measurements on each of the samples TEN200143A, TEN200156A, and SPN200173A, were made (Fig. 9). For TEN200143A and TEN200156A which were the samples with higher sulphur concentrations there was no large differences in variance and standard deviation between different beam times. For the low sulphur concentrations in sample SPN200173A there was a decrease in standard deviation and variance when the beam time was increasing. Since the effect was not very large and only effected the sample with low concentrations setting 1 (tab.1) with a beam time of 30 s was chosen for the final field work.
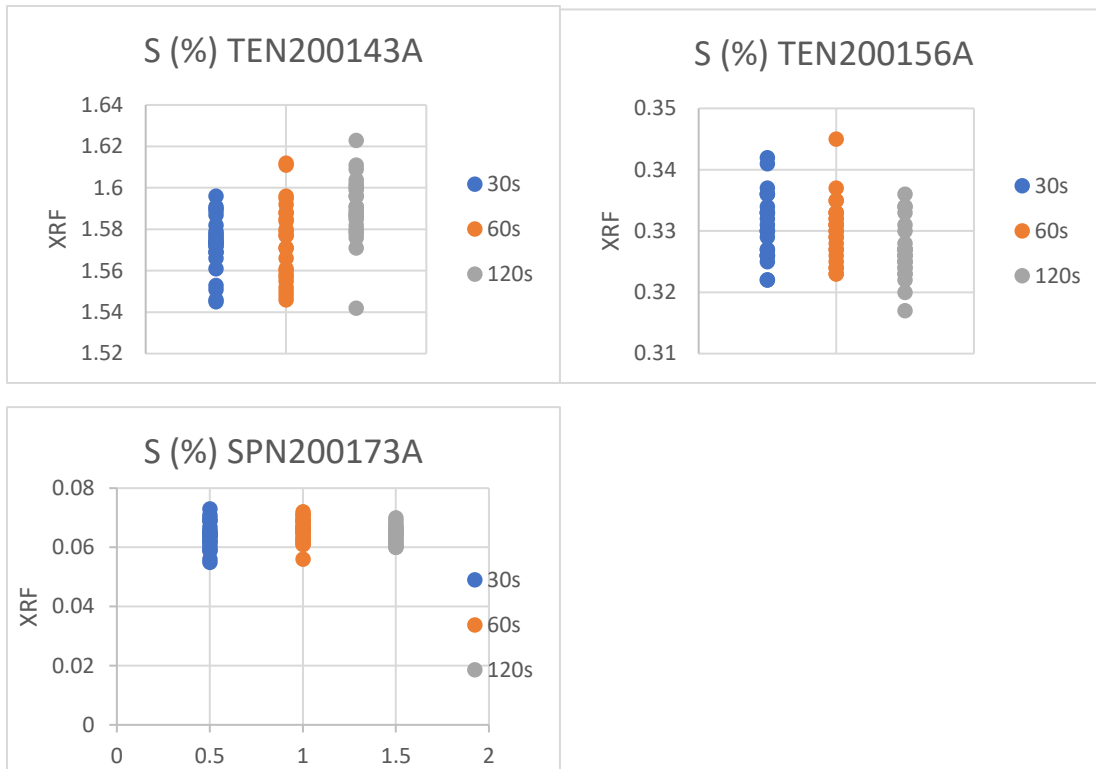
Figure 9 25 measurements of TEN200143A, TEN200156A and SPN173A with different beam times.

4.2.5. Applying the method on rock samples

The first measurement directly on rock surfaces were made in the lab with small rock samples that represent the same sites as the previous analysis. In sample TEN200156A the concentration measured with pXRF is higher compared to the laboratory IR analysis. In TEN200159A the measurements are also higher, but the results are more similar. For samples TEN200158A, UJB200041A and, SPN 200173 A the results of the pXRF measurements are lower compared to IR results.

Table 5 Rock samples of TEN200156A, TEN200158A, UJB200041A, SPN173A and TEN200159A. Average, standard deviation and, variance after 25 XRF measurements

Sample	TEN200156A	TEN200158A
Rock pXRF (S %)	0.74	0.16
Standard deviation	0.518	0.124
Varience	0.105	0.015
Reported value (S %)	0.48	0.43

Sample	UJB200041A	SPN200173A	TEN200159A
Rock pXRF (S %)	0.029	0.063	0.058
Standard deviation	0.015	0.041	0.013
Varience	0.00003	0.0027	0.00013
reported value (S %)	0.09	0.1	0.05

4.3. XRF measurements and observations in the field

The results from the field work are presented as graphs where the average of three measurements are plotted with an error bar that represent the standard deviation and the measurement error given by the instrument.

4.3.1. SPN200221B

SPN200221B was a small outcrop, approximately a meter long and half a meter high (Fig. 10). The rock was a quartzite with rust-coloured weathered surfaces. The metasedimentary rock around the main outcrop had medium crystal size and was lighter and more quartz rich. Close to the sample this was mixed with a fine crystalline dark rock (Fig. 11). The second area also contained fine crystalline darker enclaves (Fig. 12). The data from SGU shows that the S-concentration is 2.32 % and the pXRF results (Fig. 10) are 2.033 % S.
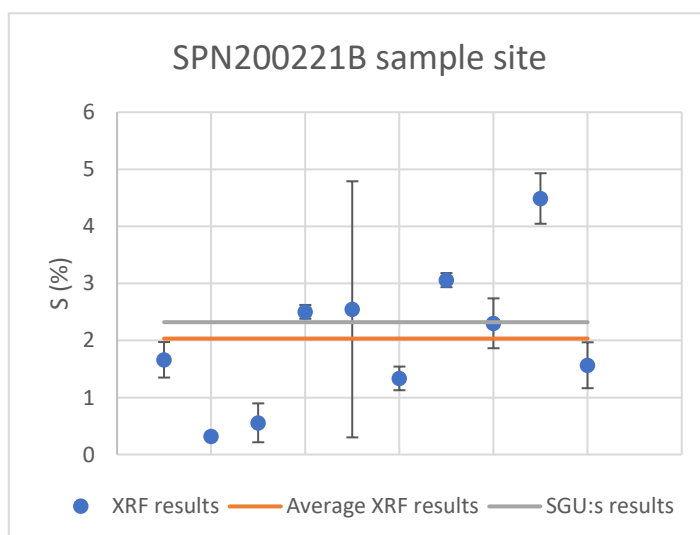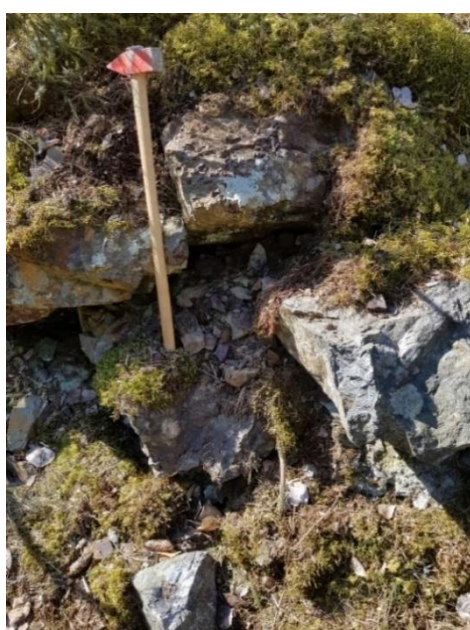
Figure 10 Sample site SPN200221B, image of the site and results of the pXRF measurement were three measurements close to each other are presented with an average and the standard deviation of the three measurements as the uncertainty

In the area with weathered surfaces outside the SPN200221B outcrop the average pXRF results are 0.247 %. (Fig.11)
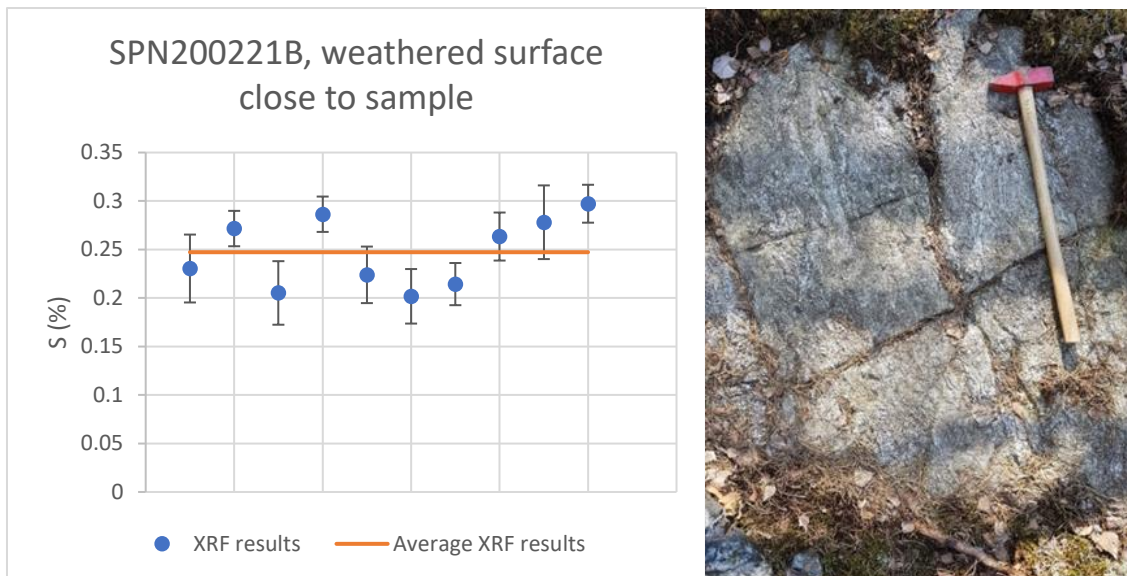
Figure 11 Area close to samples site SPN200221B image of measuring site and pXRF results

The enclaves in the area outside the SPN200221B outcrop the average of the pXRF results (Fig. 12) are 0.239 %.
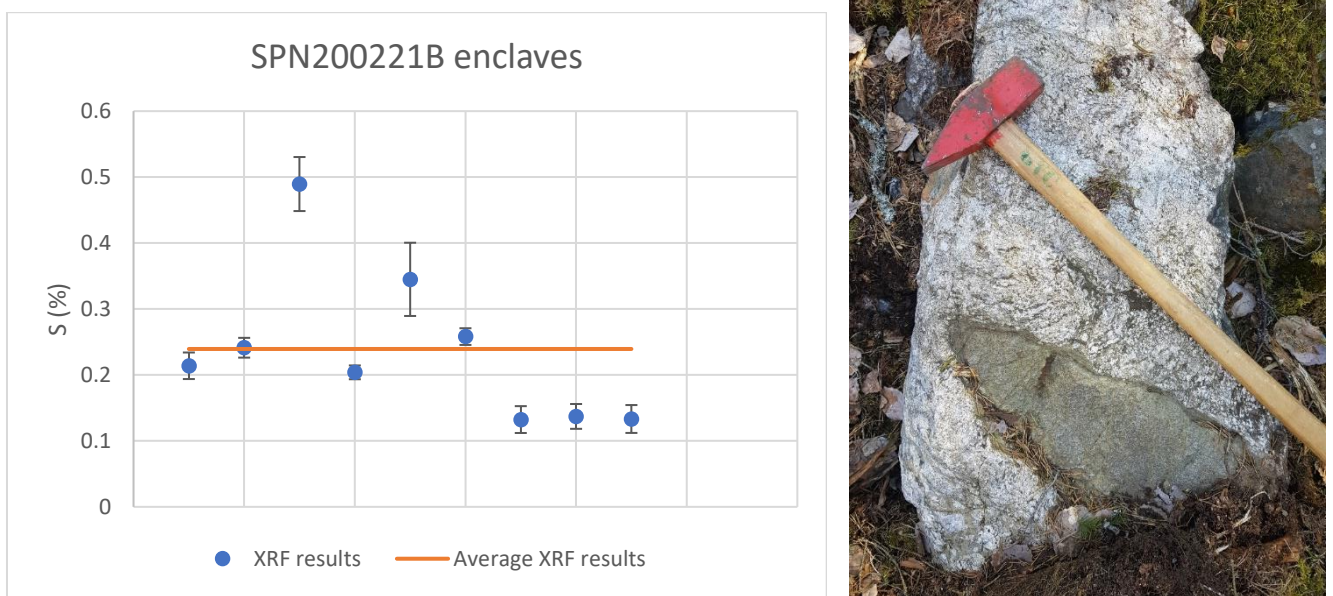
Figure 12 Enclaves in the area around samples site SPN200221B, image of measuring site and pXRF results

4.3.2. TEN200143A

TEN200143 is a small outcrop about 2 m wide 1 m high. The rock is metasedimentary very weathered and rust-coloured fine crystalline and biotite rich. It was sometimes difficult to find fresh surfaces to measure on, therefore the hammer was used to create new surfaces to measure on (Fig. 13)

Figure 13 Sample site TEN200143A. Most surfaces were weathered, to get fresh surfaces to measure a geological hammer was used.

The results from the laboratory are 2.34 % S and the pXRF results on the weathered surfaces (Fig. 14) are 2.590 % S and the unweathered surfaces are 2.751 % S.
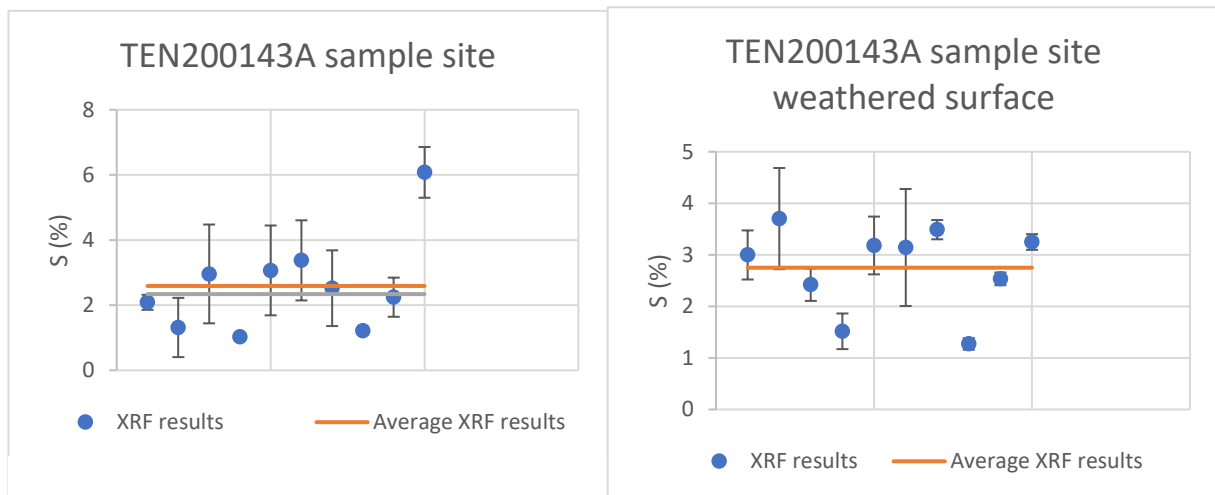
Figure 14 pXRF measurements from sample site TEN200143A on weathered and unweathered surfaces

In the area around the sample site the rock was more coarse crystalline and quartz rich. There was a pegmatite, and quartz veins and small lenses where the rock was darker and more fine crystalline. Everything was rust coloured (Fig. 15) the average of the pXRF measurements was 0.377 % S.
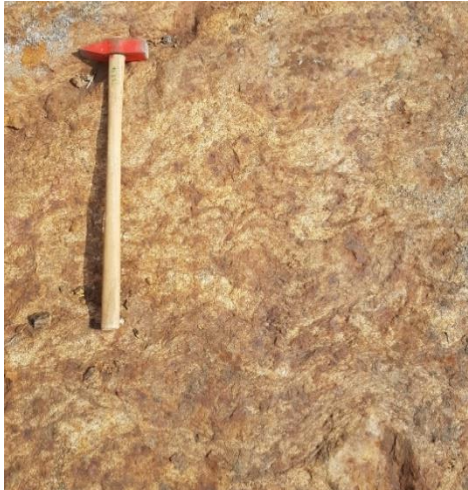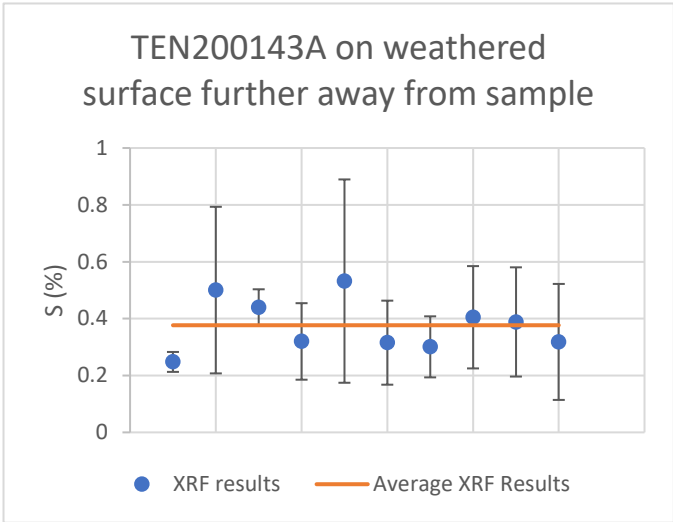
Figure 15 Area around TEN200143A image of the site and pXRF measurements

4.3.3. TEN200156A

TEN200156A was in a weathered area of metasedimentary rock. It was rich in quartz and mica; some garnets were observed, and pyrite crystals were seen in the faults (Fig. 16). It was difficult to find good surfaces to measure since the rock fell apart in already existing faults. The lab results from the area are 0.48 % S and the average of the pXRF measurements 0.205 %.
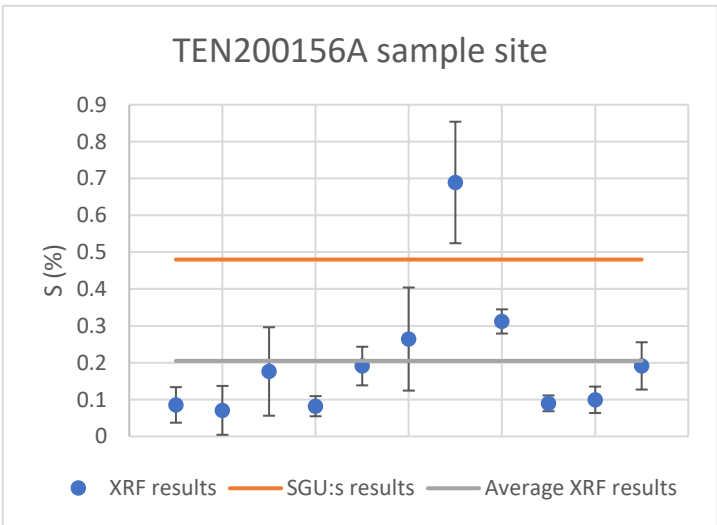
Figure 16 Sample site TEN200156A, image of the site and results of the pXRF measurements

PXRF measurements on a weathered area nearby (Fig. 17) had the average pXRF result 0.334 %.
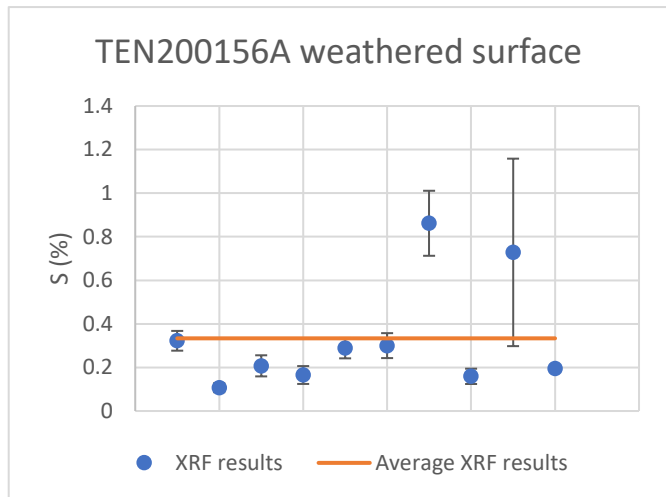
Figure 17 Near sample site TEN200156A, image of the site and results of the pXRF measurements

In addition to the measurements along two profiles that were about 2 m long were made. Profile 1 was made along the yellow pipe and profile 2 was made where there was a trace in the rock just left of profile 1 (fig. 18).

Figure 18 Road cut close to TEN200156A where pXRF measurements were made along two profiles

The results were smoothed in Excel to avoid and are presented in figure 19. This way of measuring shows the variation in the rock wall.
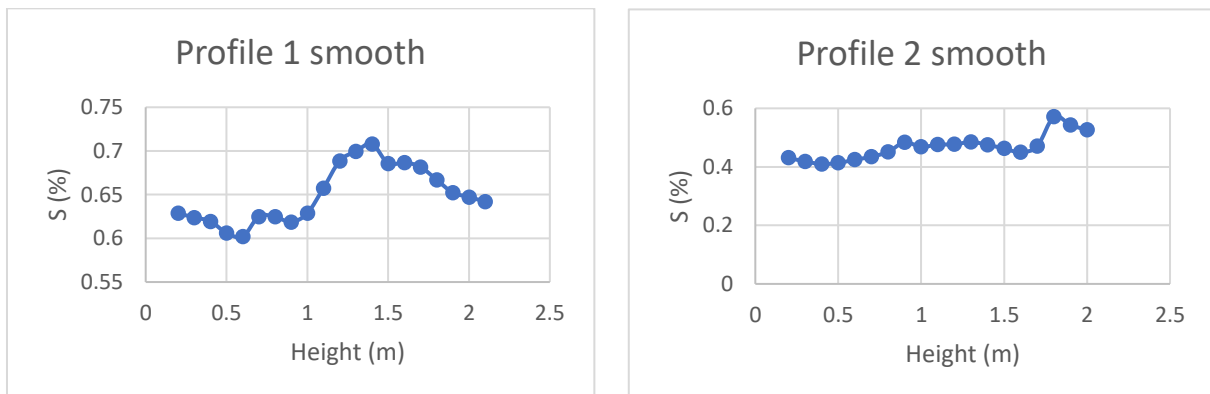
Figure 19 Profiles of pXRF measurements along a roadcut, that were smoothed to avoid nugget effects

25

4.3.4. TEN200158A

The rock in TEN200158A was similar to the previous rock TEN200143. It´s a biotite rich sedimentary gneiss that is very weathered in the faults. It is quartz rich has quartz veins, garnets, and lenses with partially melted material (fig. 20).

Figure 20 TEN200158A, weathered metasedimentary rock that fall apart in weathering planes

The lab results for TEN200158A are 0.43 % S and the pXRF measurements in the area, shown in figure 21 has an average of 0.400 % S.
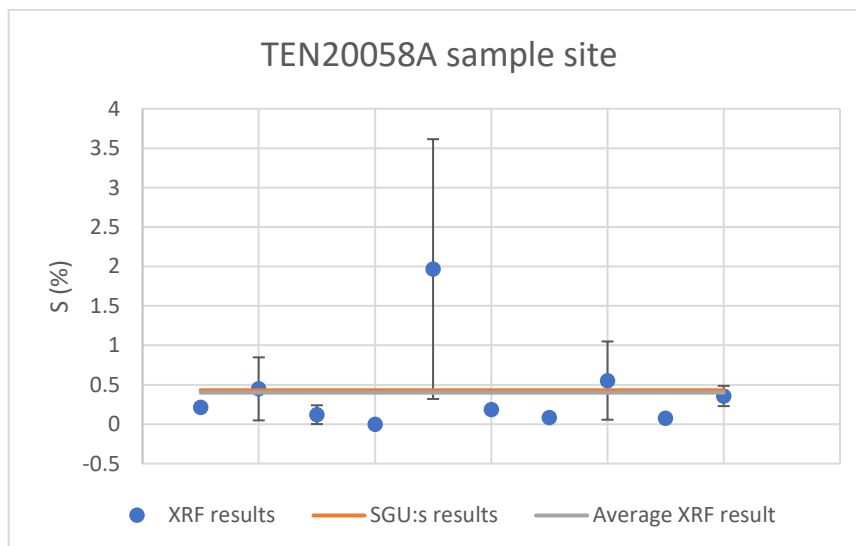
Figure 21 pXRF results for measurements at TEN200158A. Ten spots were measured with three measurements on each spot, the spots are plotted individually with the standard deviation shown in the error bar.

Three more measurement series with different amounts of rust coloured, weathered materials were made (fig. 22)

Figure 22 Weathered surfaces where measurements were made close to TEN200158A

The pXRF results from the weathered surfaces near TEN200158A (fig. 23) were 0.435 % S for surface 1, 0.214 % S for surface 2 and 0.098 % S on surface 3.
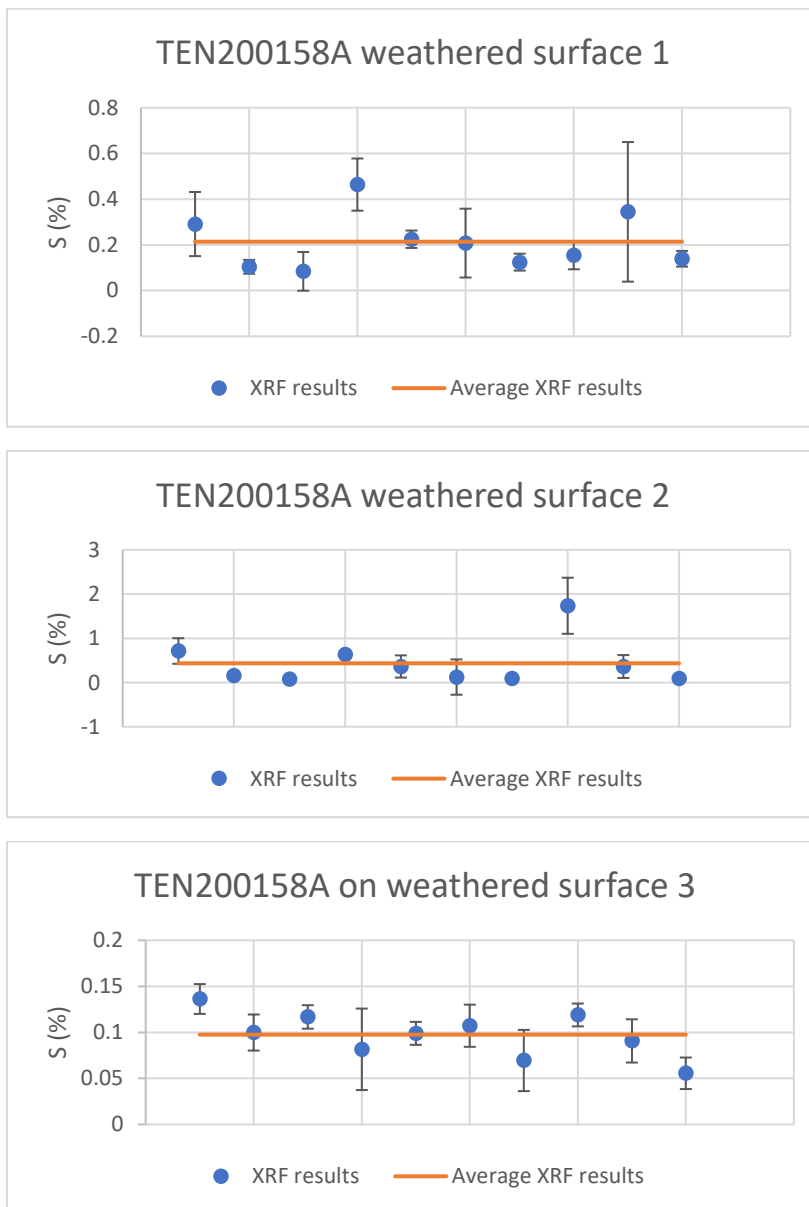
Figure 23 Results of the pXRF measurements on weathered surfaces near TEN200158A

4.3.5. UJB200041A

UJB200041A is a fine crystalline meta sedimentary rock it is biotite rich and there is pyrite in the fractures (fig. 24). The laboratory data shows 0.09 % S and the pXRF data 0.123 % S.
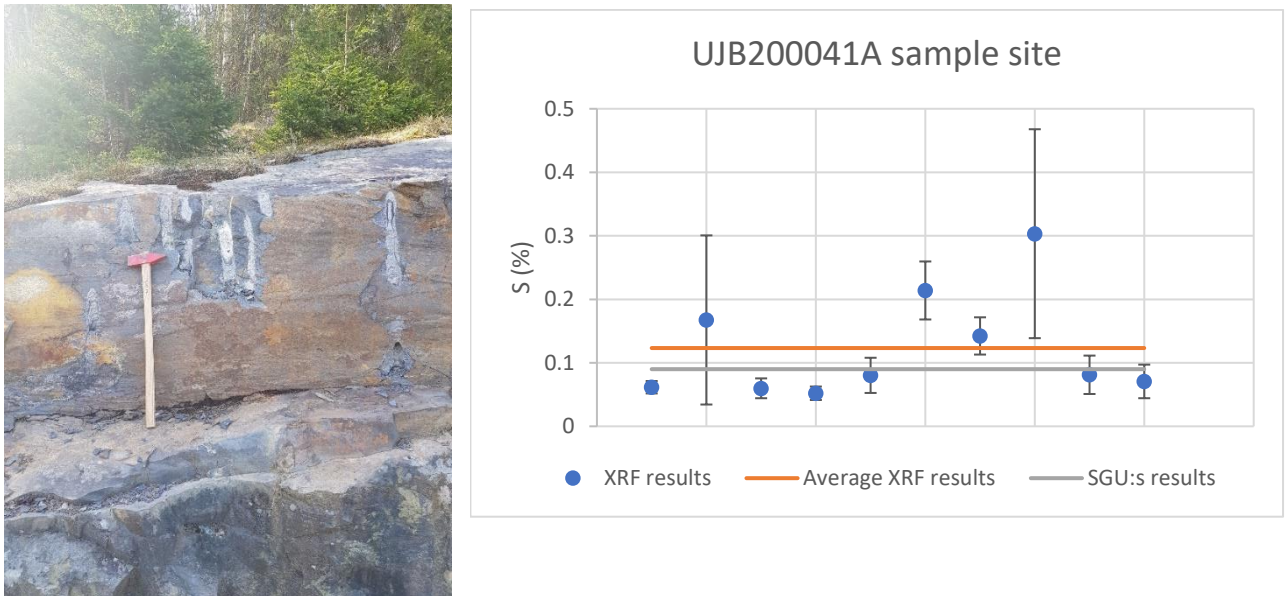
Figure 24 Sample site UJB200041A, image of the site and results of the pXRF measurements

Measurements on weathered rock just above the sample site (fig. 25) were also made. The pXRF results were 0.321 % S.
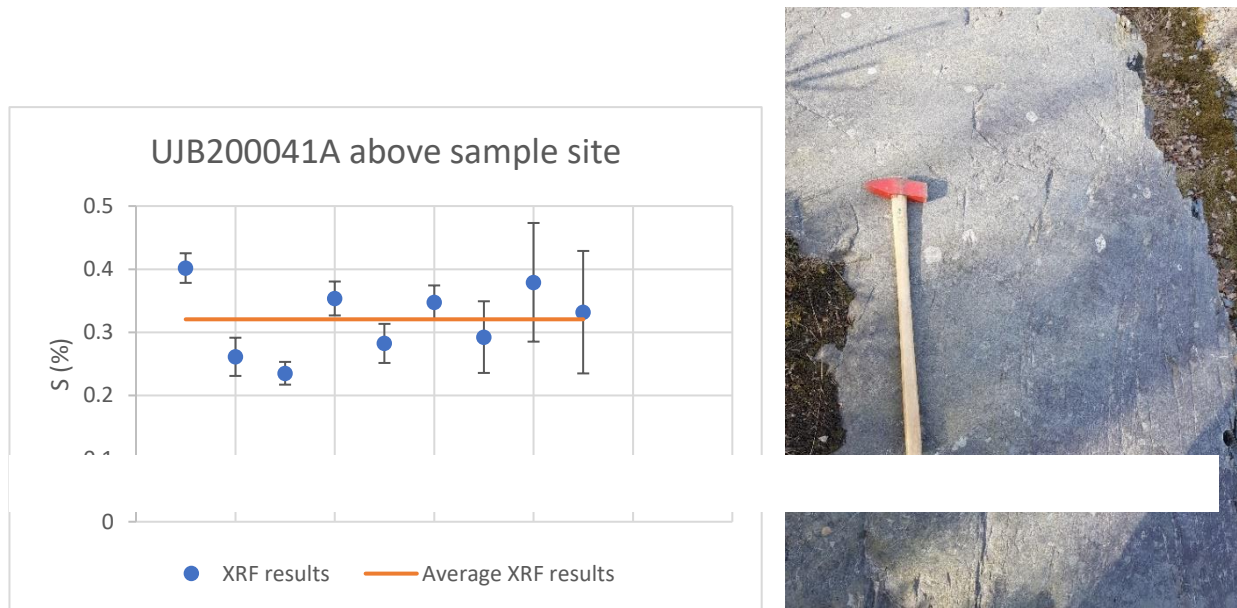
Figure 25 Above sample site UJB200041A image of the site and results of the pXRF measurements

4.3.6. Summary of all measurement sites

Figure 26 shows the results of the pXRF measurements made on the sample sites plotted against the laboratory data. The linear regression is close to one which, but individual measurements have small differences between lab and field.
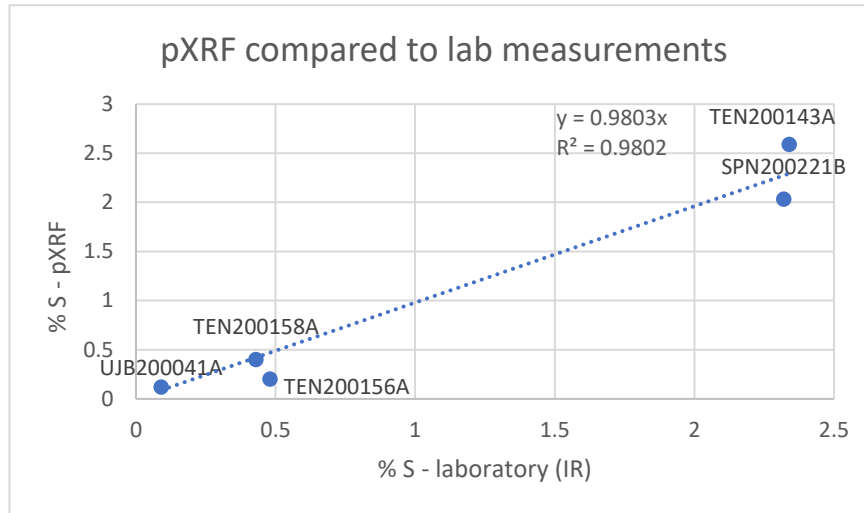
Figure 26 pXRF measurements made in the field plotted against the laboratory measurements on the same sites

4.3.7. Measurements of light elements

The pXRF cannot measure the concentration of light elements. Therefore it will interpret no signal as light elements. The concentrations of light elements were lower when the powder in the lab was measured (Fig. 27) which means that more signal was lost in the field compared to the lab.
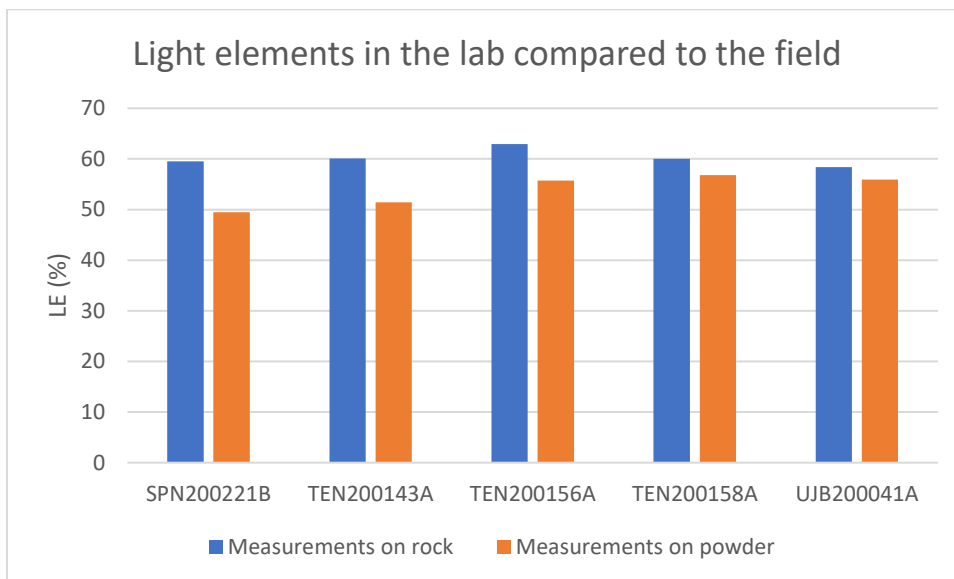
Figure 27 Light elements (LE) measured with pXRF on powder in the laboratory compared to field measurements.

5. Discussion

The pXRF measurements in Ostlänken area gave similar results as the IR measurements made in the laboratory which is a promising result for making a method using the pXRF. However, there are some uncertainties which will be discussed in this chapter.

5.1. Discussion of the method

The focus of the method was comparing the IR and the pXRF results. Therefore, it was important to get familiarised with the pXRF, and make sure that the pXRF measurements were comparable to ground truth data at the SGU sample sites. However, when using the method, it should be a priority to get as much measurements as possible from geologically interesting sites. Discussion about the use of an pXRF to measure sulphur in bedrock will be presented below.

5.1.1. Calibration and preparation

The calibration of the pXRF is important to get valid results. The samples used for calibration should be of the desired rock type as samples from other areas might not work (Hagelia & Fjermestad, 2016). This project was limited to the samples that were available, it would have been good to have a couple of more samples for the calibration especially with S concentrations > 0.5 %. The calibration is also only valid for the range that it was calibrated for which means that the calibration for higher concentrations is more uncertain. The standards were measured to get more data points in the calibration. However, that did not work (see 5.2.1). This could be caused by the standards coming from a different source compared to the samples. It is also possible that the quality of the standards where too low. SARM51 and SARM46 are certified reference materials, they are however not certified for sulphur which means the reported concentrations may vary. The SGU standard are not really standards they are reference samples used by SGU evaluate and compare different analyses (Ring, 1989).

The containers used for the calibration were smaller than a standard pXRF cup. Theoretically this should not impact the measurements as sulphur is a lightweight element that have a low characteristic energy that doesn't go very far into the material. The advantage of smaller cups would be that less material was required if one were to make a powder in the field. In the end, this project was limited to measuring on rock surfaces so that was never a problem. However, if other elements should be analysed at the same time it could be preferential to use a larger container made for XRF analysis.

Getting the optimal beamtime for the pXRF was another factor of the project. To get as many measurements as possible the beam time should be kept as short (30 s), but the results could potentially improve with longer beamtimes. However, the results could probably improve more by adding more measurements which is why 30 seconds was used for this project. No time shorter than 30 seconds was tested, it is possible that an even shorter measurement time could be used. The tests of the beamtime can be divided into two parts testing if the results are affected by beam time, and if the repeatability is affected by beam time. Therefore measurements on the powders in the laboratory were made with three different beam times to compare results. Three sample with different sulphur concentrations were selected to do even longer measurement series to test repeatability. Increasing the beam time should theoretically increase the repeatability.

The rock samples were studied to get an idea about how the method was working while measuring directly on a rock surface. The largest issue with that were that the rock samples were too small

compared to the original sample and there is no way of telling if those rocks where representative of the sample as a whole.

5.1.2. Sampling in the field

One of the key aspects of obtaining correct results is the sampling. Regardless of whether the sampling is done for lab testing or in situ testing, choosing sample sites is going to require knowledge of the geology to get representative samples. The volume analysed with one measurement is very small. Since the sample volume is so limited it is also important to make multiple measurements on each site and the possibility to make a lot of measurements is one of the big advantages with the method. For the sample area measurements were made in ten places that where evenly distributed and seemed to represent the sample well. It was also important to notice any local nugget effects, therefore three measurements were made at each spot. It is relevant to know how big the nugget effect is to be able to make an interpretation if there is one very high sulphur concentration detected.

While comparing the pXRF results with the laboratory data, the exact same areas were analysed with the pXRF that had previously been analysed by the lab. To get an appreciation of how local the effects of a sulphur nugget could be, every data point consisted of three measurements that were made close to each other. It is possible that the extra measurements were not necessary for every site, but it is easier to compare the results if the same protocol is used everywhere.

Some sample areas were easy to find, and it was clear where the rock had been removed and there were a lot of surfaces to measure on. At other sites, (TEN200143A and SPN200221B) the rock had been falling apart along already existing fractures that which made measurements harder. Additional measurements were made on other surfaces in the area surrounding the sample sites. These measurements could not be used to compare with any other data, but it can provide information about how the sulphur content can vary in an area. The two profiles near TEN200143A were for example made to further test the resolution of the method.

5.2. Discussion of the results

The results will be discussed in the chapter below. Overall, the pXRF method is working well. There are still risks of potential errors especially related to sampling which is something that needs to be taken into consideration when using the pXRF data.

5.2.1. Results from the lab work

There were two types of data provided by the laboratory, ICP-MS and IR. For sulphur contents > 0.1 % the two data sets were very similar. However, for very low concentrations ICP-MS was giving lower sulphur concentrations. This means that even when measured in an accredited lab there are uncertainties for measuring low concentrations of sulphur. These low concentrations are probably not very relevant for environmental applications, but it is a factor to consider when evaluating the pXRF method.

The calibration curves didn't have many data points due to lack of data. However, the data fit well on a linear regression, which gave an indication of the scale value for calibration. The results were very similar, regardless of what beam time was used. When making 25 measurements (fig. 9) the variance was decreasing when the beam times were increasing but only when the sulphur concentrations were low. Since the improvement from using a longer beam time was small and only relevant for low concentrations of sulphur, it was concluded that 30 s was enough to get sufficient results. For the

aim of this paper the possible improvement of adding more measurements would be larger than the potentially small measurement errors on low sulphur concentrations.

The measurements of the standards were giving higher results with the pXRF compared to the laboratory IR and the field samples were giving lower results with the pXRF compared to the laboratory IR. These differences in the pXRF measurements can depend on, for example: differences in crystal size (should be > 50 µm) or differences in minerology (Hagelia & Fjermestad, 2016). In this case it is probably the difference in mineralogy. These samples were therefore discarded when making the calibration.

5.2.2. XRF artefacts

During the calibration there were two measurements on SPN200221B and SARM51 that were measured during 60 s (tab. 6) that seemed different than the other identical measurements. That could be explained with a phenomenon called escape peaks. When the X-ray hit the silica in the detector the silica absorbs some of the energy from the X-ray resulting in a beam energy that has between lowered by the characteristic energy of silica peaks (Tanaka et al., 2017). In this case the results are similar except for one where sulphur concentration is too low and calcium concentration is too high. This could be because the instrument is interpreting some of the signals for the sulphur as escape peaks from calcium. The artefacts are easy to find in a series of measurements but if only one measurement is made it is a good idea to keep an eye on the calcium concentrations so that inaccurate measurements can be identified and removed.

Table 6 Two measurement series where one measurement inaccurate

SPN200221B, 60 s beam		SARM51, 60 s beam	
S (%)	Ca (%)	S (%)	Ca (%)
1.803	3.012	0.436	0.936
1.888	1.932	0.426	0.833
1.848	2.582	0.416	0.936
1.883	1.747	0.313	26.974
1.542	19.339	0.419	0.857

The pXRF provides a concentration of light elements (LE) which represents the signal that could not be detected as a certain element. This means that the light elements can be interpreted as an indication of the quality of the measurement (Fig 27) This means that some of the signal that can be detected in the lab is disappearing, probably due to less ideal measurement conditions. Such as the surface of the rock not being flat enough to have contact with the devise or not being able to hold the pXRF still for the required time. Another aspect for field measurements is water content. The measurements made for this paper was during dry conditions, but water can have an effect on the pXRF measurements.

5.2.3. Results from the field work

Most of the results from pXRF measurements at the sample sites had similar results as the original samples. The largest error was at site TEN200156A were the results of the pXRF measurements were 0.205 % and the laboratory measurements were 0.48 %. This was one of the sites where it was not very clear were the sample was taken and it was difficult to find surfaces to measure. It is important to know that there is a risk of measurements errors around 100 % is high and this is something that needs to be taken into consideration during remediation. The total amount of measurement sites

was limited by the data available. However, 5 sites are not enough to make statistical conclusions. Which means that the method should be studied further before being used as the only method measuring sulphur concentrations.

When looking at the error bars certain measurement sites have a large variation or a nugget effect where one measurement can be very high because the pXRF was directed towards a sulphide. This is especially common when high sulphur concentrations were detected (fig. 10, 14, 16, 21). If there are not enough measurements made these effects could skew if measurements either hits or misses these sulphide nuggets. Therefore it is important with multiple samples.

At sample sites TEN200143A, TEN200156A, and UJB200041A the measurements on weathered rock around the sites often resulted in higher concentrations compared to where the original sampling had been made. In SPN200221B the measurements on the weathered surfaces where not possible to complete since the out crop was too small and in TEN200158A the results were varying depending on the amount of weathering (fig. 23). This could indicate that there have been some secondary processes close to the surface that increased the sulphur concentrations. If measurements are made where there are no cuts where deeper rock has been exposed, it is important to note that the measurements can only be representative of the surface and not concentrations further down.

The three measurements sites on weathered rock close to TEN200158A are especially interesting because they show how different results can be if the measurements are made just a couple of metres away from each other (fig. 22). The highest sulphur concentration measured is 0.435 % and the lowest 0.098 %. This shows that the exact location of the samples has a great effect on the results. This is relevant no matter if the analysis is made with an pXRF in the field or sent away to a laboratory. The advantage with the pXRF is that it is possible to cover a larger area with measurements compared to sending a rock sample away for every analysis.

5.3. The pXRF indicates areas in need of sulphide remediation

The pXRF results can only be an indication of what the actual sulphide content of the rock is. The accuracy of the method is less than other methods, the sample size is small, and the sulphides are heterogeneously distributed. The measurement accuracy can be improved by combining the technique with other types of measurements, but those will also only be covering a small part of the rock. Therefore it is important to always evaluate the potential environmental risks by acidification and leaching in any areas where there is a risk of high sulphur concentration. At this moment there are no limits for sulphur concentrations in bedrock. The method using pXRF is working very well in indicating areas with a sulphur content of 0,5 % and above.

There are different options for remediation of areas where construction is made through bed rock with high sulphur concentrations. It is important to note that while sulphur concentration is important for acidification it is not the only factor. The size of the excavated rocks is important because it affects the surface area where reactions can take place. Remediation can be done by removing the small grain sizes. Furthermore, the sulphides need to be exposed to water and oxygen for any reaction to occur and a buffer can be used to counteract the acidification. Therefore, remediation depends on clast size and can be done by adding an impermeable layer of for example clay or adding a buffer such as calcium carbonate.

However, there is a risk of measurements errors of at least around 100 % and possibly even more. This means that when remediations are calculated it needs to be considered that the sulphide content could be higher than what was measured with the pXRF. Even if methods with larger

sampling volumes are used to confirm the results, that will make the risk of sampling errors smaller, but still possible.

The advantages using the pXRF for sulphur measurements is that a lot of elements can be analysed at the same time as sulphur, for example different types of metals. The instrument provides a quick indication if the concentrations given by the measurements are not interpreted as an absolute truth.

5.4. Method proposal - Suggestions for evaluating sulphide content in bedrock with pXRF

The results from the pXRF measurements on sulphides in Ostlänken area are promising for use as an initial screening of an area. While the scope of this project does not cover all aspects to make a complete measurement protocol some suggestions for further use and study of the pXRF measuring sulphides can be made.

5.4.1. Preparation and calibration of the pXRF

To obtain reliable data with the pXRF, calibration of the instrument is important. The calibration requires laboratory data from the area that is going to be evaluated. The calibration curve should have enough data points to make a good linear regression and it should cover sulphur concentrations in the entire range that is required for a project.

5.4.2. Measurements and quality control

One of the largest challenges of the method is the sampling. PXRF measurements should be made across the layers of sedimentary bedrock. In metasedimentary rock the measurements should be made on a fresh surface. For this project measurements were made at sites where large rock samples had already been removed which exposed surfaces to measure on. Only in a couple of cases a hammer had to be used to get a fresh surface. Measurements on weathered surfaces can also be a good complement but weathering processes can have affected the sulphur concentration.

Using a hammer to get an unweathered surface to measure can be a great tool. However, there must be an awareness that there could be surface effects of the sulphur content, and the concentrations at further depth are unknown. If there are any already existing road cuts in the area that could be a good place for measurements. Since the window of analysis of the pXRF is small and the sulphide distribution is heterogenous, many measurements are required to achieve sufficient results. The shorter beam time (30 s) is enough and will allow the user to make more measurements during testing. Furthermore, it is important to have a good geological knowledge of where the potentially high sulphur concentrations can occur, for example alum shales (Daniels, 2003) (Hagelia & Fjermestad, 2016) and mica rich sedimentary gneisses (Tullborg, 2001).

More measurements are going to lower the uncertainties. Nevertheless, there are still risks of large sampling errors that needs to be considered. Thus, some samples should always be sent to a laboratory for further analysis. This would be especially important for samples that might need further remediation.

6. Conclusions

Ostlänken is going to be a part of Sweden's new main railway between Södertälje and Linköping. Rock samples along the new railway have been analysed for sulphur content to manage risks of acidification during construction. To this end it would be beneficial to have a quick method of measuring sulphur directly in the field to enable faster decision making during the construction of Ostlänken and similar projects. This thesis has investigated the use of an pXRF for field analysis of sulphur concentrations.

The pXRF method requires careful calibration with powdered material from the rock types that are going to analysed. These samples need to have a known concentration of sulphur, e.g. from being analysed in a lab by a conventional method such as ICP-MS or IR. Furthermore, several (at least ten) measurements must be made on the same site since each pXRF measurement only cover a small volume.

In this project, measurements with the pXRF were compared with samples along Ostlänken that were previously analysed by a lab. The comparison was promising and show that the pXRF can give reliable indications of how much sulphur there is in the rock. It is important to recognize that the concentrations given by the pXRF are only representative of a small sample and since the sulphides can be distributed heterogeneously there are risks of sampling errors. However, this is also true for any method when sampling in large area.

The method using the pXRF provides results on the same day which leads to faster decision making. More measurements can be made faster compared to sending rock samples away to the lab. However, the results are not as strong due to the small sample size. In conclusion, the pXRF is an easy-to-use instrument it is quick and provides meaningful results. The pXRF could be a useful tool for measuring sulphides during construction as long as the user takes the risk of sampling errors into consideration. This could be a useful method for initial screening of an area to determine where further analysis should be made.

7. References

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