Environmental impacts of early metallurgy in Moshyttan

A study of one of Europe’s oldest blast furnaces, using three lakes records in Nora bergslag

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Abstract
The aim of this study was to assess the environmental effects of Moshyttan, one of the earliest known blast furnaces in Europe (ca. 11th century). The study was based on the analysis of three lake records in the immediate surroundings of the smelter. Fickeln lies directly downstream and is the main recipient of waterborne pollution. Mosjökälla lies directly upstream and served as the main water reservoir for the water-powered bellows. Kramptjärnen lies 1 km to the NW in a separate catchment and acts as a reference. The data includes 31 elements analyzed by X-ray fluorescence spectroscopy (XRF), organic content inferred from loss on ignition (LOI), biogenic silica (BSi) modeled from Fourier-transform infrared spectroscopy (FT-IRS) for all lakes and diatom counts for Fickeln. Two other studies provided dating of slag from the smelter and pollen- and geochemical data from Fickeln. The results show that the metallurgy and associated activities (e.g. agriculture, forest grazing and charcoal production) led to eutrophication and alkalization in Fickeln. This is indicated by the diatom community that in the background is dominated by benthic genera indicative of oligotrophy and dystrophy (Frustilia, Brachisyra and Eunotia) that during the active smelter phase is replaced by pelagic genera indicative of eutrophy (Aulacoseira and Asterionella). BSi also decreases after smelter establishment, which speculatively could indicate an overall decrease in diatom production. At the same time, a suite of elements commonly associated with iron processing (Fe, Pb and Zn) increase in the sediment.

Keywords: Diatoms, Biogenic silica, Geochemistry, Pre-industrial metallurgy, Environmental effects.
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1 Background

Paleolimnology has long been used to study the environment. While some of the early work produced theories about lake development and eutrophication that were later falsified, much of the work has stood the test of time. One good example is the study by Pennington (1943) that is surprisingly modern. The sampling techniques include overlapping cores with a complimentary surface core extracted with a pipe that’s shut from the top. The analyses combine physical properties (color, water content, dry density, and particle size), the chemical analyses available at the time (LOI and BSI) and species composition of diatoms. Despite a misconception regarding diagenesis the study manages to argue convincingly for the human role in eutrophication and make reasonable estimation of the age of the Holocene.

Another study, which widened the field of paleolimnology, is done by Mackereth (1966). It is a thorough review of the sediment geochemistry of the English Lake District. Elements are traced back through diagenesis to their origins and clever element ratios are used to provide new insights into how lakes interact with and reflect their surroundings.

Despite the success of these early studies, it was not until the environmental problems of the seventies and eighties that the full usefulness of paleolimnology became apparent. One such issue was the acidification of lakes in northern Europe. The scientific community had studied the acidity of lakes (Almer 1974) and precipitation (Barrett and Brodin 1955), but it was with the development of diatom-inferred historical pH that humans could be declared the perpetrator. These models were developed by Meriläinen (1967) but the adaptations by Renberg and Hellberg (1982) were very influential. Another issue studied successfully using paleolimnology is eutrophication. As seen above, the fact that humans played a role in eutrophication was known, but again the development of diatom transfer models was needed to provide the temporal perspective. The study by Lotter (1998) is a good example of such models.

Another important field in paleolimnology that build more on the geochemical work of Mackereth, is the study of metal pollution. An early work by Aston et al. (1973) showed how airborne Hg-pollution can spread widely to lakes without any discernable point sources. They thereby showed that regional Hg emission likely has been present in England since AD 1400 and that the emissions increased during the industrial revolution. Förstner (1976) makes a good synthesis of contemporary studies of metal pollution. He discusses both air- and waterborne pathways and the complex issues of metal solubility, complexation and biotic availability that are so important to determine which metals that are dangerous and under which circumstances. Most work on metal pollution so far had been done on a local to regional scale and often focused on pollution following the industrialization. Renberg et al. changed that in 1994 when they connected 5000 years of lead history in Swedish lakes to what historians knew about historical lead production, thus showing the need for perspective when studying pollution.

In contrast to how useful diatoms are as indicators of acidification and eutrophication, using them to complement studies of metal pollution has proven to be harder and mostly viable in extreme cases. One such example is a paper by Ruggiu et al. (1998) that examines a lake in Italy where a factory dumped around 60 tons of Cu per year into the lake without any simultaneous acidification and eutrophication. This resulted in diatom frustule deformations
and shifts in diatom community composition. Another example is Salonen et al. (2006). They studied a lake subjected to acid mine drainage (AMD) from extensive tailings (leftover material from a modern metal extraction method) where they record similar responses as Ruggiu et al. (1998) to the diatom community: decrease in total production, shifts in species composition and frustule deformities. These lakes are extreme in their exposure, something the writers themselves are keen to point out.

All in all the main contribution from the field of paleolimnology is the perspective of time that it provides. In a landscape littered with lakes like Sweden, it is an invaluable tool when environmental issues need that perspective.

2 Introduction

As the study of pollution developed from local and industrial pollution via antique and continental pollution, more examples of human impact were discovered. One great study of the Pb pollution history of South America is done by Cooke et al. (2008). They analyze the history of local Pb pollution in four lakes in the Bolivian and Peruvian Andes and find that pollution from metallurgy has been present near one of the lakes from around AD 400. Another interesting result is that in some of the lakes, the early pollution coincides with no known imperial states. This suggests that metallurgy can develop in, or at least spread to, decentralized societies.

While the pollution from metallurgy can be seen on continental scales, other effects are much more local, as a study by Pèlachs et al (2009) shows. They studied a Spanish Pyrenean valley where processing of the local iron ore required charcoal that was produced in kilns spread all over the valley. The charcoal kilns are numerous during the Antiquity, disappear after the fall of the Roman Empire and reappear in great numbers during late Middle Ages and the Renaissance. During this later phase the gradual increase in charcoal production lead to increasing deforestation and changes in composition.

In the Bergslagen area of Sweden, mining and metallurgy has been a part of society for a very long time (Damell 2002 and references therein), possibly as early as 700 BC. A paper by Bindler et al. (2009) studied this region and compared Pb concentrations and isotope ratios in the sediment of eight lakes in the in the Kolbäcksån catchment, three sites in Lake Mälaren, and two sites in the Baltic Sea. This data was also related to Pb concentrations and isotope ratios of seven raised bogs. Their results indicate that the region has a complex history of pollution with a strong signal of airborne Pb pollution from continental Europe, but data from two of the bogs show some influence of bergslagen Pb during the 15th and 16th centuries, with isotope ratios indicating that around 15 % of the Pb coming from Bergslagen. The lakes however show greater influence of Bergslagen Pb, which is most pronounced in Kalven and Noren, two lakes near the historical iron mining and processing town Norberg. In these lakes Pb starts to increase around AD 920 and peaks around AD 1500 with isotope ratios showing that around 90% and 40% respectively of the Pb in excess of the background comes from Bergslagen. In Noren this increase in local Pb is also accompanied by a suite of elements: As, Cd, Cu, Fe, Hg and Zn. The difference in Pb sources between the peat bogs and the lakes show that the mining and metallurgy in Bergslagen had a diffuse impact on the region and a more pronounced impact of the local aquatic environment.
Studying specific elements like Pb and effects such as deforestation is interesting on its own, but to understand the environmental effects of metallurgy – especially earlier processes on smaller scales – the scope has to be wider. De Laender et al. (2012) examined several lakes around Falun, a town of historical Cu mining and processing, and compare the species richness and evenness of diatoms to sediment metal concentrations and pollen-based land cover. They found no negative effects of metal load on the diversity of the diatom community. The likely explanation to this is the fact that land-use intensified at the same time as metal-loads increased and that this positive effect over-wrote whatever negative effect the metal pollutants might have had. On the other hand they admit that biodiversity might not be the best measure in this instance because the community indeed might change without it being reflected in the indexes, as long as the new species are as many as the ones they replaced. They do indeed see some changes in the dominating species, which is expected when a change in local land-use introduces more nutrients to the lake. As is discussed in the Background, nutrient availability is one of the most powerful structuring mechanisms on diatom communities.

The environmental effects of the earliest iron production were likely small, but the invention of the blast furnace changes this. As described by Magnusson (2002) based on the excavations of Lapphyttan in Norbergs Bergslag, a blast furnace is an advanced feat of engineering. The basic structure is a vertical pipe that is filled with alternating layers of iron ore and coal and at the bottom there are three holes; one where water powered bellows insert air, one where slag drains out and one where the pig-iron is extracted. In direct connection to this smelter lay all the facilities where all the secondary processes took place: heating and crushing before smelting and decarburization (removing of carbon) after smelting. The process included many experts, mostly “bergsmän” – the owners and supervisors of the smelter – and smiths that produced the wrought iron, the form in which most of the iron was traded. The process required constant attention so hired workers kept the smelter going in shifts continuously for weeks, likely at least a month. For the rest of the year charcoal kilns produced new charcoal and more iron ore was prepared for the next run. At the same time local agriculture and forest grazing was required to feed the community, but there is still much debate over which occupation was the most important for the bergsmän, agriculture or metallurgy.

These blast furnaces were spread all over the Bergslagen region and during the Middle Ages they were around 200 (Magnusson 2002). One such medieval smelter was located in “Noraskogs bergslag”, today in the municipality of Nora in the westernmost region of Bergslagen. It has been excavated by Wetterholm (1999) and he found the remains of a pipe (from the smelter itself), several pits where the secondary processes had taken place and three large heaps of slag. Though this site runs Mosjöbäcken, a stream that supplied the water that powered the bellows. It drains Mosjökälla, a lake that served as the main reservoir, holding possibly a whole year of runoff. Downstream lies Fickeln, a small forest lake that eventually drains into Mälaren. Wetterholm radiocarbon dated coal encased in slag from the heaps and found two lumps close to the bottom of one pile which were dated to AD 960 ± 80. This means that Moshyttan could predate Lapphyttan, the previously considered the oldest known smelter in Europe. Lidberg (2012) has studied this very question already and found paleolimnological data to support Wetterholm. The smelter was active for around 700 years, until 1720 when it was closed (Johansson 1881, Landerholm and Eriksson 2001).
One question has yet to be asked, especially considering what paleolimnology does best: how did such an early industrial process affect the surrounding landscape in general and the aquatic system in particular? All in all the people around the smelter had multiple of ways to impact their surroundings: agriculture, charcoal production, direct emissions from the smelter (both through the air and water) and water regulation.

2.1 Aim
The main objective of this study is to assess how the environmental conditions surrounding Moshyttan have changed in response to historical metallurgy-related activities. This objective can be split into three questions: 1) What were the background conditions in the three lakes in the immediate surroundings of Moshyttan? 2) How did these conditions change after the smelter was established? 3) How did this affect the diatom community and lake-water quality?

To address these questions I have studied three lakes in the immediate vicinity of the smelter. 1) Fickeln, a forest lake which lies 600 m downstream of Moshyttan. 2) Mosjökälla, a headwater lake a few hundred meters upstream of Moshyttan. 3) Kramptjärnen, a shallow lake 1 km NW of Moshyttan that is part of another catchment than the other two lakes. A previous thesis by Lidberg (2012) has studied the geochemistry and, for a part of the record, pollen composition of Fickeln, with regards to the timing of the establishment of Moshyttan. I have analyzed major and trace elements in Kramptjärnen and Moshyttan and re-evaluated the geochemistry of Fickeln. I have also analyzed BSi using Fourier-Transform Infrared Spectroscopy (FT-IRS) in all lakes and in Fickeln I have counted diatom on a low sample resolution covering the last 3000 years.
3 Materials and Methods

3.1 Site description
The three lakes analyzed in this study lie in the immediate vicinity of Moshyttan. The archeological data here is presented by Landerholm and Eriksson (2001) but is also available at the Swedish national heritage board (Fornsök 2012). Kramptjärnen has three basins that drain to the west and are a part of the Vänern/Göta älv catchment. The eastern basin that is sampled in this study is shallow with only one small inlet from the north that drains a small system of mires. Around this basin there are two remains of human settlement of unknown age and two small mines where Iron ore was excavated, also of unknown age. Mosjökälla is a deep headwater lake with one inlet draining a small mire. This was the main water reservoir for the hydro powered bellows of the smelter and thus its outlet in the southern end was dammed. In connection to the smelter that lies around 200 m downstream of the outlet there are two homesteads of unknown age. Written sources first show them in 1688, but they are likely older. Fickeln lies around 600 meters downstream of the smelter. Because the smelter used hydropower for the bellows it is located right at the stream, as shown in Wetterholm (1999). This also means that the slag heaps are so close to the stream the at least in the later phases of operation the stream ran through them. Fickeln has no recorded signs of human settlement in its direct vicinity. Table 1 contains coordinates of sampling sites and depth of each lake and Figure 1 shows a map of the smelter surroundings.

Figure 1. Map depicting the immediate surroundings of Moshyttan, including the three lakes examined in this study.
Table 1. Coordinates (RT90) and depth at the sampling site of each lake.

<table>
<thead>
<tr>
<th></th>
<th>Fickeln</th>
<th>Mosjökalla</th>
<th>Kramptjärnen</th>
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<tbody>
<tr>
<td>East</td>
<td>1443912</td>
<td>1443343</td>
<td>1442544</td>
</tr>
<tr>
<td>North</td>
<td>6611876</td>
<td>6612891</td>
<td>6612992</td>
</tr>
<tr>
<td>Depth (m)</td>
<td>11</td>
<td>20</td>
<td>3.3</td>
</tr>
</tbody>
</table>

3.2 Sampling and analysis

Sediment cores were taken from all three lakes in March 2012. The uppermost less-consolidated sediment was sampled with a gravity corer (Renberg and Hansson 2008) down to 40 cm depth. On site, the core was sectioned into 1 cm slices and stored in plastic sample boxes. A Russian corer with a diameter of 8 cm and a length of 1 m was used to sample as far down as possible through the rest of the sediment with an overlap between cores of roughly 20 cm. This field-estimated overlap was later adjusted based on the geochemical data. The cores were wrapped in plastic and aluminum foil and stored in wooden boxes for transportation, after which everything was stored in a walk-in cooler at + 5°C.

Before analysis the Russian cores were prepared. First the outer couple of millimeters of the half-cylinder shaped core, which may have been disturbed during sampling were scraped off. Then the cores were sectioned into 1 cm slices and stored in plastic sample bottles. All samples were freeze-dried and gently homogenized with a spatula. Even though samples are 1 cm thick, they are numbered by their bottom depth, thus a sample referred to as 54 cm means sediment from 53 to 54 cm.

The analyses were performed in several consecutive steps which allowed information from earlier steps to be used when samples were selected for the more time-consuming steps. All steps are described in detail later. The first analyses were XRF, Hg and LOI. Combined these yielded a series of major and trace element concentrations and estimated organic matter content. Based on these data, sample levels were selected for radiocarbon dating, the second analysis. The third step was FT-IRS analysis and based on these data biogenic silica was modeled. The last and most time-consuming step of the analysis (at least on a per-sample basis) was the counting of diatoms. For Fickeln the FT-IRS and diatom counting produce new data while the other analyses were presented by Lidberg (2012). However, the XRF data are slightly different after a re-evaluation of the calibration curves.

The method used in this study to determine the chemical constituents of the sediment is wavelength-dispersive XRF using a Bruker S8-Tiger WD-XRF. The XRF technique is a relatively modern analysis used on liquids and solids (often prepared as pellets bound by various media). It has applications in both the industry and the sciences, for example in archaeology, earth science and geology (West et al. 2011) and paleolimnology (Boyle 2000). The analysis is based on a calibration created at the Department of Ecology and Environmental Science at the Umeå University (Rydberg, article in prep.). Calibration curves for 31 elements are based on analysis of 10 standard reference materials. Approximately 0.5 g of dry sample was analyzed in a plastic sampling cup (ø=20 mm) with a spectrograde mylar film bottom. The major elements analyzed were Al, Ca, Fe, K, Mg, Na, S and Si. The minor elements that were analyzed and that existed in quantities above the detection limit (detection limit and accuracy for all elements in Table 2) in both lakes were Ba, Br, Cl, Cu, Mn, Ni, P, Pb, Sr, Ti, V, Y, Zn and Zr. In addition the data for Mosjökalla includes Co, Ga and
Rb. The data for Fickeln from Lidberg (2012) include the same set of elements as Mosjökälla. In total 226 samples were analyzed and after overlaps had been removed this amounted to continuous profiles with 83 samples from Mosjökälla and 105 from Kramptjärnén. To that data 79 samples from Fickeln are included.

Table 2. Calibration detection limits and analysis accuracy. Calibration limits are presented in % for major elements and ppm for minor elements. Analysis accuracy is measured as average (n=10) percent deviation from certified values. The standard reference materials are NCS-DC73310 and NCS-ZC73002.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Ca</th>
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<th>Mg</th>
<th>Na</th>
<th>S</th>
<th>Si</th>
<th>Ba</th>
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<td>ppm</td>
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</tr>
<tr>
<td>Detection limit</td>
<td>0.5</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>4.1</td>
<td>30</td>
<td>1.2</td>
<td>39</td>
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<tr>
<td>Accuracy (%)</td>
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<td>8.8</td>
<td>2.2</td>
<td>4.4</td>
<td>2.4</td>
<td>6.9</td>
<td>7.5</td>
<td>1.6</td>
<td>9.6</td>
<td>37</td>
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<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Ga</th>
<th>Mn</th>
<th>Ni</th>
<th>P</th>
<th>Pb</th>
<th>Rb</th>
<th>Sr</th>
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<th>V</th>
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<tr>
<td>Detection limit</td>
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<td>1.8</td>
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<td>6.0</td>
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</tr>
<tr>
<td>Accuracy (%)</td>
<td>2.3</td>
<td>2.4</td>
<td>1.1</td>
<td>27</td>
<td>12</td>
<td>4.0</td>
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<td>9.2</td>
<td>2.7</td>
<td>8.6</td>
<td>3.6</td>
<td>4.9</td>
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Mercury concentrations were analyzed with a Perkin Elmer SMS 100 system, but instrumental breakdown caused a reduction in the analysis accuracy of the instrument and some missing data. Data are still included as information values, but they have not been used in the statistical analyses and specific concentrations cannot be used quantitatively. To save sample material, the ash left over after the Hg-analysis was weighed to estimate loss-on-ignition. That is, rather than the conventional temperature range of 450 to 550 °C LOI was measured after combustion at 800 °C. If carbonates are present when combustion is done at this temperature they would volatilize and release CO₂, meaning that the result would not be an estimate of only organic matter (Santisteban et al. 2004), but the local bedrock is not known to contain any carbonates (Wetterholm 1999) so it was reasonable to assume that LOI here represents organic matter. Furthermore, the FT-IRS analysis is sensitive to carbonates so this assumption could be evaluated at a later stage. Carbonates were found to be lacking in all but three near-surface samples and these are affected by liming which is discussed later in this paper. The precision of the LOI analysis is consistently good with an average difference between replicates of 0.9% (σ=1.0%, n=22). Because LOI was analyzed along with Hg some samples were likewise affected by the mechanical problems with the Hg-analyzer and thus lack LOI data. These samples along with those that contained carbonates have their organic content estimated statistically later.

The FT-IRS analysis records the absorption at every other wavelength from 399 nm (violet light) to 3751 nm (mid-infrared). The basic principle is that different molecules absorb radiation at different wave-lengths and through training data-sets this can be used to quantify specific molecules. In preparation for the FT-IRS analysis a subset of samples from the three lakes was selected, with the highest temporal resolution at the onset and during early phases of estimated human impact. This means the late Medieval and early Renaissance period. 110 samples were analyzed in total; 33 from Fickeln, 35 from Mosjökälla and 42 from Kramptjärnén. The samples were ground in an agate ball mill and mixed with spectrograde KBr so that 0.22 ± 0.002 % of the mixture-mass was sediment (11 mg sample to 500 mg KBr). This dilution prevents very high absorbance values that could have left little or no light to detect. Samples were then analyzed in a Bruker Vertex 70 with an attached HTS-XT
screening unit located in a temperature controlled room at 25 ± 0.5 °C. Samples were scanned 128 times and the average spectra were reported. For a more detailed methodology see Rosén et al. (2011).

For the diatom analysis a subset of seven samples was selected from Fickeln that highlighted the period before and during the time that the smelter was operative according to Johanson (1881), Wetterholm (1999) and Lidberg (2012). Samples were digested in 10% Hydrogen peroxide at 60 °C for six hours to remove organic material, washed once with deionized water, treated with hydrochloric acid to remove the rust-colored iron hydroxides and finally washed 4 more times with deionized water. The final suspension was thoroughly mixed and a few drops were placed on a coverslip and left to dry overnight after which the dried film was carefully fixed with naphrax. For a more detailed methodology see Renberg (1990).

Identification and counting of at least 200 frustules per slide was done using a Leica DMLB microscope according to the Süsswasserflora von Mitteleuropa (Krammer and Lange 1986, 1988, 1991 A, 1991 B).

### 3.3 Dating, modeling and statistics

Statistical analysis and modeling were important parts of this study. Some analyses, such as the age-depth relationship and BSi modeled from FT-IRS, produce parameters that are integral parts of the project. Others, like principal component analysis (PCA), are tools to reduce the complexity of large data sets and extract significant patterns from the large number of parameters. Finally, some analyses allow certain absent values to be estimated so that as much information as possible is available for the other statistical analyses. All tests are done are at α = 0.05, but the nature of this study is exploratory and they must be viewed in that context.

From Mosjökälla and Kramptjärnen a total of nine samples were dated at the Tandem laboratory at the University of Uppsala. Based on these data the module CLAM (CLassical Age Modeling, Blaauw 2010) in R version 2.11.1 was used to model the age-depth relationship. This model uses the whole probability distribution of each calibrated 14C age, a way to take into account the inherent uncertainties that arise when radiocarbon dates are translated to calendar years. It produces a best fit age for each sediment level along with a 95% confidence interval expressed as minimum and maximum age. The graphical output shows the probability distribution of calibrated age for each dated sample, the best fit curve and confidence interval (in this case approximately ± 60 years).

As a complement to the dating, the first time that spruce pollen appears in large quantities in the sediment was determined; this was a relative estimate of the first sample where spruce pollen is strikingly present. This timing of spruce immigration can be used as a chronological marker (Giesecke and Bennett 2004) to evaluate how the age-depth models of the three lakes match each other. It is also possible to compare the immigration in these lakes to data available in the European Pollen Database (2013), where the nearest lake is Lilla Gloppsjön (Almquist-Jacobson 1994). To ensure comparability, the uncalibrated dates presented for Lilla Gloppsjön are used in a new model based on the method described above.

The BSi model is based on a method developed by Rosén et al. (2011), where the absorbance at specific wave-length intervals in the FT-IRS-spectra, which correspond the silica cell-wall of diatoms, is compared to a training dataset of 725 samples from 91 Swedish lakes. The
modeling was performed by partial least-squares regression in SIMCA-P+ 12 and has a coefficient of determination ($r^2$) of 0.85.

Several LOI values (n=14) in the data-set of Fickeln and Mosjökälla were missing or contained errors as is mentioned earlier. These were modeled statistically so that the organic matter content for all samples could be used for further statistical analysis. Five random reference samples with LOI data were excluded from each lake so that the model could be evaluated. For Fickeln the best model was non-linear and based on Br, an element associated almost exclusively with organic material (Rasmussen et al. 1998). The model follows Equation 1 and is represented graphically in Figure 2. Both the factor and the power are significant ($p_{\text{factor}} = 3.1 \times 10^{-12}$, $p_{\text{power}} = 9.3 \times 10^{-16}$) and this model is slightly better at predicting the reference values than the best linear model. The average discrepancy between modeled and actual values is 5.6 % for the non-linear model compared to 5.9 % for the linear.

Fickeln: $\text{LOI} = 16.87 \times \text{Br}^{0.202}$

(1)

Mosjökälla has two LOI outliers that represent surface samples that are affected by direct liming to the lake surface (Länsstyrelsen Örebro län 2010), which caused the Ca concentrations in the surface sediment to increase by an order of magnitude. These samples were excluded and new values were modeled along with the missing samples. The best correlation for Mosjökälla was with Cl and the best model was also non-linear (Equation 2, Figure 2 b). Both parts of the model are significant ($p_{\text{factor}} = 3.0 \times 10^{-3}$, $p_{\text{power}} = 9.3 \times 10^{-10}$) and it is better at predicting the reference values than the best linear model. The average discrepancy between modeled and reference is 8.5 % compared to 9.4 % for the linear.

Mosjökälla: $\text{LOI} = 4.165 \times \text{Cl}^{0.377}$

(2)
The PCA is often called dimension reduction. Essentially it is multiple regressions performed in all multiple dimensions; in this case each element or diatom genus in the lake sediment is one dimension. This study also used z-score transformed data. This means that instead of the absolute values, the input was how many standard deviations that individual value deviated from the mean, thus each parameter is scaled equally and given equal weight. Each regression is called a principal component, which represents a unique fraction of the total variance. This study extracted principal components with eigenvalues >1. Along with the principal components, the PCA produces two important parameters: scores and loadings. For each principal component and dimension there is one score that explains how much of the variance of that dimension that is explained by that principal component. In more common statistical terms, the score is a correlation coefficient between an element and a principal component. Because all elements have scores for all principal components the scores can be used to group the elements. This study assumed that a correlation coefficient >0.5 (or < -0.5) was relevant for grouping.

For each level of data that the different dimensions are measured in (in this case each measured sample depth) and each principal component, there is a loading. This loading represents how much that sample level is influenced by that principal component. If the data input was in relative units, as in this study, then the loading represents, on a relative scale, how much that group of elements differs from their average. If the group of elements that co-varies has common properties, then the loadings can be used to explain the relative development of that group in more abstract terms. For instance, as shown later in this thesis, one principal component in each lake groups elements associated with silicate erosion together. The loadings then represent a parameter that can be used instead of the concentration of each and every element in said group – the number of dimensions has been reduced. Because the PCA picks up on relative changes over time, it is important to select samples to highlight relevant periods.

The PCA in this study uses samples between 1000 BC and AD 1800, to focus on the period between AD 960 and 1720 where the smelter was operational (Johansson 1881, Landerholm and Eriksson 2001) without including industrialization and with a reasonable amount of background. For each lake two analyses were done, one on all samples and one that only included samples with data for both geochemistry and BSi. This was done to provide loadings for all sample levels and scores for all variables. The different analyses on each lake proved to be so similar that they are used interchangeably: when looking at the parameters as a conglomerate, BSi is important and the subset PCA is used, but when looking at the loadings of individual sample levels, it is important to include all samples so the whole-set PCA is used to provide greater resolution.
4 Results
The Results section of this paper goes through core correlation, depth adjustment and dating of Mosjökälla and Kramptjärnen. Then the new data for Fickeln – BSi, PCA (of all available data) and diatoms – are presented along with some of the geochemistry from Lidberg (2012) for reference. Lastly all data for Mosjökälla and Kramptjärnen – geochemistry and PCA – are presented.

4.1 Core correlation, adjustment and dating
To merge the different cores into one continuous series they were wiggle-matched based on the depth measured on site and sediment composition, after which overlapping data were removed. Figure 3 shows each core and the concentration of two elements chosen to show the wiggle-matching.

In Mosjökälla five samples were dated. The sediment was rich in well preserved macrofossils so each date is based on a leaf fragment (species not identified). In Kramptjärnen four samples were dated based on bulk sediment. This means that when comparing these lakes to Fickeln, which was also dated on bulk sediment, events in Kramptjärnen and Fickeln could appear older because of the so called catchment effect. This effect is assumed to be caused by carbon that has been stored in the catchment (e.g. in soils or wetlands) before being deposited in the sediment, making the bulk dates appear older than the actual time of deposition. Uncalibrated 14C-ages are shown in Table 3 and the age-depth models in Figure 4. When dates are presented it is always the best fit. The age uncertainty increases with distance from a radiocarbon dated sample, especially when extrapolating below the oldest dated level. The average uncertainty (expressed as a 95 % confidence interval), excluding backwards extrapolation, is ± 60 years and the maximum is ± 135 years.

Based on these age-depth models the timing of spruce establishment can be used to compare and then validate the models. In Kramptjärnen spruce was established at a depth of 101 cm which is dated to 680 BC ± 70. The corresponding depth and date for Mosjökälla is 66 cm and 440 BC ± 80 and for Fickeln 117 cm and 650 BC ± 100. Compared to Lilla Gloppsjön, the nearest lake in the European pollen database (2013), which lies 22 km NNW of Moshyttan, where spruce was established at 740 BC ± 90 (Almquist-Jacobson 1994), both of the lakes dated by bulk sediment are within the margin of error of the reference. The differences between the age-depth models of the lakes in this study are discussed in depth later.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Depth (cm)</th>
<th>Type</th>
<th>Reference number</th>
<th>C-14 age (y)</th>
<th>± (y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mosjökälla</td>
<td>22</td>
<td>Leaf</td>
<td>Ua-44229</td>
<td>722</td>
<td>30</td>
</tr>
<tr>
<td>Mosjökälla</td>
<td>34</td>
<td>Leaf</td>
<td>Ua-44230</td>
<td>1069</td>
<td>30</td>
</tr>
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<td>Mosjökälla</td>
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<td>Leaf</td>
<td>Ua-44231</td>
<td>1797</td>
<td>33</td>
</tr>
<tr>
<td>Mosjökälla</td>
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<td>Leaf</td>
<td>Ua-43941</td>
<td>2789</td>
<td>45</td>
</tr>
<tr>
<td>Mosjökälla</td>
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<td>Leaf</td>
<td>Ua-43942</td>
<td>3386</td>
<td>30</td>
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<td>Bulk</td>
<td>Ua-44227</td>
<td>738</td>
<td>32</td>
</tr>
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<td>Bulk</td>
<td>Ua-44228</td>
<td>1148</td>
<td>31</td>
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<td>Bulk</td>
<td>Ua-43939</td>
<td>1566</td>
<td>30</td>
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<tr>
<td>Kramptjärnen</td>
<td>111</td>
<td>Bulk</td>
<td>Ua-43940</td>
<td>2768</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure 3. Core matching for a) Mosjökälla and b) Kramptjärnen. The first core in each was taken with an H/H sediment corer while the rest were taken with a Russian corer. The alternating black and grey lines are data for each separate core and the actual depth has been wiggle-matched to produce a single profile.
Figure 4: Age-depth models for a) Mosjökälla and b) Kramptjärnen, using linear interpolation and CLAM (Blaauw 2010) in R. The black line is best fit, the grey area is the 95% confidence interval and the small areas along the black line are the calibration probability distribution of each radiocarbon dated sample.

4.2 Fickeln

In the thesis by Lidberg (2012), which presents most of the data from Fickeln that will be used in this study, there are four cores that cover ¾ of the postglacial history of the lake. The sediment is brown gyttja with an average of 60% organic material and 12% Si. In the lower sections this silicon is almost entirely BSi. Lidberg makes a more detailed presentation of the geochemical data, but Figure 5 provides a selection of elements from the sediment together with the new BSi-data.

The PCA of the geochemistry data of Fickeln was done on all samples between 10 and 132 cm (BC 1100 to AD 1892, n=64) as well as the subset of samples with data for BSi (n=27). The all-samples PCA returned four principal components that explain 52, 16, 14 and 7% (89% together) of the variance of the data. The BSi-PCA also returned 4 PC’s that explain 52, 18, 13 and 8% (91% together) of the variance. Loadings of all principal components are presented in Figure 5 and scores are presented in two-dimensional matrixes in Figure 6.

PC1 has positive scores for elements associated with mineral matter: Na, K, Rb, Ti, Zr, Mg, Al, Sr, Zn, and Pb. It has negative scores for elements associated with organic matter: BSi, Cl, Br and LOI. The loadings for PC1 are very stable throughout most of the 3000 year sequence until 32 cm (AD 1630) where they increase drastically. They stay elevated until 16 cm (AD 1820) after which they return to values around 0. PC2 has positive scores for a group of elements often associated with iron ore processing (Bindler et al. 2009): Zn, Fe and Pb, as well as other elements: P, Co, Mn. It has negative loadings for BSi and Si. The loadings show a peak between 60 and 32 cm (AD 1150-1630). During this period certain elements of this group show large absolute changes. In comparison with the background averages, the peak in Fe (at 38 cm, AD 1560) is 8% units higher and the corresponding lowest point for BSi is 15% units lower.
Figure 5. Fickeln. A summary of the geochemistry from Lidberg (2012) plus BSi and PCA loadings. Note that the XRF data are based on a new calibration, so the absolute values are not exactly equal to the ones previously published. The grey lines mark important changes in sediment history: a=16 cm (AD 1820), b=32 cm (AD 1630) and c=60 cm (AD 1150).

PC3 has high scores for Ba, Sr, V, Al and Ca. These are associated mostly with mineral matter erosion but also authigenic precipitation (Engstrom and Wright 1984). The loadings for PC3 fluctuate around zero, but with greater variance than the other principal components. It has relatively low loadings between 84 and 50 cm (AD 340-1420). PC4 has positive scores for S and Cu and a negative score for Si. The loadings are stable through the whole sediment history until 20 cm (AD 1770) where they increase sharply. This means that little happens to PC4 within the periods of interest so whatever process is driving these changes in S and Cu is of low importance here.
The diatom analysis of Fickeln is shown in Figure 7, where all major genera are presented. A stable background is visible between BC 1100 and AD 810, when the community is dominated by Eunotia, Frustulia, Brachisyra and Navicula. From AD 1090 to 1470 these genera decrease and the community instead becomes dominated by Aulacoseira, Asterionella, Fragilaria and Navicula. After this the community returns to an in-between state dominated by Eunotia, Navicula, Achnantes and Frustulia. Table 4 provides ecological information about the eight genera that dominate the sediment at any point.

Table 4. A list of the eight Genera that dominate the diatom composition. Ecological information on habitat-, nutrient- and pH preferences is provided where it is available and classification is adequate. Loadings on PC2 (from the diatom-PCA below in the text) are a relative measurement of how the genus is affected during the period of active metallurgy in Moshyttan.

<table>
<thead>
<tr>
<th>Genus</th>
<th>Habitat</th>
<th>Nutrients</th>
<th>pH</th>
<th>Loading PC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frustulia</td>
<td>Benthic</td>
<td>1</td>
<td>Acid</td>
<td>-2.07</td>
</tr>
<tr>
<td>Brachisyra</td>
<td>Benthic</td>
<td>Oligotrophic</td>
<td>Acid</td>
<td>-0.93</td>
</tr>
<tr>
<td>Eunotia</td>
<td>Benthic</td>
<td>Oligo-dystrophic</td>
<td>Acid</td>
<td>-0.91</td>
</tr>
<tr>
<td>Navicula</td>
<td>Benthic</td>
<td>2</td>
<td></td>
<td>-0.17</td>
</tr>
<tr>
<td>Achnantes</td>
<td>Benthic</td>
<td>2</td>
<td>2</td>
<td>0.52</td>
</tr>
<tr>
<td>Fragilaria</td>
<td>Benthic</td>
<td>2</td>
<td>2</td>
<td>0.68</td>
</tr>
<tr>
<td>Asterionella</td>
<td>Pelagic</td>
<td>Eutrophic</td>
<td>Neutral</td>
<td>1.11</td>
</tr>
<tr>
<td>Aulacoseira</td>
<td>Pelagic</td>
<td>Oligo-Eutrophic</td>
<td>Neutral</td>
<td>3.29</td>
</tr>
</tbody>
</table>

1. No information available on ecology
2. The genus is ecologically diverse and this study does not have enough data on species to provide ecological information

a. Krammer & Lange-Bertalot 1986
b. Krammer & Lange-Bertalot 1991 A
c. Battarbee et al. 2011
d. Hutchinson 1967
e. Raynolds 1998
Figure 7. Percentage of total number of diatoms in Fickeln based on genus. Rare genera constituting <5% of the total count in every sample have been excluded and genera have been ordered by their loading to the second PC described below in the text.

The diatom data were also analyzed by PCA and the result is presented in Figure 8. The seven samples are 24, 46, 54, 62, 70, 78 and 132 cm, but they are labeled by sample year and plotted by score to the two principal components that explain 65 and 25 (90% in total) of the variance in the data. In the figure the loadings of each genus are also plotted. Because loadings go above one, they have been normalized to fit the scale. The second PC clearly separates the samples corresponding to the period when the blast furnace was active (AD 1090, 1310 and 1470) from the samples from before establishment (1100 BC, AD 540, 810) and after closure (AD 1730). It is also apparent that the most recent sample is very similar to the before-establishment group if the whole community structure is taken into account. The genera that affect PC2 the most have the loadings (not normalized): Aulacoseira (3.29), Asterionella (1.11), Fragilaria (0.68), Eunotia (-0.91), Brachisyra (-0.93) and Frustulia (-2.07).
Figure 8. Fickeln. PCA scores and loadings from the diatom-PCA. The seven filled circles represent each sample and values are scores of the first two components that explain 90 % of the total variance. Open circles are loadings for each genus. The scale has been normalized so that loadings do not exceed 1. The eight clustered circles without labels are GO, MR, NE, PE, SN, SB and TE.

4.3 Mosjökälla

The 4 cores from Mosjökälla do not cover the whole post-glacial history of the lake. If the dating is extrapolated backwards to the deepest sample at a sediment depth of 256 cm it was deposited ca. BC 5700. The whole sequence is brown gyttja of which 50 % of the weight is organic material and 17 % is Si, of which most is diatomaceous: BSi. The major, mineralogic elements of the sediment are: Ca, Fe, Al, S, K, Na and Mg. They are shown in Figure 9 along with a selection of minor elements (Zn, Ti, Pb, Cu, Cl and Hg).

The recovered sediment sequence starts around 1000 years after lake stabilization is visible in Kramptjärnen (presented below, chapter 4.4), so all of it is relevant as a background. Between 256 and 72 cm (5700-700 BC) conditions are stable with no systematic changes. Between 72 and 26 cm (700 BC-AD 1150) the redox-sensitive elements Fe and P show four distinct peaks. Many other elements clearly show similar patterns with four peaks, but in general the two more recent peaks are more distinct. These elements include: S, Al, Cu, Br and Mn (not shown). Between 46 and 26 cm (AD 400-1150) when the two more recent peaks occur, LOI increases by 25 % and Si decreases by 34 %. Pb deviates from the general pattern with the so-called Roman Pb peak (Renberg et al. 1994, 2001) at 56 cm (30 BC). This has little to do with local environmental effects, but is important as a chronological maker, which is discussed later.
Between 26 and 6 cm (AD 1150-1790) the sediment composition changes: BSi decreases sharply by 70% at the same time that LOI decreases by 34%. Many of the mineral matter associated elements increase: Si (32%), Ca, K (840%) and Na. BSi stands for the largest absolute change decreasing by 14% units. The minor elements Ti and Pb also increase and just as with Fickeln, the increase in Pb predates the other elements and starts at 34 cm (AD 970), 8 cm and 180 years earlier. Above 6 cm (AD 1790) the dating is uncertain due to the sediment being less consolidated. This greatly influences the age-depth model in the recent sediment and because the period has little relevance to the questions of interest in this study the patterns here are of no specific importance.

The PCA on all samples between 82 and 6 cm (1045 BC to AD 1790, n=41) in Mosjökälla reveals three components; two of them are very influential and explain 35% of the variance each, while the third explains 17% (87% together). The BSi-PCA with a subset of samples (n=16) similarly reveals three components of which two were especially influential (38, 35 and 17%; 90% all together). Loadings for all principal components are presented in Figure 9 and scores in Figure 10.

PC1 has positive scores for a diverse group of elements associated with both mineral matter and authigenic formation: Mn, S, Cu, Al, Sr, Fe, Ba, P, Br and Ca. The loadings show great variance throughout the whole period analyzed by the PCA. Like most its associated elements, the loadings pick up the two distinct peaks between 46 and 26 cm and the two more diffuse peaks below that. PC2 has positive scores for a group of elements associated with mineral matter: Rb, K, Pb, Zr, Ti, Mg, Na and Zn and negative scores for BSi and P. The loadings are stable until 26 cm (AD 1150) where they increase drastically. PC3 has positive scores for a group of biophilic elements: LOI, Cl and Br as well as for V, and a negative score for Si. The loadings increase steadily to a peak just before the 26 cm event, after which they drop back to pre-46 cm levels.
Figure 9. Mosjökälla. Major elements, six minor elements and loadings of each principal component. The grey lines mark important changes in sediment history: a=26 cm (AD 1150) cm and b=72 cm (700 BC).
4.4 Kramptjärnen
The seven cores from Kramptjärnen cover the entire post-glacial history of the lake, from isolation around 8000 BC to the present. The sediment is silty grey in the deepest decimeter after which it turns into dark, brown gyttja for the rest of the Holocene. The sediment is highly organic with on average 36 % of the dry weight lost on ignition. Almost as much (28 %) is Si, of which the majority is organic in origin (diatomaceous), i.e. BSi. The other major elements, Ca, Fe, Al, S, K, Na and Mg, are minerogenic. Figure 11 shows these major constituents along with a selection of minor elements, Ti, Br and Cu.

From 501 to 366 cm (9600 - 6600 BC) the lake and its surroundings are going through primary succession, so these early landscape developments are of little relevance to the question at hand. The apparent stabilization around 366 cm (6600 BC) is however a good reference level, and is used to constrain the background of the other lakes. Between 366 and 55 cm (6600 BC to AD 400) conditions are generally stable, but some trends are still clear. The difference between the average of the five first and last samples of this period shows that Si increases by 16 % over time while Fe, Al, K, S and LOI decrease. Fe decreases by 44 % and LOI 20%. Ca, K, Na and Mg remain stable compared to the other major elements. The minor elements generally follow the above groups with Cu, Zn and Mn decreasing over time and Ti, P, Cl, Sr, Br and Hg remaining stable. Pb is generally below the detection limit (6 ppm) from lake stabilization until 44 cm (AD 730), but once during this entire time two consecutive samples (87 and 89 cm, 350 and 260 BC) show a peak that, while below the method detection limit is exactly when the Roman Pb peak occurs in Fickeln. This is relevant and discussed later as a chronological marker.

At 55 cm (AD 400) BSi increases slightly (11 %) but because it stands for more than a third of the total sediment weight at this point, this affects the other concentrations and thus all other elements (aside from total Si, of course) decrease; e.g. Fe, LOI and Ca decrease by 20, 19 and 17 % respectively. At 39 cm (AD 890) BSi (and Si) has started decreasing to and below its pre-55 cm levels, while elements such as LOI, Br, Cl, Zr, Pb, K, Na, Zn and S have increased well above their pre-55 cm levels. At 38 cm (AD 1140) some of these elements (S, Zr, LOI and Cl)
stabilize while others (Pb, K, Zn, Na) continue to increase. On the decreasing side BSi continues to decrease to an all-time low of 17.4%. It is worth noting that Pb starts increasing already at 44 cm (AD 725) preceding the other elements by 5 cm and 170 years. There is another sharp event at 4 cm where Ca and Mg increase by an order of magnitude, but as mentioned earlier this is due to liming and of low interest to the questions of interest here.

The PCA with all samples from 115 to 6 cm (1000 BC to AD 1800, n=52) returned three principal components that explain 42%, 22% and 20% each (84% together) of the total variance in the data. The analysis with the subset of the samples that include BSi (n=23) also returned three components and they explain 46%, 22% and 20% (88% together) of the variance. Loadings of all components are presented in Figure 11 and scores in Figure 12.

PC1 has positive scores for elements associated with mineral matter (Ca, K, Ti, Na, Mn, Mg and Zr) and elements associated with both mineral matter and iron production (Pb and Zn, Bindler et al. 2011). It also has positive scores for LOI and Cl. PC1 has negative scores for BSi, P and Si. The loadings for PC1 are very stable until 30 cm where they increase drastically.

PC2 has positive scores for a diverse group containing elements associated both with mineral matter and authigenic formation (Engstrom and Wright 1984): Fe, Al, Cu, V, P, Ni, Mg and Mn. The loadings for PC2 are negative following the Si-event between 55 cm and 39 cm. Other than that the loadings fluctuate greatly but without any apparent direction. PC3 has positive scores for the biophilic elements Br, Cl and LOI. It also has positive scores for the mineral matter-associated Sr, Ba and Zr, where at least Zr is known to be enriched in relatively coarse mineral particles (Taboada 2006). It has a negative score for Si. The loadings for PC3 are negative between 55 cm and 39 cm and very positive between 39 cm and 30 cm after which they return to fluctuations around zero.
Figure 11. Kramptjärnen. Major elements, five minor elements and loadings of each principal component. The grey lines mark important changes in sediment history: a=39 cm (AD 890), b=55 cm (AD 400) and c=366 cm (6600 BC).
Figure 12. Kramptjärnen. Score plots from the BSi-PCA. Values in parentheses after axis labels indicate how much of the total variance that PC explains.
5 Discussion
The Discussion section will first go through two points of organization: firstly a division of the lakes’ common history into clearly defined phases, and secondly a generalized ordering of elements in all lakes into functional groups based on the PCA. Then the results of Fickeln, Mosjökälla and Kramptjärn will be discussed. Because Fickeln is the lake downstream of the blast furnace and has the most data available, the conclusions will be strongest there. The other lakes lack direct paleoecological data but through comparisons with Fickeln inferences are still possible. Lastly all results will be synthesized to answer the questions asked in the aim.

5.1 General organization
To answer the questions regarding the environmental effects of the smelter and related activities, it is important to look at the lakes and their immediate surroundings holistically. As shown in Table 5 the elements in the three lakes can be divided into four distinct groups, with some elements that cannot be defined because they change groups between lakes. There is also a fifth group of ore-related elements that is unique for Fickeln and will be discussed there.

The erosion group includes elements widely viewed as related to silicate erosion and deposition in a clastic phase: K, Na, Rb, Ti, Zr and Mg (Engstrom et al. 1985, Koinig et al. 2003, Boës et al. 2011). Silicon is not so much a group as variations in concentration and composition of total Si. Therefore it is not referred to directly; instead the specific fraction is used. The biophilic group is organic content inferred from LOI and two elements strongly related to organic matter: Br and Cl (Rasmussen et al. 1998). In Kramptjärn, this group is not clearly separated from the erosion group, but this is attributed to that lake being so dominated by BSi that the boundaries between the other groups are clouded.

The final group, the authigenic elements, is a diverse group with one thing in common: their dissolved forms can become insoluble in the lake water and precipitate. The mechanisms of this precipitation are different however. Fe, Mn and Al form insoluble oxides or complexes with organic matter; S and P can form insoluble compounds directly with Fe and Mn, while also being important constituents in organic material; Ca and Cu can be bound to organic complexes; Ni and Cu can be bound to Fe/Mn-oxides. (Macereth 1966, Engstrom and Wright 1984, Du Laing et al. 2009, Rydberg et al. 2012). It is therefore clear that these processes are influenced by the composition of the organic matter and the redox potential of the water and sediment. pH can also play a role, especially for Al, but with no way of estimating the pH, this cannot be discussed. Additionally, many elements are only partially associated with this group, which means that the specific mechanisms driving the authigenic formation varies between lakes.

Why these authigenic processes are so pronounced in these lakes is an interesting matter. Kramptjärn and Mosjökälla are headwater lakes. Therefore groundwater input to the them is relatively important and the availability of dissolved Fe and Al is likely good compared to Fickeln, which has a small inlet, and other lakes further down the river continuum. Indeed Fickeln has the least pronounced authigenic formation in this study. The relatively low importance of stream-transported matter also serves a secondary effect: the clastic contribution of elements like Fe and Al remain low so they do not dominate and mask the authigenic processes.
Table 5. A matrix with elements and how they are grouped by the PCA of each lake. Four basic groups are identified: Erosion, Authigenic, Biophilic and Silicon. Between these are elements that are grouped differently in different lakes. Five elements also have an extra dimension in that they are clearly associated with the metallurgy in Fickeln. Subtraction signs means that the elements is negatively correlated to a group and groups in parenthesis means that the element has a correlation to a secondary group.

<table>
<thead>
<tr>
<th></th>
<th>Fickeln</th>
<th>Mosjökalla</th>
<th>Kramptjärnen</th>
<th>Group</th>
</tr>
</thead>
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<tr>
<td>K</td>
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</tr>
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<td>Mg</td>
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<td>Erosion (Authigenic)</td>
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<tr>
<td>Ni</td>
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<td>BSi</td>
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To describe the anthropogenic changes to the environment there must be reference points: a background, an active smelter phase and post-metallurgy phase with a possible recovery. A relevant start to the background phase is 6600 BC when the sediment of Kramptjärnen no longer shows the great changes associated with early succession and landscape development. For the end of the background phase, Lidberg (2012) argues that small-scale forest grazing was established or intensified in the immediate surroundings of Fickeln around AD 200 based on pollen of Rumex, Plantago, Juniperus and Ericaceae found in the sediment record. New data (unpublished) shows that while Rumex indeed establishes around AD 200, the others are present in the area already from at least 1000 BC. Archaeological evidence for
organized settlement in Riddarhyttan, 50 km to the west of Moshyttan, exists from around 400 BC (Damell 2002), so these dates are plausible.

While there seems to be a human presence in the general area, the geochemistry indicates no direct changes during this early pollen phase. Between AD 400 and 890, BSi increases in Kramptjärnen, possibly indicating a change in lake productivity and between 700 BC and AD 1150 redox conditions (and possibly organic matter composition) change in Mosjökälla. In Fickeln, Lidberg (2012) detected slight increases in mineral matter after AD 200. With these diffuse signals in mind, the period before AD 400 is here considered a background with no human influence. The period between AD 400 and 1020, where human presence and impact is probable given the pollen data, is considered a phase of early settlement.

For the active smelter phase Lidberg (2012) proposes a start date of AD 1020 based on changes in charcoal particles and geochemistry in Fickeln and the radiocarbon dated slag from Moshyttan. This is supported by changes in geochemistry of the other lakes that takes place well within the uncertainty of the age-depth models; the sediment of both Kramptjärnen and Mosjökälla record changes in mineral matter, BSi and organic matter. As for the end of the active smelter phase, according to Johansson (1881) the blast furnace at Moshyttan was closed AD 1720, which Landeholm and Eriksson (2001) support based on historical maps. The geochemistry of Fickeln gives further support because the ore-related elements decrease after 1630, well within the margin of error of the age-depth model. The post-metallurgy phase ends with the industrialization and is defined rather conservatively here to AD 1800 to avoid confusing signals from modern pollution.

To summarize, the sediment history of the three lakes surrounding Moshyttan is divided into four phases: I) background, before AD 400; II) early settlement, between AD 400 and 1020; III) active smelter, between AD 1020 and 1720; IV) post-metallurgy, between AD 1720 and 1800.

5.2 Fickeln

The background and early settlement phases of Fickeln are characterized by stable conditions in most elements and principal components. The exception is the authigenic group (as indicated by PC3), that fluctuates more than the other principal components during the background and decreases during the early settlement phase. Some information is available in the Fe/Mn-ratio. If the deep water of the lake was anoxic, authigenic Fe and Mn would be mobilized; however, Mn is released to a higher degree (Koinig et al. 2003, Engstrom and Wright 1984). In other words, a stable Fe/Mn-ratio indicates stable redox conditions. As Figure 13 shows, the redox conditions are stable throughout the background and early settlement phases, which together with the known affiliation of authigenic Al and Ca (the major elements connected to the authigenic group in Fickeln during these phases) to organic complexes discussed earlier, indicates that the fluctuations of PC3 here likely are tied to changes in organic matter composition. The diatom assembly during the background and early settlement phases is stable and dominated by benthic genera that seem to be favored by oligotrophy or mild dystrophy (Table 4).
The Active smelter phase starts with a great increase in the metallurgy group and a decrease in BSi, as suggested by PC2. The erosion and biophilic groups (as indicated by PC1) remain stable throughout this phase. One thing to note is that the absolute decrease in BSi outweighs the increase in the erosion group. This would imply an actual decrease in diatom production inferred from BSi accumulation. Indeed, if the rest of the sediment were to dilute BSi so that the concentration decreases from 17 to 4 %, the overall sedimentation rate would have to increase four times. While average deposition rates based on so few dated samples must be used with care, Figure 13 indicates no changes in deposition rate until halfway through the active smelter phase (AD 1420) and then the increase is only around the double.

Another observation is that the erosion group (indicated by PC1) remains stable throughout the active smelter phase, which is very different from what happens in the other lakes. There the erosion groups show marked increases, while the biophilic groups decreases slightly. The cause of this difference is unclear, but Landeholm and Eriksson (2001) note no sites of human settlement close to Fickeln. It is possible that little agriculture or forestry took place in the immediate surroundings of Fickeln, unlike Mosjökälla and Kramptjärnen where a couple of sites are documented near each lake. From the studies of Lapphyttan it is also reasonable to infer that the water most likely went through at least two dams, one at the outflow of Mosjökälla (there is still a dam here) and one close to the smelter that was used to control water flow (Magnusson 2002). Depending on how those dams were build, they could collect parts of the sediment transported in the stream, preventing it from reaching Fickeln.

The diatom assemblage changes almost immediately as the Active smelter phase begins. Simultaneously the benthic species indicative of oligotrophy decrease and give way to pelagic species that prefer more nutrients and less acidity. First the Aulacoseira genus increases (around AD 1090) and by AD 1310 Asterionella formosa, a pelagic species commonly associated with eutrophication (Krammer & Lange-Bertalot 1991 A) has established in Fickeln. Simultaneously the amount of Isoetes spores decreases (Lidberg 2012). This is a benthic plant and thus sensitive to increased sediment deposition and light competition from
pelagic algae. The obvious mechanisms behind these changes is eutrophication and alkalization because they are commonly seen as the most important for structuring diatom communities (Reynolds 1998). The smelter must have worked through substantial amounts of charcoal that produced N, P, base cations and alkalinity that ended up in the stream and subsequently in Fickeln. Another effect of the metallurgy that logically must have affected diatoms is changes to the hydrological cycle. Again from Lapphyttan (Magnusson 2002), it is reasonable to assume that the smelter was active for around one to a couple of months each year, probably during spring. It is also known that there is a succession of diatom species throughout the year as the water temperature and nutrient availability changes (Kirilova et al 2008). Concentrating the water from the spring flood or perhaps the whole year, to a couple of months must affect this cycle. While this is purely speculation, but a month-long pulse of water rich in nutrients, and that causes significant turbulence in the lake should provide perfect conditions for blooms of pelagic algae. There is, however, no reason that all these algae are diatoms. In fact, changes in trophic status could very well benefit other phytoplankton competitors (Tilman et al. 1986) and lead to a decrease in the total diatom biomass. This would also be in line with the major decline in BSi, that indicates an over-all decrease in diatom production.

At the end of the Active smelter phase, around AD 1680, the sediment composition changes again. The metallurgy and biophilic groups decrease rapidly while the erosion group increases, as indicated by PC2 and PC3. This continues into and through the post-metallurgy phase. At the same time, the diatom community changes and at AD 1730 the community is very similar to how it was composed in the Background. There are some differences though, and some genera never recover to their former abundance (e.g. Brachisyra). This could mean that the new condition actually is an alternative steady state, but more specific diatom species data are required to assess this. According to the new pollen data (unpublished) Isoetes starts recovering around AD 1560 and by AD 1750 it has returned to early settlement levels, indicating that at least functionally, the system has recovered to benthic production.

To summarize, the human impact in Fickeln during the active smelter phase seems to be connected to activities directly relating to the smelter. Water regulation and export of nutrients and alkalinity are all mechanisms that can cause the ecological response observed in the diatom community and abundance of isoetes, even if more detailed data, mainly on diatoms, would be required to establish a direct causality.

5.3 Mosjökälla
Both the background and early settlement phases in Mosjökälla are characterized by stable conditions with little systematic changes over time, with one exception: the fluctuations in the authigenic group, as indicated by PC1. This begins in the late background period (700 BC) and continues through the early settlement and ends right in the beginning of the Active smelter phase. The authigenic group in Mosjökälla is more extensive than in the other lakes and includes elements associated with different mechanisms of precipitation; it includes elements associated with organic complexes (Fe, Al, Mn, Ca and Cu), elements associated with oxic formation (Fe, Mn, P, Ni) and elements associated with anoxia (Fe, S). Using the Fe/Mn ratio discussed earlier, Figure 14 indicates periodically recurring anoxia in the deep waters of Mosjökälla and the lake is 20 m deep, so this is plausible. The fact that Br partakes in the fluctuations also suggests that some changes in the organic matter must be taken into account. Müller et al. (1996) imply that Br is associated with high molecular mass organic
matter from phytoplankton in the Black sea. This material should also readily partake in the formation of stable organo-mineral complexes and possibly provide a stable phase for P, so that it is not released in the anoxic deep waters of the lake. Such a change in the phytoplankton community should be visible in the diatom community and thus within the scope of paleolimnology. Unfortunately the lack of such data at present places these conclusions outside of the scope of this study. One alternative mechanism is the establishment of spruce in the area. With the new pollen data and the alternative dating model discussed in chapter 5.5, this happens around 740 BC. It is logical that a spread of spruce through the catchment should alter the organic matter composition and affect authigenic formation, but the fluctuations would still require explaining.

At the end of the early settlement phase and the beginning of the active smelter phase (AD 870 - 1150) the biophilic and erosion groups show a peak, as indicated by PC2 and PC3. This coincides with a relative decrease in minerogenic Si, indicated by the highest BSi/Si-ratio in sediment history (Figure 14). The reason for this event and how it relates to the last peak in the authigenic group, that occurs at about the same time is unknown. After this and through the active smelter phase, however, the biophilic group and BSi decrease rapidly while erosion and minerogenic Si increases, indicated by PC2, PC3 and the BSi/Si-ratio. The concentration of Pb reaches relatively high levels in the sediment, but it is still low compared to other studies that detected signs of metal poisoning in diatoms. The Pb concentration in Fickeln is for example one order of magnitude lower than in the lake studied by Salonen et al. (2006). Additionally, as De Laender et al. (2012) showed, these intermediate metals loads seem to be negligible in comparison to other human impacts (e.g. land use-induced eutrophication).

A more likely cause for increasing erosion is the establishment of agriculture and forestry in the immediate surroundings of Mosjökälla, which is supported by Lidberg (2012) because

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**Figure 14. Mosjökälla.** Average rate of sediment deposition (Dep. rate), ratios of BSi/Si and Fe/Mn and loadings on PC1. The decrease in BSi/Si-ratio during the active smelter phase indicates increasing concentrations of minerogenic Si. PC1 describes the authigenic group and the corresponding fluctuation in the Fe/Mn-ratio (Koinig et al. 2003) implies that anoxia likely plays a part in the variation of PC1. Roman numbers and the grey lines separating them represent the phases: I (background) < AD 400 < II (early settlement) < AD 1020 < III (active smelter) < AD 1720 < IV (post-metallurgy) < 1800.
this happens a couple of hundred years after he detected signs of agriculture in Fickeln and after the smelter had been established. Another mechanism that logically should affect sediment composition is the increased fluctuations in water level caused by water regulation (discussed in chapter 5.2). This should increase erosion and negatively affect littoral diatoms. It is at this point not possible to determine how much of the decrease in LOI and BSi that is dilution (from increasing mineral matter) and how much is actually a decrease in accumulation, but BSi decreases by 33% during the active smelter phase. This means that to cover the whole decrease, the overall sedimentation rate would have to increase by 50%. Figure 14 shows the average deposition rates and while it seems to increase during the AD 870 - 1150 event, there are no indications of such an increase for prolonged periods of time. It is possible that the diatom community in Mosjökälla suffered the same fate of competition as is Fickeln. The patterns of the decrease in BSi are similar and both lakes experienced changes to the water cycle and increased influx of mineral matter and most likely nutrients, but without data on the diatom community composition this cannot be clarified in this study.

The Post-smelting phase is only covered by two samples, but what can be seen is a continuation of the patterns in the Active smelter phase: even more erosion and lower BSi, as indicated by PC2. The biophilic group is an exception and seems to stabilize, as indicated by PC3. This implies that even if the smelter closed, the agriculture and forestry in the immediate vicinity of Mosjökälla continued.

To summarize, the background phase of Mosjökälla sees some changes to the redox conditions and possibly organic matter composition, but the causes are unknown. Around 130 years into the active smelter phase elements associated with erosion increase while BSi and LOI decrease. The likely cause is a combination of agriculture, forestry and water regulation, but to what extent this actually decreases diatom production is uncertain. Unlike in Fickeln where the post-metallurgy phase saw signs of recovery, the data presented in this study show no such signs in Mosjökälla.

5.4 Kramptjärnen
Kramptjärnen has a complete sediment history which shows the development from deglaciation, through lake stabilization during the primary succession, to a stable lake background. This follows that basic pattern described by Engstrom et al. (2000), with initially high concentrations of products of erosion and leaching (Ca, Ti, Si), that slowly become replaced by organic material (both autochthonous and allochthonous) and BSi. The major increase in LOI, temporarily anoxic conditions indicated by the Fe/Mn-ratio (Figure 15) and increases in associated authigenic elements (Fe, Mn, S) seen in one sample at a depth of 489 cm could be an indication of the alder-thickets implied in many lakes of the chronosequence.
Figure 15. Kramptjärn. Ratios of Fe/Mn and BSi/Si, average deposition rate (Dep. rate) and the concentrations of Si and LOI. The Fe/Mn-ratio implies an event of anoxia shortly after lake isolation, but the stability of the ratio throughout the rest of sediment history, indicates stable redox conditions in the lake. Values of Si and LOI over the last 7000 years show the strong negative correlation. Grey lines are the transitions between four phases in the landscape development. Roman numbers and the grey lines separating them represent the phases: I (background) < AD 400 < II (early settlement) < AD 1020 < III (active smelter) < AD 1720 < IV (post-metallurgy) < 1800.

The background and early settlement phases then show a sediment composition heavily dominated by BSi. This is because this basin acts as a headwater lake with its only inlet running through a mire, so the input of mineral matter and allochthonous organic matter is low compared to BSi. Compared to the other lakes, Kramptjärn has a high average concentration of BSi with 26% (17% for Mosjökälla and 12% for Fickeln). In a broader perspective this is not unheard of. For instance, the training data-set used by Rosén et al. (2010) for the FT-IRS model has lakes with BSi concentrations ranging from 2 to 61%. This BSi dominance is reflected in the PCA that places LOI together with the erosion group on the same side of PC1, with BSi on the other end. LOI also has a weaker score to PC3, which is strongly associated with Cl and Br. It is reasonable to assume that PC3 is a good indicator for biophilic elements, and the much of the association between LOI and BSi on PC1 is dilution. Just like in the other lakes there is an authigenic group (here implied by PC2) that shows little correlation to the other groups. Like in Fickeln, the authigenic group in Kramptjärn consists of elements associated with organic matter complexation (e.g. Fe, Al, Cu), but unlike in Fickeln it also includes elements the precipitate on their own, like Fe, Mn and P. This difference is probably an effect of Fe, Mn and P being so strongly associated with metallurgy, that their variation during the active smelter phase in Fickeln overshadows any possible association with the authigenic group.

At the end of the early settlement phase (around AD 890) BSi starts decreasing after its peak during the early settlement phase, and simultaneously the other groups increase. The development continues into the early active smelter phase but by AD 1140 the biophilic and
authigenic groups have stabilized (as indicated by PC2 and PC3) while the erosion group starts increasing rapidly, as indicated by PC1. This development matches the pollen indicators described by Lidberg (2012). He found the very first indications of farming at AD 880 and detected slight changes in forest composition between AD 950 and 1300. It is worth noting that around Kramptjärnen, the signs of inferred human impact predate the smelter by 130 years.

These changes to the catchment of Kramptjärnen apparently caused increased erosion of fine-grained mineral material. It is likely that this caused a decrease in diatom production, just like in the other lakes, because the decrease in BSi can only be explained by dilution if the deposition rate increases by around 65%. This is unlikely since the average deposition rate (Figure 15) decreases during the active smelter phase. The post-metallurgy phase sees no disappearance of the human impact and this is not so surprising considering that the impact likely consists of small-scale agriculture and forestry, which seems to outlive the metallurgy.

5.5 Synthesis
The dating and age-depth modeling of the cores is crucial to compare events within this study as well as to other lakes in the literature. Figure 16 shows Pb for each of the lakes in this study with the Spruce immigration, Roman Pb peak and the medieval rise in Pb (defined as the first time the concentration rises above 6 ppm, the detection limit) pointed out. Kramptjärnen and Fickeln, which are both dated on bulk sediment, match each other with an average difference between events of 20 years. When comparing Fickeln to Mosjökälla, dated on leaf fragments, events in Fickeln appear on average 240 years older.

Figure 16. Concentrations of Pb in the three lakes (in ppm) over that last 3000 years. The headings denote three events used to match the age-depth models: a) Spruce immigration, b) Roman Pb and c) Earliest medieval Pb. The events in the three lakes are pointed out with arrows, linked by lines and marked with corresponding letters. The grey areas are reference events; Spruce immigration in Lilla Gloppsjön at 740 ± 90 BC (Almquist-Jacobson 1994) and Roman Pb peak at AD 0 +200/-100 (Renberg et al. 2001). The dashed arrow is spruce immigration according to the new pollen data at 740 BC (unpublished).

The reference points above the chart include the Roman Pb peak as proposed by Renberg et al. (1994, 2001) and it supports the theory that the age-depth model of Mosjökälla is more accurate. Figure 16 also includes dates on spruce immigration from a lake in the Bergslagen area: Lilla Gloppsjön (Almquist-Jacobson 1994) 22 km NNW of Mosshyttan. This lake is also dated on bulk sediment, so it is logical that it should match Fickeln and Kramptjärnen more closely. The new pollen data (unpublished) also shows a good match between Fickeln and Lilla Gloppsjön, showing that the relative method used in this study produces reasonably accurate estimates of spruce immigration.
Based on the good match between lakes and to the Roman Pb peak, and to a lesser extent to the data on spruce immigration, the catchment effect is assumed to be 240 years. As shown in Figure 17, where an alternative age-depth model has been established for Fickeln that includes a 240 year catchment effect, events there match both Mosjökälla and the outside chronological markers. Establishing these kinds of effects is prone to circular logic; the patterns are clear because I fixed my data so the patterns would be clear. It is therefore logical to present the uncorrected dates, but because so many things add up in the sediment if the catchment is taken into account, it is important to discuss the effect when making comparisons.

Looking at the three lakes and their surroundings holistically, what were the background conditions? Fickeln clearly was an oligo- and slightly dystrophic forest lake, as indicated by the diatoms, BSi and LOI. In Mosjökälla and Kramptjärnen, the BSi and LOI are similar to the values of Fickeln, and no other geochemical parameters show any major deviations, so it is reasonable to assume that they were similar in respect to pH and trophic status. The pollen data (Lidberg 2012) indicate a forested landscape dominated by Birch, Pine, Alder and Spruce. The geochemistry, as synthesized by the PCA and showed in Figure 18, is stable over longer time-periods. The erosion, biophilic and diatom groups dominate sediment composition and covary with each other. Seemingly superimposed is the authigenic group that fluctuates without much correlation to the other groups. As discussed for each individual lake, there is some development in the early settlement phase that could be attributed to human activities, but no conclusions can be drawn in this study.

At the onset of the Active smelter phase, the erosion group increases in Kramptjärnen and Mosjökälla but in Fickeln it remains low until late in the phase. The increase in Kramptjärnen and Mosjökälla most likely has to do with the establishment of agriculture and forestry in their catchments. In Fickeln the great delay probably has two reasons. Firstly there is no evidence of agriculture in the immediate surroundings of the lake and secondly whatever material that was transported in Mosjöbäcken (from Mosjökälla) could have been trapped in the dams. While Fickeln sees no apparent increase in erosion, the metallurgy group increases. This timing issue is very interesting and has been investigated by Lidberg (2012). This study does provide a greater context to the developments in Fickeln and if the catchment
effect is taken into account the first clear signs of an active smelter proposed by Lidberg take place around AD 1190. Using the alternative age-depth model the early increase in Pb however takes place at AD 930 in Fickeln and AD 960 in the other lakes. This is then very close to the earliest slag dates from around AD 960 by Wetterholm (1999). Unfortunately very little is known of how these early smelters are established, but speculatively it could have been active for 200 years on a smaller scale or by different techniques.

While the activities surrounding the smelter change the sediment composition, the biota of the lake is also affected. Through a combination of increased nutrient input, increased pH and changes in the hydrological cycle the diatom community changes and partially moves into the pelagic. At the same time, the benthic plant Isoetes decreases. This seems to imply that these changes in water quality are accompanied by increased DOC, but the connection is complex (e.g. LOI decreases during this time) and little can be concluded presently. Mosjökälla and Kramptjärnen lack paleoecological data and the main changes in the geochemistry during the active smelter phase are different; they see an increase in the erosion group rather than the metallurgy group. There are also differences in how BSi changes (Figure 18), where Fickeln has a more drastic decrease that happens earlier than in the other lakes. This indicates that the directly metallurgical processes may affect the diatom community differently from agriculture and forestry.

The post-metallurgy phase sees some major changes in Fickeln. If the catchment effect is taken into account the smelter associated group decreases rapidly from AD 1730. This is only 10 years after the smelter was closed (Johansson 1881). At the same time the erosion group increases rapidly. This is likely because that after smelter closure, the dams break down and the human presence around the stream is seen in Fickeln. In conjunction with these changes the Isoetes seems to recover to early settlement levels, indicated by the amount of spores in the sediment. Simultaneously the diatom community changes and by AD 1800 (using catchment effect-adjusted dates) it is again statistically similar to the background, but slight qualitative differences could be indicative of an alternative state rather than a recovery.

To further develop this study, more detailed data on the diatom community of Fickeln, both increased resolution and improved species data, would be very interesting. This would clarify how the lake was affected by the metallurgy, with respect to alkalization and eutrophication. It would also show whether the post-metallurgy diatom community can be considered recovered, or if it represents an alternative state. Similarly, diatom data on Mosjökälla would provide a better understanding of how impacts from changes in land-use differ from the more directly metallurgy-related impacts. Because this study already includes so many parameters, it would provide a very good parallel to other studies of impacts from metallurgy, e.g. the study by De Laender et al. (2012). To broaden the scope of this study, analyses of stable Pb isotope composition would provide another proxy to more precisely match the sediment records in this study, which would provide a more conclusive answer to when signs of metallurgy are first detected in Fickeln. Pb isotope data would also provide a way to separate between Pb sources to shed some light on the balance between long-range atmospheric-, local atmospheric- and directly waterborne Pb transport. Again this study would then be a good parallel to similar studies in other areas, such as in Norberg (Bindler et al. 2009).
Figure 18. BSi in each lake, loadings on PC2 of the diatom-PCA in Fickeln, Isoetes % of total pollen in Fickeln and principal component loadings that synthesize the geochemistry of all three lakes. These PC loadings have their associated groups written out and groups after hyphens are negative correlators. Roman numbers and the grey lines separating them represent the phases: I (background) < AD 400 < II (early settlement) < AD 1020 < III (active smelter) < AD 1720 < IV (post-metallurgy) < 1800. Grey bars above the chart summarize important events from the new pollen data (unpublished).
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6 References


