

# **HOLOCENE PALEOHYDROLOGY OF VIANKIAAPA MIRE, SODANKYLÄ, FINNISH LAPLAND**

Master thesis

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## ABSTRACT

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<p>In 2011 AA Sakatti Mining Oy published a promising ore discovery in Sodankylä, Finnish Lapland. The need for more knowledge led to the start of Sakatti geoenvironments -project in collaboration with the University of Helsinki. As a part of this project, the Holocene paleohydrology of Viiankiaapa mire was reconstructed. Viiankiaapa mire is located on the eastern side of Kitinen River and has developed in close connection to it. It is a large aapamire complex consisting of multiple smaller minerotrophic mire sites and bogs. Viiankiaapa conservation area was first established in 1988. A large portion of Viiankiaapa is now part of the Natura 2000 conservation network.</p> <p>To study the development and paleohydrology of Viiankiaapa mire, a 4.3 meter peat core (VA310315, 7497803 N/0490511 E) was collected using a Russian peat sampler. From the peat core, six specimens from increasing depth levels were sampled for age determinations to establish reliable chronology. Dating was conducted at LUOMUS Laboratory of chronology at the University of Helsinki, using <sup>14</sup>C AMS dating method. Peat stratigraphy was studied on site and humification determined using von Post method. Physical properties of the peat (LOI<sub>550</sub> and water content) were determined in 2 cm resolution. The colour of the ash was determined using Munsell soil color chart. Same resolution was used in geochemical analyses of 17 individual elements (C, N, S, P, K, Ca, Mg, Na, Fe, Al, Cu, Ni, Zn, Ti, Mn, Pb, Si). C, N, and S contents were determined using gas chromatography, while all the other elements were analyzed using ICP-MS.</p> <p>From the element contents, multiple ratios were calculated in order to study the Holocene deposition pattern of individual elements. Element/Ti profiles show an increase in mineral material input in c. 8 000 – 6 000 cal. BP, c. 4 800 – 3 000 cal. BP, and 2 500 – 1 900 cal. BP, suggesting enhanced flooding of Kitinen and increased humidity. Early Holocene (11 700 – 8 200 cal. BP) is indicated as a period of higher detritic material input. Waterlogged conditions, however, have most likely not been continuous during early Holocene. This is suggested by the occurrence of dark red color of iron oxide (FeO) in the ash. The occurrence of iron sulphides (possibly pyrite, FeS<sub>2</sub>) in the ash of the bottom section of the core suggests that waterlogged conditions were reached during Mid -Holocene. The 8.2k event is showcased in the profiles of multiple elements, including the main nutrients (C, N, P). These elements show significant increase after the cold event. Ca/Mg, Ca/K, and Mg/K ratios were used to estimate the trophic state of the mire and the sources of the mineral material. Also the accumulation of Pb was studied more closely. All of these factors suggest that atmospheric input and groundwater alone could not have transported the entire volume of the mineral material, and therefore river Kitinen may be considered as the main water and nutrient source until the damming of the river in 1984 and 1995.</p>			
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<p>Vuonna 2011 AA Sakatti Mining Oy julkaisi merkittävän malmiesiintymän löytymisen Sodankylässä, Suomen Lapissa. Lisäinformaation tarve johti Sakatti geoenvironments- projektin aloittamiseen yhteistyössä Helsingin yliopiston kanssa. Osana tätä projektia Viiankiaavan Holoseenin aikainen paleohydrologia rekonstruoitiin. Viiankiaapa sijaitsee Kitisen joen itäisellä puolella ja on kehittynyt läheisessä yhteydessä siihen. Viiankiaapa on suuri aapasuokompleksi, joka koostuu useista pienemmistä minero- ja ombrotrofisista suoalueista. Viiankiaavan suojelualue perustettiin ensimmäisen kerran vuonna 1988. Sittenmin suuri osa suoalueesta on otettu osaksi Natura 2000 verkostoa.</p> <p>Viiankiaavan paleohydrologian rekonstruomiseksi 4,3 metrin turvesarja (VA310315, 7497803 N/0490511 E) kairattiin käyttäen venäläistä suokairaa. Turvesarjasta kuusi näytettä esikäsiteltiin radiohiiliajoitusta varten. Ajoitukset toteutettiin LUOMUS Ajoituslaboratoriossa Helsingin yliopistossa käyttäen <sup>14</sup>C AMS- ajoitusmenetelmää. Turvestratigrafia ja turpeen maatuneisuus määritettiin käyttäen von Post - menetelmää. Turpeen fysikaaliset ominaisuudet (LOI<sub>550</sub> ja vesipitoisuus) määritettiin kahden senttimetrin resoluutiolla. Tuhkan väri määritettiin käyttäen Munsellin väriluokitusta. Samaa resoluutiota käytettiin myös geokemiallisissa analyyseissä, joissa 17 yksittäisen alkuaineen (C, N, S, P, K, Ca, Mg, Na, Fe, Al, Cu, Ni, Zn, Ti, Mn, Pb, Si) kokonaispitoisuudet määritettiin. C, N ja S pitoisuudet määritettiin käyttäen kaasukromatografiaa, kun taas muut alkuainepitoisuudet analysoitiin käyttäen ICP-MS-laitteistoa.</p> <p>Alkuainepitoisuuksista määritettiin useita suhdelukuja, joita hyödynnettiin Holoseenin aikaisten alkuaineiden kerrostumismallien tutkimiseksi. Alkuaine/Ti -suhdeluvut osoittavat mineraaliaineksen kulkeutumisen Viiankiaavalle lisääntyneen c. 8 000 – 6 000 kal. BP, 4 800 – 3 000 kal. BP ja 2 500 – 1 900 kal. BP. Tämä viittaa Kitisen joen lisääntyneeseen tulvintaan ja lisääntyneeseen ilmastosta kosteuteen. Varhais-Holoseenia (11 700 – 8 200 kal. BP) karakterisoi lisääntynyt mineraaliaineksen kerrostuminen. Vedellä kyllästyneet olosuhteet eivät kuitenkaan todennäköisesti ole vallinneet yhtäjaksoisesti koko Varhais-Holoseenin ajan. Tähän viittaa tummanpunaisen rautaoksidin esiintyminen tuhassa. Rautasulfaattien (mahdollisesti pyriitin, FeS<sub>2</sub>) esiintyminen turvesarjan pohjaosan tuhassa viittaa siihen, että vedenkyläiset olosuhteet saavutettiin Keski-Holoseenin aikana. Useat tulokset, mukaan lukien pääravinteet (C,N,S), osoittavat 8,2k tapahtuman Viiankiaavan kehityshistoriassa. Nämä tulokset osoittavat merkittävää kasvua kylmän ilmastovaiheen jälkeen. Ca/Mg, Ca/K ja Mg/K suhdelukuja käytettiin Viiankiaavan trofisen tilan arvioimiseen. Niitä hyödynnettiin myös suolle kerrostuneen mineraaliaineksen lähteiden tutkimukseen. Myös lyijyn akkumulaatiota tarkasteltiin lähemmin. Kaikki tekijät viittaavat siihen, että ilmakehän laskeuma ja pohjavesi eivät ole voineet kuljettaa kaikkea mineraaliainesta Viiankiaavalle, minkä vuoksi Kitisen jokea voidaan pitää pääasiallisena veden ja ravinteiden lähteenä Viiankiaavalla aina joen patoamiseen saakka vuosina 1984 ja 1995.</p>			
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## 1. INTRODUCTION

### 1.1 Holocene epoch in Finland

The Holocene, representing the most recent geochronological epoch, has been the interest of scientific studies of wide range (Mackay et al. 2003 p.4). At higher latitudes long-term climate changes are driven by not only changes in precipitation and temperature, but also by various feedback mechanisms associated predominantly with changes in the sea ice and vegetation (Ojala et al. 2008). In Finland the interpretations of Holocene climate have mainly been based on studies of past vegetation patterns and climate related to them (eg. Seppä 1996a, Mäkelä and Hyvärinen 2000). In addition, especially in northern Finland paleolimnological studies have been used to reconstruct and model climatic changes during Holocene (eg. Korhola et al. 2005).

Table 1 Blytt-Sernander chronozones for the European Holocene. Based on Roberts (2014, p. 159).

Pollen stage	Inferred climate	Pollen zone	Approximate age (BP)
Subatlantic	Cool/wet	VIII	present - 2 600
Sub-boreal	Warm/dry	VIIb	2 600 - 5 700
Atlantic	Warm/wet	VIIa	5 700 - 7 800
Boreal	Warm/dry	V/VI	7 800 - 10 500
Preboreal	Cool/dry	IV	10 500 - 11 700

Peat stratigraphy has also been used to create a framework for climatic changes during Holocene. Especially in Nordic countries the origin of paleoclimatic studies is thought to lie in various types of mires that cover the landscape (Birks and Seppä 2010). Phases of faster and slower peat growth can be linked to climatic factors, such as temperature and precipitation. Alex Blytt and Swede Sernander, pioneers in paleoclimatic studies from peat in the late 1890s and early 1900s, created the Blytt-Sernander Scheme describing the climatic subdivision of Holocene as seen in peat stratigraphy (Blytt 1876). When

radiocarbon dating became possible the original division was redefined based on chronology (Mangerud et al. 1974). This division and its correlation with pollen zones is shown in Table 1. The Blytt-Sernander Scheme has later been replaced by dividing the Holocene into Early – (11 700 – 8 200 cal. BP), Middle – (8 200 – 4 300 cal. BP), and Late Holocene (4 300 – present) phases. This is mainly because the subdivision proposed earlier is not recognized as applicable in larger context and is useful only in local and perhaps regional scale (Walker et al. 2012).

The Holocene epoch began approximately 11 700 years ago (Roberts 2014 p.128). At this time the edge of the Scandinavian ice sheet was at the Salpauselkä zone of Finland, at the coast of Gulf of Finland, and Finnish Lapland was only starting to be released from continental glacier (Taipale and Saarnisto 1991 p.241). The northernmost parts of Finland were deglaciated approximately 11 500 years ago (Johansson and Kujansuu 2005) First few thousand years of Holocene in Finland were therefore characterized by melting of ice sheet and processes related to it. Deglaciation was a result of gradually rising temperatures at a time of rapid climate warming which is shown especially by changes in vegetation during early Holocene (Taipale and Saarnisto 1991 p. 242). Over northern Europe modern summer temperatures were reached during the first thousand years of Holocene (Roberts 2014 p. 128). Based on pollen record, the annual mean temperatures in southern Finland were still below 0.0 °C 10 700 – 10 000 cal years BP, but steadily rising (Heikkilä and Seppä 2003). The so-called 8.2 ka BP event, which occurred at the end of early Holocene, has been proposed as a boundary between early and middle Holocene. This event is clearly visible in the isotopic records from Greenland ice cores (eg. Rasmussen et al. 2007), and also somewhat in Finnish pollen record (Heikkilä and Seppä 2003). It is a short-lived event of cooling, disrupting the pattern of gradual warming (Walker et al. 2012). Increased erosion and decrease in organic matter influx is also recorded in lakes with varved sediments of southern central Finland around 8 000 BP, which may be associated with the 8.2 ka BP event (Ojala et al. 2008).

Holocene thermal maximum (HTM) in Finland has been dated at around 7 000–4 500 cal. years BP (Heikkilä and Seppä 2003, Ojala et al. 2008). During this time temperature reached as much as 1.5-3.0 °C higher than the modern one (Heikkilä and Seppä 2003, Ojala et al. 2008). In addition to pollen and varve records, HTM in Finnish Lapland has also been recorded by lake-level changes (eg. Korhola et al. 2005). At this time there was a reduction of lake-levels by approximately 4–6 m resulting from lower precipitation and

higher evaporation (Ojala et al. 2008, Korhola et al. 2005). Ojala et al. (2008) combined paleoclimatological interpretation of seasonally resolved varve record with a sum of growing degree days reconstruction based on pollen data, and stated that maximum summer temperature in Finland was reached 6 500-4 500 cal. years BP. This study agrees with the lake-level reconstructions conducted in Finnish Lapland (Korhola et al. 2005) because higher summer temperature at higher latitudes is associated with lower precipitation and higher evaporation.

HTM was followed by progressive cooling separate from the 8.2 ka BP event (Roberts 2014 p. 219). The cooling pattern was noted in northern Europe, including Finland, where tree line started to move towards south, and *Pinus* and *Picea* became more dominant in the pollen record supplanting formerly dominant *Betula* (eg. Heikkilä and Seppä 2003). During the next 2 000 years after cooling began, winters became gradually colder and/or longer with higher net accumulation of snow. At the same time the season for highest productivity became shorter and possibly colder. These changes have been indicated by increasing influx of mineral matter and decreasing influx of organic matter in varve lakes across Finland (eg. Ojala et al. 2008). Higher seasonality and more variable climate regime, that characterize the present climate of Fennoscandia, are thought to be results from the gradual cooling (Tikkanen 2005).

There has been a lot of discussion on what caused the climatic changes during Holocene. Orbital forcing is considered a major factor even when its effects are on multi-millennial timescale (Mackay et al. 2003 p.10). Coupled with changes in solar and greenhouse gas forcing, orbital changes are thought to be the main driver of climatic changes during Holocene (Ojala et al. 2008). During early Holocene, northern hemisphere summer solstice was at the time of perihelion. This resulted in higher summer insolation, affecting summer temperatures (Mackay et al. 2003 p.11). The melting of Laurentide and Scandinavian ice sheets also resulted in large freshwater influx to the Atlantic Ocean, affecting ocean currents and the temperatures of the air masses above Atlantic. Despite this, not all climatic changes during Holocene can or should be related to external factors. Various feedback mechanisms affect climate at all times. The spreading of forests and declining sea ice, for example, caused changes in albedo feedbacks, which had a direct effect on the climate. Winter warming around 6000 years BP for example can be directly linked to decrease in sea-ice cover (Heikkilä and Seppä 2003).



Developments in the studies of climatic conditions during Holocene have shown that at least five events of changing climate can be distinguished during the last 11 700 years BP. O'Brien et al. (1995) stated that these events occur at *c.* 0 – 600, *c.* 2 400 – 3 100, *c.* 5 000 – 6 100, *c.* 7 800 – 8 800 and *c.* 11 300 calendar years BP, and that they were events of colder and drier conditions. Holocene paleoreconstructions based on peat deposits have been conducted also in Finland (eg. Korhola 1995, Välranta et al. 2007). Radiocarbon dating of basal peats in Finland suggests that the period between 4 300 – 3 000 cal. BP represented a time interval of intensive peat initiation (Korhola 1995). According to Korhola (1995) this may reflect increased atmospheric humidity and higher temperatures. A number of paleoclimatic records have also indicated that *c.* 2 700 cal. BP there was a phase of increased precipitation. Some studies conclude that this “wet-shift” was one of the largest climatic events of late Holocene (Barber 1985, Charman 1990).

## **1.2 The aim of this study**

In 2011 an international mining company, Anglo American, publicly announced a promising ore discovery named as Sakatti, in Sodankylä, Finnish Lapland (Brownscombe et al. 2015). Ore prospecting had already begun in 2004 and to this date studies are still continuing in the area. The deposit is located underneath the Viiankiaapa Natura 2000 area. This increases the need for further investigations on the Quaternary history and development of the mire. This need led to the initiation of the Sakatti geoenvironments - project in collaboration with the University of Helsinki. As a part of this project, this thesis investigates the mire hydrology, processes related to it, and its development during Holocene. To assess and prevent possible environmental impacts of ore prospecting and potential future mining, all aspects of Viiankiaapa mire hydrology should be understood. The aim of this study is to reconstruct the Holocene paleohydrology of Viiankiaapa mire. The goal is to better understand the connection between the development of Viiankiaapa mire and the flooding activity of river Kitinen, flowing in the immediate surroundings of Viiankiaapa mire. Based on historical writings and conversations with the locals, river Kitinen is known to have flooded significantly in the past before the construction of multiple dams in 1984 and 1995. The floods are believed to have brought mineral material and additional nutrients to the mire ecosystem, and therefore affected the development of Viiankiaapa mire (Lappalainen 1970). This study aims to answer the questions:

- 1) What are and/or have been the main water sources of Viiankiaapa mire?
- 2) What is the significance of the flooding of river Kitinen for the development of Viiankiaapa mire?
- 3) How has the mire and its hydrology changed since the damming of river Kitinen?

The hypothesis for this study is that river Kitinen has had a significant effect on the development of Viiankiaapa mire. Flooding, and the presence of allogenic material is expected to show in the geochemical record of the mire. It is also believed that Viiankiaapa mire has had more than one source of water and nutrients throughout its history.

### **1.3 Peatlands in Finland**

Peatland or a mire is a peat-forming ecosystem defined by wetland vegetation adapted to wet conditions (Pajunen 2005). In order for a mire to develop a surplus of water is needed. The surplus may have either climatic origin or be caused by changes in the hydrological setting (Huttunen and Tolonen 2006). In geological terms, mire is an area where peat layer of at least 0.30 m covers an area of 20 hectares (Maunu and Virtanen 2005). About one quarter of Fennoscandia is categorized as peatlands (Parviainen and Luoto 2007). In Finnish Lapland one third of the entire area is categorized as peatlands (Maunu and Virtanen 2005).

The end of the Weichselian ice age represents a beginning of the development of many present peatlands in Finland (Lindholm and Heikkilä 2006a). Retreating ice revealed land, which had been drastically deformed by the activity of the former glacier. As the ice sheet retreated the meltwater draining system shaped the landscape even further, and together with post-glacial land uplift, created numerous basins for the mires to develop. Based on the records on Geological Survey of Finland there are over 10 500 separate mires in Finland (Maunu and Virtanen 2005).

Mire initiation and expansion may happen in three different ways: paludification, the filling-in of lake basins, and the primary mire formation (Pajunen 2005). Paludification occurs when forest vegetation is replaced by mire vegetation. The change is initiated by increased soil moisture, which in most cases is a result from rising groundwater table (Pajunen 2005). The filling-in of lake basins occurs, where shallow lakes are filled by

plant detritus or floating peat mats expand across the entire lake (Pajunen 2005). In the primary mire formation, the wetland vegetation occupies an area either emerged from water or released from ice (Huttunen and Tolonen 2006). Topography, regional climate, and the type of underlying mineral soil have an effect on the primary mire formation (Pajunen 2005). Peatlands are most common in watershed areas formed by till (Virtanen 2008). The rate of peat increment is determined by multiple factors such as water permeability, bottom soil nutrient content, topography (determining water runoff patterns), plant ecology and the water balance of the mire (Mäkilä 2006).

Peatlands may be and have been categorized based on various factors, such as shape, chemistry, or vegetation structure. Based on the source of water and nutrients, aka their trophic state, mires can be categorized into either ombrotrophic or minerotrophic (Pajunen 2005). Ombrotrophic mires (often referred to as bogs) are fed by only precipitation, whereas minerotrophic mires may be fed by groundwater or surface runoff in addition to precipitation. Minerotrophic mires may also be referred to as fens. In practice, due to difficulty of establishing trophic state by hydrological means, fens and bogs are often recognized by the absence, presence or abundance of fen-indicator species of vegetation (Gorham and Janssens 2005).

The peatlands in Fennoscandia and also in other parts of the northern hemisphere are usually categorized into mire complexes and mire complex zones where each type of mire complex is most abundant. Mire complexes contain large areas of peatlands reflecting similar climatic conditions, vegetation, topography (micro- and macro-), peat stratigraphy and hydrology. Finnish peatlands may be divided in four main types of mire complexes: aapamires, blanket bogs, palsamires and raised bogs (Parviainen and Luoto 2007). Finland has been divided into mire zones based on the occurrence of different mire complex types in different part of Finland. Mire complex zones of Finnish Lapland, consisting of types of mire complexes mentioned earlier, are presented in Figure 1. Although, some scholars prefer to narrow the classification down to only aapa mires and bogs (Maunu and Virtanen 2005).

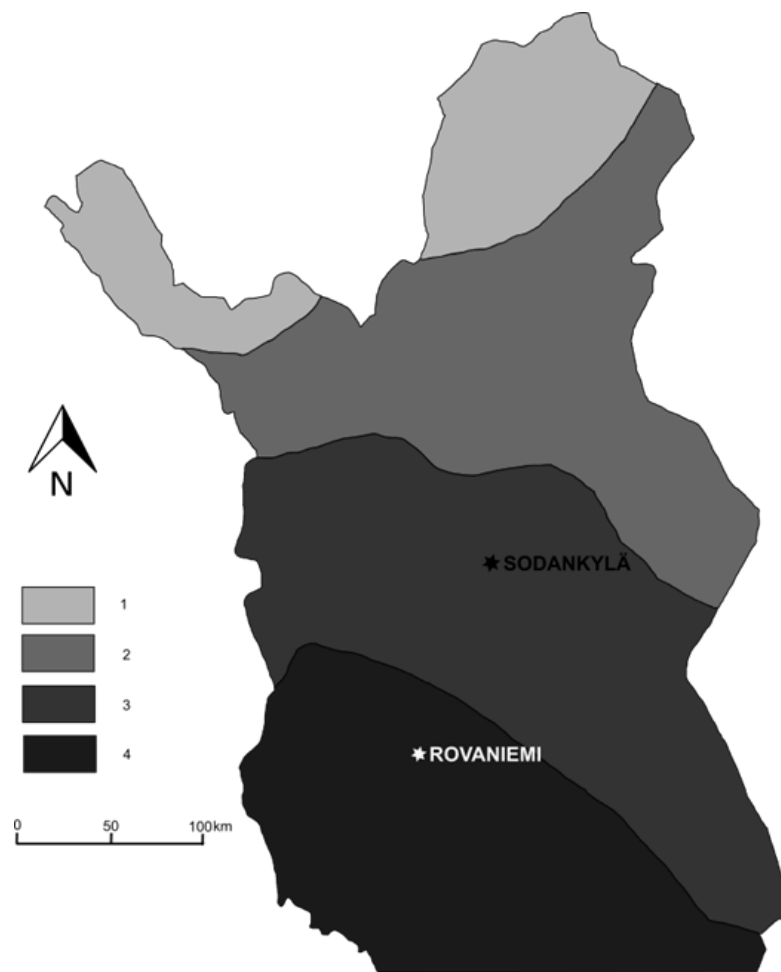


Figure 1 Mire complex zones of Finnish Lapland. 1: Palsamires and fell-top mires; 2: Aapamires of Forest Lapland; 3: Aapamires of Peräpohjola region; 4: Aapamires of Ostrobothnia. The types of mire massifs also follow somewhat same zonation accordingly: 1: Palsamires and orohemiarctic mires; 2: Pounikko aapamires; 3: Flark aapamires; 4: Sedge aapamires. Modified from Lindholm and Heikkilä (2006b) and Maunu and Virtanen (2006).

### *1.3.1 Aapamires of Finland*

Aapamires cover the largest part of Finland (Seppä 1996b) and they are dominant especially in northern and central Finland. Aapamires are also the oldest type of mire complexes (Virtanen 2008). Northern Finland is commonly divided into zones of aapamires of Ostrobothnia, aapamires of Peräpohjola region, aapamires of forest Lapland, and palsamires (Figure 1) (Maunu and Virtanen 2005). Aapamires of Peräpohjola region represent the basic type of aapamires. They mainly occur in the regions of Salla, Pelkosenniemi, Sodankylä and Kittilä (Maunu and Virtanen 2005).

Aapamires were originally described more than a century ago by Cajander A. K. (1913). Cajander A. K. (1913) narrated aapamires as large, wet and generally treeless peatlands, characterized by surface pattern of wet flarks and strings. In open parts of the mire strings, representing hummock level, and flarks form a structure where strings are perpendicular to water flow (Lindholm and Heikkilä 2006b). Later on the definition of aapamires has become more detailed (eg Seppä 1996b, Maunu and Virtanen 2005). They are usually treeless in middle parts and in marginal areas either *pine* or *spruce* mires occur (Maunu and Virtanen 2005). Central parts of the mire are usually covered by minerotrophic vegetation while marginal belts consists of ombrotrophic vegetation (Korhola and Tolonen 1996). The surface of an aapamire is most commonly flat or gently sloping (Lindholm and Heikkilä 2006b). Aapamires are categorized as minerotrophic peatlands (fens) due to nutrients originating from outside of their confines, from groundwater or surface runoff (Charman 2002 p. 6). Despite this, aapamire complexes can include some ombrotrophic areas, which are out of reach of spring floods (Pajunen 2005).

The mire complex zones, such as the Peräpohjola aapamires, have a strong connection to Finnish ecoclimate and the hydrological zones of Finland (Solantie 2006). Aapamires generally occur in areas where precipitation in summer is higher than evaporation and therefore open water surfaces are present throughout the year (Solantie 2006, Parviainen and Luoto 2007). Finnish climatic conditions, especially in northern Finland, are ideal for the development of aapamires due to short summers, long winters and spring floods (Parviainen and Luoto 2007). Aapamires in northern Finland may preserve their minerotrophic state despite accumulation of peat, due to abundant snowmelt waters washing humic acids from the mires (Lindholm and Heikkilä 2006b). Seasonal flooding and winter freezing on the upper peat layer influence the structure of strings and flarks (Seppä 1996b, Lindholm and Heikkilä 2006b). These structures are more apparent in the north, where ground frost reaches deeper in the peat (Lindholm and Heikkilä 2006b).

Mire massif types were first introduced by Cajander (1913) and later developed and re-evaluated by a number of researchers (eg. Ruuhijärvi 1988). Aapamires have been divided into three main categories: sedge aapamires, flark aapamires and pounikko aapamires (Lindholm and Heikkilä 2006b). Their zonation in Finnish Lapland is presented in Figure 1. In sedge aapamires relatively dry lawn surfaces dominate. Strings are usually very low or non-existent. In larger sedge aapamires, especially in the northern part or the zone there are wide flark fens and obvious string pattern (Lindholm and Heikkilä 2006b). Flark

aapamires represent the most typical type of aapamires. Within their confines, a variety of wet flark fens are abundant and a regular string-flark pattern can be identified. In pounikko aapamires flarks are often large and wet and the strings form a non-uniform net-like pattern. In average, the northernmost aapamires are poorer than the southern aapamires. Strings are often dominated by *Sphagnum fuscum* and dense beds of *Betula nana* (Lindholm and Heikkilä 2006b).

Peat in aapamires varies in depth and structure. It is mainly composed of the remnants of *Carex*, *Spagnum* and *Bryales*-vegetation. Most common peat type in aapamires is *Carex*-dominant. Remnants of *Menyanthes trifoliata*, *Equisetum* and *Phragmites australis* are also often found. *Bryales*-dominant peat is more common in the deeper parts of aapamires in central Lapland. (Virtanen 2008 p. 19).

### 1.3.2 Biodiversity of Finnish aapamires

Large mire complexes and their biodiversity in regional scale is controlled by climate. Main mire types within large complexes are a result of small scale variations in temperature and moisture. Finally, changes within mire types result from changes in surface structure. (Kaakinen et al. 2008 p. 34-35). The proportion of patterned fens from the entire mire surface in Finnish Lapland is presented in Figure 2. The abundance of patterned fens (with string-flark-pattern) is highest in central Lapland, and a part of Viiankiaapa mire is located in the area where more than 50 percent of the mire surface is covered with patterned fens.

When comparing aapamires with ombrotrophic bogs, peat in the surface parts of the mire is often less acidic and there are more nutrients available for vegetation. Higher pH results from surface – and/or groundwater input. In the margin areas of aapamires it's possible to have ombrotrophic areas that are outside of the influence of surface runoff and/or groundwater seepage. These areas are often characterized by pine mires and ombrotrophic pine bogs (Lindholm and Heikkilä 2006b). Minerotrophy within one aapamire can change from oligotrophic to mesotrophic and finally to eutrophic, which makes their biodiversity much higher in comparison to bogs. Local bedrock may also have an effect on the fertility of the aapamire. For example, in northern Finland in Peräpohjola aapamire zone mesotrophic and eutrophic vegetation is more common than in aapamires in other parts of Finland. (Kaakinen et al. 2008 p.36-37).

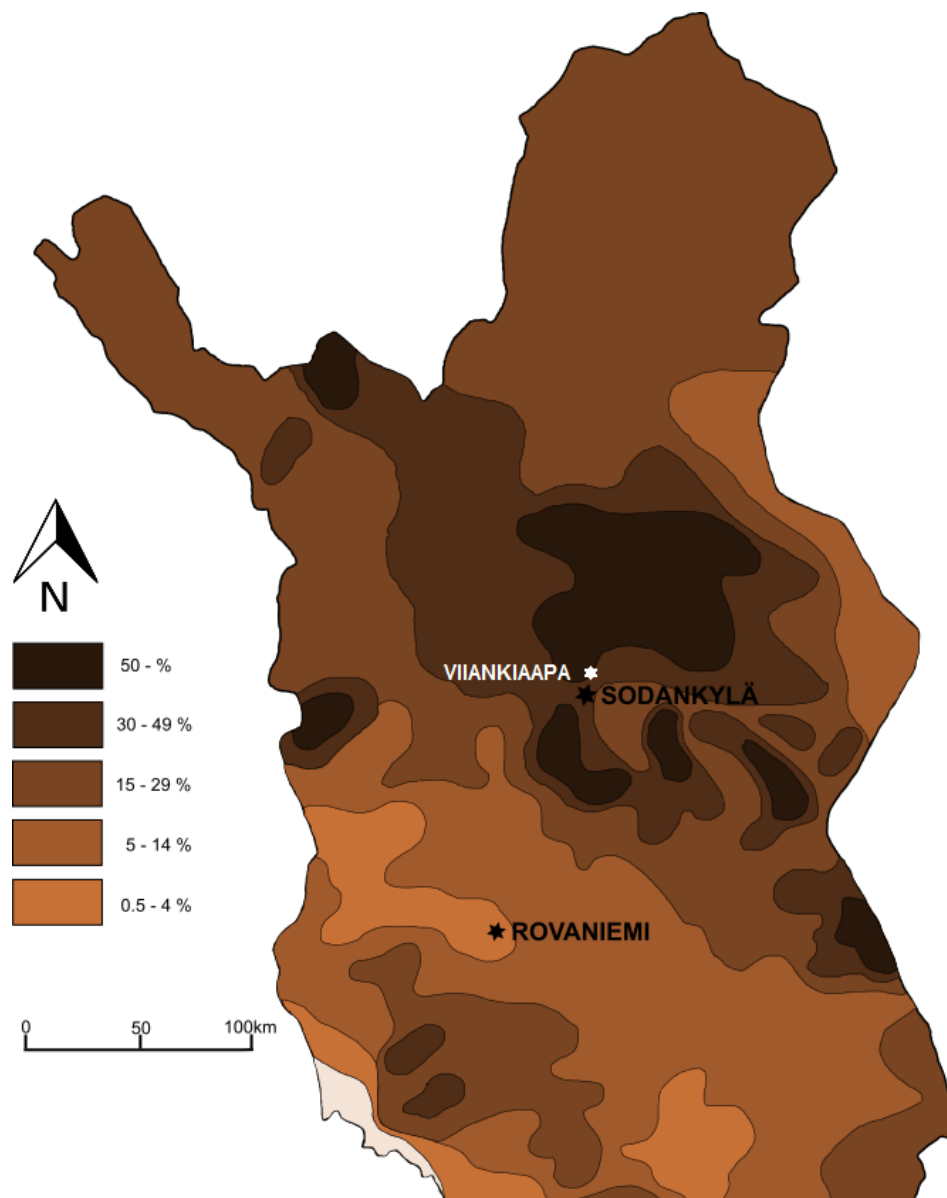


Figure 2 The proportion of patterned fens of the entire mire surface. Viiankiaapa mire is positioned in an area where there are mires which have more than 50 % or 30 – 49 % of the entire area covered with patterned fens. According to Lindholm and Heikkilä (2006).

#### 1.4 Mire hydrology

Hydrological processes are of great importance when studying mire formation, local vegetation, and peat accumulation, both in the past and at current state. Hydrology is one of the key factors determining the type of mire, which can develop in a certain area (Charman 2002, p. 41). Water table depth is one of the most important ecological factors

in most mire systems (Charman 2002, p.47). Hydrological processes are mainly a result of factors related to climate and landscape, which dictate local water exchange patterns (Price and Waddington 2000). Changes in the hydrological and topographical features of mires give rise to different types of mire waters, concerning nutrients, calcium content and acidity. These factors influence the vegetation composition and patterns within a mire (Bleuten et al. 2006).

Water and energy exchange between soil, vegetation, and atmosphere essentially drive all hydrological processes within and outside mires (Price and Waddington 2000). Once a mire has received water, it moves through the peat or is stored for a certain period of time (Charman 2002, p. 43). The rate at which water moves within a mire is affected by water pressure and resistance. Darcy's law that is most commonly used to evaluate groundwater movement applies to peatlands as well. The basic form of Darcy's law is shown in Formula 1 in which  $k$  represents the hydraulic conductivity and  $\delta h / \delta l$  the hydraulic gradient.

$$Q = -k(\delta h / \delta l) \quad (1)$$

Water outflow from a peatland may take place as surface runoff, seepage or pipe flow, and as evapotranspiration. Subsurface outflows are most commonly seepage to mineral soil underneath and around the mire. Surface runoff, however, is usually the predominant outflow from the mire. It is often linked to the fluctuations in water table. Since the upper parts of the peat layer tend to have higher hydraulic conductivity, rising water table accelerates surface runoff. (Charman 2002 p. 49-51.)

Aapamires' hydrology is often very complex and mires receive water from both atmospheric and telluric sources (Price and Waddington 2000). When classified according to hydrologic criteria aapamires are minerogenous systems. In contrast, bogs that receive water solely from atmosphere (precipitation) are ombrogenous (Bourbonnier 2009). According to Bleuten et al. (2006) water-flow in fens (minerotrophic mires) is most commonly the through-flow type, meaning that most of the horizontal waterflux is close to the surface or at it. Based on the studies made at Siperian fens, groundwater usually discharges into the fens by vertical flow (Bleuten et al. 2006).

Vegetation is important not only because plants use water and nutrients, but also because vegetation patterns affect the distribution of rain, snow and fog precipitation and also



evaporation (Price and Waddington 2000). Non-forested peatlands such as aapa mires receive more precipitation on average than forested mires at same areas. Especially at higher latitudes seasonal changes control water tables and hydrology at mires. During summer evapotranspiration is generally higher than precipitation, resulting in lowered water tables (Bourbonnier 2009). During spring water tables are at their highest due to spring flooding.

Mires receive majority of their nutrients from water. Nutrients originate from different sources in different parts of the mire complex. Surface water influence means that additional nutrients are arriving to the mire from moving surface water. In the case of older aapa mires this water usually originates from lake and river flooding (Laitinen et al. 2007). More common than the influence of surface water is the effect of groundwater movement through the mire. Groundwater derived from mineral soil transports nutrients to the mire. Groundwater flowing directly from mineral soil to or through a mire is sometimes referred to as specific groundwater (Laitinen et al. 2007).

### **1.5 Humification of peat**

The term humification describes how decomposed the peat is. Decomposition is a measure of how much of the original fibrous structure of the vegetation remains, and how big proportion of the peat no longer has recognizable plant material (Rydin and Jeglum 2006 p. 84). One of the most used visual methods to describe peat humification is the von Post humification method (Rydin and Jeglum 2006 p. 84). This method separates ten categories for peat humification and it can be easily used in field for no special equipment is needed. Categorization is based on observations made while squeezing a block peat in hand. Each class with description is presented in Table 2.

Peat humification is somewhat related to climatic factors, such as temperature and especially hydrology. As humification is a measure of decay, it mainly reflects the hydrological changes in the active upper layer of the peat: the acrotelm (Chambers et al. 2012). Decomposition is much faster in the aerated acrotelm, than in the anaerobic catotelm, and therefore humification represents the environmental conditions at the time of peat accumulation (Chambers et al. 2012). Higher temperatures and drier conditions lead to accumulation of further decomposed peat. In contrast, colder and more humid climate results in less decomposition. These variations, preferably combined with other proxies, can be used to reconstruct past climate changes, and also changes in peatland

hydrology. Using multi-proxy approach is recommended partly because changes in botanical composition of the peat affects its decomposition and therefore humification (Chamber et al. 2012). In addition to changes in precipitation mire paleohydrology in fen environments can be affected by changes in groundwater levels and flooding events of nearby rivers.

Table 2 The von Post classification for peat humification. The categorization is based on visualization and feel of the peat. Translated from Lappalainen et al. 1984.

Class	Description	Class	Description
H1	Undecomposed: plant structures unaltered, colorless water when squeezed	H6	Strongly decomposed: plant structures somewhat indistinct, but clearer in squeezed peat, 1/3 of peat passes between fingers
H2	Mostly undecomposed: plant structures distinct, nearly colorless water when squeezed	H7	Strongly decomposed: plant structures indistinct but recognizable, 1/2 of peat passes between fingers
H3	Very weakly decomposed: plant structures distinct, somewhat turbid, brown water when squeezed, no peat passes between fingers	H8	Very strongly decomposed: plant structures almost unrecognizable, 2/3 of peat passes between fingers
H4	Weakly decomposed: plant structures distinct, muddy, dark, and very turbid water when squeezed, no peat passes between fingers	H9	Almost completely decomposed: plant structures almost unrecognizable, nearly all peat passes between fingers
H5	Moderately decomposed: plant structures clear, but becoming indistinct, turbid brown water when squeezed, 1/10 of peat passes between fingers	H10	Completely decomposed: plant structures unrecognizable, all peat passes between fingers

## 1.6 Peat geochemistry

The chemical composition of peat is closely related to not only the type of ecosystem, and peat, but also the trophic state of the mire (Rydin and Jeglum 2006 p. 93). Fen environments, in contrast to bogs, usually tend to have higher values of nutrients, such as phosphorus (P) and nitrogen (N). Nutrient levels also commonly have decreasing trend with increasing depth (Rydin and Jeglum 2006 p. 93). Trophic state also has to do with the origin of water in the mire. As minerotrophic mires receive water, and therefore also nutrients, from other sources than atmosphere, the amount of nutrients depends on the chemistry of the underlying mineral soil or bedrock, overlying sediments, and the occurrence of floodwater washing over the mire (Rydin and Jeglum 2006 p. 155).

In the study of Gorham and Janssens (2005) elements were categorized into three groups: lithophilic, biophilic, and halophilic. This categorization is derived from the original Goldschmidt classification (Goldschmidt 1937) to fit the studies of peatland geochemistry. According to Gorham and Janssens (2005), for example, aluminum (Al), iron (Fe), lead (Pb), manganese (Mn), calcium (Ca), and zinc (Zn) are lithophilic elements, meaning that they are most commonly components of rock-forming minerals. From these especially aluminum is largely derived from windblown material. Also zinc and lead may result from deposition of combusted particles, but they may also be concentrated in bodies of metal ore or coal (Gorham and Janssens 2005). Elements such as iron and manganese are influenced by redox processes in the environment. Calcium is a lithophilic element that is easily mobilized into the groundwater by weathering and as carbonic acid ( $\text{H}_2\text{CO}_3$ ) is an important minerotrophic input into fen environments (Gorham 1956). Biophilic elements are those strongly concentrated in organic material. According to Gorham and Janssens (2005) these include carbon (C), nitrogen (N), sulfur (S), phosphorus (P), and potassium (K). Halophilic elements derived primarily from sea spray include, for example, chlorine (Cl), and sodium (Na).

Lead record in peat has set a starting point for geochemical studies to reconstruct paleoenvironmental changes (Bindler 2006). However, lead can only be used on a timescale extending to the beginning of relatively modern human societies, such as the Roman Empire around 2 000 years ago, using lead on daily basis, and therefore it does not provide any information on the environment at higher latitudes (eg. Finland) during early and mid-Holocene (11 700 – 8 000 cal. years BP). In addition to lead, other metals

found in peat, such as mercury, can be used to reconstruct historical metal production (Bindler 2006).

Decomposition of organic matter into inorganic compounds like carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), and ammonia ( $\text{NH}_3$ ), and processes related to it are thought to be one of the most important factors related to peat geochemistry. It affects the quantitative record of organo-bound elements such as earlier mentioned mercury, and their concentrations (Bindler 2006). Plant taking up nutrients and other elements immobilize chemical compounds until possible future decomposition. The breakdown of organic matter leading to the release of inorganic molecules is referred to as mineralization (Rydin and Jeglum 2006 p.166). Compared to other ecosystems, mineralization in mires is slow, and often higher in fens than bogs. Lowered water tables in peatlands may result in lowering of pH (Bindler 2006). Lowered pH would in turn affect the chemical composition of peat by increasing mineralization (Rydin and Jeglum 2006 p. 166.)

Carbon (C) is one of the most studied elements when regarding peatland geochemistry. Carbon is being added to peat through atmosphere  $\text{CO}_2$  used by plants. Analysis of the variability in carbon accumulation rates is used as a method for reconstructing past climate changes. Increased accumulation is connected with a more positive precipitation-evaporation relation (Mäkilä and Saarnisto 2008). In aapa mires the rate of carbon accumulation is slower than in ombrotrophic bogs. This results from more efficient oxic decay due to higher input of nutrients and oxygenated water. Oxygen is being transported to deeper peat layers via the roots of sedges. Many aapamires in Finland are approaching a stage where primary production no longer compensates the loss of carbon resulting in declining net carbon accumulation rates from the base up (Mäkilä and Saarnisto 2008). This makes aapamires also a significant source for greenhouse gases.

Nitrogen (N) is largely confined to organic forms, but it is also present in peatlands as inorganic molecules that are a result of ammonification, mineralization of nitrogen. The transfer between inorganic types of N, involving several microbial processes, such as nitrification and denitrification, is dependent on the redox potential and pH of the mire (Rydin and Jeglum 2006 p.166-167). On the other hand, emissions of  $\text{N}_2\text{O}$  from minerotrophic peatlands increases when water tables are lowered (Strack et al. 2008). In terms of water movement N is included in dissolved or particulate organic matter (Rydin and Jeglum 2006 p. 165). C/N- ratio can be used as a proxy for decomposition of peat (Bindler 2006). The decay of plant material and litter results in loss of C and therefore

decreasing C/N. In acrotelm, the C/N ratio decreases with depth as carbon is used as energy source for micro-organism and nitrogen confined in protein organisms (Malmer and Holm 1984).

Major and trace elements (Si, Al, Fe, Ti, Ca, Mg, K, Na, S, and P) are used to assess atmospheric deposition of dust and the composition of aerosols in peat. Method is mainly applied to ombrotrophic bogs since they receive all of their input through atmosphere (Weiss et al. 2001). In former studies it has been stated that even in pH 4 in organic-rich peatland waters, fine-grained mineral particles seem not to weather any further after deposition (Weiss et al. 2001). These studies covered peatlands with only atmospheric input (eg. Steinmann and Shotyk 1997) and there is no record of how major and trace elements are preserved in fen-like environments, where in addition to atmospheric input, mineral material may also originate from surface water runoff.

Sulphur (S) is especially abundant in peats and is an element that is strongly affected by waterlogged conditions which tend to reduce the amount of sulphur. The behavior and occurrence of sulphate ( $\text{SO}_4^{2-}$ ) differs considerably between waterlogged undrained peat and drier conditions. In water-saturated conditions, sulphates and other oxidized forms of sulphur can be reduced by *Desulphovibrio* bacteria to gas (hydrogen sulphite,  $\text{H}_2\text{S}$ ) or to pyrite (iron sulphide,  $\text{FeS}$ ). To which the sulphur is being reduced to, depends on the availability of iron. Processes related to sulphur are generally more important in fen environments rather than bogs. (Charman 2002, p.55.)

### **1.7 Age determination of peat**

Peatlands are considered as rich archives of paleoenvironmental information, but without a reliable chronology reconstructions are somewhat useless (Walker 2005 p.41, Charman 2002 p.121). Especially ombrotrophic peat bogs have been used to reconstruct paleoclimate due to their development being closely related to precipitation. Peat deposits are mainly autochthonous meaning that their material originates within the mire (Mäkilä and Saarnisto 2008). In most cases, this increases peats reliability when used in dating, especially when dating ombrotrophic mire deposits. There are four main types of dating used in peatland environments: radiometric methods, time markers, incremental counts and techniques based on peat accumulation (Charman 2002 p.121).

The most common technique for dating peat one of the radiometric methods, which provide absolute timescale comparable with other types of sedimentary record (Charman

2002 p.121). Radiocarbon dating is based on the decay of  $^{14}\text{C}$ -isotope in dead organic matter, such as peat. It, as were other radiometric dating methods, was developed in the middle of twentieth century (Roberts 2014 p.13).  $^{14}\text{C}$  is formed in the upper atmosphere and oxidized in to  $\text{CO}_2$ , which is later being used by plants in photosynthesis, and animals while breathing. The rate of the decay must be known, as does the original amount of  $^{14}\text{C}$  in the atmosphere. In radiometric dating the rate of decay is expressed in half-life which for  $^{14}\text{C}$  is  $5\,730 \pm 40$  years (Godwin 1962). Half-life of  $^{14}\text{C}$  sets the timescale for radiocarbon dating. Maximum age for  $^{14}\text{C}$ -datable material is around 40 000 radiocarbon years. Most peatlands, especially in the northern hemisphere, are much younger than this and therefore are suitable for radiocarbon dating (Charman 2002 p.122). The relation between the radioactive  $^{14}\text{C}$ -isotope and the stable  $^{12}\text{C}$ -isotope can be measured to a great precision using AMS (Accelerator Mass Spectrometry). Based on the relation, the age of the sample can be calculated (Walker 2005 p.21).

Peat contains large proportions of organic material and it is approximately 50 percent of carbon (Charman 2002 p. 121). Fossil pollen and various plant macrofossils (such as seeds, leaves, wood fragments etc.) provide information about the past surface vegetation, which can be linked to climate, hydrology and/or human activities in the area. In addition, they provide good quality datable material for AMS-radiocarbon dating (Walker 2005 p.41). Sphagnum or other moss leaves and stems are considered some of the best peat components to date, when available (Charman 2002 p. 123). In addition to specific fossil remains found in peat, it is also possible to do AMS-dating on bulk peat samples.

Although radiocarbon dating is widely used in dating peat, it is not without error. Problems causing error are associated with assumptions of the atmospheric concentration of  $^{14}\text{C}$ , and depositional and post-depositional processes (Charman 2002 p. 122). Peat contains organic material from various sources and depending on the material dated, it can be of various ages. In peatlands for example, roots of surface vegetation may bring so called ‘younger carbon’ to the horizon being dated. This is difficult to take into account and may cause significant error on the age determined (Charman 2002 p. 123). This problem can be reduced by choosing dated material carefully and by pretreating (sieving, acid washing) the sample. Also radiocarbon ages do not automatically represent calendar years and therefore need calibration. Calibration curves used today are based on radiocarbon ages of various records such as tree rings (dendrochronology), corals, and varve sediments (Walker 2005 p. 32-37).

## **2. GEOLOGICAL SETTING**

### **2.1 Deglaciation and the development of Baltic basin**

During the Quaternary period Finland and especially Finnish Lapland has been covered by continental ice-sheets in multiple occasions. In between of these glaciations there has been warmer interglacial intervals during which the Baltic basin has been occupied by water (Taipale and Saarnisto 1991 pp.231 and 235). Also land uplift has been and still is a considerable phenomenon around the Baltic basin revealing more land from water (Eronen et al. 2001). It has been estimated that since the ice started to melt and retreat the central Lapland area has risen as much as 500 meters due to isostatic uplift (Mörner 1980 in Tikkanen 2006).

There are four main stages that can be recognized in the Holocene history of the Baltic basin after the last glaciation: Baltic Ice Lake, Yoldia Sea, Ancylus Lake, and Litorina Sea. These stages have mainly been influenced by factors related to the retreat of the ice-sheet which include land uplift and changes in eustatic sea-level (Eronen et al. 2001). When it comes to the development and history of northern Finland and Viiankiaapa mire, the Ancylus Lake phase is the only one to be considered.

As the ice-sheet retreated even further the isostatic uplift became faster than the rise of sea level. The Baltic basin reached its second freshwater phase, Ancylus Lake, around 10 500 cal BP (Andrén et al. 2011). During the Ancylus Lake phase the highest shore was reached in northern parts of Finland, including Finnish Lapland (Ojala et al. 2013). The highest shore acts as a divider between subaquatic and supra-aquatic terrain (Tikkanen 2006). In Sodankylä the highest Ancylus shore is at 186 m a.s.l. (Johansson & Kujansuu 2005).

### **2.2 Deglaciation of Finnish Lapland**

In Lapland the Late Weichselian glacier melted on supra-aquatic land and subaquatic conditions existed only in western part of northern Finland, including Sodankylä, which was partly covered by Ancylus lake phase (Lunkka et al. 2004, Ojala et al. 2013). The reconstruction of the deglaciation in Sodankylä region as in all of northern Finland is based on studies of subglacial meltwater activity, till stratigraphy, proglacial, marginal and lateral meltwater processes and especially the development of ice lakes (Johansson 2007, Lunkka et al. 2004). Their formation required for the ice margin to have retreated

downslope along the main river valleys (Kujansuu 1967). Ice lakes are indicated in the geological record by the presence of raised shorelines and outlet channels, coarse outwash sediments and fine-grained glaciolacustrine sediments (Johansson 2007). The last remains of the Scandinavian ice sheet retreated from western Lapland around 10 000 years ago (Hughes et al. 2015). Altogether it is thought that the deglaciation in Finnish Lapland region lasted 1 600 years, beginning 11 500 BP when the northernmost corner was released from ice after Younger Dryas (Johansson 2007).

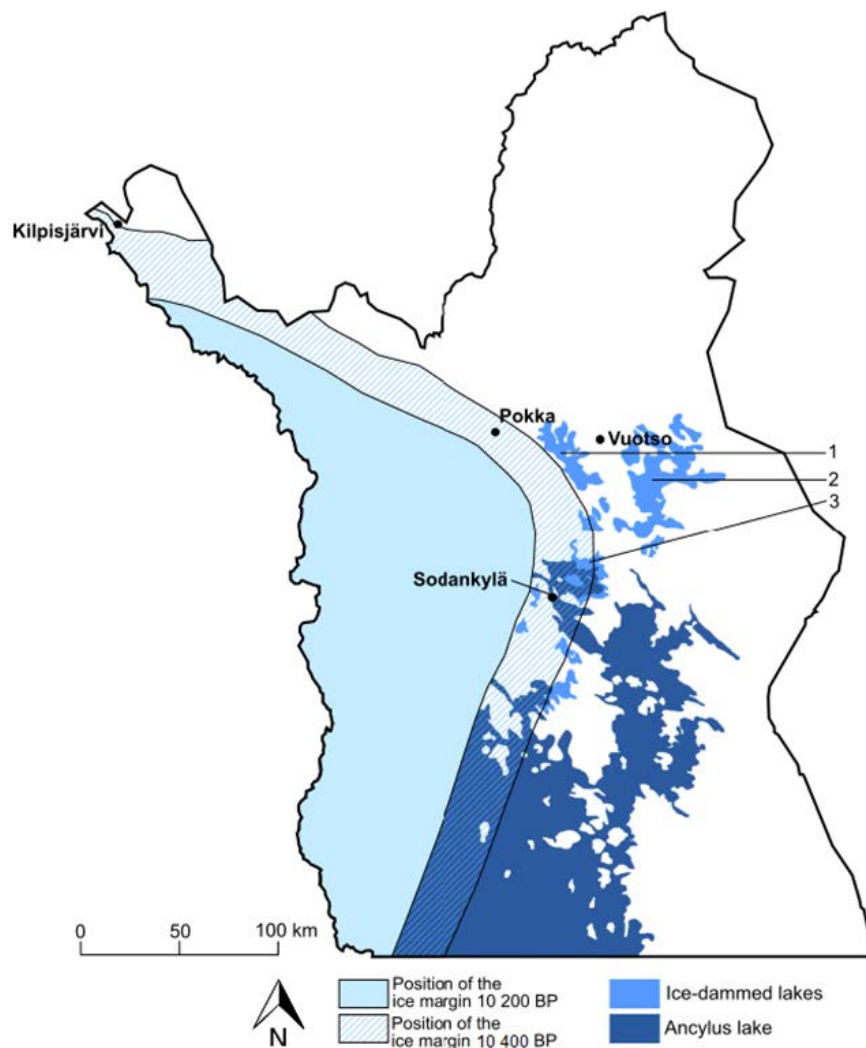


Figure 3 The position of the ice margin 10 400 BP and 10 200 BP in context with the known positions of Moskuvaara ice lake (3), Porttipahta ice lake (2) and Ice lakes of Saariselkä region and Posoaapa Ice lake (1) at their largest extension. In darker blue color the map also shows the approximate position of Ancylus lake 10 400 cal BP. The positions of the ice margin are based on interpretation by Johansson and Kujansuu (2005). Locations of the ice lakes and Ancylus lake are based on interpretation by Johansson (2005). It must be stated here, that there were many more ice lakes in the area of Finnish Lapland during deglaciation, that are not presented in this Figure (see. Johansson and Kujansuu 2005 and Johansson 2005)



The study area is located close to the ice divide which has had considerable effect on the movements of the continental ice sheet, deglaciation and on the glaciomorphological features of the area (Johansson 1995, Johansson et al. 2011). Sodankylä region was released from ice around 10 300 years ago and it was occupied by pro-glacial ice lakes. In addition to ice lakes, meltwaters produced a series of shallow meltwater channels (Johansson 2007). Smaller meltwater channels are of great importance when reconstructing the deglaciation in detail (Johansson 2007, Lunkka et al. 2004). During this time the ice sheet stagnated in many places and melted in situ. This is indicated by the absence of eskers in central Lapland area, including Sodankylä region, where only few small eskers have been identified (Johansson 2007, Väisänen 1988). Because of the fragmentation and in situ melting of the ice, most of the ice lakes in the area were filled with blocks of ice in addition to meltwaters.

The main ice lake in the area referred to as Moskuvaara Ice Lake had its highest level at 207 meters above current sea level. At its maximum extend it covered an area of 400 km<sup>2</sup> including the current basin of Viiankiaapa mire. Around 10 400 cal. BP Moskuvaara ice lake was draining towards the present Luiro valley. Later 10 300 cal. BP the water level of the ice lake dropped to 195 meters a.s.l. At this time Moskuvaara ice lake was draining towards south through the Hirviäkuru gorge. The lake was collecting meltwaters from the edge of the glacier and they entered Moskuvaara ice lake around the present Matarakoski area. Here the Matarakoski delta was deposited (Johansson 2005). After the ice sheet further retreated the water from Ancylus lake occupied the basin and Moskuvaara ice lake was connected to it. The highest shoreline north of Sodankylä is estimated to 186 meters and it was formed during the Ancylus Lake stage. The position of the edge of the ice sheet 10 400 cal. BP and 10 200 cal. BP, along with the locations of ice lakes and Ancylus lake, are presented in Figure 3.

### **2.3 Viiankiaapa mire**

Viiankiaapa mire is located in the municipality of Sodankylä, approximately 15 kilometers north-east of the city center, 188 – 190 meters above sea level. It is on the eastern side of Kitinen River and has developed in close connection to it (Lappalainen 2004). Viiankiaapa is a large aapamire complex consisting of multiple smaller minerotrophic mire sites and bogs, with most of the area being categorized as minerotrophic peatland (Metsähallitus 2006). It is one of the largest peatlands in

Sodankylä area. Measured from basic maps the total area of Viiankiaapa is 5 385 ha (Lappalainen 2004). When taken into account all parts of the mire complex (including Käppäläaapa and Eliasaapa, Figure 4) the area of the entire aapamire complex is 7 135 ha (Lappalainen et al. 1981).

It belongs to the northern aapamires of Peräpohjola region (Figure 1) and represents a typical aapamire. Mire site types categorized by the dominant tree species, and their relative abundance in the Viiankiaapa area are presented in Table 3. Viiankiaapa is characterized by large flarks and ridges that may be several kilometers in length. Large open flarks are particularly abundant in the center of the mire. The habitats of Viiankiaapa mire are mostly in their natural state. The road between Kersilö and Moskuvaara (Figure 4) has, however, to some extent affected the natural flow of waters through the mire (Pääkkö 2004). The northern side of the road is referred to as Viiankiaapa N, and the southern side as Viiankiaapa S.

Table 3 The distribution of mire site types of Viiankiaapa mire based on their minerotrophy. From the Table it is clear that mesotrophic fens are the most common in Viiankiaapa area. Translated from Pääkkö 2004.

	area		Minerotrophy							
			Ombrotrophic		Oligotrophic		Mesotrophic		Eutrophic	
Mire site type	ha	%	ha	%	ha	%	ha	%	ha	%
Spruce mires	378	7			33	9	272	72	73	19
Pine mires	1197	23	54	5	743	62	337	28	63	5
Fens	3231	64			546	17	2685	83		
Eutrophic fens	305	6							305	100
Combined	5111	100	54	1		26	3294	64	441	9

Viiankiaapa mire was mapped in most part in 1965 by the Geological survey of Finland. In this survey 3 960 hectares were investigated in altogether 309 individual study points (Lappalainen and Pajunen 1980). From each study point the total thickness of the peat layer was measured and also the mire site type was defined. From stratigraphic study points the entire peat layer was described in detail, making observations about the type and degree of humification of the peat. The type of the underlying mineral soil was determined from each study point.

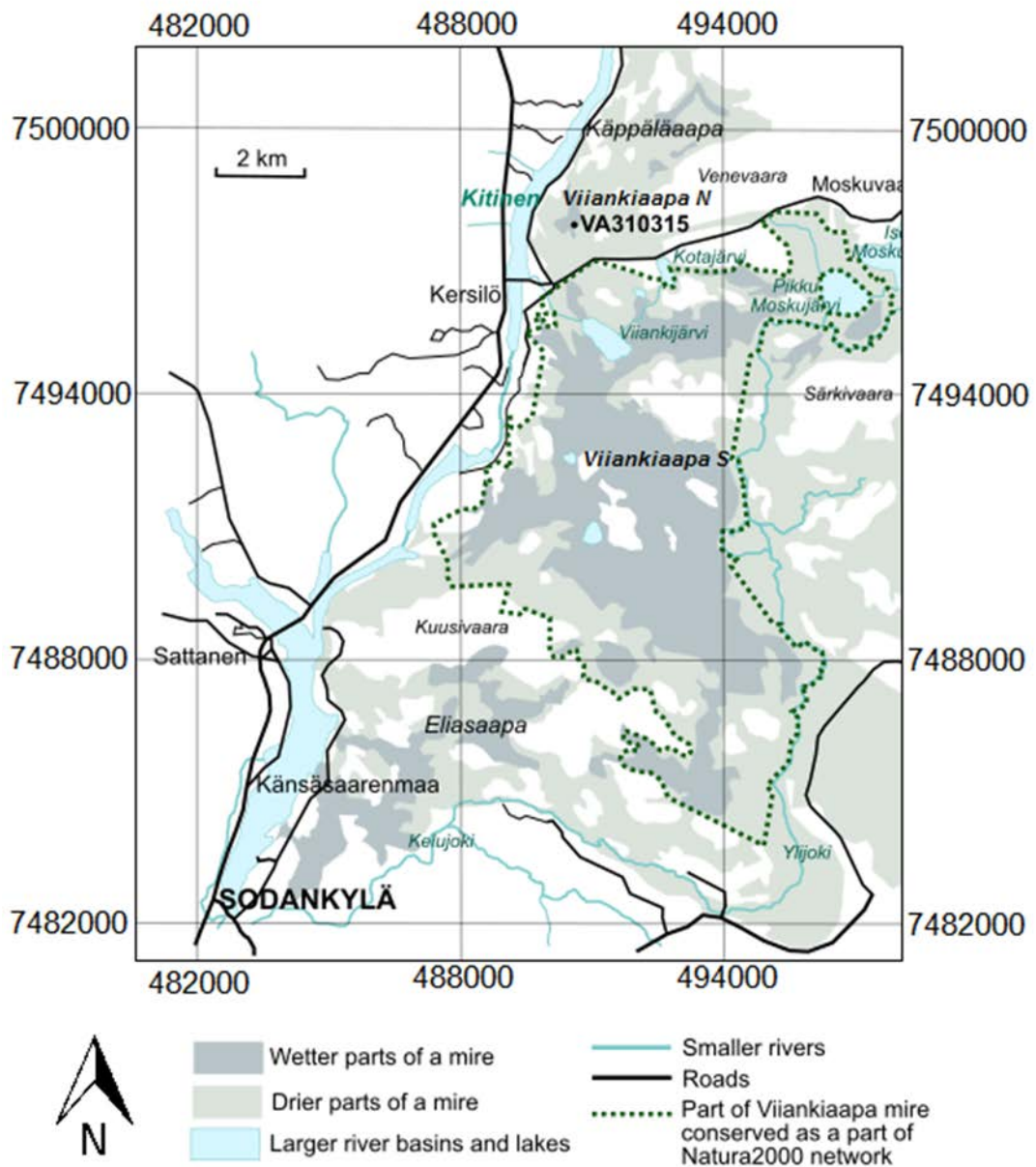


Figure 4 A basic map of the Viiankiaapa surroundings. The study site is located in the northern part of the mire complex in the area of Viiankiaapa N. The ore deposit found in the area is located between Viiankiijärvi and Kuusivaara, underneath the Natura 2000 area. Viiankiaapa is mainly composed of wet and difficult to traverse regions which are shown in the map with darker grey color. From the map the closeness of Kitinen river can also be understood. In many parts the river is directly connected to the mire. In other parts it is separated from the mire with riverbanks mainly composed of sand. The location of the coring site VA310315 is also shown.

From surveyed 3 960 ha, 2 175 ha had a peat layer of over one meter and 1 225 ha has over two meters. The total volume of peat in the studied area was 90.7 million m<sup>3</sup> (Lappalainen 2004). The underlying soil varied from tills to sandy layers. Lake muds were found in the deepest parts of the mire. From the main peat types Sedge peat was found dominant in 66 %, Bryales peat in 34 % and wooden peat in 5 % of the mire region (Lappalainen and Pajunen 1980). The average humification was 4.5. The collected data was supplemented in 1975 by another 95 study points from the northern parts of the complex (Viiankiaapa N, Figure 4). This data is addressed in more detail in Chapter 2.3.1.

Table 4 The Natura habitats of Viiankiaapa Natura 2000 area (situation 1.5.2004). Significantly important (prioritized) habitats are marked with \*. Data for habitats marked with \*\* is obtained from SutiGis-database that is based on surveys done in the area. Modified from Metsähallitus 2006.

Code	Habitat	%	ha
3160	Natural dystrophic lakes and ponds	3	198
3260	Water courses of plain to montane levels with <i>Ranunculus fluitantis</i> and <i>Callitriche</i> - <i>Batrachium</i> vegetation	1	66
6450	Northern boreal alluvial meadows**	< 1**	4**
7110	Active raised bogs**	1**	55**
7140	Transition mires and quaking bogs**	2**	94**
7310	Aapa mires*	87	5738
7220	- Petrifying springs with tufa formation ( <i>Cratoneurion</i> ) within aapa mires**	< 1**	0.5**
7230	- Alkaline fens within aapa mires**	7**	417**
91D0	- Bog woodlands within aapa mires**	11**	694**
7220	Petrifying springs with tufa formation ( <i>Cratoneurion</i> ) outside aapa mires**	< 1**	0.1**
7230	Alkaline fens outside aapa mires**	< 1**	24**
91D0	Bog woodlands outside aapa mires**	5**	287**
9010	Western taiga*	9	594
	- Spruce forests	3	198
	- Pine forests	2	132
	- Mixed coniferous forests	3	198
	- Mixed forest	1	66
9060	Coniferous forests on, or connected to, glaciofluvial eskers**	< 1**	13**
	Habitats outside the Natura 2000 classification**	3**	179**

Viiankiaapa started to form during and after the draining of Moskuvaara ice lake. Eino Lappalainen (1970) studied the development history of Viiankiaapa mire as a part of his PhD thesis. For this purpose a 6.7 meter peat core was collected for diatom and pollen analyses. In the earliest stage sandy layers were deposited in the bottom of the basin. The sand layer was later covered with gyttja, which is an indication of a lake phase in the development history of Viiankiaapa mire (Lappalainen 2004). Before the overgrowing of the lake, approximately half a meter of coarser grained gyttja was deposited. The deepest parts of the peat layer were comprised mostly of the remnants of *Bryales* vegetation. When moving towards the surface, *Sedge* peat becomes more and more abundant.

Table 5 Endangered or threatened plant species found in Viiankiaapa Natura 2000 – area. According to Metsähallitus 2006.

Plant species	Nature directive-species	Endangerment class
Vascular plants		
<i>Carex heleonastes</i> *		Endangered*
<i>Carex appropinquata</i>		Endangered
<i>Dactylorhiza inc. ssp. cruenta</i>		Endangered
<i>Dactylorhiza lapponica</i>		Endangered
<i>Dactylorhiza traunsteineri</i>		Endangered
<i>Saxifraga hirculus</i>	X	Endangered
<i>Dactylorhiza incarnata ssp. incarnata</i>		Threatened
Mosses		
<i>Hamatocaulis vernicosus</i>	X	Endangered
<i>Palustriella decipiens</i>		Threatened
<i>Palustriella falcate</i>		Threatened

\*Finland's international species of responsibility

According to Lappalainen (1970) the macroscopic composition of the peat indicated that Viiankiaapa mire was first dominated by eutrophic fens and later moderately minerotrophic fens (flark fens and herb-rich flark fens). The pollen record, combined with the stratigraphy, states that the final overgrowing of the lake happened during the beginning of transition from birch dominated forests to pine forests, approximately 8 600 years ago (Lappalainen 1970). The hydrology of Viiankiaapa mire is affected by the old

river basins and runoff channels formed during the melting of the continental ice sheet (Lappalainen 2004).

Some of these basins can be discovered from underneath Viiankiaapa mire by coring. The bedrock in the area of Viiankiaapa mire has also affected the development history of the mire. There are both alkaline volcanic rocks and acidic quartzites in the area. Alkaline volcanic rocks are often connected with more rich peatlands such as fens (Metsähallitus 2006). Viiankiaapa conservation area was first established in 1988 (Metsähallitus 2006). A large portion (altogether 6 595 ha) of Viiankiaapa is now part of the Natura 2000 conservation network (Figure 4). The Natura 2000 area consists of 11 individual habitats that are listed in the Habitats directive (92/43/EEC) of European Union. These habitats and their relative abundance in Viiankiaapa mire are listed in Table 4. Altogether ten plant species classified as either endangered or threatened are found in Viiankiaapa area. Seven of these species are vascular plants including *Hudson Bay Sedge* (*Carex heleonastes*) which is Finland's international species of responsibility (Metsähallitus 2006). All endangered or threatened plant species of Viiankiaapa mire are presented in Table 5. In addition, Viiankiaapa mire is considered as a very important birdlife conservation area with 91 individual species, from which 21 are classified as endangered (Metsähallitus 2006).

### 2.3.1 Study site

The study site is located in the northern part of Viiankiaapa mire complex (Viiankiaapa N, also referred to as Käppäläaapa, see Figures 4 and 6). The total area of Viiankiaapa N and Käppäläaapa is 770 ha from which 355 ha is treeless (Pääkkö 2004). This location was chosen due to it being outside the confines of the Natura 2000 area (no coring was allowed inside the Natura 2000), and due to earlier studies stating that there should be lake mud above the underlying sand. The occurrence of lake mud is important since the aim was to study the entire development history of the mire. Lake muds have been deposited in the Moskuvaara ice lake stage (appr. 10 300 yr. BP) and represent the beginning of the mire development. The aim was also to establish a reliable age for the mire which could be achieved when material from the contact between peat and underlying sand could be dated.

The coring site VA310315 is located on a treeless and difficult to traverse part of the mire (See Fig. 6). This was especially apparent during field work in summer time. The mire in

the area was highly wet and moving around in the area took a lot of time. The vegetation in the immediate surroundings of the coring site resembled that of flark fens and minerotrophic fens (Figure 5). The vegetation patterns gave information of the minerotrophic state of this part of the mire.



Figure 5 Pictures taken from the immediate surroundings of coring site VA310315. Images show that the vegetation mainly consists of different types of sedges. *Menyanthes trifoliata* and *Betula nana* were abundant. Stunted pines could be seen closer to the mire margins. The flark-string pattern is difficult to identify from these images but it was apparent on sight.

In the summer of 1975 the Geological Survey of Finland mapped the area of Viiankiaapa N. This investigation consisted of altogether 91 coring points where the thickness of the peat, its average humification, mire site type, and the underlying soil was determined. In this study the average ash content was determined at 3.6 % and pH value at 4.4. (Lappalainen and Pajunen 1980.) The average humification in the area was 4.3. The locations and details of each coring site are shown in Appendix 1.



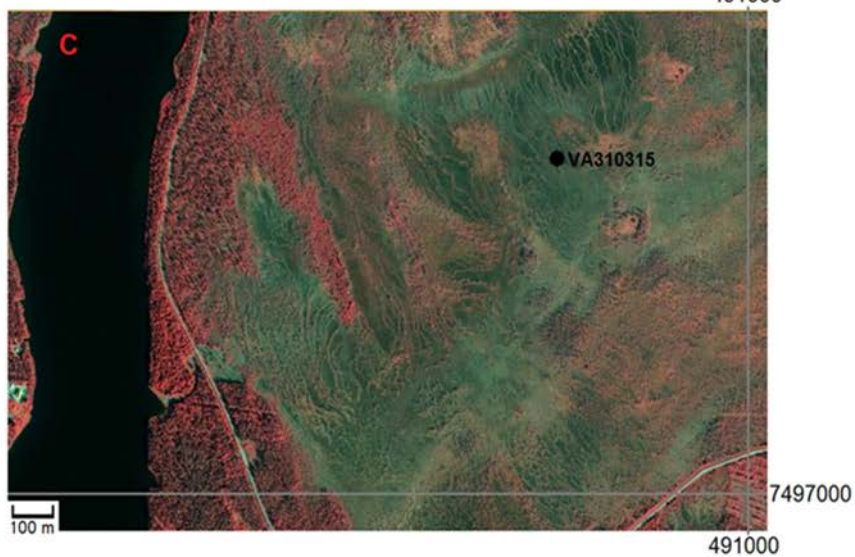
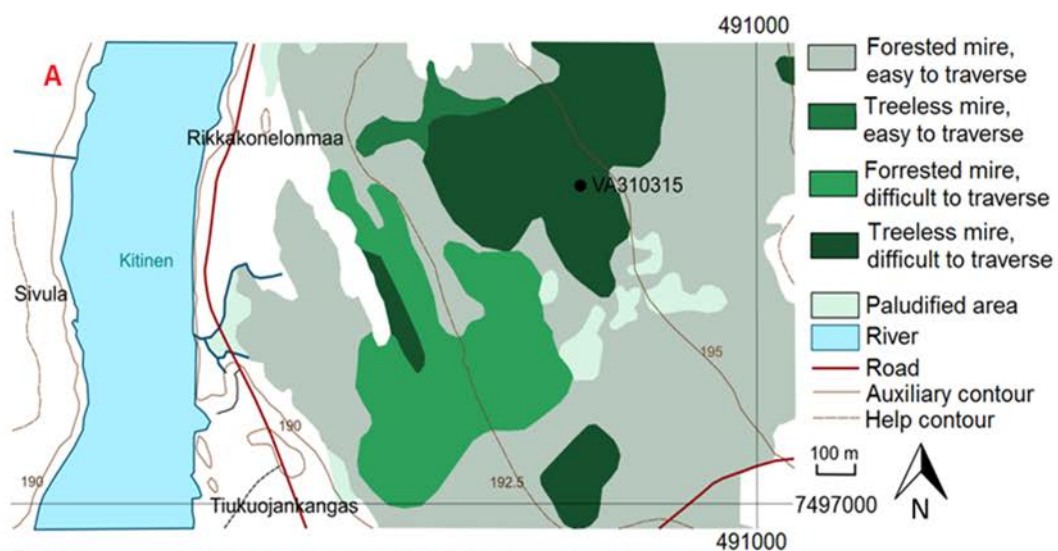




Figure 6 (Previous page) In Figure 7A there is a simplified terrain map showing the main features of the area. Coring site is located in an area classified as treeless mire that is difficult to traverse. This is mainly due to the fact that it is a wet flark-string patterned part of the mire. Figure 7B is a true-color aerial image of the area. In the figure treeless parts of the mire can be clearly identified. Also the orientation of the flark-string pattern is somewhat visible. Kitinen is seen in the figure in very dark blue color. Figure 7C is a false-color aerial image of the same area. In this figure vegetation is highlighted with red color. Green color shows areas that remain unchanged while the image was taken (no trees moving in the wind etc. Flark-string pattern is better visible in the false-color image due to higher contrast between vegetated and non-vegetated areas.

The study site may be hydromorphologically categorized as floodplain mire. The basic concept of this mire type is presented in Figure 7. Floodplain mires, or fens, form in association with a river system. In the case of Viiankiaapa, the Kitinen river. They receive a significant amount of annual water income through seasonal flooding which affects the groundwater table. The peats in these kinds of surroundings are often waterlogged all year round. (Charman 2002, p.12.)

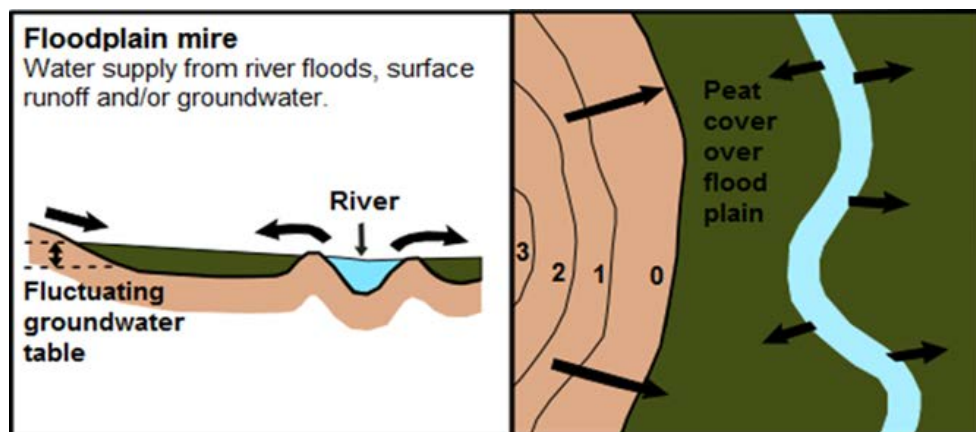


Figure 7 Floodplain mire or fen represents one key hydromorphological mire type, and is relatively abundant in aapa mires of northern Finland. Here, the mire receives water from river floods, surface runoff and/or groundwater. The groundwater table often fluctuates seasonally following spring and autumn flooding events. The black arrows in the Figure represent the movement of water. Figure according to Charman 2002 (p. 7).

### **3. MATERIAL AND METHODS**

#### **3.1 Coring and sampling**

A 4.3 meter peat core (VA310315, 7497803 N/0490511 E) was collected 31.3.2015 using a 1 meter Russian peat sampler. At the time of coring, the thickness of the snow cover was 80 cm and the frost layer 30cm. All together five sections were collected (30 – 130cm, 110 – 210cm, 190 – 290cm, 270 – 360cm and 340 – 430cm). The frozen top part of the core was sampled by chopping off and measuring frozen peat pieces. In addition to the peat core two surface vegetation samples were collected for closer review.

The same site was revisited 15.8.2015. The entire 4.3 meter core was cored anew and described on site. This time a smaller 50 cm Russian peat corer was used. No peat samples were collected. A smaller corer and easier conditions allowed for a representative underlying sediment sample to be collected.

#### **3.2 Age determination**

Six samples from increasing depth levels were subsampled for age determinations. Subsamples were collected at depths 35 cm, 125 cm, 205 cm, 275 cm, 340 cm, and 430 cm. The sample from depth 430 cm is representing the basal age of Viiankiaapa mire and the beginning of peat increment. Each sample consisted of terrestrial plant remains like seeds and pieces of birch leaves and wooden particles. All samples were dated at LUOMUS Laboratory of Chronology at Helsinki University, using  $^{14}\text{C}$  AMS dating method (Tikkanen et al. 2004).

Collected dating samples were pretreated using a standard procedure for plant material (acid-alkali-acid treatment) (eg. Ramsey 2004). Obtained  $^{14}\text{C}$  ages were calibrated to calendar years using Intcal13 calibration curve (Reimer et al. 2013) and Oxcal 4.2 software (Bronk-Ramsey 2009). Calibration was done on the behalf of the dating laboratory.

#### **3.3 Peat stratigraphy**

The von Post method was used in the field to determine humification of the peat. Different groups of vegetation remnants were identified visually and their relative volume was estimated based on method dividing the entire volume of peat into six parts. From these parts two main factors and two initial factors were identified if present. In this case initial

factors were present only in volumes less than 1/6 of the entire sample volume and therefore they are not mentioned in Table 7. In addition the wetness of peat was determined on a scale from 1 to 5 with 5 being mostly water and 1 being entirely dry.

### **3.4 Water content**

Water content of the peat was determined in 2 cm continuous resolution throughout the core for depths between 30 cm and 430 cm. Since the top 30 cm was frozen at the time of coring water content determinations from this section were done in longer intervals.

Porcelain crucibles were acid-washed, dried and weighed before use. Sample between 3 and 5 grams was placed in the crucible and weighed again. Each sample was dried in an oven in  $105 \pm 2$  °C for 23 hours to ensure all water had evaporated. After heating samples were cooled for 15 minutes in desiccator and weighed again.

### **3.5 Loss-on-ignition, ash content and the color of the ash**

Loss-on-ignition (LOI<sub>550</sub>) was determined to reveal mineral material content (ash content, AC) of the peat. Ash residue after ignition is a mixture of primary ash from the peat forming plants, and secondary ash derived from mineral constituents (Rydelek 2013). Determination was done at the same 2 cm continuous resolution as the previously described water content. Dried and weighed samples were crushed by hand using a scoopula and heated in porcelain crucibles in an oven at 550 °C for 2 hours to remove all organic material. After heating samples were allowed to cool in desiccator for 30 minutes before weighing again.

Continuous LOI<sub>550</sub> and AC analyses were conducted for depths between 30 cm and 430 cm. Since the top 30 cm was frozen at the time of coring determinations from this section were done in longer intervals and with bigger sample size.

#### *3.5.1 The color of the mineral material*

For the mineral material, obtained via AC determinations, a color was defined using the Munsell Soil color chart (Munsell 1975). This was done because the color of the ash changed in samples representing different depths from pinkish to dark red. The change was so distinctive that it is thought to give information on the redox-conditions of the mire. For the comparison with chemical concentrations, the color needed to be documented using a widely known and simple method.

### 3.6 Peat geochemistry

Prior to any chemical analyses the entire peat core (depths 30 – 430cm) was divided into 2 centimeter sections, packed in LDPE bags, frozen and dried using a SCANVAC CoolSafe™ freeze dryer. Drying time was four days. After drying samples were grind by hand through the LDPE bag. No mechanical grinder was used in order to avoid sample contamination. Due to grinding being done by hand, it is possible that the samples are not fully homogenized. This may have a slight effect on the analytical results. Error is monitored by the use of parallel samples being measured.

#### 3.6.1 *Metal and non-metal analyses*

For the multi-element analyses 14 individual elements (Fe, Ti, Al, Zn, Cu, Ni, Pb, Si, P, K, Mn, Mg, Ca, and Na) were chosen. These elements were thought to provide most information on the development history and hydrology of the mire. Also possible comparison with other similar studies affected the selection of these particular elements.

To analyze the alkali and earth alkali metal concentrations of the samples, the solid peat samples needed to first be wet digested. This was done by weighing approximately 0.25 g of sample into PFA vessels and measuring in 9 ml of 71 % suprapure nitric acid (HNO<sub>3</sub>) on top. The vessels were sealed mechanically and heated using CEM Mars 5 microwave accelerated reaction system. Method EPA 3052 (EPA 2014) for total concentration determinations from organic samples and sediments was selected due to the organic nature of the samples. The method 3052 is designed for total sample decomposition with the use of appropriate acid mix for different types of sample matrixes. In this case only nitric acid was used, since there was no need to break down siliceous material within samples.

To monitor the results of the wet digestion and the analyses, 11 reference samples (Moss M3, Steinnes et al. 1997) were put through the same pretreatment process as the actual samples. In addition 10 zero samples (only nitric acid) and 12 parallel samples were prepared and analyzed. After wet digestion all samples were moved to 15 ml HDPE test tubes and centrifuged. Samples were diluted 1:20 using class I water (Milli-Q) as diluent. Final volume of the samples was 10 ml. The results for the reference materials are presented in Appendix 4.

The analyses were conducted using an ICP-MS (Inductively coupled plasma mass spectrometry) analyzing machinery. To first learn about the approximate concentrations

of the samples, a semi-quant-analysis was conducted for 60 selected samples. Based on the results, a calibration of nine levels was designed and prepared for each element being analyzed. Multiple levels needed to be used since some elements were present in wide concentration range. The ICP-MS was programmed to fit the analysis of the samples and the analysis of all 14 elements was carried out at once.

### 3.6.2 *CNS-analysis*

The analyses of carbon and nitrogen contents were conducted with gas chromatography using solid samples. In this case, Vario Elementar MICRO cube- unit was used. The analysis is conducted of three stages: catalytic combustion, reduction, and gas chromatographic determination. No sample preparation was needed other than drying and grinding. Dried and grinded samples were weighed at approximately 5 mg and packed in a tin boat and burned at 1150 degrees. The program calculated the content automatically based on known standards and zero samples. In this case sulfanilamide was used as a standard. The results were also monitored by parallel samples, and the use of 13 samples of reference material Moss M3 (Steinnes et al. 1997). The results for the reference materials are presented in Appendix 5.

Also sulfur content was obtained from most of the samples. However it was not obtainable from all samples since its levels were below the detection limit. For these samples a percentage was given but it will not be reported since it's based on an assumption rather than absolute values.

### 3.6.3 *Data processing*

#### *Concentration calculations*

For the CNS-analyses, the data could be collected without any further processing since the software used calculated values automatically based on the weight of the sample, used standards, and zero-samples. All numeric data is shown in Appendix 2.

For the analyses conducted using ICP-MS a calculation needed to be performed to derive the true concentrations of the solid peat sample. Since the sample was first weighed, soluted in 9 ml of 71 % nitric acid, and then diluted 1:20 for analyses, the true concentration could be calculated using Formula 2.

$$content (\mu g / g) = \frac{[9 \times 20 \times (c_{sample} - c_{zero})]}{m_{sample}} \quad (2)$$

, with the  $m_{sample}$  being the weight of the sample,  $c_{sample}$  the measured concentration, and  $c_{zero}$  the concentration of zero-samples (samples with only nitric acid and class I water). Samples whose measured concentration was above or below the detection limit were completely left out of interpretation. All processed numeric data for ICP-MS analyses is shown in Appendix 3.

#### *Accumulation rate calculations*

Accumulation rates were calculated for the peat itself and to carbon and lead. For the determination of peat accumulation rate (PAR, mm yr<sup>-1</sup>), the age-depth model (Figure 8) was used. In the calculations for element accumulation rates (EAR), the PAR was taken into account. For dry bulk density, an average for Finnish Bryales and Sedge peats (82.5kg/m<sup>3</sup>) was used (Mäkilä 1994). In these simple calculations, the effect of peat decay and packing were not taken into account, but will be discussed later on. For the EARs Formula 3 was used.

$$EAR = r \times E \times \rho \quad (3)$$

, where  $r$  is the PAR (m yr<sup>-1</sup>),  $E$  is the concentration of the element (g/g), and  $\rho$  is the dry bulk density of the peat.

#### *Statistical methods*

The statistical analyses for geochemical and physical (LOI<sub>550</sub>) properties were carried out using IBM SPSS Statistics 22 software. The purpose for the statistical analyses and grouping of the different elements and properties, was to determine the controlling factors of mineral material input to Viiankiaapa mire.

To identify significant correlations between different variables, the Spearman rank correlation coefficient (eg. Ranta et al. 1991) was calculated. All variables analyzed and calculated were taken into account. The spearman correlation matrix gives information on which variables are connected to each other, and may therefore be used to asses deposition patterns at Viiankiaapa mire.

## 4. RESULTS

### 4.1 Chronology

All of the six ages obtained with  $^{14}\text{C}$  dating are presented in Table 6. It can be noted that the ages are in chronologically logic order with oldest ages at the bottom of the peat core. As the depth increases also the statistical error increases. Age at the bottom (Hela 3728), when calibrated to calendar years, has a span of 420 years. This marginal may be seen as relatively good result for an age this old.

Table 6 The measured and calibrated  $^{14}\text{C}$  BP ages for the peat core VA310315.

Lab code	Sample	depth (cm)	$\delta^{13}\text{C}(\text{‰})$	Obtained age yr. BP	Calibrated $^{14}\text{C}$ age-range yr. BP *
Hela-3732	Remnants of vegetation	35	-28,3	$767 \pm 20$	670 – 730
Hela-3724	Remnants of vegetation	125	-27,1	$3\,883 \pm 24$	4 240 – 4 415
Hela-3725	Remnants of vegetation	205	-29,4	$5\,702 \pm 26$	6 410 – 6 555
Hela-3726	Remnants of vegetation	275	-27,8	$6\,967 \pm 28$	7 705 – 7 920
Hela-3727	Remnants of vegetation	340	-26,7	$7\,088 \pm 28$	7 850 – 7 960
Hela-3728	Remnants of vegetation	430	-28,8	$8\,836 \pm 32$	9 735 – 10 155

\*Reimer et al. 2013

#### 4.1.1 Age-depth model

By presenting the calibrated ages' mean and their range graphically, a simple age-depth model may be obtained. Model for the core VA310315 is presented in Figure 8. From the model the peat accumulation rate can be observed and calculated. The accumulation rate remains relatively constant until depth 275 cm. The increment rate of the top is similar to depths greater than 340 cm. In the case of core VA310315 the accumulation rate for these sections is approximately 0.4 mm/year.

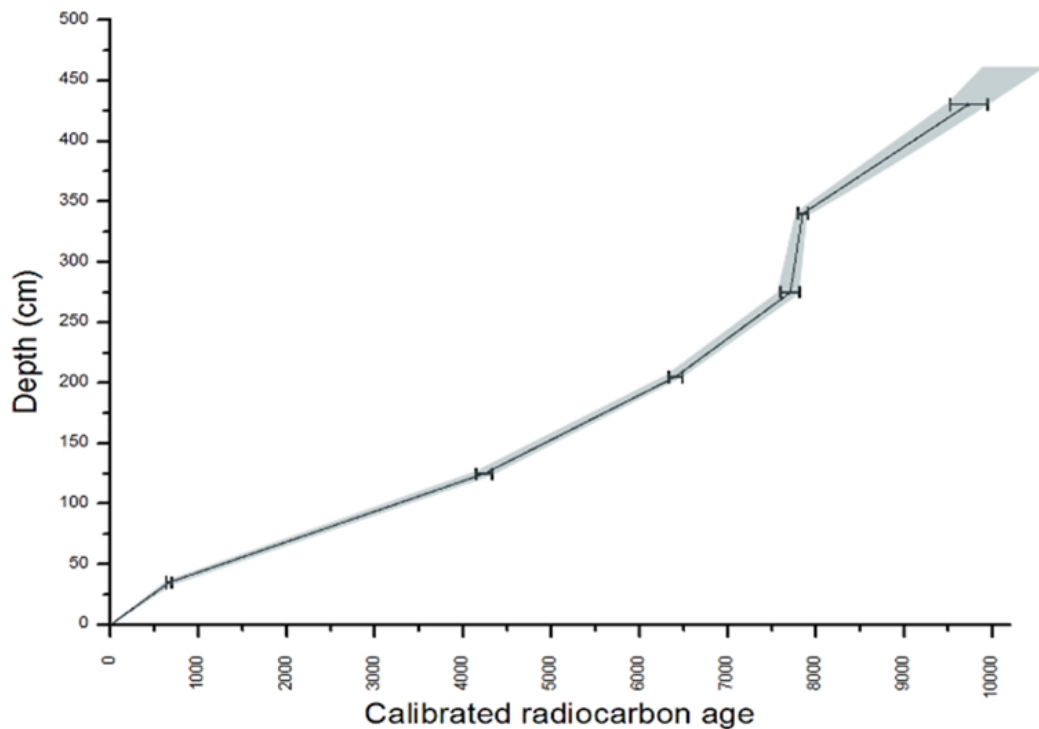


Figure 8 An age-depth model for the core VA310315. From the model a sharp increase in peat accumulation rate can be seen at depth interval 275cm to 340cm.

At depths 275- 340 cm there is a distinct increase in the increment rate. Approximately 8 000 to 7 800 cal BP there appears to be a phase with significant increase in peat increment rate up to a few mm/year. As stated earlier the statistical error increases with increasing depth. However the error alone is not adequate to explain the drastic change in the increment rate. Also since all samples were similar to one another, and treated/collected the same way, there is no reason to suggest that either Hela-3726 or Hela-3727 is erroneous.

#### 4.2 Peat stratigraphy

Peat stratigraphy at the Viiankiaapa mire study site is presented in Table 7 and in Figure 9. To determine the relative proportions of each type of peat, peat sample volume was divided into six parts. Visually defined main factors (C *Carex*, S *Sphagnum* and B *Bryales*) were given a number from 1 to 6 based on their relative abundance and volume in the sample. The changes in humification were very gentle and no sudden or clearly



defined layers could be seen. An increasing trend in humification with depth can be identified. Wetness of peat remained normal (3/5) throughout the core apart from the top 50cm which had higher water content. One of the 50 cm sections cored is presented in Figure 10.

Also the composition of peat remained relatively unchanged throughout the core apart from Bryales apparently becoming more abundant with increasing depth. Peat consisted of mainly remnants of *Carex* (C) and *Bryales* (B) vegetation. *Sphagnum* (S) was only identified at depths 200 – 230cm, and 400 – 430cm. Layer 100 – 130cm consisted of only *Carex* pieces. Remnants of *Menyanthes*, especially seeds, were particularly abundant at depths 100 – 130cm, 130 – 150cm, and 150 – 160 cm. They were present throughout the core but in relatively small numbers. *Menyanthes trifoliata* is a common peatland plant accustomed to relatively wet environments. At depth 250 - 300cm cyclicity of color and humification was apparent. Thin layers (1 – 3cm) of lighter and darker peat could be seen. At this depth humification varied from 5 to 6 with lower humification being connected to lighter color in peat and vice versa.

Depth of the peat layer was altogether 430cm ending in a very thin layer (approximately 1cm) of lake mud (Figure 10). Below the bottom lake mud layer there was sand from depth 430 to depth of approximately 440 cm. Using a small Russian peat corer we were unable to core any deeper.

Table 7 The results for the peat stratigraphy described on study site 15.8.2016.

Starting depth (cm)	Ending depth (cm)	Main factor 1	Main factor 2	Humification H	Wetness B	Notes
0	50	B2	C4	3	4	
50	100	B1	C5	3	3	
100	130		C6	4	3	Multiple <i>Menyanthes</i> seeds
130	150	B1	C5	4	3	Multiple <i>Menyanthes</i> seeds and wood fragments ( <i>Betula</i> )
150	160	B1	C5	4	3	Multiple <i>Menyanthes</i> seeds
160	200	B1	C5	5	3	
200	230	B3	C3	5	3	Also includes regular <i>Sphagnum</i> fragments (S)
230	250	B2	C4	6	3	
250	290	B2	C4	6	3	At depth of 250-300cm cyclicity of darker and lighter colored peat sections. Also changes in humification from 5 (lighter) to 6 (darker).
290	300	C3	B3	6	3	
300	310	B2	C4	5	3	
310	340	B2	C4	7	3	
340	350	C3	B3	7	3	
350	390	B3	C3	6	3	
390	400	B2	C4	7	3	
400	430	C3	B3	7	3	Considerably darker colored layer. Also includes regular <i>Sphagnum</i> fragments (S).
430	431			Lake mud		
431	440			Sand		

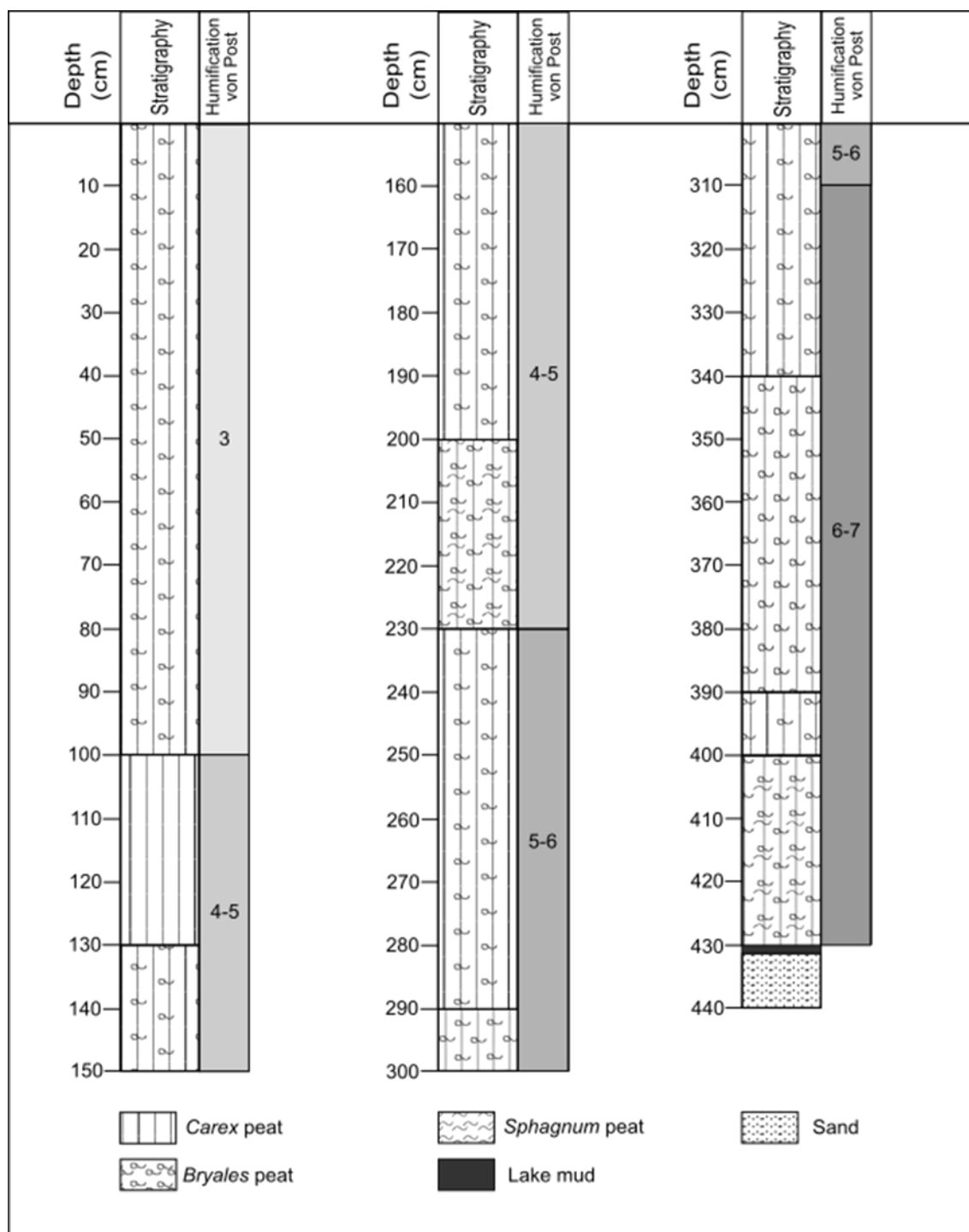


Figure 9 Peat stratigraphy of core VA310315 (7497803 N/0490511 E). The relative abundance of each main factor in relation to one another has been drawn to the figure. Although the borders of each layer are shown by continuous lines there were no clear layers in the peat core. Lines are drawn to clarify the image. Also the humification of peat is shown. As can be seen from the figure humification increases with increasing depth.



Figure 10 A 50 cm section of the peat cored 15.8.2015. This image demonstrates the uniform quality of the peat in general. There are no clear changes in the humification or the type of the peat. In this image slight changes in the color of the peat can be identified with close observations. Visible changes were easier to point out in the field where the lighting could be changed by moving the sample to shadow. The section shown here is from depth 250 - 300 cm.

#### **4.3 Water content, ash content and the color of the ash**

The average water content (percentage of fresh sample) for the core VA310315 was 89.3 %. The water content fluctuated between values 84.8 % (minimum value at depth 190-192 cm), and 93.9 % (maximum value at depth 112-114 cm). The results for the entire core are presented in Figure 11. The maximum and minimum values are both seen in the graph (Figure 11). Also the storing of the peat core may have affected the distribution of the water content throughout the core. The top 30 cm has the highest error since this section was frozen during the time of sample collection. The mean value of 89.3 % is a typical value for mires in their natural state (Kivinen 1948, p. 154).

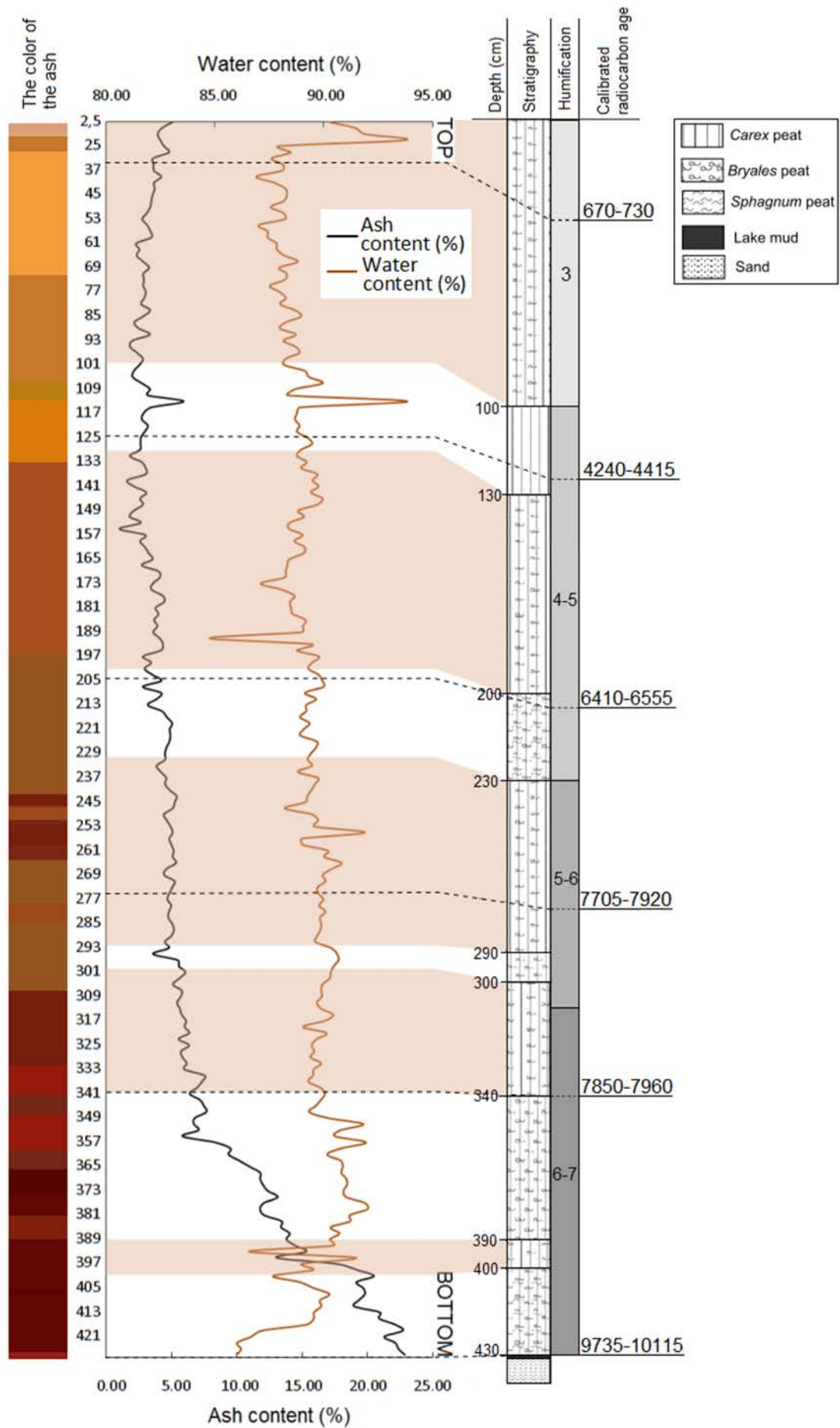




Figure 11 (Previous page) The results of the water content and AC determinations plotted in the same graph with peat stratigraphy, humification, established chronology and ash color. The colors are based on Munsell Soil color charts (1975), and have been determined visually. The colors presented here are as close to the actual color as technically possible.

Results for the AC are presented as percentage of dry weight. The average ash content was determined at 6.2 %. This is a relatively high value for a mire, and it indicates mineral material being transported to the mire (Large et al. 2009). The ash content fluctuated between values of 1.1 % (minimum value at depth 154 – 156 cm) and 22.9 % (maximum value at the very bottom). The ash content in general has higher accuracy compared to the water content since it has not been affected by the storing of the core. From the top to approximately 150 cm the ash content has a decreasing trend. Lowest values are located at the mid sections of the core. From 150 cm the ash content has an increasing trend with increasing depth. Highest values are located at the bottom which is typical for all mires.

The color of the ash was determined using Munsell soil color charts (1975). Altogether 16 individual shades were identified. All the Munsell color IDs and color names are presented in Table 8. The top 70 cm of the core had a lighter yellowish and pinkish colors possibly indicating waterlogged conditions. From 70 cm to approximately 240 cm the color stays yellowish brown. At 240 – 262 cm the ash has a darker reddish color that can clearly be separated from the top 240 cm of the core.

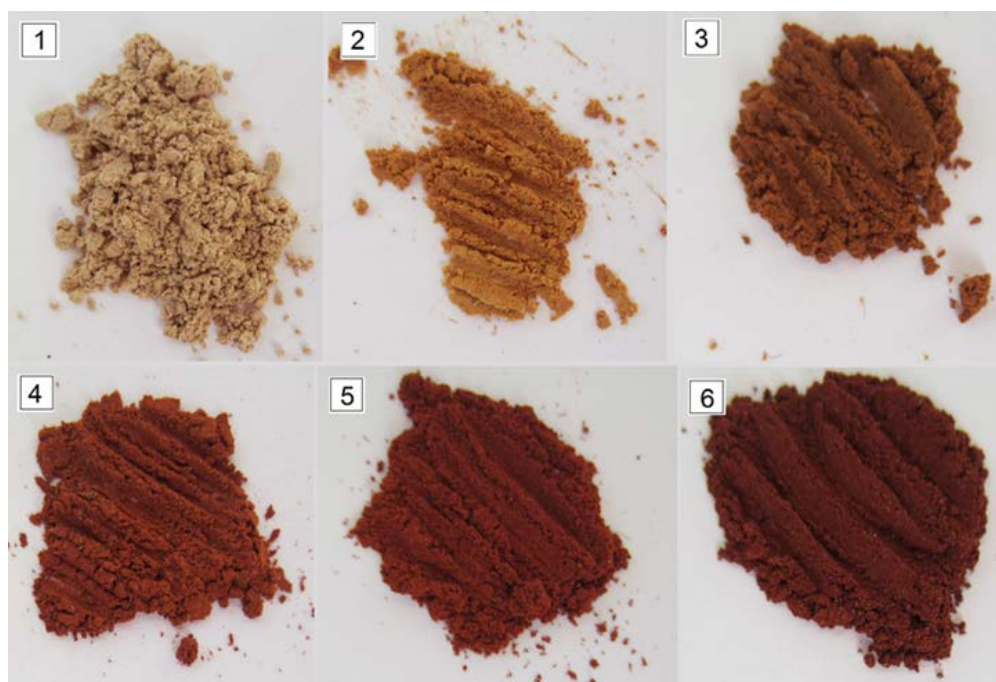


Figure 12 (Previous page) Ash from six different samples at different depths. Sample number 1 is from the top 5 cm of the core, 2: 122 – 124 cm, 3: 238 – 240 cm, 4: 350 – 352 cm, 5: 362 - 364 cm, 6: 420 – 422 cm. The change in the color of the ash is distinct in these images taken in the same lighting and surroundings.

Table 8 Results of the color determination of the mineral material in core VA310315. The color has been determined in 2 cm resolution.

Depth (cm)	Color ID (Munsell)	Color name	Depth (cm)	Color ID (Munsell)	Color name
0 - 5	7.5 YR 7/4	Pink	276 - 282	5 YR 5/6	Yellowish red
5 - 8	10 YR 7/4	Very pale brown	282 - 306	7.5 YR 5/6	Strong brown
8 - 30	7.5 YR 6/6	Reddish yellow	306 - 322	5 YR 5/6	Yellowish red
30 - 70	10 YR 7/6	Yellow	322 - 330	5 YR 4/6	Yellowish red
70 - 104	7.5 YR 6/6	Reddish yellow	330 - 338	2.5 YR 4/8	Red
104 - 110	10 YR 6/6	Brownish yellow	338 - 346	5 YR 4/6	Yellowish red
110 - 130	7.5 YR 6/8	Reddish yellow	346 - 356	2.5 YR 4/8	Red
130 - 194	7.5 YR 5/8	Strong brown	356 - 364	2.5 YR 4/6	Red
194 - 240	7.5 YR 5/6	Strong brown	364 - 372	2.5 YR 3/6	Dark red
240 - 244	5 YR 4/6	Yellowish red	372 - 378	10 R 3/6	Dark red
244 - 248	5 YR 5/6	Yellowish red	378 - 386	10 R 4/6	Red
248 - 250	2.5 YR 4/6	Red	386 - 400	10 R 3/6	Dark red
250 - 256	5 YR 4/6	Yellowish red	400 - 402	2.5 YR 3/6	Dark red
256 - 262	2.5 YR 4/6	Red	402 - 426	10 R 3/6	Dark red
262 - 276	7.5 YR 5/6	Strong brown	426 - 430	2.5 YR 4/4	Reddish brown

#### 4.4 Peat geochemistry

The results for all geochemical analyses have been listed and interpreted individually. In Chapter 5 different proxies will be compared to one another to form a vision on the development history of Viiankiaapa mire.

##### 4.4.1 Metalloid contents

The metalloids analyzed either by gas chromatography or ICP-MS include carbon (C), nitrogen (N), Sulphur (S), and phosphorus (P). The results for these elements are presented as percentage of dry weight, or as ppm (parts per million) in Figure 13.

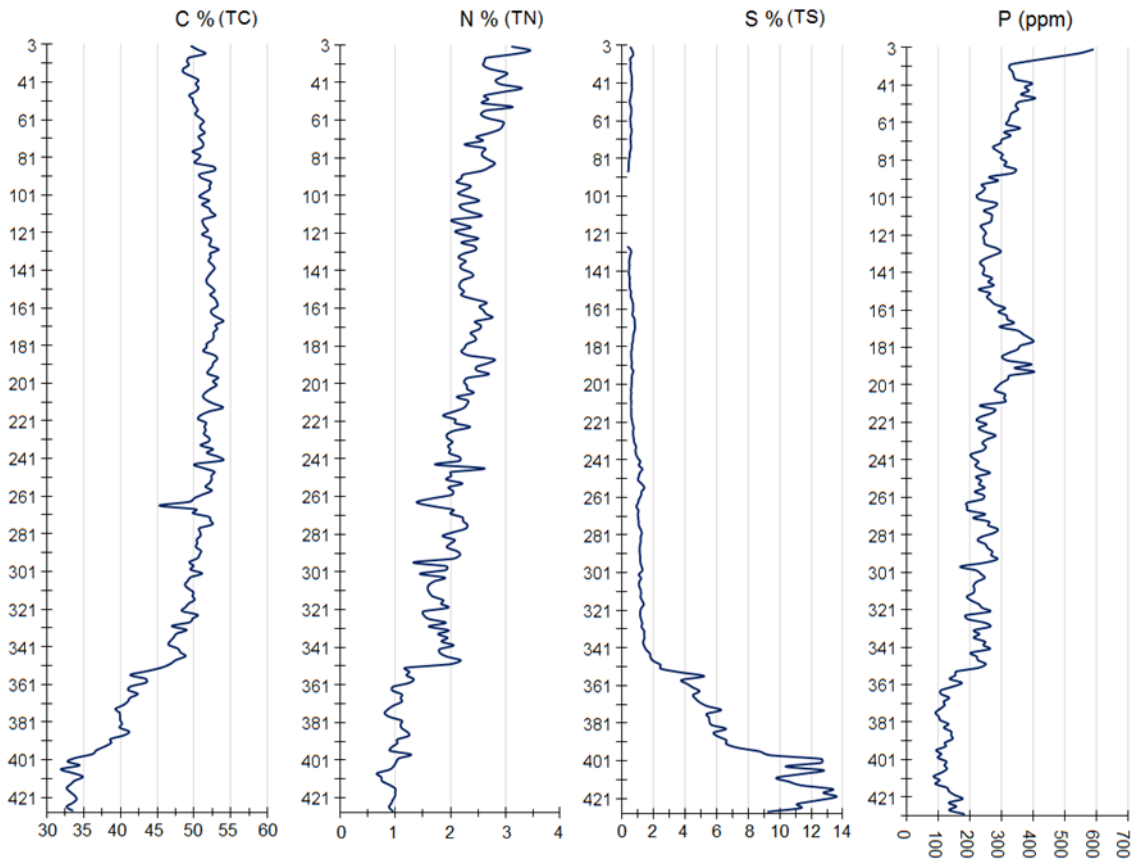


Figure 13 The total carbon (TC), total nitrogen (TN), total sulfur (TS), and phosphorus (P) contents for the core VA310315. The values of TC, TN and TS are presented as percentage of dry weight. The values for P are presented as parts per million (ppm).

### *Carbon content*

The total carbon content (TC) was measured in 2 cm intervals. The results are shown in Figure 13 where the TC (percent of dry weight) has been plotted with depth. On average the TC of the peat core VA310315 was 48.51%. Maximum value was 54.03% at depth 168 – 170 cm. Minimum value was 39.93 % at depth 406 – 408 cm. TC shows slight increasing trend with decreasing depth until approximately 180 cm from which downward the carbon content decreases notably. For the top 260 cm, the fluctuation of the carbon content stays within five percent range. From 260 cm downward the fluctuation is stronger, and at depths 262 – 272 cm a drop of nearly ten percent in TC is recorded. At the bottom part of the core the carbon content shows two distinctive drops: the first at depths 348 – 358 cm where TC drops from 47.59 % to 41.36 %, and the second at depths 386 – 404 cm where TC drops from 41.22 % to 32.84 %.



### *Nitrogen content*

While the TC (Figure 13) fluctuates within 20 percent range, the changes in total nitrogen content (TN) fit in less than five percent variation (Figure 13). Like TC, the TN is shown as total percentage of dry weight. The average TN for the entire core VA310315 is 2.03 %. The maximum value is 3.45 % at depth 8 – 13 cm. Minimum value is 0.67 % at depth 408 – 410 cm. Overall the TN has a notable decreasing trend with decreasing depth. Steepest changes can be observed at depths 242 – 248 cm, 260 – 270 cm, 294 – 396 cm, and at 348 – 354 cm. All of these changes have close to one percent range within relatively short interval of peat. Especially the drop from 2.19 % to 1.18 % is notable since at depths greater than 354 cm the TN never exceeds 1.5 % while top of this shift the nitrogen content hardly undercuts 1.5 %

### *Sulphur content*

The total sulfur content (TS) of the core VA310315 is presented in Figure 13. It is shown as total percentage of dry weight. The gap at depths 90 – 128 cm (values for 98 – 100 cm (0.29 %), 108 – 110 cm (0.26 %), and 118 – 120 cm (0.34 %) are successfully measured but cannot be seen in Figure 13 due to scale) is due to the concentration being below detection limit. The average TS for the core is 2.31 %. The maximum value is 13.63 % at depth 420 – 422 cm. The minimum value recorded is 0.26 % at depth 108 – 110 cm. The TS stays relatively constant with slight increase with decreasing depth until approximately depth 340 – 342 cm. From this depth downward the sulphur content increases drastically. Strong variations were also recorded at the bottom section of the core.

### *Phosphorus content*

The phosphorus content has a clear decreasing trend with decreasing depth. All the values are presented in Figure 13. The average value for the core VA310315 is 250.26 ppm. Maximum value is 590.86 ppm at the very top (0 – 5 cm), and the minimum value of 91.20 ppm is located at depth 412 – 414 cm. Biggest change in the P content is at the top where values drop from the maximum of 590.86 ppm to 326.23 ppm in 30 cm interval. The next peak values are at depth interval 150 – 210 cm. At this depth there are also steep changes in the P content. At depth 348 – 358 cm the values drop below 200 ppm and don't exceed it before the bottom. At depths greater than 358 cm the fluctuation of the

values is less than at depths smaller than 358 cm. A notable feature of the P content is that values seem to have intervals of more subtle changes in contrast to intervals with steep changes. This feature seems to carry out throughout the core.

#### 4.4.2 Semi-metal and metal contents

Altogether twelve metal concentrations were analyzed from the core VA310315. These include alkali metals sodium (Na), and potassium (K), alkaline earth metals calcium (Ca), and magnesium (Mg), transition metals iron (Fe), manganese (Mn), copper (Cu), nickel (Ni), titanium (Ti), and zinc (Zn), and post-transition metals aluminum (Al), and lead (Pb). All metal concentrations are presented as ppm. The only semi-metal analyzed was silicon (Si).

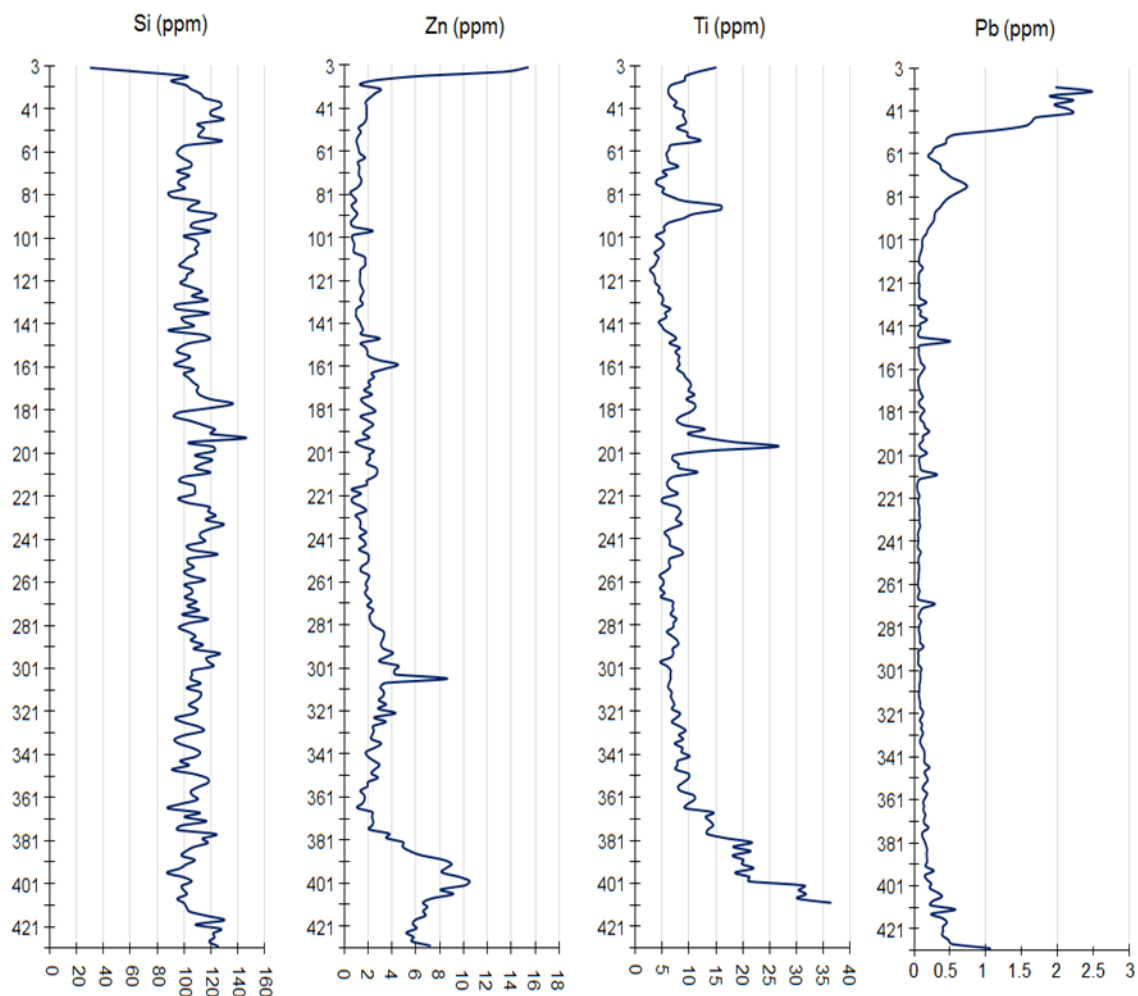


Figure 14 The silicon (Si), zinc (Zn), titanium (Ti) and lead (Pb) contents of core VA310315. Values are presented as parts per million. In order to show changes in Pb content the top four results were left out of the graph. They were all above 3 ppm and are reported in Appendix 3.

### *Silicon content*

Unlike most of the elements analyzed, silicon (Si) has no clear decreasing or increasing trend with decreasing depth. The results for the ICP-MS analysis of Si are presented in Figure 14. The average Si content for the core VA310315 is 107.57 ppm. The maximum value is 146.41 ppm at depth 192 – 194 cm, and the minimum value is 30.79 at the very top (0 – 5 cm). Excluding the top eight centimeters, the silicon values are above 80 ppm throughout the core (see Fig. 14). The strongest change of Si content is at depths 170 – 192 cm. In this interval the Si content fluctuates over 40 ppm.

### *Zinc content*

Zinc (Zn) content of core VA310315 is presented in Figure 14. The concentration of Zn fluctuates between maximum value of 15.40 ppm at the very top (0 – 5 cm), and minimum value of 0.53 ppm at depth 78 – 80 cm. The average Zn content for the core is 2.80. The maximum content is anomalously high and the second highest value of 10.53 ppm (396 - 398 cm) is nearly 5 ppm smaller. The previously mentioned 10.53 ppm is one of three notable rises in the Zn content (excluding the peak at the top). From top downward the first peak is at depth 152 – 162 cm. The second, and most distinctive, one is recorded at depth 294 – 308 cm.

### *Titanium content*

Titanium (Ti) content of core VA310315 is presented in Figure 14. The average concentration is 9.15 ppm for the values below highest detection limit. For the bottom section (410 – 430 cm) no values could be reported since they were above maximum detection limit. The maximum value reported is 36.39 ppm at depth 408 – 410 cm. As can be seen from Figure 14, the concentration of Ti has two distinctive peaks. From top downward the first peak is recorded at depth 72 – 98 cm. Here values rise from 3.94 ppm to 15.91 ppm in 10 cm interval. The second peak is recorded at depth 182 – 200 cm. Here values increase from 7.74 ppm to 26.67 ppm in only 12 cm interval. In addition, a notable increasing trend with decreasing depth can be identified in the bottom section of the core.

### *Lead content*

The lead (Pb) content of the core VA310315 is presented in Figure 14. A notable feature of the Pb concentration is that the highest values located at the top 60 cm of the core are as much as 26 times higher than the average of 0.39 ppm. From Figure 14, the values for the top 20 cm were left out in order to show variations more clearly. The maximum value

of 10.31 ppm is located at the very top (0 – 5 cm). The minimum value of 0.050 ppm is recorded at depth 212 – 214 cm. The Pb content has notable peaks at depths 74 – 76 cm, 144 – 150 cm, 204 – 210 cm, and 266 – 274 cm. From depth 390 cm the lead content has an increasing trend towards the bottom. The value at the very bottom (1.06 ppm) is 2.7 times the average value.

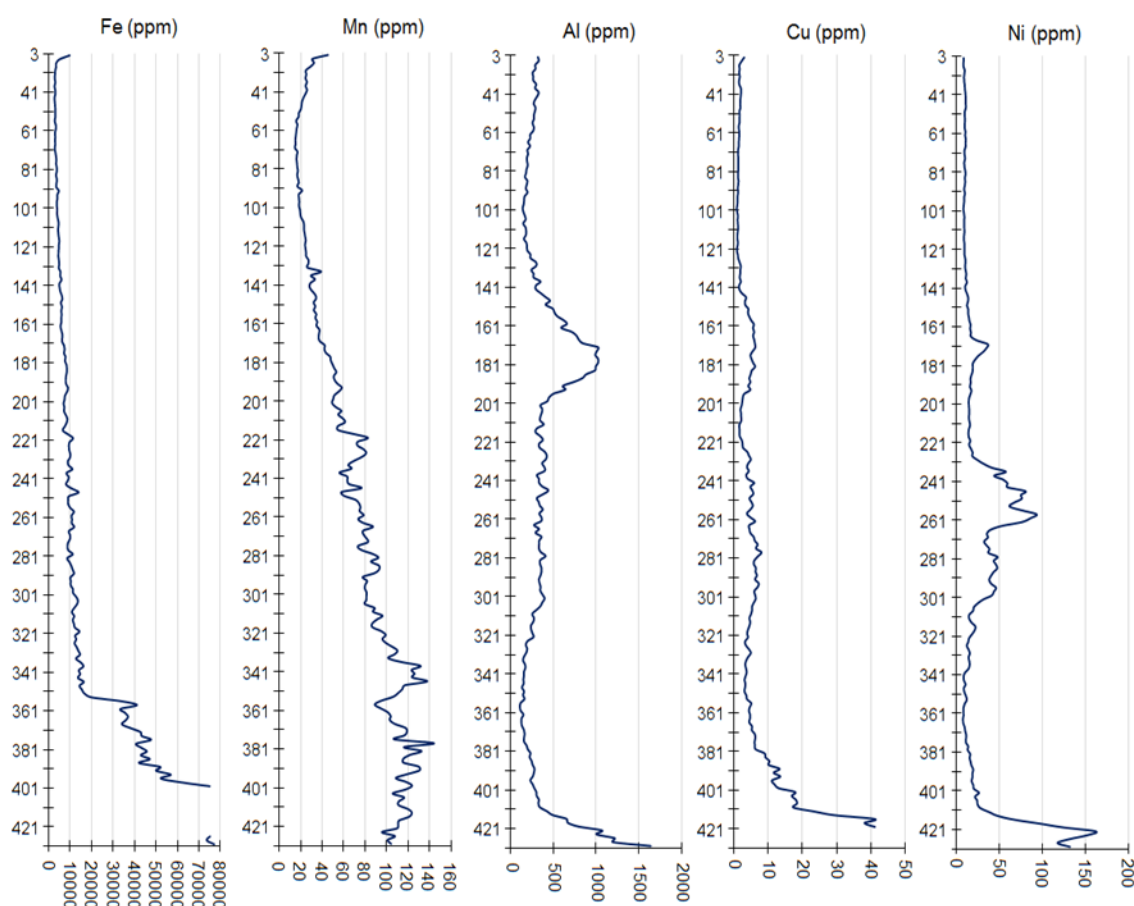


Figure 15 The iron (Fe), manganese (Mn), aluminum (Al), copper (Cu) and nickel (Ni) contents of core VA310315. All values are presented as parts per million (ppm). For Fe, the contents at depth 400 – 424 cm were above detection limit and therefore cannot be reported. For copper the values above 40 ppm (above maximum detection limit) are also not presented.

### *Iron content*

Of all metal elements analyzed, iron has the highest average concentration of 13402.22 ppm (~1.34 %). The results have been presented in Figure 15. The iron content of core VA310315 has a slightly increasing trend with decreasing depth until the depth of 356 cm. From here downward the iron content increases drastically and reaches its maximum value (maximum value under the highest detection limit) of 77203.58 ppm at the very

bottom (428 – 430 cm). The minimum value of 2861.11 ppm is recorded at depth 42 – 44 cm.

#### *Manganese content*

Manganese content of the core VA310315 is presented in Figure 15. From the top until depth 70 cm the Mn concentration has a slight decreasing trend with decreasing depth. At this depth of 68 – 70 cm the minimum value of 14.85 ppm is recorded. From 70 cm to 376 cm the trend is increasing with decreasing depth. This trend is interrupted with strong decrease at depth interval 342 – 368 cm (see Fig. 15). The bottom section (376 – 430 cm) again has a decreasing trend. The maximum value of 144.45 ppm is detected at depth 376 – 378 cm. From depth 190 cm downward the fluctuation of the Mn content is far greater than at the top 190 cm.

#### *Aluminum content*

The aluminum content of the core VA310315 is presented in Figure 15. The average for the core is 363.10 ppm. The maximum value of 1639.18 ppm is recorded at depth 428 – 430 cm, and the minimum value of 116.15 ppm at depth 356 – 358 cm. The Al content has two notable peaks one of which at the bottom (400 – 430 cm), and the other at depth 138 – 200 cm. The short-term fluctuation is relatively smooth, and at depth interval 200 – 300 cm the aluminum content stays relatively constant.

#### *Copper content*

The copper content of the core VA310315 has similar features than previously described aluminum content. The results are presented in Figure 15. The highest values are recorded at the bottom. The maximum of 38.20 ppm is recorded at depth 416 – 418 cm. The minimum value of 1.02 ppm is detected at depth 120 – 122 cm. The Cu concentration has three intervals of higher values: 138 – 200 cm, 218 – 316 cm, and 364 – 430 cm. These intervals may be compared with changes in aluminum content.

#### *Nickel content*

Nickel (Ni) content has similar features to Cu and Al contents (Figure 15). Rises of the values are situated relatively similar to previously described elements, but changes are steeper and shorter lasting. The first clear peak is recorded at depth 162 – 178 cm. The second interval of higher, and strongly fluctuating values, is recorded at depth 224 – 308 cm. The last high peak is recorded at the bottom section of the core (406 – 430 cm). The

average value for nickel is 25.06 ppm, with maximum value of 162.46 ppm at depth 420 – 422 cm, and minimum value of 7.66 ppm at depth 364 – 366 cm.

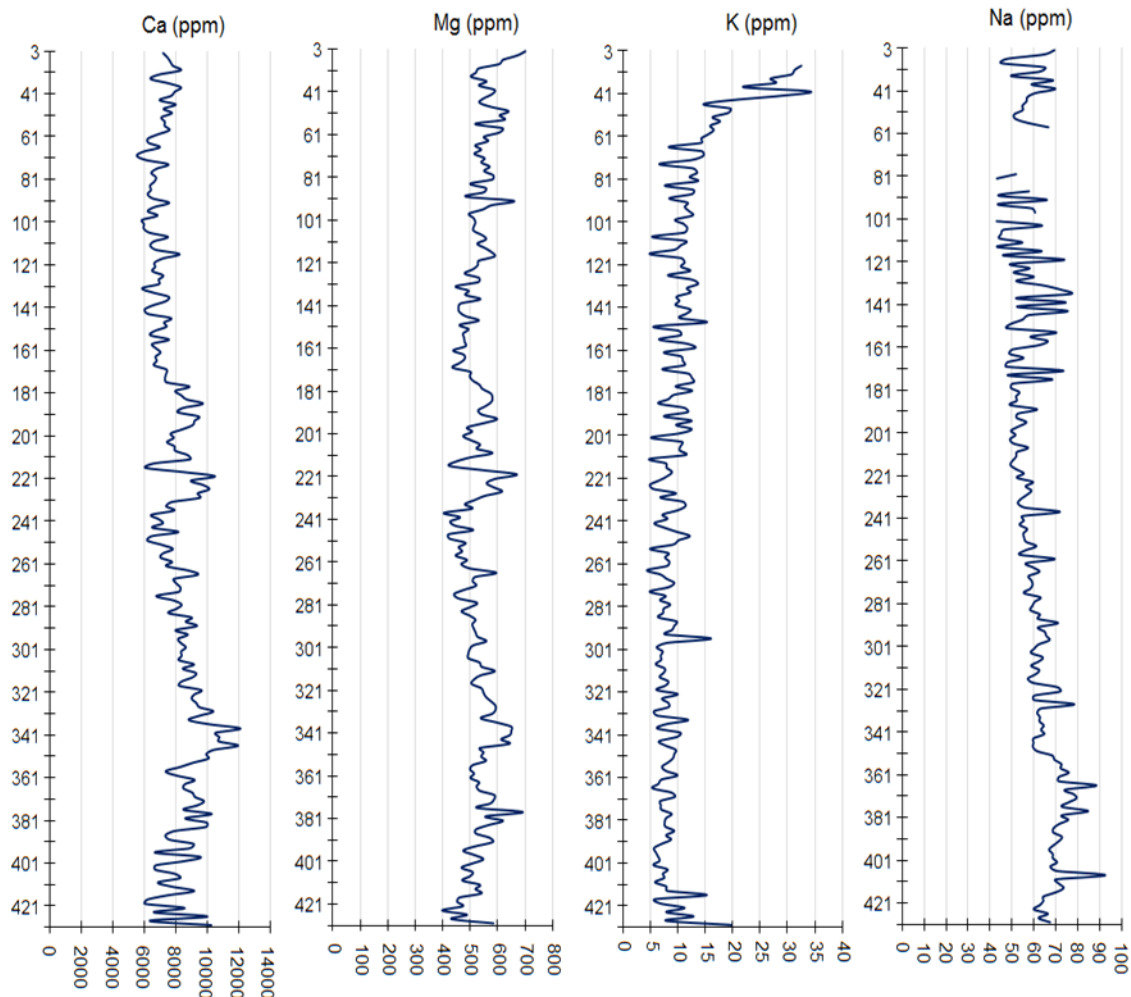


Figure 16 The calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) contents of core VA310315. All results are presented in ppm (parts per million). In order to show changes in potassium content more clearly the top three values have been left out of this figure. They are presented in Appendix 3. Ca and Na were analyzed separately since their calibration was not successful in the first run. Also results for Na that were below detection limit (approximately 40 ppm) have been left out.

### *Calcium content*

Calcium (Ca) content of core VA310315 is presented in Figure 16. Like silicon (see. Figure 14), the Ca content has no clear increasing or decreasing trend with decreasing depth. Another similar feature is that periods of stronger and milder fluctuation seem to occur. The strongest fluctuation occurs at the bottom section of the core, at depths greater than 380 cm. The average calcium content for the core is 7920.06 ppm, with maximum

value of 12135.44 ppm at depth 336 – 338 cm, and minimum value of 5533.76 ppm at depth 68 – 70 cm.

#### *Magnesium content*

Magnesium (Mg) content of core VA310315 is presented in Figure 16. The fluctuation pattern seems to agree with calcium content in various parts. Another similar feature is that periods of stronger and milder fluctuation seem to occur. The average magnesium content for the core is 530.97 ppm, with maximum content of 693.27 ppm at depth 374 – 376 cm, and minimum value of 405.51 ppm at depth 234 – 236 cm. The strongest short term change occurs at depth 212 – 218 cm where values rise from 425.54 ppm to 671.26 ppm in six centimeter interval.

#### *Potassium content*

Potassium (K) content has a slightly decreasing trend with decreasing depth. Its results are presented in Figure 16. The maximum value of 246.02 ppm for K content is recorded at the very top (0 – 5 cm). This value is anomalously high since it's more than 20 times the average value of 12.29 ppm. The minimum value of 4.47 ppm is recorded at depth 262 – 264 cm. Also potassium concentration seems to have intervals of stronger and milder fluctuation throughout the core.

#### *Sodium content*

Sodium content of the core VA310315, presented in Figure 16, shows very slight increasing trend with decreasing depth. The top 180 cm is characterized by very strong fluctuations in the values. At depths greater than 180 cm fluctuation is far less. The average sodium content for the core is 60.62 ppm, with maximum value of 92.58 ppm at depth 406 – 408 cm, and minimum value, above lowest detection limit, of 41.84 ppm at depth 60 – 62 cm. Sodium does not seem to have notable similarities with other elements analyzed.

## 5. DISCUSSION

### 5.1 Peat growth and humification as indicators of climatic changes during Holocene

Studies of peat growth patterns and humification are a widely used methods for reconstructing Holocene paleoclimate and peatland hydrology especially in Europe (Payne and Blackford 2008). These methods are based on the assumption that under drier conditions water tables in peatlands are lower resulting in intensified decomposition. Drier conditions also affect the peat accumulation, enhancing the growth of peat forming plants. In contrast, waterlogged conditions lead to lower level of humification and lessened peat accumulation. Nilssen and Vorren (1991) concluded that peat characteristics (eg. color and humification) are a result of changes in the balance precipitation and temperature. However, it must be noted that as Large et al. (2009) stated, low level of decay and low density of peat should mostly reflect the environment of deposition and near surface processes.

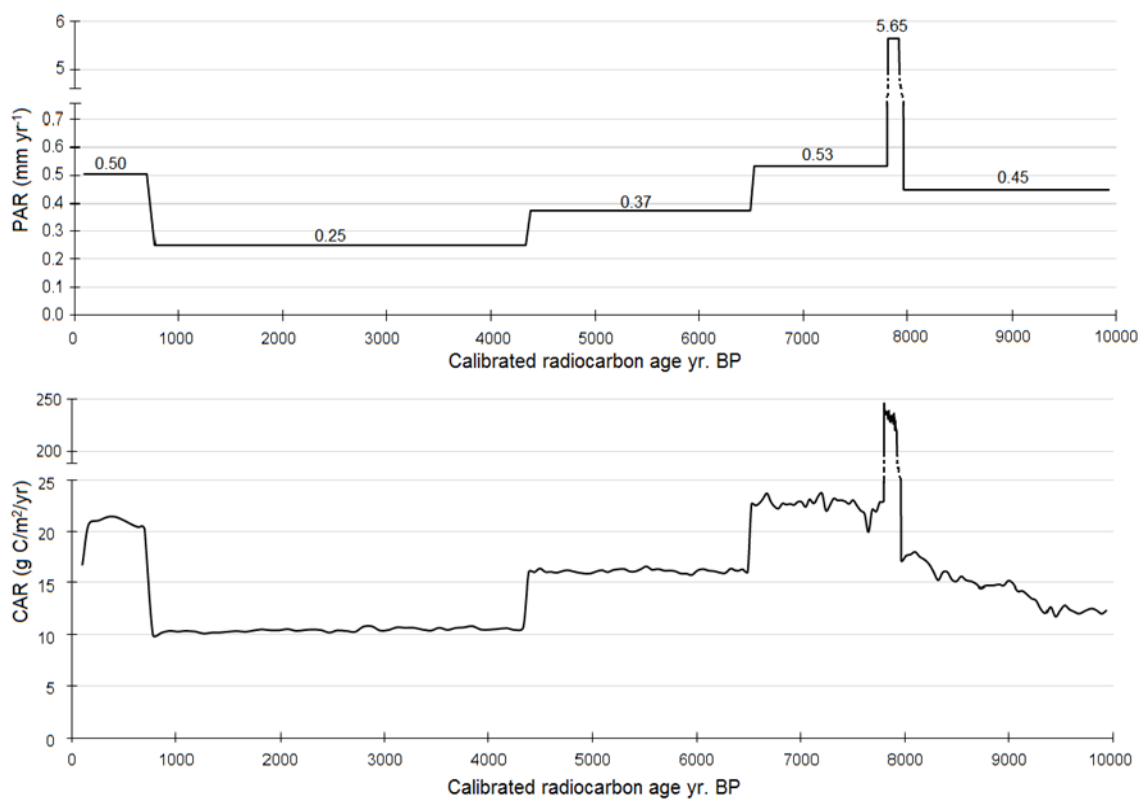


Figure 17 The results for PAR (mm yr<sup>-1</sup>) and CAR (g C/m<sup>2</sup>/yr) for the core VA310315 presented with calibrated radiocarbon age. In both graphs the peak at approximately 7 800 yr BP is cut to show the smaller scale variations better.



Peatlands in the northern hemisphere often have the highest rates of peat accumulation due to cool, humid climates (Rydin and Jeglum 2006). Also carbon is sequestered in peatlands as long as peat accumulation exceeds humification (van der Linden et al. 2014). Changes in both climatic and hydrological conditions affect peat and carbon accumulation rates (PAR and CAR) (eg. Korhola et al. 1996 and Mäkilä et al. 2001). Changes in the hydrology of mires affect the carbon accumulation process. Lower water tables increase the thickness of the oxygenated acrotelm and decrease the rate of litter deposition into the waterlogged peat layer, resulting in a lower CAR (van der Linden et al. 2014). However, in the PAR and CAR calculations for the core VA310315, the decay of the peat was not taken into account. Also for the dry bulk density, an average value for Finnish peats was used (Mäkilä 1994). Due to these generalizations, the results for PAR and CAR may only be treated as average values, and are used to support other results and conclusions. The results for both PAR and CAR with calibrated  $^{14}\text{C}$  age are presented in Figure 17. Both indexes are also presented with depth in Figure 18.

In the results of CAR (Figure 17) early Holocene (11 700 – 8 200 cal. BP) is characterized with steady increase in carbon accumulation. During early Holocene Viiankiaapa mire was only starting to develop towards a large minerotrophic mire and the increase in CAR is in line with this. At the end of early Holocene, right after the so-called 8.2k event, there is a drastic increase in both PAR and CAR. This most likely has to do with the drier and warmer conditions enhancing peat growth and carbon accumulation (Seppä and Birks 2002, Hyvärinen and Alhonen 1994). In Figure 18 the approximate location of the cooling event is shown with a green line. After this short-lived event of high PAR and CAR, the both values show steady decrease until late Holocene where values increase again. This may have to do with drier (eg. Korhola et al. 2005) and cooler conditions during late Holocene and decreased flooding of river Kitinen, resulting in lower water tables.

In the case of Viiankiaapa mire, the peat was relatively poorly humified and uniform throughout the core. The humification increased slightly towards the bottom which is a common feature in mires. The humification of the core VA310315 was studied using the von Post method on site. This method may be considered as reliable when applied to fresh material, as was the case here (Nilssen and Vorren 1991). In addition, C/N ratio was calculated using the results for TC and TN (Figure 13). The results for the C/N ratio are presented in Figure 18 along with PAR and CAR. C/N ratio is a relatively good indicator for properties of organic material in peat. It reflects the ratio of carbon and nitrogen that

is affected by the processes of decay (Malmer and Holm 1984). The ratio is highest in *Sphagnum* peat (36.9 on average) and lowest in *Bryales* peat (16.7 on average). As remnants of *Sphagnum* vegetation disappear the C/N ratio decreases rapidly (Kivinen 1948, p. 128).

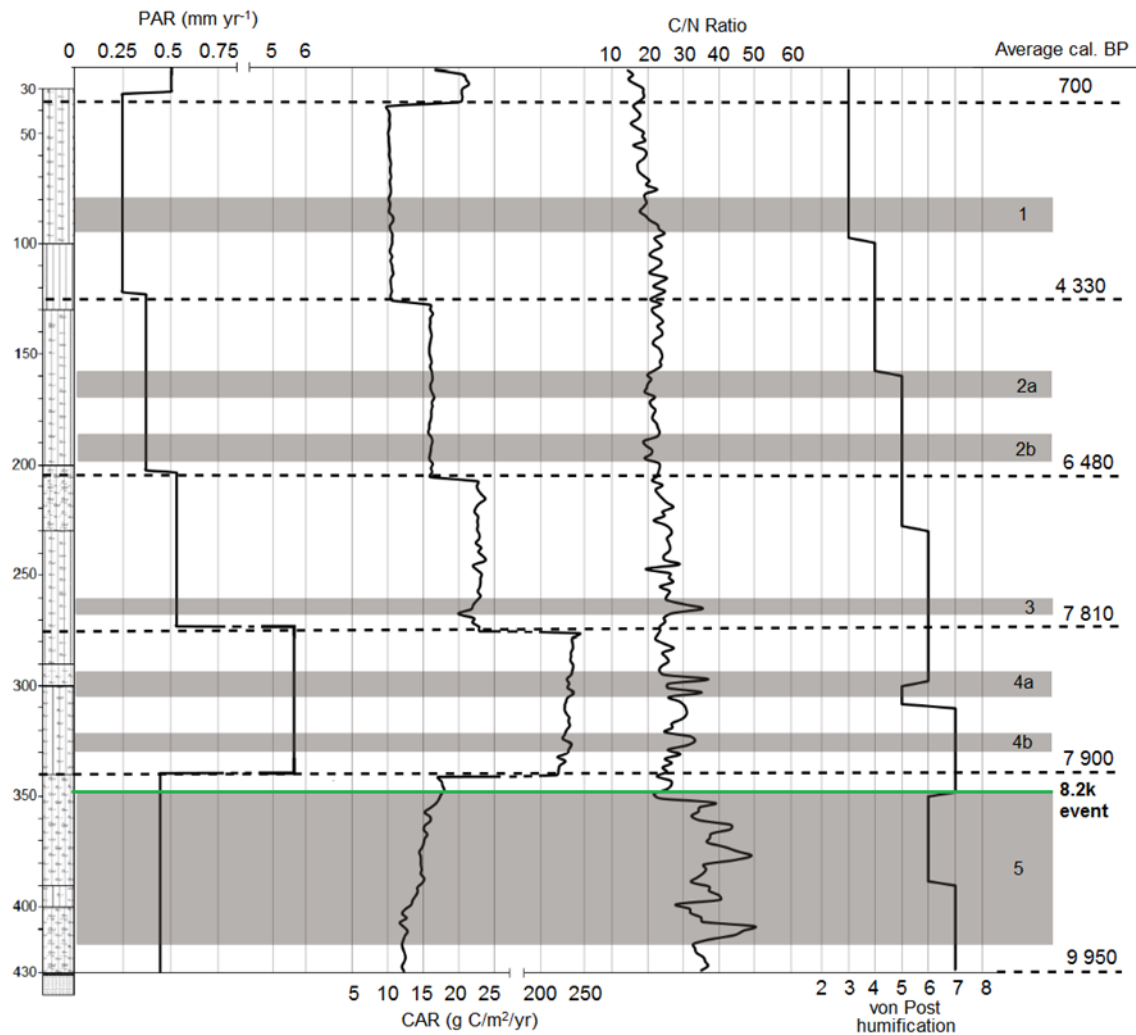


Figure 18 Peat stratigraphy (see Fig. 9), PAR, CAR, C/N ratio, and von Post humification of core VA310315. Calibrated average ages are presented along with the approximate location of the 8.2k event. Phases of notable change are highlighted in grey color.

The C/N ratio of core VA310315 typifies the pattern of increasing humification with decreasing depth. The average value is 25.88. The maximum value is 49.92 at depth 408 – 410 cm. The minimum value is 14.48 at depth 0 – 5 cm. This trend gives an indication of the environment becoming wetter in time. The same pattern is indicated by PAR and CAR which both generally decrease in time. Strongest fluctuations in C/N ratio occur at

depths greater than 350 cm. In this section, the values shift over 20 units within one meter of peat. In Figure 17, notable changes have been highlighted in grey color (phases 1 – 5). The top boundary of phase 5 is situated at approximately same age range than the 8.2k event ending early Holocene (eg. Roberts 2014, p. 159). This event of abrupt and short-lived cooling, increased the rate of decay substantially. In temperature reconstructions from northern Fennoscandia, Seppä and Birks (2002) recorded this event as a slow-up of the gradual warming pattern of early Holocene. Change to colder and drier conditions is clearly visible in the chemistry of core VA310315. Both TC and TN show (Figure 13) an increase during and after the 8.2k event which is linked to the decreased rate of decay. The 8.2k event is followed by drastic increase in PAR and CAR, indicating enhanced peat growth right after the cooling event.

The time interval of increased PAR, based on radiocarbon dating (Figure 8) of the core, show at least three notable peaks (phases 4a and 4b) in the C/N ratio. The peaks seem to be connected to changes in TN rather than TC (Figure 13). Time interval of *c.* 7 800 – *c.* 7 900 cal. BP fits within the 7 800 – 8 800 cal. BP interval of recorded cooler temperatures and decreased precipitation (Hughes et al. 2000, O'Brien et al. 1995). In contrast, it also fits together with recorded high July mean temperatures concluded by Seppä and Birks (2002). Based on the results from Viiankiaapa mire and previous studies, this was a time of higher temperatures and drier conditions resulting in high peat increment rate (Seppä and Birks 2002, Hyvärinen and Alhonen 1994).

At depth 250 – 300 cm changes in humification were also visually detectable and sections of lighter and darker colored peat was recorded (see Table 7). Phases 3 and 4a are situated in this interval of approximately 500 years. Phase 4a is visually determined to have lower humification in disagreement with C/N ratio. The cause for this is difficult to speculate, but it is possible that Viiankiaapa mire experience a short-lasting event of higher water table resulting in decreased decay.

## **5.2 The trophic state of Viiankiaapa mire**

Minerotrophic mires (fens) receive their inorganic element and nutrient input from atmosphere, surface runoff and/or groundwater (Pajunen 2005). The assessment of a mires trophic state gives information on the likely sources of nutrients and other inorganic elements, and their movement and changes within the deposit (Weiss et al. 2001). To determine whether or not a mire is minerotrophic, a number of methods may be used. The

most common method is based on studies of past and modern vegetation patterns (eg. Kultti et al. 2003). For example, *Sphagnum* vegetation is typical for bogs, where the water table is typically lower than in minerotrophic fens. Here, however, the trophic state of Viiankiaapa was assessed with the use of Ca/Mg ratio. The use of this method is based on the assumption that peat deposit with a Ca/Mg ratio lower than, or similar to, local rainwater average, is ombrotrophic. Otherwise the mire has to have a non-atmospheric source of calcium and is therefore minerotrophic (Weiss et al. 2001).

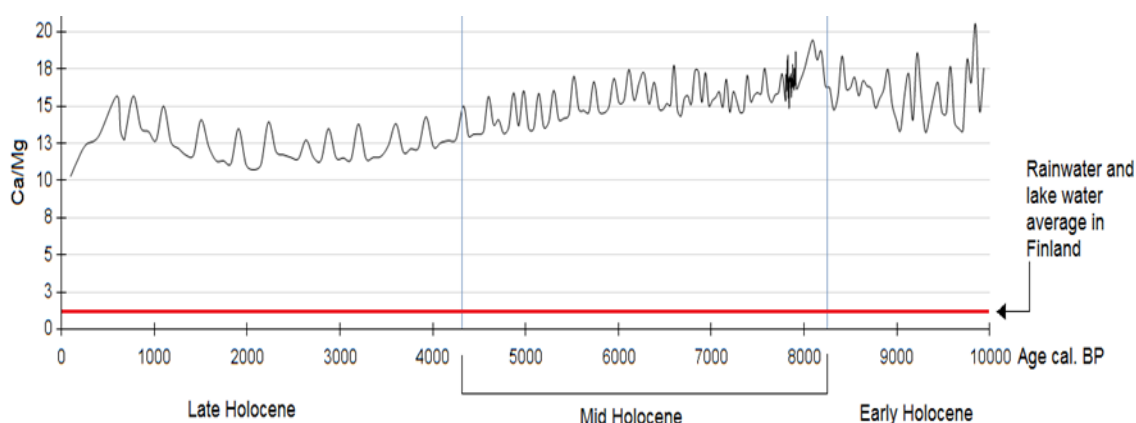


Figure 19 The Ca/Mg ratio of core VA310315 presented with calibrated radiocarbon age. With the red line the average Ca/Mg ratio of rainwater and lake waters of Finland is shown (Reinmann et al. 1996, Lahermo et al. 1994). Lowest values of the ratio are at the top of the core, and highest values close to the bottom. The approximate boundaries of early -, mid -, and late Holocene are shown.

The Ca/Mg ratio for peat core VA310315 is shown in Figure 19. Rainwater and lake water average 1.5 is based on Reinmann et al. (1996) and Lahermo et al. (1994). As Figure 19 indicates, Viiankiaapa has not experienced ombrotrophic state during its development. The result is expected due to the mires close location to a river, and due to near-surface groundwater tables in the area. Thin red line indicates the average trend of the changes. Throughout the core Ca/Mg ratio stays relatively constant, when excluding the short term variations. Short term fluctuation increases at the bottom section of the core. This pattern agrees with C/N ratio, and Fe/Ti profile, indicating variations in the water table at Viiankiaapa (see Fig. 18 and 20). High Ca contents, relatively high ash content (Figure 11) and high Ca/Mg ratio, all suggest waterborne mineral material input at Viiankiaapa. Lowest values recorded at the very top may have to do with reduced flooding due to damming of river Kitinen.

### 5.3 Mineral material transported to Viiankiaapa mire

The most important and straightforward, indicator of mineral material being transported to a mire, is the ash content (AC) (see Figure 11). AC of core VA310315 is relatively high, indicating strong influx of mineral material, especially in the bottom section of the core. It is mainly due to secondary effect of the underlying soil, but in the case of Viiankiaapa this does not solely explain the unusually high ash content. A common feature for ash content is that it usually increases when transitioning from sphagnum peat to sedge and bryales peat (Kivinen 1948, p. 119). In latter mentioned peat types flooding often brings secondary mineral material to the mire.

The question needing to be answered is whether the mineral material is derived from airborne deposition, flooding events, or diagenetic precipitation (Large et al. 2009). Due to the location of Viiankiaapa mire, the flooding events of river Kitinen may be considered as the most likely option. The assessment of post-depositional processes, including redox and precipitation of dissolution reactions, is also crucial since they may result in misinterpretation of the geochemical data (Weiss et al. 2001).

#### 5.3.1 Correlation between variables

The results for the Spearman rank correlation coefficient (eg. Ranta et al. 1991) are presented in Table 9. In Table 9 all high ( $> |\pm 0.5|$ ) correlations are identified with bold type. Only statistically significant values are presented. In addition to chemical variables, also peat, carbon, and lead accumulation rates (PAR, CAR, PbAR) along with ash content (AC) and loss-on-ignition (LOI<sub>550</sub>) are taken into account.

The highest positive correlation is between Fe and Mn (0.962). These elements are both affected by the redox conditions at the mire (Koinig et al. 2003). Sulfur, which is also affected by the presence or absence of oxygen, also shows strong correlation with both Fe (0.895) and Mn (0.904). All of these elements are mainly derived from mineral material being transported to a mire by other means than atmosphere. This is supported by the fact that they all also correlate well with AC, and have a high negative correlation with the carbon content of the peat core (Table 9). Similar, but less significant pattern is also shown by Zn, Cu, Ca and Na. All of the mentioned elements are common in rock-forming minerals (Goldschmidt 1937).

Very strong ( $> 0.9$ ) positive correlation is also between the main nutrients N and P (0.921), that are both a vital part of plant growth. Phosphorus and nitrogen are often the

limiting factors for plant growth in peatlands (Verhoeven et al 2001). Main nutrients, including C, N, P, and K, all have negative correlation with the AC. Carbon correlates positively with all the other nutrients, but has a negative correlation with all the other metals (excluding Al with relatively low correlation of 0.322). This refers to major part of the ash being other than plant accumulated mineral material (Wei et al. 2012). Negative correlation with most of the metals is also shown by other main nutrients, supporting the previously made conclusion.

AC and LOI<sub>550</sub> show high correlation with altogether ten elements, including C, N, S, P, Zn, Fe, Mn, Cu, Ca, and Na. They both also correlate significantly with PAR (0.594), AC positively and LOI<sub>550</sub> negatively. S, Fe, Mn, Zn and Cu, that all have a significant positive correlation with the AC, are all lithogenic elements whose main source is mineral material, and in the case of Viiankiaapa mire, the bedrock surrounding the basin (Tyrväinen 1983). These high correlations refer to surface waters and groundwater being the main source for mineral material in Viiankiaapa mire. Ni that is also categorized as lithogenic element, shows higher positive correlations with only Al (0.706), Cu (0.758), and PAR (0.560). Copper shows high correlation also with Zn (0.701). All these features refer to non-atmospheric material being the main contributor of AC.

While CAR shows very limited correlations with the other variables, PAR has high correlation with eight individual variables (Table 9). These include CAR, N, Zn, Fe, Mn, Cu, Ni, and Ca, from which negative correlation is only with N (-0.531). The peat accumulation rate correlating positively with lithogenic elements suggest that concentrations of these elements are connected to the growth rate of the peat layer. It is evident that the same climatic and hydrological processes affecting peat accumulation have also affected the accumulation of these elements. This is supported by the negative correlation of PAR and CAR with mainly atmospherically derived Pb (-0.376 and -0.566).

Although most of the elements seem to have a high correlation with one of more other variables, there are also few that do not show correlations above  $|\pm 0.5|$  with any other element. These elements include Si, Pb, Ti, and Mg. From these Si and Mg are a vital part of plant metabolism. Pb does however have a negative correlation with CAR (-0.566) suggesting that lead does not accumulate in the plant material significantly, as stated earlier. Pb and Ti are mainly atmospherically derived elements, and Ti is also known to withstand chemical weathering better than other elements analyzed (Weiss et al. 2001).

Table 9 Spearman  $\rho$  matrix for the geochemical and physical properties of core VA310315. Only statistically significant values are presented. High ( $>|\pm 0.5|$ ) correlations are indicated in bold type. All values within detection limits were used in calculations (N<sub>total</sub> = 205)

	AC	LOI <sub>550</sub>	PAR	CAR	PbAR	C	N	S	P	Si	Zn	Ti	Pb	Fe	Mn	Al	Cu	Ni	Ca	Mg	K
AC																					
LOI <sub>550</sub>																					
PAR	<b>0.594**</b>	<b>-0.594**</b>																			
CAR	0.268**	-0.268**	<b>0.891**</b>																		
PbAR	0.428**	-0.428**	0.374**	0.163*																	
C	<b>-0.757**</b>	<b>0.757**</b>	-0.262**	0.145*	<b>-0.609**</b>																
N	<b>-0.761**</b>	<b>0.761**</b>	<b>-0.531**</b>	-0.246**	-0.148*	<b>0.613**</b>															
S	<b>0.896**</b>	<b>-0.896**</b>	0.489**	0.165*	0.258**	<b>-0.663**</b>	<b>-0.815**</b>														
P	<b>-0.663**</b>	<b>0.663**</b>	-0.413**			<b>0.560**</b>	<b>0.921**</b>	<b>-0.749**</b>													
Si																					
Zn	<b>0.651**</b>	<b>-0.651**</b>	<b>0.503**</b>	0.332**	0.497**	-0.481**	-0.486**	<b>0.643**</b>	-0.380**												
Ti	0.459**	-0.459**			0.297**	-0.374**	-0.167*	0.409**		0.141*	0.413**										
Pb			-0.376**	<b>-0.566**</b>	<b>0.607**</b>	-0.487**			0.145*		0.148*	0.397**									
Fe	<b>0.855**</b>	<b>-0.855**</b>	<b>0.679**</b>	0.475**	0.180*	<b>-0.530**</b>	<b>-0.869**</b>	<b>0.895**</b>	<b>-0.745**</b>		<b>0.574**</b>	0.387**	-0.213**								
Mn	<b>0.881**</b>	<b>-0.881**</b>	<b>0.680**</b>	0.441**	0.286**	<b>-0.607**</b>	<b>-0.847**</b>	<b>0.904**</b>	<b>-0.735**</b>		<b>0.675**</b>	0.439**		<b>0.962**</b>							
Al			0.168*	0.260**		0.322**			0.229**	0.267**	0.229**		-0.216**								
Cu	<b>0.695**</b>	<b>-0.695**</b>	<b>0.532**</b>	0.345**	0.225**	-0.386**	<b>-0.623**</b>	<b>0.782**</b>	-0.491**		<b>0.701**</b>	0.499**		<b>0.740**</b>	<b>0.760**</b>	0.471**					
Ni	0.387**	-0.387**	<b>0.560**</b>	0.480**			-0.389**	0.460**	-0.281**	0.219**	0.431**		-0.368**	0.446**	0.463**	<b>0.706**</b>	<b>0.758**</b>				
Ca	<b>0.565**</b>	<b>-0.565**</b>	<b>0.512**</b>	0.405**	0.328**	-0.417**	-0.450**	0.456**	-0.290**	0.188**	0.345**	0.369**		<b>0.677**</b>	<b>0.660**</b>		0.374**	0.173*			
Mg				-0.193**	0.322**	-0.333**			0.159*			0.184*	0.366**			-0.365**	-0.269**	-0.425**	0.469**		
K	-0.450**	0.450**	-0.468**	-0.358**		0.196**	0.610**	-0.495**	<b>0.623**</b>		-0.260**		0.372*	<b>-0.596**</b>	<b>-0.572**</b>		-0.435**	-0.356**	-0.389**	0.212**	
Na	<b>0.569**</b>	<b>-0.569**</b>	0.264**		0.322**	<b>-0.580**</b>	<b>-0.558**</b>	<b>0.569**</b>	<b>-0.514**</b>		0.397**	0.302**	0.174*	<b>0.541**</b>	<b>0.580**</b>	-0.225**	0.437**		0.314**	-0.190**	

\*\* : Correlation is significant at the 0.01 level (2-tailed).

\* : Correlation is significant at the 0.05 level (2-tailed).

The highest correlation for Ti is with Cu (0.499) suggesting that they also have a common source, which is most likely the mafic and ultramafic rocks surrounding Viiankiaapa mire.

### *5.3.2 Ti normalized profiles and elements in connection to mineral material transported to Viiankiaapa mire*

Common accessory Ti-bearing minerals, such as rutile ( $\text{TiO}_2$ ), ilmenite ( $\text{FeTiO}_3$ ) and titanite (“sphene”,  $\text{CaTiSiO}_5$ ), are generally resistant to chemical weathering in acidic solutions (Weiss et al. 2001). This allows titanium to be used as a reference element in soils and sediments, such as peat. Ti normalization is also used to remove the effect of natural changes in dust input and compensate for differences in bulk density of the peat (Ferrat et al. 2012). For the core VA310315 Ti normalization was carried out on the top 410 cm of the core, since no values for Ti could be obtained from the bottom 20 cm. Results are presented in Figure 20.

Ti normalization was applied on four metal elements (Fe, Al, Si, Cu), and all alkaline and earth alkaline metals (Ca, Mg, Na, K) analyzed. Fe, Al, Si and Cu, categorized as lithophilic elements, were chosen for the normalization due to their main lithogenic origin (Margalef et al. 2013). Alkaline and earth alkaline metals were chosen since their input to the mire can be used to estimate the surface runoff and minerotrophy of the mire (Gorham and Janssens 2005).

From Ti normalized elements lithophilic Fe, Si, Cu and Al show similar patterns indicating periods of higher mineral material influx. At least eight (I-VIII, Figure 20) notable peaks are recorded. The same patterns are also shown in alkaline and earth alkaline metal graphs (Figure 20). The ninth peak is only shown in Fe/Ti curve, is indicated in Figure 20 with red box. The sudden rise in Fe/Ti values indicate a strong Fe enrichment relative to Ti. Si/Ti, Ca/Ti, Mg/Ti and Na/Ti show significant similarities with each other. Excluding Na, these elements are important factors in plant metabolism (Weiss et al. 2001). Peaks I, VI and VII are clear in all elements, although they don't seem to have notable correlation with the concentration curves. Peak III is strongest in Al/Ti and Cu/Ti and with these elements it seems to correlate with higher total contents (Figure 15). Peak II especially showcased in Si/Ti, Ca/Ti, Mg/Ti and Na/Ti curves, respectively, mainly has to do with enrichment of these elements relative to Ti. Peak VIII has the lowest correlation between individual curves, and is mainly visible in Fe/Ti, Cu/Ti



and Na/Ti values. All ratios, excluding Fe/Ti and Cu/Ti have decreasing trend in values at depths greater than 300 cm.

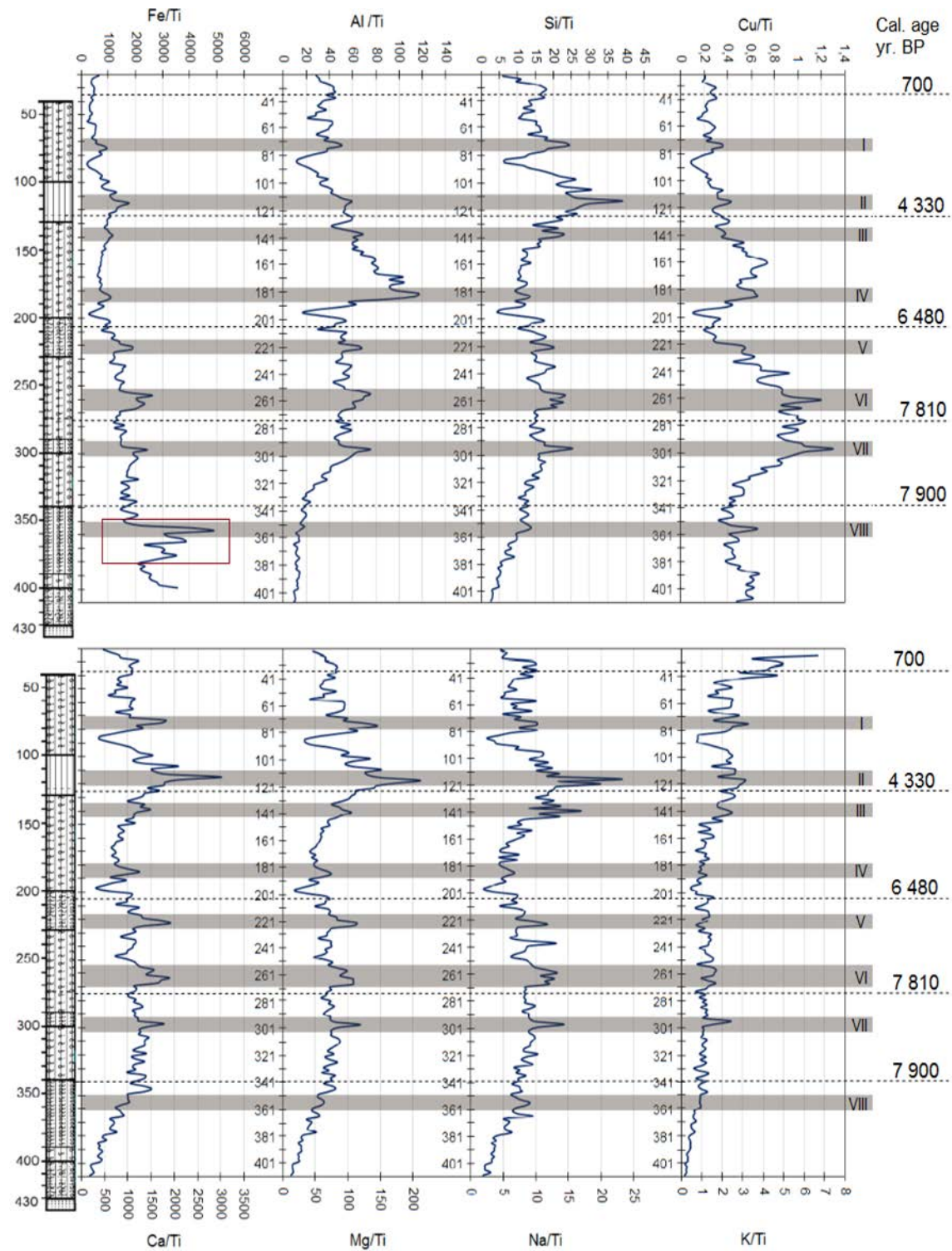


Figure 20 The element/Ti profiles for Fe, Al, Si, Cu, Ca, Mg, Na, and K. Eight most clearly visible peaks are highlighted in grey color and numbered (I – VIII) using roman numerals. Peak distinctive for only Fe/Ti is highlighted with red box. Peat stratigraphy (see Fig. 9) and average calibrated radiocarbon dates are also shown.

All Ti normalized profiles, excluding K/Ti and Fe/Ti, show increase during mid-Holocene. This pattern is most notable in Cu/Ti profile, where high values occur during time interval 8 000 – 6 500 cal. BP. In other profiles the pattern is notable, but not as significant. Similar trend is also recorded in concentrations of Al, Cu, and Ni (see Figure 15), respectively. The higher levels of these elements during mid-Holocene are in keeping with higher temperatures recorded during this time interval (Ojala et al. 2008, Seppä and Birks 2002). At the same time lower precipitation is recorded by Seppä and Birks (2002). Together with the results of this study, other publications disagree with lowered precipitation during the time interval 8 000 – 6 500 cal. BP (eg. Korhola et al. 2005). Korhola et al. (2005) recorded higher lake levels in northern Finland during this time period. C/N ratio together with higher metal concentrations during mid-Holocene suggest high water table with frequent influx of mineral material with flooding events.

The period of higher mineral material influx is followed by a stage of lessened deposition of various elements. This event (interval between peaks IV and V in Figure 22) is shown in all Ti normalized profiles, and especially in Ni and Cu concentrations. Korhola et al. (2005) report lowered lake water levels during this time, suggesting lessened flooding and decrease in mineral material influx. Peaks II and III represent a period of higher peat accumulation related to increase in temperatures. Element/Ti profiles of elements related to plant growth, including Si, Ca, Mg, and K, and also Na (not a significant part of plant metabolism), show strong increase during time interval 3 200 – 4 800 cal. BP. Fe, Al, and Cu, do not show similar peaks during this period of time. Korhola (1995) stated in his study that 4 300 – 3 000 cal. BP southern Finland experienced higher temperatures and increased humidity resulting in enhanced peat initiation. Peaks II and III (Figure 22) fit in the time period suggesting that similar rises in temperature and precipitation were also experienced in northern Finland. Increased temperatures and humidity would also explain the higher deposition of halophilic element Na, derived mainly from ocean spray (Weiss et al. 2001).

A number of paleoclimatic records have indicated that c. 2700 cal. BP was a phase of increased precipitation. Some studies conclude that this “wet-shift” was one of the largest climatic events of late Holocene (Barber 1985, Charman 1990). In geochemical records of Viiankaapa, this event is recorded especially in the concentration profile of titanium (Figure 14). Margalef et al. (2013) connects high Ti contents to increased detritic input to the mire, supporting the theory of increased precipitation and enhanced flooding in

Viiankiaapa area. However, other records apart from Ti concentration, do not showcase this event of increased humidity as clearly. Ti normalized profiles indicate a sudden drop in the values, suggesting lower input of these elements. Korhola et al. (2000) stated in their study that five distinctive cooling episodes could be identified in diatom-based model for northern Fennoscandia. One of these episodes, recorded approximately 3 000 cal. BP, is in keeping with the Ti normalized profiles from Viiankiaapa. All profiles display a drop in element/Ti values during time interval 3 300 – 2 500 cal. BP. After this period values show another sudden increase (peak I, c. 2 500 – 1 900 cal BP, Figure 20) suggesting that this “wet-shift” is recorded in northern Finland later than in other records (Barber 1985, Charman 1990).

The so-called “Little-ice-age” took place in Finland approximately 700 cal. BP ago (eg. Luoto et al. 2008). Since the records from Viiankiaapa have far poorer resolution within the top 30 cm section, this event is difficult to identify. However, multiple concentration profiles (Ti, Zn, Ca, Mg, K, P, N, C, and Si) showcase dropping values during this time, suggesting colder temperatures and drier conditions. Ti normalized profiles seem to be showing drops in values earlier, during time interval 1 600 – 700 cal. BP (Figure 20).

Most of the element/Ti values (excluding K/Ti) and concentrations of Si (Figure 14) and Ca (Figure 16) show decreasing values in the very top part of the peat core. This may have to do with the damming of Kitinen, and reduced flooding resulting from it.

### 5.3.3 *Post-depositional processes affecting the element contents of Viiankiaapa mire*

From the analyzed elements, concerned by post-depositional processes in the northern latitudes, mainly S, and Fe (also Mn, and N) are affected by the redox conditions in the mire (Charman 2002). In the case of Viiankiaapa, this is reflected by not only the occurrence of microscopic iron ore, also referred to as “bog iron” (Naucke et al. 1993), but by the changing color of the ash (See Figures 11 and 12). It should be noted here, that the ore granules found in the core were not analyzed further, and sulfur and iron may exist in multiple different compounds (eg. Dellwig et al. 2001). When oxygen is available diluted iron oxidizes into iron oxide. Iron oxide (Fe(II)O) has a distinctive dark red color, that is seen in the ash of core VA310315. Manganese usually precipitates as manganese(II)carbonate (MnCO<sub>2</sub>) that has reddish brown color (Koinig et al. 2003). Red color of the ash together with the high Fe and Mn contents indicates higher mineral

material influx during early Holocene. In the study of Margalef et al. (2013) high Fe/Ti ratio (Figure 20 in this study) was also connected to drought events. This together with the color of the ash could indicate that early Holocene was an unstable period of time and included both wetter and drier periods. This theory is in keeping with the C/N ratio that shows strong variations during early Holocene (Figure 18).

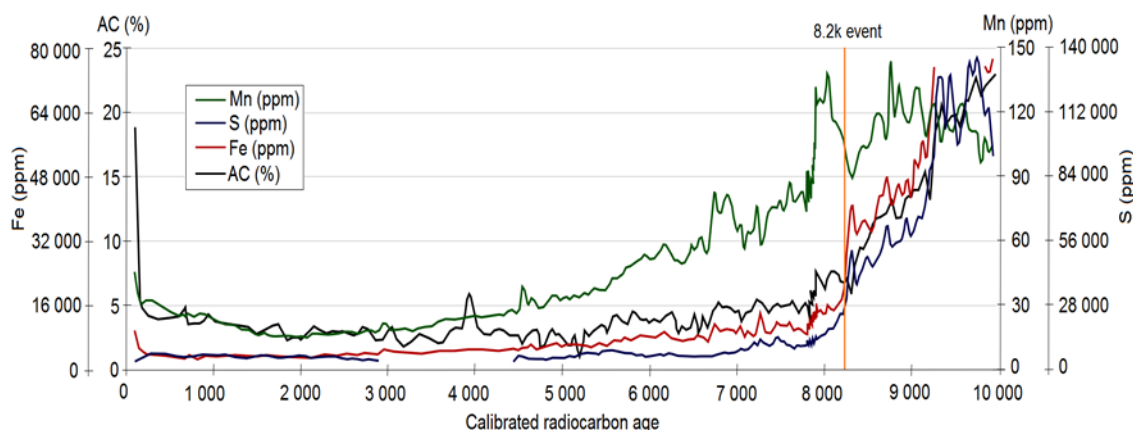


Figure 21 The concentrations of Mn, Fe, and S, along with AC for the core VA310315 presented with calibrated radiocarbon age. The approximate position of the 8.2k event is shown with orange line. Correlations between all the variables presented here is shown in Table 9. The chemical elements are presented in parts per million, and the ash content as percentage of dry weight.

Diagenetic precipitation under anoxic conditions has most likely also occurred at Viiankiaapa. This is indicated by the high observed concentrations of not only iron, but also sulfur in the bottom section of the peat core (Figure 21). Under waterlogged conditions, sulphates and other oxidized forms of sulfur can be reduced to hydrogen sulfite or iron sulfite (pyrite,  $\text{FeS}_2$ ) (Charman 2002) As Dellwig et al. (2001) stated in their study pyrite enrichments may only be explained by processes related to paleoenvironmental changes affecting water level of the mire. Iron and sulfur contents of the core VA310315 strongly correlate with each other ( $r = 0.895$ ), and with AC (S:  $r = 0.896$ ; Fe:  $r = 0.855$ ). This suggests that reduction of pyrite under anoxic conditions may be a significant factor at Viiankiaapa along with the oxidation of iron. The significant increase in Fe, Mn, and S content, and AC with decreasing depth occurs at peat deposits older than approximately 8 200 yr BP (350 – 360 cm, the 8.2k event). As one important source for iron is mineral material transported by periodic flooding (Dellwig et al. 2001),

the results of Fe, Mn, and S contents, Fe/Ti, and S/Ti (not shown) ratios, and AC suggest a period of major flooding events during early Holocene, interrupted by a drought events. Based on these factors, it is likely that the mire did not experience continuous waterlogged conditions, resulting in anoxic conditions, during early Holocene. Waterlogged conditions reached during mid-Holocene may have induced the reduction of sulfur in the deeper parts of the peat core. Concentrations of elements such as Ti, Zn, Al, Cu, and Ni also support this theory since their concentrations increase in the bottom section of the core.

#### 5.3.4 *Sources of the mineral material*

From the lithogenic elements Si, Fe, Al, and Ti, generally found in atmospheric dust (Weiss et al. 2001) only Fe significantly correlates ( $r = 0.89$ ) with the ash content (Figure 25). The correlation of the other elements is far more insignificant, although Ti does show some similarities with AC (see Figures 11 and 19). This indicates that the origin of mineral material in Viiankiaapa mire is not predominantly atmospheric deposition, but also water transported material. Different sources of mineral material would explain the changes in the Ti normalized profiles presented in Figure 19. From the Ti normalized elements previously mentioned Si, Fe, Al, and Ti, have terrestrial origin. Also Cu may be considered lithogenic even if it may also have anthropogenic origin. Alkaline and earth alkaline metals, however, may also have marine origin. Due to the continental location of Viiankiaapa, it may be assumed that marine material has only a minor influence on the peat geochemistry.

Based on the results of the geochemical analyzed of the core VA310315, it is safe to say that Viiankiaapa mire has more than one water source. However it is far more complicated to evaluate what the main sources are in individual time intervals. Most of the metal elements (Fe, Al, Cu, Ni, Zn, Mn, Ti) and Si, found in atmospheric dust, derive from weathering of the continental crust, and consequently have continental origin (Weiss et al. 2001, Berner and Berner 2012). Alkaline and earth alkaline metals, however, can have either terrestrial, or marine origin. Especially sodium (Na) is categorized as halophilic element (Gorham and Janssens 2005). In the case of Viiankiaapa mire, especially during the mid – and late Holocene, ocean spray may be considered as a minor factor due to continental location of the mire.

Table 10 The average values for the element/element ratios. \* based on Berner and Berner 1997 in Weiss et al. 2001. \*\* based on unpublished measurements done in Viiankiaapa region as a part of the Sakatti-project. Averages for the peat core VA310315 are also presented. (GW groundwater, SW surface water)

Element/ element ratio	Upper continental crust average*	Continental rainwater average*	Marine and coastal rainwater average*	GW, SW and spring water samples in Viiankiaapa region**	Averages for core VA310315
Ca/Mg	2	1 – 10	1 – 3	2.2	14.9
Ca/K	1	0.5 – 2	2 – 3	9.6	887.7
Mg/K	1.75	2 – 6	0.5 – 1	4.3	57.8

Ratios Ca/Mg (Figure 19), Ca/K, and Mg/K (not presented) may all be used to assess not only the trophic state of a mire, but also the possible sources of mineral material (Weiss et al. 2001). All of the calculated ratios have higher values than rainwater average, suggesting that floodwaters and/or groundwater flow are needed to explain them. Averages based on Berner and Berner (2012), and average results of groundwater, surface water and spring water samples from Viiankiaapa region, are presented in Table 10. Values for peat core VA310315 are significantly higher than the values measured from local groundwater and river water samples (Work Package III of Sakatti-project, unpublished results, Table 9). Since values for the core VA310315 are multiplex compared to those of different water sources it is clear that mineral material transported to the mire by flooding is the only factor capable of explaining these values.

Against atmospheric input being the most important source of mineral material is also the Pb content of the core VA310315 (Figure 14). Pb has mostly anthropogenic origin (lead pollution) that is showcased as higher values in the top section of the core (Figure 14). In mires that receive waters from other sources than atmosphere it is also possible that the source of Pb is not solely atmospheric (Wei et al. 2012). In their study Wei et al. (2012) calculated correlations between TOC (total organic carbon), Pb concentration, and Pb/Ti ratio, concluding that lead correlates significantly with TOC and LOI. This suggests that plant material affects the accumulation of lead and Pb is mainly derived from organic materials. In core VA310315 however, there were no significant correlations between LOI<sub>550</sub>, Pb, C contents or Pb/Ti (not presented) (Table 9), suggesting that the main source of lead in Viiankiaapa mire is atmospheric input (Wei et al. 2012). From the Pb profile it is clear that before approximately 3 000 cal. BP the values had only few minor peaks,

suggesting that the atmospheric input is less significant when it comes to the development of Viiankiaapa. Peaks at c. 140 cm and 200 cm (Figure 14), do correlate with element/Ti profiles (Figure 20), which might indicate shorter time intervals of higher atmospheric input. The accumulation rate of lead (PbAR, g Pb/m<sup>2</sup>/yr) is presented in Figure 22, shown with calibrated <sup>14</sup>C age. During early Holocene (c. 11 700 – 8 200 cal. BP) the accumulation rate of lead seems to decrease slightly to its average level. The pattern is disrupted by the sudden increase after the 8.2k event also visible in the PAR and CAR (Figures 17 and 18), respectively. After the cooling event, three smaller peaks can be identified, having an age of approximately 7 700, 6 550, and 4 950 cal. BP (Figure 21), all fitting in mid Holocene age range. The expansion and development of civilization is shown as increased values from c. 3 000 cal. BP towards present time (Bindler 2006).

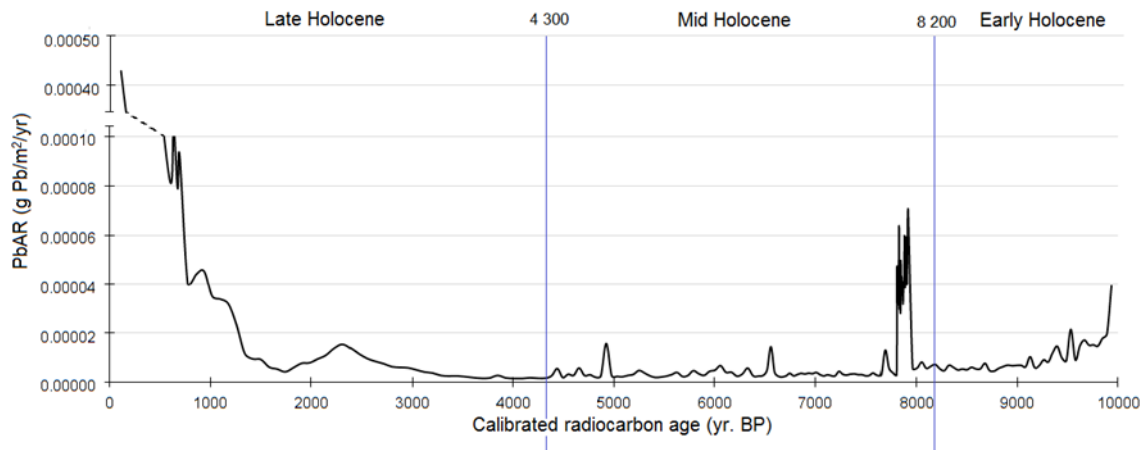


Figure 22 The accumulation rate of lead (PbAR, g Pb/m<sup>2</sup>/yr) in core VA310315, presented with calibrated radiocarbon age. The approximate boundaries of early -, mid -, and late Holocene are also shown.

## 6. SUMMARY

Various geochemical and physical proxies and methods were used to assess the Holocene development and paleohydrology of Viiankiaapa mire, located in Sodankylä, Finnish Lapland. The main events showcased by the obtained results are summarized as follows.

### *Early Holocene 11 700 – 8 200 cal. BP*

Early Holocene in the development history of Viiankiaapa mire was characterized by high mineral material input due to meltwaters of the Scandinavian ice sheet, and floods of the

initial river Kitinen washing over the young mire. Most of the metal profiles are showing high values at the bottom of the peat core VA310315. Part of this phenomenon is due to the secondary effect of the underlying mineral soil, but it cannot explain all of the element concentrations. From the element/Ti profiles, especially Fe/Ti and S/Ti profiles are indicating of increased flooding events, interrupted by drier periods as displayed by the Fe/Ti profile and the color of the ash. This is supported by C/N ratio indicating strong fluctuation during early Holocene. The main nutrient levels (C, N, P, K, and to some extend Ca) show lowest values during early Holocene suggesting higher water table and variable peat accumulation rate. CAR shows relatively constant increase throughout early Holocene supporting the interpretation of a growing and relatively unstable young mire. This is supported by PAR. The 8.2k event terminating early Holocene is clearly visible in the element concentration profiles where metals show generally decreasing values. Nutrients show strong increase in values after the cooling event.

#### *Mid Holocene 8 200 – 4 200 cal. BP*

Mid Holocene was the time interval of generally higher temperatures (Holocene thermal maximum, HTM) and events of higher and lower mineral material input to Viiankiaapa mire. All accumulation rates calculated showcase an event of high growth rate of the mire following the 8.2k cooling event. Ti normalized profiles showcase two distinct events of increased mineral material input (c. 8 000 – 6 500 cal. BP and c. 4 800 – 3 200 cal. BP, latter extending to late Holocene), in keeping with other Holocene records from Finland. The wet event at c. 8 000 – 6 500 cal. BP is recorded in multiple profiles and the observation is parallel with elevated lake-levels recorded in northern Finland. Lower lake levels, and resulting reduced flooding, following the wet event is also recorded at Viiankiaapa mire. The end of mid Holocene is characterized with again higher mineral material input, in keeping with increased peat initiation reported in southern Finland. All results combined indicate that mid Holocene was a time of stabilization for Viiankiaapa mire, and that its main water and nutrient source remained terrestrial rather than atmospheric.

#### *Late Holocene 4 200 cal. BP – present*

The beginning of late Holocene is characterized by increased mineral material input in keeping with recorded higher temperatures and increased humidity. Many of the element profiles (including S, Fe, Mn, Al, Cu, and Ni) show relatively constant values throughout



late Holocene, suggesting only minor changes in mineral material input to Viiankiaapa mire. This refers to stabilized groundwater and surface water flow patterns through the mire, since all these elements are present in bedrock surrounding Viiankiaapa mire. Ti normalized profiles showcase an event of cooler and drier conditions 3 000 cal. BP, in keeping with the other studies conducted in Finland. The wet-shift reported in other studies 2 700 cal. BP is also indicated at the geochemical record of Viiankiaapa mire. To less extend this event is also showcased by a number of other analyzed elements. More modern events, such as the Little ice-age, are less clear in the geochemical record of Viiankiaapa mire. However, the development of the modern civilization is shown very clearly in the profile of lead Pb. The very top of the core VA310315 shows decreasing values relative to multiple elements indicating decrease in mineral material input and, therefore flooding of Kitinen. This could be connected to the damming of the river.

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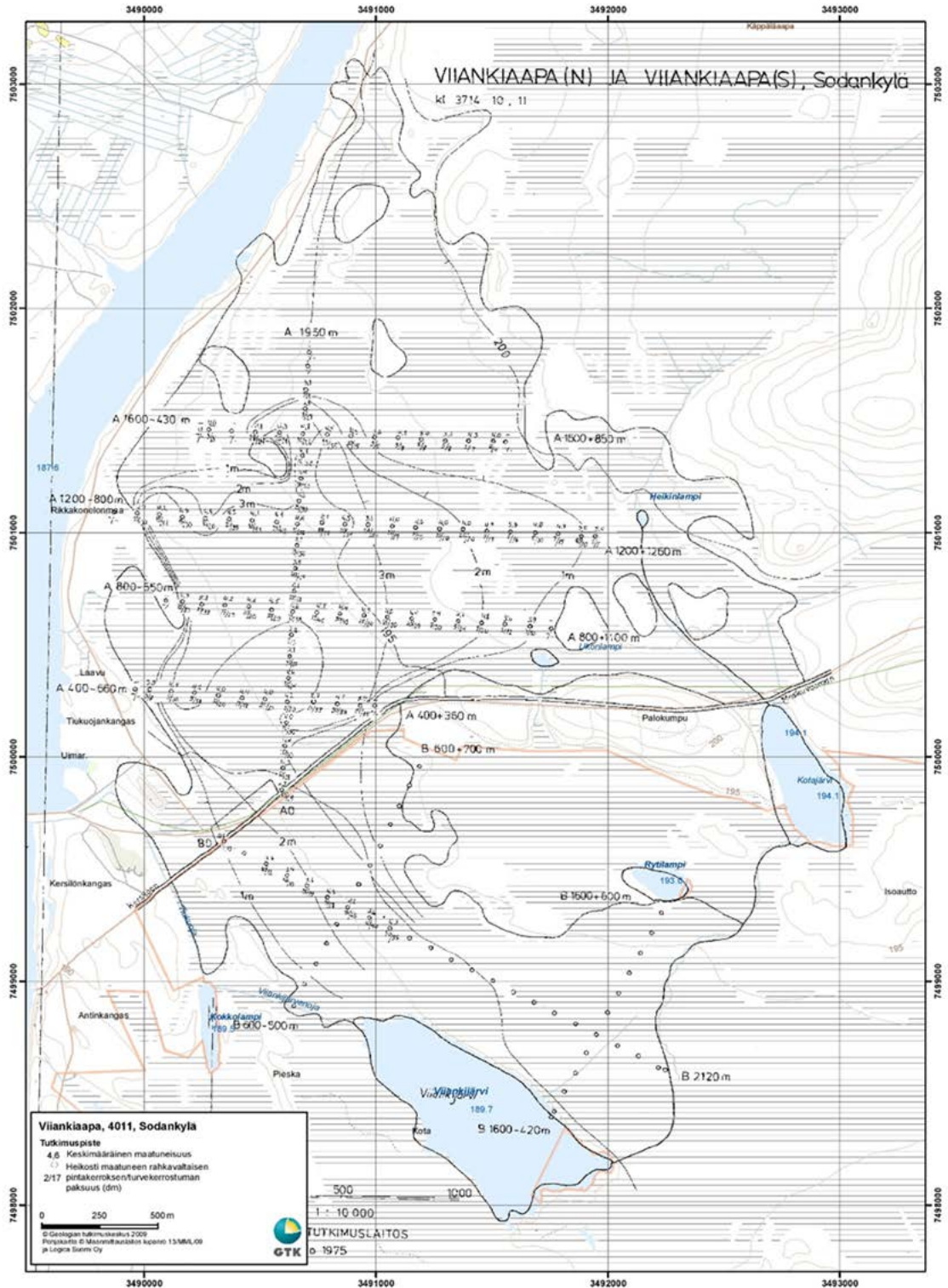
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## 9. APPENDICES

Appendix 1 The main results of the study of the northern part of Viiankiaapa mire complex mapped in 1975. The upmost number on each point represents the average humification. The lower number is the poorly humified top layer/the entire peat layer in dm. (Geological survey of Finland, 2009).



Appendix 2 Result of the CNS-analysis. Also measured weights of the samples and C/N ratio are shown.

Sample	Depth (cm)	C %	N %	C/N ratio	S %	Weight (mg)
1-P	0 - 5	40.26	2.78	14.48	0.41	11.86
2-P	0 - 8	49.67	3.12	15.93	0.56	9.37
3-P	8 - 13	50.63	3.45	14.66	0.68	6.84
4-P	13 - 20	51.56	3.15	16.36	0.72	6.28
5-P	20 - 25	49.39	2.65	18.67	0.54	6.30
1	31	49.09	2.62	18.77	0.56	5.63
2	33	49.32	2.60	18.99	0.55	5.78
3	35	48.56	2.74	17.71	0.55	5.81
4	37	48.65	3.03	16.05	0.60	6.32
5	39	49.71	2.94	16.92	0.64	5.85
6	41	50.64	2.82	17.93	0.64	5.94
7	43	50.26	2.91	17.30	0.62	5.18
8	45	50.64	3.30	15.37	0.65	5.58
9	47	50.30	2.97	16.92	0.61	5.89
10	49	49.37	2.62	18.89	0.57	5.63
11	51	49.84	2.69	18.52	0.52	5.79
12	53	49.89	2.58	19.30	0.52	5.44
13	55	50.24	3.13	16.07	0.59	6.12
14	57	50.54	2.64	19.12	0.61	5.55
15	59	50.19	2.56	19.65	0.58	5.99
16	61	50.80	2.68	18.95	0.53	6.00
17	63	51.37	2.96	17.36	0.55	5.94
18	65	50.90	2.95	17.24	0.57	5.08
19	67	50.94	2.89	17.61	0.63	5.36
20	69	51.50	2.70	19.07	0.59	5.76
21	71	50.65	2.47	20.53	0.55	5.16
22	73	51.02	2.59	19.68	0.56	5.39
23	75	51.31	2.26	22.67	0.58	5.95
24	77	51.01	2.63	19.41	0.57	5.37
25	79	49.84	2.59	19.29	0.50	5.81
26	81	50.87	2.58	19.71	0.49	5.50
27	83	50.57	2.69	18.83	0.45	5.71
28	85	50.15	2.81	17.86	0.43	5.97
29	87	52.70	2.71	19.48	0.44	5.92
30	89	52.85	2.57	20.67	0.41	5.98
31	91	50.79	2.23	22.79		5.28
32	93	51.04	2.20	23.23		5.74
33	95	52.31	2.12	24.72		5.31
34	97	52.12	2.37	22.02		5.56
35	99	52.17	2.27	23.00	0.29	5.77
36	101	51.34	2.14	23.95		5.25
37	103	50.76	2.36	21.50		5.23
38	105	52.11	2.52	20.70		5.58
39	107	51.12	2.18	23.49		5.82
40	109	52.06	2.21	23.72	0.26	5.52
41	111	52.33	2.39	21.92		5.97
42	113	52.91	2.56	20.66		5.66
43	115	51.30	2.03	25.33		5.11
44	117	51.24	2.17	23.57		5.87
45	119	51.53	2.38	21.68	0.38	6.03
46	121	51.93	2.09	24.88		5.49
47	123	51.12	2.25	22.74		5.16
48	125	52.26	2.51	20.83		5.69
49	127	52.29	2.20	23.82		5.37
50	129	52.15	2.44	21.35	0.39	5.76
51	131	53.39	2.46	21.71	0.59	5.92
52	133	52.26	2.24	23.35	0.55	5.72
53	135	52.31	2.15	24.30	0.50	6.03

54	137	52.01	2.28	22.78	0.47	5.68
55	139	52.51	2.19	23.92	0.48	5.79
56	141	52.84	2.20	24.04	0.46	5.28
57	143	52.43	2.37	22.12	0.44	6.03
58	145	52.02	2.41	21.55	0.50	5.97
59	147	51.72	2.23	23.21	0.49	5.78
60	149	51.81	2.17	23.90	0.50	5.89
61	151	52.44	2.17	24.14	0.50	5.82
62	153	52.83	2.25	23.47	0.59	5.89
63	155	52.22	2.20	23.76	0.55	5.34
64	157	52.88	2.41	21.93	0.64	5.41
65	159	53.14	2.66	20.00	0.70	5.67
66	161	53.22	2.53	21.04	0.70	5.65
67	163	52.42	2.60	20.14	0.71	5.48
68	165	52.43	2.65	19.77	0.67	6.04
69	167	53.17	2.76	19.28	0.80	5.80
70	169	54.03	2.45	22.07	0.82	5.18
71	171	52.98	2.55	20.74	0.82	5.65
72	173	53.19	2.53	21.04	0.82	5.11
73	175	52.70	2.37	22.25	0.75	5.63
74	177	52.71	2.44	21.62	0.72	5.92
75	179	52.51	2.46	21.37	0.71	5.97
76	181	51.76	2.30	22.49	0.64	5.44
77	183	51.74	2.26	22.90	0.65	5.56
78	185	51.29	2.20	23.36	0.59	5.88
79	187	52.74	2.33	22.68	0.59	5.80
80	189	53.20	2.80	19.02	0.61	5.82
81	191	52.68	2.70	19.51	0.64	5.93
82	193	52.52	2.48	21.21	0.61	5.88
83	195	52.07	2.48	20.98	0.73	5.22
84	197	51.90	2.70	19.23	0.65	5.40
85	199	53.32	2.31	23.11	0.64	5.23
86	201	52.61	2.25	23.37	0.62	5.35
87	203	53.11	2.30	23.05	0.62	5.71
88	205	52.29	2.31	22.68	0.58	5.33
89	207	51.57	2.42	21.29	0.60	5.51
90	209	51.24	2.12	24.20	0.57	5.89
91	211	51.71	2.32	22.28	0.60	5.68
92	213	52.79	2.30	22.99	0.59	5.61
93	215	53.97	2.24	24.13	0.59	5.41
94	217	52.09	2.05	25.46	0.60	5.66
95	219	50.95	1.87	27.21	0.60	5.89
96	221	50.58	2.09	24.24	0.64	5.63
97	223	51.68	2.09	24.72	0.68	5.95
98	225	51.44	2.36	21.77	0.75	5.28
99	227	51.61	2.07	24.91	0.71	5.59
100	229	51.38	1.94	26.47	0.72	5.61
101	231	52.07	1.95	26.72	0.76	5.95
102	233	52.02	2.04	25.49	0.79	5.65
103	235	50.92	1.96	25.92	0.90	5.28
104	237	52.61	2.00	26.31	0.86	5.61
105	239	51.78	1.99	26.06	0.89	5.63
106	241	53.31	2.17	24.56	1.00	5.23
107	243	53.94	2.17	24.88	1.17	5.91
108	245	50.11	1.73	28.90	1.08	5.75
109	247	51.23	2.62	19.55	1.30	5.81
110	249	52.80	2.01	26.27	1.14	5.73
111	251	52.39	2.02	25.95	1.07	6.06
112	253	52.43	1.93	27.12	1.04	5.21
113	255	52.17	2.22	23.48	1.28	5.65
114	257	51.59	1.97	26.14	1.43	5.94

115	259	52.45	2.05	25.53	1.25	6.04
116	261	51.28	2.03	25.25	1.22	5.91
117	263	50.09	1.66	30.17	1.09	5.38
118	265	49.43	1.39	35.47	1.03	5.82
119	267	45.34	1.67	27.13	0.92	5.58
120	269	50.33	2.06	24.65	1.05	5.76
121	271	49.85	2.00	24.96	1.02	5.22
122	273	52.07	2.22	23.50	1.04	5.54
123	275	52.27	2.23	23.49	1.06	5.43
124	277	52.52	2.31	22.77	1.08	5.71
125	279	50.76	2.28	22.24	1.19	5.67
126	281	50.85	2.05	24.77	1.27	5.70
127	283	50.92	1.86	27.31	1.20	5.60
128	285	50.41	2.08	24.19	1.21	5.29
129	287	50.48	2.00	25.23	1.17	5.34
130	289	50.28	1.94	25.88	1.13	6.09
131	291	50.98	2.12	24.00	1.13	5.28
132	293	50.78	2.18	23.27	1.16	5.33
133	295	50.50	2.05	24.63	1.16	5.36
134	297	49.40	1.33	37.01	1.19	5.42
135	299	49.97	1.93	25.89	1.27	5.46
136	301	49.57	1.92	25.76	1.30	5.43
137	303	51.13	1.45	35.16	1.08	5.65
138	305	49.61	1.90	26.04	1.22	5.29
139	307	49.18	1.71	28.84	1.11	5.36
140	309	48.79	1.61	30.36	1.09	5.42
141	311	49.24	1.59	30.88	1.19	5.81
142	313	49.96	1.62	30.88	1.23	5.86
143	315	49.82	1.68	29.66	1.19	5.39
144	317	50.12	1.87	26.86	1.30	5.41
145	319	49.32	1.84	26.94	1.39	5.44
146	321	48.86	1.96	24.89	1.23	5.35
147	323	48.41	1.51	32.15	1.17	6.05
148	325	50.51	1.52	33.31	1.17	5.93
149	327	49.84	1.61	30.93	1.23	5.59
150	329	49.45	1.92	25.70	1.29	6.05
151	331	47.01	1.61	29.15	1.26	5.32
152	333	49.02	1.97	24.92	1.42	5.51
153	335	47.68	1.78	26.78	1.41	5.87
154	337	47.28	1.95	24.22	1.43	5.82
155	339	46.80	1.84	25.40	1.35	5.93
156	341	46.59	2.06	22.65	1.42	5.44
157	343	47.85	1.81	26.50	1.55	5.83
158	345	48.18	1.81	26.65	1.78	5.52
159	347	48.88	1.94	25.23	1.82	5.55
160	349	47.59	2.19	21.75	2.00	5.64
161	351	46.86	2.00	23.39	2.46	5.80
162	353	45.68	1.18	38.76	2.46	5.63
163	355	43.59	1.26	34.64	3.71	5.39
164	357	41.36	1.21	34.28	5.23	5.35
165	359	43.45	1.34	32.31	3.80	5.57
166	361	43.53	1.25	34.71	4.12	5.77
167	363	41.47	0.96	43.34	4.50	6.01
168	365	41.07	0.95	43.24	4.93	5.26
169	367	42.38	1.12	37.86	4.52	6.00
170	369	41.38	1.10	37.47	4.68	5.49
171	371	41.04	1.12	36.72	4.96	5.58
172	373	40.41	0.97	41.55	5.44	5.89
173	375	39.35	0.87	45.09	6.30	5.50
174	377	39.91	0.81	49.11	5.40	5.53
175	379	39.97	0.90	44.25	5.53	5.36

176	381	40.01	1.12	35.75	5.56	5.55
177	383	40.24	1.10	36.43	5.70	5.69
178	385	39.94	1.12	35.57	6.61	5.77
179	387	41.22	1.22	33.81	5.83	5.79
180	389	40.52	1.25	32.29	6.10	5.62
181	391	38.68	1.04	37.24	6.63	5.53
182	393	38.78	1.04	37.25	6.63	5.94
183	395	37.88	0.94	40.10	7.33	5.65
184	397	36.75	0.91	40.33	8.75	5.92
185	399	36.23	1.29	28.09	9.41	5.83
186	401	33.96	1.07	31.73	12.65	5.21
187	403	32.84	1.02	32.07	12.66	5.35
188	405	34.47	0.98	35.04	10.39	5.35
189	407	31.93	0.90	35.44	12.81	5.39
190	409	33.51	0.67	49.92	11.38	5.66
191	411	34.93	0.75	46.82	9.81	5.95
192	413	33.86	0.76	44.30	10.58	5.74
193	415	33.27	0.89	37.29	11.37	5.32
194	417	32.72	1.00	32.84	13.38	5.45
195	419	33.17	1.00	33.32	12.78	5.80
196	421	33.79	1.00	33.69	13.63	5.57
197	423	34.07	0.96	35.62	12.43	5.64
198	425	33.52	0.93	36.18	11.10	5.49
199	427	32.69	0.89	36.89	11.39	5.75
200	429	33.52	0.96	35.06	9.28	5.94

Appendix 3 The processed results for the ICP-MS analysis of core VA310315.

Depth (cm)	P	Si	Zn	Ti	Pb	Fe	Mn	Al	Cu	Ni	Ca	Mg	K	Na
2.5	590.86	30.79	15.40	14.97	10.31	9886.2	45.64	326.32	3.16	8.49	7218.88	702.28	246.03	69.38
4	547.17	70.23	13.49	11.59	7.99	5184.5	31.28	334.45	2.39	8.38	7492.33	672.20	132.59	64.64
10.5	472.59	102.84	6.51	9.34	4.94	3667.7	32.72	294.32	1.74	8.17	7673.55	620.55	62.29	47.96
16.5	396.52	90.49	2.61	9.21	3.72	3590.0	29.34	297.91	1.84	9.53	7853.09	607.17	32.56	45.20
25	329.37	101.46	1.33	6.78	1.99	3223.1	25.00	263.99	1.69	9.41	8341.37	532.81	31.32	65.00
31	326.23	105.76	3.05	6.21	2.49	3085.6	25.52	271.96	1.88	8.87	6960.02	522.20	30.81	62.73
33	336.30	112.68	2.63	6.21	1.90	2968.2	24.76	271.31	1.67	9.07	6414.53	505.14	26.97	49.64
35	339.27	115.51	2.19	6.78	2.23	3281.5	26.06	305.84	1.73	9.74	7495.48	560.67	27.91	68.72
37	346.20	127.15	1.82	7.72	1.96	2870.4	24.84	292.78	2.21	9.93	8351.57	533.03	22.05	58.99
39	397.82	127.65	1.88	7.30	2.15	3251.2	26.17	333.04	2.24	10.55	7959.33	589.76	34.18	69.90
41	375.09	120.46	1.88	9.06	2.22	3261.8	24.78	320.27	2.17	10.83	7726.69	581.80	28.97	60.81
43	387.82	120.43	1.89	8.89	1.71	2861.1	22.91	292.43	2.02	10.71	6985.96	551.28	20.11	57.10
45	362.75	129.66	1.86	9.27	1.65	3009.5	21.54	276.96	1.97	11.02	8020.86	535.11	14.74	56.67
47	407.63	110.49	1.67	9.41	1.55	3168.6	21.03	297.67	2.06	11.03	7242.15	576.47	19.64	54.81
49	355.28	115.23	1.21	7.76	1.13	3282.9	20.46	290.14	1.76	9.53	7779.26	641.02	19.28	55.03
51	345.77	112.51	1.41	9.70	0.57	3169.8	18.50	279.02	1.85	9.78	7106.26	608.35	16.39	51.13
53	353.48	111.07	1.19	9.80	0.46	3235.1	18.30	279.62	1.77	10.08	7316.35	626.51	17.78	51.55
55	332.44	128.48	1.03	12.15	0.44	2968.4	15.96	263.13	1.75	9.74	7312.21	519.85	15.99	57.37
57	326.92	101.78	1.13	6.62	0.29	3518.9	17.24	277.48	1.55	9.64	7617.26	618.96	16.64	66.67
59	322.68	96.38	1.22	6.35	0.25	3502.8	16.50	272.24	1.70	10.64	6876.27	607.52	15.63	
61	316.65	95.18	1.34	5.82	0.20	3099.4	16.12	236.12	1.73	10.23	6239.82	551.75	14.33	41.84
63	360.01	99.32	1.76	6.07	0.28	3198.4	15.69	236.52	1.67	11.07	6295.16	566.33	14.41	
65	309.80	105.36	1.16	6.31	0.37	3137.1	15.26	210.70	1.58	10.67	7007.70	519.93	8.43	59.15

67	329.85	105.15	1.29	8.04	0.38	3210.8	15.56	234.46	1.57	10.70	5983.21	541.41	14.48	
69	302.07	95.00	1.26	5.19	0.46	3011.0	14.85	203.18	1.37	9.33	5533.76	516.72	14.77	
71	298.04	104.17	1.23	5.88	0.53	3274.7	17.25	210.93	1.31	9.59	6122.90	553.67	12.71	
73	273.81	97.29	1.45	4.15	0.67	3564.2	16.53	196.99	1.46	10.18	7544.45	541.84	6.71	41.99
75	286.63	95.98	1.39	3.94	0.75	3755.5	16.42	199.83	1.42	9.14	6824.14	572.13	12.88	
77	304.88	100.87	1.07	5.36	0.67	3634.3	16.81	206.56	1.43	9.33	6463.47	551.87	13.61	
79	298.15	88.58	0.53	5.08	0.55	3922.2	17.07	192.94	1.41	10.28	6756.12	585.67	12.22	51.96
81	316.79	91.17	0.78	6.80	0.46	3954.5	17.70	187.82	1.36	10.78	6666.46	582.19	13.65	43.26
83	310.37	111.23	1.03	9.25	0.40	3550.8	16.95	175.54	1.35	9.92	6371.05	501.22	7.72	
85	347.16	106.00	0.63	15.91	0.36	3981.1	17.78	202.78	1.51	10.31	6443.39	558.64	12.91	
87	335.59	103.50	0.83	15.91	0.30	3824.1	18.46	194.94	1.42	9.80	6230.65	549.90	12.71	57.86
89	261.97	123.65	1.11	10.91	0.29	3651.8	17.22	185.73	1.26	9.00	6552.04	486.21	8.54	43.90
91	290.13	121.25	0.86	9.00	0.28	4864.6	21.67	204.72	1.39	10.12	7602.30	660.15	11.85	66.05
93	239.04	107.06	0.57	6.29	0.24	4215.1	18.51	170.01	1.21	9.04	6667.62	579.68	11.34	43.63
95	248.30	105.53	0.78	5.37	0.19	4223.2	18.60	164.94	1.25	9.18	6235.80	548.06	12.11	59.24
97	239.26	119.62	2.41	5.43	0.17	3884.6	18.92	160.86	1.18	8.68	6852.17	497.10	12.78	60.63
99	221.68	100.11	0.72	3.81	0.13	3962.2	18.61	148.35	1.00	8.24	5877.95	513.57	9.60	
101	230.81	108.71	0.72	4.78	0.11	4146.4	19.53	156.34	1.11	8.77	6005.12	520.18	11.15	43.12
103	285.19	111.10	0.87	5.35	0.12	4072.1	19.89	174.09	1.33	9.35	5973.73	514.74	11.81	63.86
105	276.96	108.28	0.82	4.68	0.10	4323.6	20.57	182.52	1.23	9.19	6345.66	513.76	11.29	46.16
107	244.75	109.96	0.85	3.59	0.08	4702.0	22.71	154.56	1.30	8.93	7520.91	544.77	5.39	45.17
109	268.99	103.46	1.71	4.38	0.07	4718.4	23.38	182.10	1.38	9.26	6643.78	559.14	11.58	44.36
111	269.49	99.87	1.76	4.03	0.08	4514.3	23.27	188.53	1.28	9.37	6389.60	527.11	10.60	54.82
113	265.45	96.81	1.77	3.65	0.13	4599.6	23.88	185.95	1.17	8.98	6744.01	554.33	9.53	43.34
115	235.17	107.03	1.37	2.74	0.08	4862.6	24.43	163.11	1.18	8.80	8264.83	579.19	4.93	63.69
117	243.41	102.56	1.35	3.42	0.07	5105.9	24.95	191.33	1.35	9.46	7229.80	589.96	10.74	46.03
119	251.58	101.80	1.33	3.71	0.07	4899.5	24.33	198.21	1.14	9.47	6671.45	532.22	11.31	74.00
121	243.74	97.41	1.33	3.75	0.08	4846.6	24.72	202.08	1.02	9.30	6709.79	529.46	10.66	49.48
123	245.87	106.51	1.47	4.56	0.07	4743.7	25.22	238.25	1.30	9.56	6525.22	511.64	12.34	58.15
125	249.18	113.74	1.63	4.28	0.08	4674.3	25.24	240.14	1.44	10.51	7215.57	481.06	8.28	50.90
127	284.28	106.10	1.46	5.06	0.08	4921.5	27.54	303.55	1.82	10.55	6926.64	533.33	12.63	60.10
129	298.70	117.80	1.35	5.22	0.18	5076.9	27.38	305.25	2.18	10.18	6956.14	531.03	13.78	52.05
131	272.33	93.71	1.58	5.02	0.06	4878.7	26.52	249.52	2.01	10.95	5872.78	448.26	11.73	64.15
133	244.60	94.70	1.08	6.57	0.10	5674.7	39.29	275.20	1.98	11.60	6570.15	495.23	12.40	72.25
135	232.19	118.81	0.99	5.57	0.08	5509.8	29.86	276.65	1.86	10.93	7575.77	484.35	9.90	77.01
137	244.78	98.68	1.04	5.80	0.18	6120.6	33.61	355.26	2.17	12.31	7398.90	538.43	10.37	51.87
139	245.41	100.77	1.29	4.40	0.08	5171.7	29.24	303.75	1.68	10.34	6561.35	466.35	9.71	74.65
141	242.81	107.42	1.43	4.96	0.09	5212.6	28.54	301.21	1.75	10.74	6019.69	458.28	12.37	52.37
143	270.94	88.52	1.59	5.52	0.06	5558.4	30.76	357.61	2.48	12.49	6257.32	462.37	11.63	75.49
145	258.79	114.23	1.43	6.85	0.08	6224.7	33.81	412.25	3.72	13.81	7717.25	485.79	10.41	57.57
147	275.45	119.57	3.01	7.65	0.51	6502.5	34.68	466.14	3.42	13.47	7277.55	532.83	15.33	55.04
149	228.27	103.67	1.43	6.38	0.08	5847.3	32.33	416.14	3.45	12.42	7416.90	462.85	5.71	49.70
151	264.42	96.69	1.80	8.30	0.07	6368.7	33.84	497.68	4.36	13.92	6672.91	495.29	10.26	47.66
153	254.18	95.34	1.96	7.49	0.07	6048.0	32.51	518.48	4.26	13.68	6406.88	475.86	10.64	70.17
155	266.38	104.77	2.03	8.19	0.09	6187.4	34.74	550.80	4.61	14.55	7591.09	478.92	6.65	58.56
157	280.05	99.67	2.90	8.02	0.10	6051.5	33.95	623.99	5.18	15.24	6531.10	481.09	11.72	66.38
159	312.32	92.96	4.53	8.29	0.15	6061.7	35.70	663.46	5.97	16.64	6742.18	484.66	13.22	62.41
161	291.20	107.72	3.46	7.79	0.12	5668.3	34.89	597.22	5.74	16.01	7050.52	439.33	7.58	50.39

163	317.17	99.96	2.32	8.93	0.08	6003.5	37.67	716.07	6.05	17.09	6729.19	477.98	10.71	48.91
165	319.21	103.71	2.52	9.41	0.06	6472.0	37.38	773.70	5.74	16.86	6811.13	480.94	10.97	55.37
167	339.89	106.86	2.03	10.19	0.06	6476.1	36.96	800.49	6.06	23.52	6629.07	461.20	11.32	48.02
169	294.48	110.90	2.20	10.37	0.07	6381.9	38.00	850.04	6.28	36.57	7428.94	437.07	7.25	47.46
171	352.06	109.58	1.68	9.92	0.09	7337.4	42.55	1025.03	6.38	35.12	7409.94	502.27	11.99	73.60
173	369.28	112.10	2.34	11.05	0.12	7609.6	42.37	1013.12	5.62	31.26	7335.45	499.40	12.64	48.07
175	390.21	120.74	1.44	9.52	0.07	7313.8	43.66	994.53	4.98	25.68	7427.54	510.01	12.95	68.57
177	401.54	136.71	1.67	11.00	0.08	8026.5	47.73	1026.06	5.30	21.87	8892.10	534.50	9.68	50.36
179	361.39	119.95	2.24	11.15	0.15	7741.2	48.28	1027.76	5.76	19.16	7996.86	546.33	12.70	49.65
181	352.29	96.78	2.60	10.24	0.11	8459.3	49.96	998.81	6.33	19.27	8359.42	575.70	9.32	53.47
183	323.58	92.57	1.39	8.46	0.09	8651.	51.48	990.69	5.35	18.97	8707.52	582.54	8.38	51.93
185	301.93	105.00	1.95	7.74	0.14	8540.0	53.45	889.51	5.04	17.55	9752.13	578.80	6.57	52.31
187	319.80	114.85	2.46	9.00	0.16	8244.0	51.16	844.68	4.65	16.43	8483.69	557.89	11.25	49.31
189	396.05	123.44	1.95	12.98	0.21	8079.0	51.79	742.73	4.93	16.73	8143.55	530.06	11.90	61.51
191	342.15	120.14	1.57	9.77	0.13	8275.6	54.48	617.17	4.36	15.87	9491.63	543.96	7.54	52.84
193	404.82	146.41	2.13	13.19	0.13	9152.8	58.60	643.68	4.93	17.57	9217.56	599.61	12.58	52.24
195	326.52	103.82	1.00	18.56	0.08	8695.6	55.87	510.80	3.17	16.24	9103.66	550.27	9.77	56.66
197	321.33	121.85	1.47	26.67	0.10	7746.5	51.65	455.34	2.76	14.80	8435.68	490.15	12.62	53.17
199	300.04	122.93	2.50	13.70	0.18	7572.1	50.57	433.85	2.61	14.34	7693.26	508.77	10.35	49.69
201	287.53	108.39	2.12	7.23	0.08	7081.1	49.52	353.97	2.43	14.62	7891.90	475.58	5.20	51.71
203	280.35	121.28	2.18	6.92	0.08	7487.5	52.71	377.55	2.08	15.02	7461.13	504.57	10.88	49.20
205	311.54	113.36	1.88	8.10	0.09	7287.4	58.15	369.25	2.22	15.00	7947.09	537.44	10.55	50.87
207	308.67	108.36	2.66	8.08	0.11	8180.5	55.27	354.05	2.26	14.53	7978.37	525.71	10.42	57.46
209	312.60	119.81	2.80	11.63	0.32	8838.7	59.54	351.51	2.30	15.30	8762.75	582.56	11.57	52.33
211	232.21	99.83	2.58	7.18	0.09	8507.7	61.46	391.87	1.73	15.96	8935.38	503.64	4.90	52.09
213	279.63	96.52	1.90	6.10	0.05	7603.7	54.84	313.92	1.78	14.57	6606.23	449.22	7.94	50.46
215	270.50	107.55	1.89	5.97	0.05	6747.5	55.04	298.66	1.82	13.99	6086.78	425.54	8.01	49.36
217	235.20	108.28	0.63	6.58	0.05	9207.1	69.35	353.51	1.84	14.41	8522.62	549.26	9.02	51.96
219	221.96	107.99	1.42	7.96	0.08	11533.2	82.86	383.34	2.46	16.24	10520.61	671.26	8.16	55.49
221	253.45	95.94	0.72	5.21	0.05	9886.4	73.56	338.17	2.68	14.78	8991.69	594.40	6.69	52.30
223	227.63	102.72	0.71	5.10	0.07	9574.7	73.24	345.80	2.84	16.94	9744.98	561.20	4.99	59.68
225	247.81	119.26	1.46	7.73	0.08	9679.6	79.07	403.81	4.06	18.96	10154.42	586.06	5.65	56.33
227	282.09	118.12	1.84	8.46	0.07	10207.7	81.23	429.16	4.53	18.79	9409.48	617.52	9.76	58.97
229	255.39	123.80	0.97	8.11	0.08	10096.2	76.96	418.42	5.09	25.03	9574.91	555.40	6.87	56.92
231	239.97	116.26	1.31	7.60	0.08	9051.3	69.63	375.09	4.33	32.32	7762.25	516.99	11.06	54.17
233	251.36	129.90	1.39	8.71	0.09	9386.7	64.65	400.77	3.96	41.83	7406.95	481.91	11.50	52.81
235	241.44	120.54	1.35	6.85	0.07	11193.3	67.44	404.01	4.50	57.66	7910.21	508.01	10.00	55.89
237	203.81	112.60	1.87	5.47	0.05	8438.7	56.37	315.67	3.76	44.03	6464.27	405.51	7.31	71.93
239	209.58	112.31	1.29	6.18	0.06	9494.3	63.62	337.21	4.20	54.25	6929.65	464.66	8.17	54.72
241	227.80	115.74	1.69	6.51	0.06	9004.7	63.64	338.12	6.03	59.61	7195.45	428.27	5.81	55.55
243	217.70	102.26	1.79	6.52	0.05	8265.3	65.47	374.39	4.96	59.35	6526.25	447.35	7.54	53.58
245	233.53	106.28	1.25	8.36	0.10	10844.2	77.00	448.14	5.56	80.34	8182.25	512.62	9.83	57.03
247	264.00	125.24	1.98	8.84	0.07	14091.2	58.52	386.10	5.76	75.14	6479.58	422.87	12.26	55.32
249	220.22	103.21	2.06	6.51	0.06	9572.0	60.65	314.00	4.70	76.13	6192.28	425.75	10.22	55.66
251	236.68	103.08	1.97	6.29	0.07	9183.5	71.19	335.15	5.27	67.03	7112.74	484.61	9.27	56.50
253	229.09	107.54	1.47	6.52	0.07	9232.9	74.71	348.69	5.66	62.14	7835.71	459.41	5.02	61.19
255	246.96	100.19	1.42	5.66	0.07	10172.8	75.92	382.36	4.88	76.68	7222.11	471.99	8.37	56.26
257	216.08	104.72	2.09	4.53	0.07	11931.3	75.20	341.95	3.94	93.45	7048.92	448.50	7.74	53.62



259	245.39	115.85	1.99	5.23	0.06	10812.0	78.90	366.72	5.01	86.33	7784.69	489.73	8.54	69.58
261	240.68	100.61	1.81	5.27	0.06	11048.3	73.88	362.35	6.33	76.67	7419.87	468.84	8.14	56.63
263	190.67	105.63	1.96	4.64	0.08	10910.7	78.46	280.66	4.60	53.10	8783.19	500.88	4.47	59.76
265	191.98	106.23	1.75	5.49	0.06	12039.7	87.69	338.48	4.71	39.70	9427.15	596.52	6.90	62.64
267	194.04	100.73	1.97	4.78	0.07	9554.2	78.53	298.05	4.94	35.60	7904.18	518.73	8.04	57.68
269	248.93	109.63	2.30	7.03	0.29	10095.5	78.74	366.49	5.91	36.71	8040.25	510.45	9.44	58.93
271	210.83	102.53	1.94	6.96	0.13	10136.8	81.59	340.95	6.24	32.35	8317.98	523.23	8.31	59.49
273	261.08	111.56	2.45	7.09	0.08	9178.4	82.86	339.61	7.09	35.05	8225.82	479.09	4.94	58.44
275	258.65	98.90	2.18	6.62	0.06	8899.6	73.55	336.87	6.57	38.64	6777.85	442.36	7.85	55.52
277	289.22	118.23	2.16	7.71	0.10	9308.5	76.69	358.33	8.19	37.43	7858.15	458.87	6.83	63.05
279	277.19	103.64	2.28	7.12	0.08	11403.9	87.04	415.00	7.19	47.99	8390.88	525.91	8.70	60.48
281	239.20	96.25	2.65	7.11	0.07	8786.2	92.69	354.37	6.17	43.61	8060.62	503.39	7.50	59.38
283	225.12	103.43	3.30	5.90	0.08	9838.2	85.71	349.33	5.92	46.19	7560.42	469.68	7.40	58.50
285	249.79	108.84	3.36	6.84	0.09	10722.8	92.97	365.67	6.56	47.55	9025.49	499.01	6.53	62.88
287	256.26	105.29	3.22	7.80	0.09	11326.6	93.50	367.73	6.47	43.08	8655.71	520.75	9.86	61.91
289	271.96	114.40	3.09	8.02	0.14	11924.7	89.07	356.95	6.85	40.09	9371.68	509.23	9.44	71.06
291	268.27	107.54	3.29	6.96	0.06	10306.0	78.09	337.89	6.32	38.33	7997.76	514.11	9.01	62.03
293	287.64	126.97	4.11	7.14	0.06	10463.4	82.16	344.31	7.37	40.78	8787.67	521.53	7.74	64.98
295	244.81	117.09	3.49	6.65	0.06	10436.2	80.42	356.62	7.06	46.30	8176.86	528.69	16.15	65.71
297	169.52	118.40	2.96	4.68	0.06	11426.4	80.07	352.88	6.11	43.70	8344.48	560.58	8.12	67.19
299	220.57	121.89	4.54	5.91	0.11	11519.5	81.73	379.86	6.34	41.16	8660.30	511.48	6.24	62.28
301	235.85	106.35	4.23	6.65	0.09	12947.1	81.55	403.56	6.53	31.53	8356.62	498.95	7.31	60.23
303	247.56	106.33	4.27	6.55	0.09	13793.0	81.42	377.59	5.96	25.11	8401.01	494.41	6.96	58.82
305	222.91	105.17	8.65	6.61	0.09	13313.5	79.97	354.50	5.46	20.49	8218.93	494.81	7.03	64.09
307	212.36	112.68	3.47	6.31	0.08	11908.7	89.12	305.59	5.45	19.37	9183.86	535.69	6.06	62.29
309	214.76	102.13	3.03	6.14	0.08	10984.5	87.65	260.08	5.15	14.94	8465.35	543.07	7.71	58.83
311	211.77	112.40	3.33	6.81	0.07	12052.8	96.37	279.29	4.67	14.92	9304.08	591.11	7.50	62.54
313	191.06	112.51	3.29	6.66	0.08	11370.8	91.22	272.46	4.90	17.79	9094.52	539.22	6.78	60.79
315	203.67	109.14	2.90	6.96	0.09	11942.9	87.01	244.25	4.68	22.15	8394.52	515.18	8.34	57.32
317	228.21	103.66	3.53	7.31	0.09	12413.8	87.11	246.77	4.28	21.32	8241.87	506.53	7.81	59.72
319	239.57	110.30	2.86	6.86	0.13	14539.0	95.32	262.02	4.01	18.31	9643.42	541.78	6.21	70.73
321	264.36	107.14	4.31	8.40	0.12	12530.5	99.46	273.50	4.25	14.91	9213.03	549.60	10.07	72.07
323	187.07	93.66	2.52	7.69	0.08	12992.1	96.41	205.49	3.43	13.91	9029.21	558.04	7.24	60.19
325	193.76	99.66	3.51	6.83	0.11	12221.1	99.36	185.58	3.61	12.21	9329.91	575.60	8.33	60.12
327	248.03	110.76	2.43	8.26	0.10	13202.2	105.33	200.83	4.49	14.38	9525.85	592.77	8.45	78.49
329	265.60	114.83	2.50	9.42	0.13	13999.1	110.40	190.68	5.09	15.73	10417.74	593.88	5.72	63.20
331	213.13	100.72	2.38	8.16	0.10	14739.7	107.69	164.27	4.37	14.18	9538.91	581.54	6.32	61.60
333	230.81	92.96	2.28	8.94	0.08	12876.7	101.84	152.87	3.74	15.16	8853.13	539.76	11.95	62.86
335	212.86	96.74	3.11	7.38	0.11	15106.5	114.39	175.50	3.45	15.47	10183.13	595.87	8.02	62.64
337	248.16	106.61	2.59	8.81	0.14	16351.1	131.94	178.90	3.68	14.13	12135.44	651.21	6.33	64.58
339	243.60	112.35	1.85	8.62	0.15	14246.5	123.74	162.15	3.89	9.87	10557.62	651.19	10.53	63.32
341	263.55	108.89	1.97	10.17	0.15	14843.7	126.28	162.89	3.57	8.42	10803.72	645.61	9.92	64.75
343	203.12	97.28	2.46	7.97	0.15	13787.9	124.31	156.25	3.25	8.90	10746.61	614.06	6.68	59.89
345	221.72	103.99	2.98	7.90	0.22	16519.2	138.15	160.21	3.51	10.68	11993.56	644.44	7.79	59.95
347	226.31	91.16	2.60	7.55	0.15	14494.3	117.28	140.22	3.40	8.67	10427.14	536.77	9.68	59.68
349	251.05	107.33	2.28	9.93	0.17	15644.2	115.00	164.52	3.24	9.42	9959.80	550.21	9.44	61.68
351	228.01	117.63	2.84	9.99	0.19	16772.5	111.11	152.52	3.80	11.19	10112.89	541.37	9.19	68.45
353	156.55	118.34	2.00	9.03	0.14	19914.0	106.28	169.79	3.98	12.18	9120.23	558.46	8.27	69.49

355	154.61	111.12	1.98	7.99	0.12	33781.5	95.34	123.96	5.20	9.66	8295.88	510.93	7.19	72.65
357	136.82	105.24	1.37	8.46	0.18	41288.4	89.33	116.15	4.81	8.37	7378.28	500.87	8.01	72.29
359	175.00	106.79	1.69	10.88	0.16	33642.7	95.03	124.36	4.53	8.22	8066.27	515.65	10.03	75.96
361	147.43	110.29	1.73	11.09	0.13	35722.0	101.50	156.50	4.88	8.46	9220.07	502.37	7.08	71.50
363	109.43	97.52	1.53	9.86	0.14	37125.3	104.13	135.52	4.85	7.66	8618.28	533.61	6.55	71.26
365	108.61	88.16	1.10	9.29	0.13	35924.6	103.32	132.79	4.62	8.02	8507.73	524.53	5.46	88.54
367	134.90	112.00	2.38	14.51	0.16	34293.5	107.89	139.95	5.44	9.59	9084.17	536.50	8.89	74.32
369	117.61	100.50	2.33	13.12	0.14	38461.4	117.83	163.34	5.38	10.25	9243.57	589.38	9.55	78.06
371	120.00	116.87	2.43	13.92	0.14	42992.1	119.35	171.15	6.25	11.46	9820.43	588.51	6.89	79.50
373	105.14	98.09	2.39	14.55	0.20	43486.5	116.76	164.55	6.40	11.30	9371.17	573.97	6.99	75.71
375	91.23	95.25	2.10	13.55	0.13	47837.4	107.86	163.90	6.19	11.07	8518.43	526.82	7.08	72.99
377	101.59	124.06	3.79	13.40	0.12	40941.8	144.45	194.39	6.22	13.79	10306.87	693.27	8.95	84.80
379	106.69	113.94	3.54	17.00	0.15	43201.2	116.55	207.64	6.56	13.23	8622.48	556.84	7.92	72.79
381	132.35	117.95	4.96	21.77	0.17	45851.1	132.86	238.89	9.11	16.18	9998.19	620.95	7.70	75.71
383	118.22	107.32	4.90	18.26	0.18	43094.1	122.10	228.95	9.33	15.47	9956.97	570.11	7.84	71.64
385	140.82	101.46	5.49	21.51	0.18	47278.3	115.99	251.97	10.53	16.58	7914.21	523.44	9.43	69.10
387	141.00	98.47	6.44	18.14	0.18	42230.7	115.92	263.28	10.28	17.63	7355.01	521.98	7.95	68.93
389	145.18	108.29	8.21	20.15	0.18	52084.0	129.93	285.96	13.47	19.72	7624.52	571.89	8.86	72.87
391	121.28	102.02	9.01	19.90	0.17	50192.0	131.13	279.61	11.73	18.69	9171.94	583.45	7.17	71.55
393	123.30	96.80	8.55	22.04	0.28	57052.6	119.60	266.59	13.66	18.77	8924.08	519.97	5.75	69.06
395	93.58	87.41	8.20	18.62	0.16	52370.8	108.94	237.87	11.26	17.67	6682.72	476.23	6.07	67.00
397	109.43	99.90	9.60	21.30	0.18	61865.9	118.41	263.57	11.97	19.64	9555.99	514.94	6.49	68.66
399	98.62	105.89	10.53	21.13	0.24	75178.7	124.01	282.73	13.18	20.38	8602.84	549.45	6.76	68.69
401	125.75	98.44	10.15	31.52	0.22		117.48	307.58	17.97	26.36	6743.27	509.30	5.65	70.61
403	119.93	99.94	8.08	30.43	0.32		106.02	310.54	17.02	21.74	6701.05	469.87	8.19	67.52
405	127.62	102.24	9.15	31.82	0.39		116.57	336.67	18.23	24.23	7964.66	510.33	7.37	70.39
407	109.64	95.20	7.42	30.25	0.27		111.81	331.98	18.53	24.71	8293.09	500.47	7.59	92.58
409	85.33	100.16	6.61	36.39	0.23		111.45	348.60	17.48	28.08	6880.32	472.97	5.93	69.91
411	104.39	102.09	6.99		0.58		120.19	429.60	23.36	37.98	7776.83	536.82	8.02	71.56
413	91.20	104.49	6.62		0.24		123.87	497.19	29.51	48.24	9189.48	520.32	8.09	73.65
415	127.72	117.78	6.83		0.40		121.35	659.08	41.18	67.87	7525.19	541.80	15.35	70.06
417	134.39	130.23	5.98		0.46		111.90	673.75	38.20	97.03	6220.01	461.51	5.84	64.41
419	153.24	108.80	5.76		0.41		111.16	801.76	41.18	125.05	6055.24	454.30	6.99	64.44
421	177.30	127.74	6.08		0.41		110.20	1071.41	41.18	162.46	8584.68	474.53	11.31	62.80
423	133.83	122.10	5.22		0.40		95.89	1008.35	41.18	152.31	6627.03	399.79	7.96	60.05
425	157.46	122.90	5.84		0.48	75304.5	108.04	1222.66	41.18	132.15	10046.30	489.25	12.96	66.46
427	134.92	118.98	5.66		0.53	73808.7	101.31	1196.46	41.18	117.81	6357.23	434.04	7.95	62.18
429	181.64	125.50	7.20		1.06	77203.5	104.47	1639.18	41.18	132.27	10281.14	586.13	19.87	67.46

Appendix 4 The results for the analyzes of the reference material with ICP-MS. SD = standard deviation, CV = coefficient of variation, RP = recovery percentage. Below the announced concentrations and used methods by Steinnes et al. 1997.

Sample	Mg	Al	Si	P	K	Ti	Mn	Fe	Ni	Cu	Zn	Pb	Ca	Na
Moss M3-1	652.59	109.14	52.30	840.55	4206.38	1.11	456.79	80.11	0.80	3.07	20.62	3.16	1896.18	123.17
Moss M3-1	618.69	102.13	48.51	809.42	3986.59	1.18	432.99	77.53	0.74	2.91	20.18	3.06	2474.96	176.82
Moss M3-2	589.40	120.01	75.71	778.43	3774.25	2.35	414.63	97.14	0.74	2.87	19.92	2.90	1778.80	116.43
Moss M3-3	612.73	146.38	53.64	787.38	3919.67	1.01	422.09	81.94	0.74	2.87	20.33	2.99	1914.47	117.30
Moss M3-3	620.80	152.21	60.02	800.35	4000.80	1.05	431.31	80.83	0.75	2.95	21.21	3.07	1953.20	119.98
Moss M3-4	662.86	113.34	65.01	886.81	4329.03	2.21	466.70	91.42	0.89	3.19	21.64	3.34	1959.14	121.64
Moss M3-4	679.35	116.38	60.20	896.07	4364.16	1.77	475.90	90.40	0.84	3.28	23.39	3.43	2017.05	125.22
Moss M3-5	659.63	123.88	67.30	884.55	4298.94	2.23	462.33	94.17	0.84	3.21	21.79	3.27	1954.16	121.00
Moss M3-5	691.19	128.88	77.56	929.92	4510.16	3.04	485.67	103.94	0.83	3.29	23.27	3.55	2095.55	130.57
Moss M3-6	633.17	110.38	62.53	859.43	4172.23	2.02	452.40	96.01	0.79	3.19	20.86	3.18	1878.47	113.07
Moss M3-6	603.66	102.39	54.95	799.83	3961.49	1.84	426.89	81.04	0.72	2.96	19.76	3.03	1763.79	105.33
Average	638.55	120.47	61.61	842.98	4138.52	1.80	447.97	88.59	0.79	3.07	21.18	3.18	1971.43	124.59
SD	32.72	15.73	8.89	48.96	215.49	0.63	22.53	8.32	0.05	0.16	1.19	0.19	183.30	17.67
CV	5.12	13.06	14.42	5.81	5.21	34.72	5.03	9.39	6.53	5.12	5.62	6.02	9.30	14.18
RP	87.95	66.93	94.79	80.28	100.94		89.59	64.20	82.32		83.38	95.43	104.86	102.97
Steinnes et al. 1997	726	180	65	1050±70	4100		500	138±12	0.96		25.4±1.1	3.33±0.25	1880	121
Method	MS	MS	ES	ES	MS		MS	Multi	MS		Multi	Multi	MS	ES

Appendix 5 The results for the reference materials in CNS-analysis. SD = standard deviation, CV = coefficient of variation.

Sample	S %	C %	N %
Moss m3	0.67	45.45	0.28
Moss m3	0.67	45.22	0.18
Moss m3	0.65	44.64	0.17
Moss m3	0.74	44.55	0.22
Moss m3	0.73	44.11	0.21
Moss m3	0.79	44.03	0.29
Moss m3	0.78	44.08	0.23
Moss m3	0.69	42.25	0.20
Moss m3	0.67	41.93	0.10
Moss m3	0.65	42.00	0.11
Moss m3	0.80	44.10	0.42
Moss m3	0.70	44.03	0.18
Moss m3	0.67	43.95	0.14
Average	0.71	43.87	0.21
SD	0.05	1.09	0.08
CV	7.30	2.49	39.00