



Weathering of volcanic tephra and its impact on soil formation south of Vatnajökull glacier

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**Faculty of Life and Environmental Sciences
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Dissertation submitted in partial fulfilment of a
Philosophiae Doctor degree in Geography

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Abstract

Frequent tephra deposition and a steady influx of aeolian material of diverse origin dominate soil formation in Iceland. Little is known about the weathering behaviour, mineral formation and alteration of tephra and Icelandic soils after tephra deposition. This thesis presents the results from extensive studies on soil mineralogy and pedogenesis in various Icelandic soil types and different soil environments.

The sampling sites were selected according to the presence of the light coloured rhyolitic tephra from the Öræfajökull eruption in 1362 CE and a dark-coloured basaltic Veiðivötn tephra from 1477 CE in the volcanically active area south of Vatnajökull, SE Iceland.

All investigated soils were acidic and dominated by sand. Indicated by Fe_o/Fe_d ratios above 0.75, they classify as being in an early stage of chemical weathering and soil development. The major portion of the clay size particles are mainly derived from amorphous and poorly crystalline constituents (allophane and ferrihydrite). However, traces of layer silicates (smectite, hydroxy interlayerd minerals and secondary chlorite) were found at all sites. The determining factor of pedogenesis in the histosols was the OM, but the aeolian transport of tephra over long distances and re-deposition as well as local site conditions, rather than the primary composition of the parent material, were the important factors in the development of all investigated soils and the alteration of minerals. Icelandic soils develop in a very dynamic environment. None of the profiles represented a well-developed-pedon, but appeared disturbed over time, showing signs of external influences.

Útdráttur

Tíð eldgos með tilheyrandi gjóskufalli og stöðugt áfök vindborinna efna af ólíkum uppruna setja mestan svip á jarðvegsþróun á Íslandi. Skortur er á þekkingu á veðrun, myndun og ummyndun steinda í gjósku í íslenskum jarðvegi í kjölfar gjóskjufalls. Í þessari ritgerð eru niðurstöður umfangsmikillar rannsóknar kynntar, sem tekur til steindafræði og jarðvegsþróunar í mismunandi jarðvegsflokkum og í breytilegu umhverfi jarðvegsmyndunar.

Rannsóknarsvæðið er á virku eldfjallasvæði sunnan við Vatnajökul á Suðausturlandi Á öllum sýnatökustöðum sem notaðir voru í rannsókninni finnast ljóslituð, súr gjóska frá Öræfajökulsgosi frá 1362 e.Kr. og dökklituð, basísk gjóska úr gosi í Veiðivötum árið 1477 e.Kr.

Öll jarðvegsýni í þessari rannsókn reyndust súr og sandkennd. Hlutfall $Fe_o/Fe_d > 0.75$ gefur til kynna að efnaveðrun og jarðvegsþróun sé skammt á veg komin. Meginhluti agna í leirstærð felst í myndlausum (e. amorphous) eða ófullkomlega kristölluðum (e. poorly crystalline) efnum (allófan og ferrihýdrít). Engu að síður fundust ummerki um lagsiliköt á öllum sýnatökustöðum (smektít, steindir með hýdroxýl jónir milli laganna og síð-steindina klórít). Lífræn efni voru ráðandi þáttur jarðvegsþróunar í mójörð (e. histosol), en flutningur gjósku með vindi yfir langar vegalengdir, tilflutningur gjósku og staðbundnir umhverfisþættir réðu meiru um jarðvegsþróun og ummyndun steinda en frumsamsetning móðurefnisins. Íslenskur jarðvegur þróast í síbreytilegu umhverfi. Ekkert jarðvegssniðanna mátti skilgreina sem vel þróað og öll sýndu þau ummerki um rask og áhrif frá ytri umhverfisþáttum.

Zusammenfassung

Die Bodenbildung in Island ist von häufigem Eintrag von Tephra und äolischem Material unterschiedlicher Zusammensetzung dominiert. Bis dato ist wenig über die Mineralogie, insbesondere Tonmineralogie und Bodenbildung infolge von Tephraeintrag in isländischen Böden bekannt. Die vorliegende wissenschaftliche Arbeit präsentiert die Ergebnisse einer umfassenden Studie an unterschiedlichen Bodentypen und Entstehungsmilieus zu diesem Thema.

Das Untersuchungsgebiet südlich des Vatnajökull wurde in der Vergangenheit regelmäßig mit Tephra bedeckt. Zwei bedeutende historische Tephraschichten, eine helle rhyolitische Tephra vom Ausbruch des Öraefajökull im Jahr 1362 n.Chr. und eine schwarze basaltische Tephra vom Veidivötn-Ausbruch 1477 n.Ch., sind in allen Profilen deutlich ausgeprägt.

Die pH-Werte der untersuchten Böden lagen im sauren Bereich, Sand war die vorherrschende Korngrößenfraktion. Auf Grundlage des Fe_o/Fe_d Verhältnisses (> 0.75) konnten alle Böden als jung, demnach am Beginn ihrer Pedogenese, eingestuft werden. Amorphe und schwachkristalline Bestandteile (Allophan, Ferrihydrit) machten den größten Teil an der Tonfraktion aus. Entgegen bisheriger Untersuchungen, aus denen hervorgeht, dass pedogene Schichtsilikate in isländischen Böden kaum vorhanden sind, konnten Smektit, hydroxy-interlayered Minerale und sekundärer Chlorit nachgewiesen werden. Unterschiede im Verwitterungsverhalten waren nicht nur zwischen der basaltischen und der rhyolitischen Tephra, sondern auch in den Böden erkennbar. Die Untersuchungen ergaben, dass die Bodeneigenschaften und die unterschiedliche Mineralogie der untersuchten Böden nicht nur vom Ausgangsmaterial, sondern vor allem vom eingetragenen äolischen Material (hauptsächlich basaltisches vulkanisches Glas) und den jeweiligen Standortbedingungen abhängig sind.

Umweltdynamische Einflüsse (u.a. Vulkanismus, Erosionserscheinungen) waren in allen Böden erkennbar. Keines der untersuchten Bodenprofile konnte als „gewachsener Boden“, sondern vielmehr als eine Abfolge von mehr oder weniger dünnen Boden- und Tephraschichten betrachtet werden.

List of papers

Paper 1

Bonatotzky, T., Ottner, F., Erlendsson, E. Gísladóttir, G., 2019. The weathering of volcanic tephra and how they impact histosol development. An example from South East Iceland. *Catena* 172, 634-646. <https://doi.org/10.1016/j.catena.2018.09.022>

Paper 2

Bonatotzky, T., Ottner, F., Erlendsson, E., Gísladóttir, G., 2021. Weathering of tephra and the formation of pedogenic minerals in young Andosols, South East Iceland. *Catena* 198C, 105030. <https://doi.org/10.1016/j.catena.2020.105030>

Paper 3

Bonatotzky, T., Ottner, F., Erlendsson, E., Gísladóttir, G.
The impact of environmental factors on early stage Andosol development south of Vatnajökull, Iceland. *Manuscript submitted to the international peer-reviewed European Journal of Soil Science (EJSS-380-21)*.

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Abbreviations

Ö1362	Tephra from Öräfajökull eruption in 1362 CE
V1477	Tephra from Veidivötn eruption in 1477 CE
KF	Study site Kálfafell
RV	Study site Reynivellir
SD	Study site Steinadalur
KV	Study site Kvísker
KMK	Study site Kvíármýrarkambur
SAR	Soil accumulation rate (mm/yr)
SOM	Soil organic matter
LOI	Loss on ignition
SOC	Soil organic carbon
Al	Aluminium
Fe	Iron
Si	Silica
Fe _o , Al _o , Si _o	Ammonium oxalate extractable Fe, Al, Si
Fe _p , Al _p	Sodium pyrophosphate extractable Fe, Al
Fe _d	Citrate-bicarbonate-dithionite extractable Fe
NaF	Sodium fluoride solution
XRD	X-ray diffraction
DSC	Differential scanning calorimetry
TG	Thermogravimetry
SRO minerals	Short-range order minerals

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1. Introduction

1.1 The dynamic Icelandic environment

Iceland is situated between latitudes 63°23' and 66°32' North and longitudes 13°30' and 24°32' West, close to the Arctic Circle. Its location in the middle of the North Atlantic Ocean, near both oceanic and atmospheric fronts, makes it highly sensitive to climate changes (e.g. Einarsson, 1980; Hannesdóttir et al., 2015). The weather and climate are generally characterized by strong winds, frequent precipitation, mild winters and cool summers (Ólafsson et al., 2007). Glacier variations and volcanic activity over the last centuries highly impacted and formed the Icelandic environment (Björnsson and Pálsson, 2008; Hannesdóttir et al., 2015; Ingólfsson et al., 2010; Vilmundardóttir et al., 2015; 2014; 2010). All these factors greatly influenced the surface geomorphology and soil properties.

Situated on the Mid-Atlantic Ridge and above the Iceland mantle plume, Iceland is one of the most active and productive volcanic regions in the world (Einarsson, 2008). Volcanic eruptions are common and have a recurrence interval of 2–5 year (Compton et al., 2015; Pagli and Sigmundsson, 2008; Thordarson and Larsen, 2007). The bedrock consists mostly of basaltic igneous rocks, while tephra composition ranges from basaltic to rhyolitic (Thordarson and Larsen, 2007).

Explosive hydro-magmatic basaltic eruptions represent the most common volcanic activity in Iceland during the Holocene (e.g. Thordarson and Höskuldsson 2008), thus most of the tephra layers in Icelandic soils and sediments are of basaltic composition (e.g. Larsen and Eiriksson, 2008). Eruptions producing rhyolitic tephra are less common, but at least 24 eruptions have produced silicic tephra in historic times (Gudmundsson et al., 2008; Larsen et al., 1999), that is since 874 CE. The ejecta composition of each volcanic system to have remained relatively stable and geochemically different from other systems throughout the Holocene (Jakobsson, 1979). Thus, it is possible to identify the sources of Holocene tephra (Larsen et al., 1999). Based on written documents and tephra studies, an accurate reconstruction of the historical eruptions in Iceland is possible (Óladóttir, 2009; Thorarinsson, 1944).

Tephra may be deposited nearby the source-volcano or transported over long distances and preserved in glaciers, soils and lakes far away from its source. Amongst other factors, dispersal and deposition depend on the eruption magnitude and prevailing wind directions at the time of eruption and which can change throughout the event. Vegetation and lakes in the area of deposition are also of great importance for the preservation of the tephra. Deposited on un-vegetated land, tephra becomes very unstable and cannot withstand erosion by wind and water, whereas deposition on vegetated land or in lakes it will be (at least partly) sheltered from the wind (e.g. Óladóttir, 2009).

Many of the volcanic systems in Iceland have produced a high volume of tephra. The eruption of the Öraefajökull central volcano in 1362 CE is the most voluminous explosive

silicic eruption to have occurred in Iceland in historical times, producing up to 10 km³ (or even more) of light grey, acidic, un-compacted tephra (Gudmundsson et al., 2008; Larsen et al., 1999; Sharma et al., 2008). According to Thorarinsson (1958) the vast quantity of the erupted ejecta was carried to the southeast (Fig. 1.1), but tephra from this eruption has been identified in Western Europe (Pilcher et al., 2005) and in Greenland ice-cores (Palais et al., 1991). Based on the chemical composition, the rhyolitic Ö1362 tephra can be distinguished from other Icelandic tephra deposits with a similar SiO₂ content of 72.71% on average (e.g. historical Hekla tephra) by its high FeO (average 3.30%), low MgO (close to zero), low CaO content (<1.2%) and high Na₂O (around 5%) values (e.g. Larsen et al., 1999; Sharma et al., 2008; Wolff-Boenisch et al., 2004).

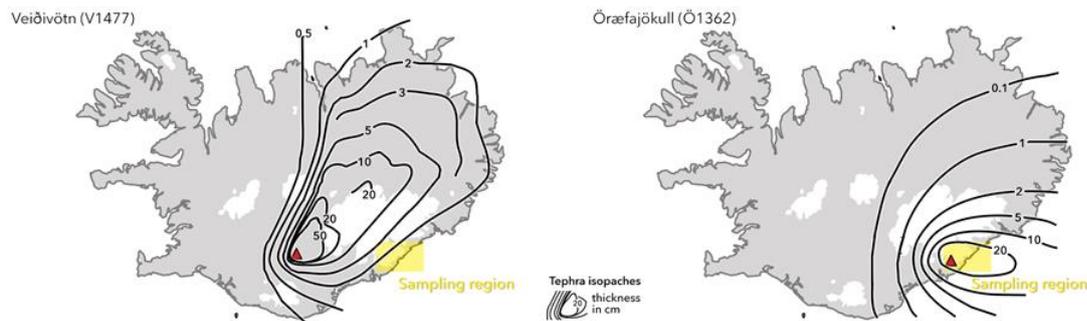


Figure 1.1 Isopach maps of the distinctive tephra layers from the Veidivötn eruption in 1477 CE (left) and the Öraefajökull eruption in 1362 CE (right). On both maps the respective source volcano is marked by a red triangle. Isopach maps have been modified from Thorarinsson (1958) and Larsen (1984). The particular research area is marked by a yellow rectangle. (Maps produced by Benjamin D. Hennig)

The 1477 CE eruption in the Veidivötn-Bárðarbunga volcanic system is thought to be the largest explosive basaltic eruption in Iceland during the last 1200 years. Over 10 km³ of basaltic tephra from a 60–65 km long fissure along the Veidivötn lake basin was dispersed towards east, northeast and north (Fig. 1), depositing a layer of tephra up to 12 m thick in sum (Larsen, 1984; Larsen et al., 2014). Tephra from the 1477 CE eruption has been identified at many proximal and distal sites in Iceland as a visible horizon, in soils, lake sediments and offshore marine cores (Abbott et al., 2021). Compared to the rhyolitic tephra, V1477 has a lower SiO₂ content of c. 50%, about half of Na₂O (approx. 2.5%), but a multiple of the MgO (6–7%) and FeO (approx. 13%) content (e.g. Lawson et al., 2007; Streeter and Dugmore, 2014).

When Iceland was first settled by Norse in the late 9th century, the environmental conditions were very different to the contemporary environmental conditions. Human colonisation introduced grazing livestock and land-use which highly affected the natural environment and induced a significant change in the Icelandic terrestrial environment. In particular, the loss of woodland and other vegetation has left many places barren. In conjunction with harsh climate and frequent volcanic eruptions the result was an increased and severe soil erosion and thus drastically decreased soil quality and depletion of soil organic carbon (Eddudóttir et al., 2020; Gísladóttir et al., 2010; Kardjilov et al., 2006; Lal, 2004; 2003; Óskarsson et al., 2004). Large areas became prone to wind and water erosion processes, forming wide areas of sandy deserts and sources of dust. The main source areas for dust in Iceland nowadays are the highlands in central Iceland and the sandur plains along the south coast, where the surface is made up of loose sediment (Arnalds et al., 2016).

1.2 Pedogenesis and weathering in Icelandic soils

The high frequency of volcanic activities in Iceland has great impacts on soil development and environmental stability. Most Icelandic soils are developed in volcanic ejecta and are rich in volcanic glass. Andosols are thus the predominant soil order, covering 86% of the island, while Histosols cover about 1% of the Icelandic surface (Arnalds and Óskarsson, 2009). All Icelandic soils, even highly organic Histosols, exhibit andic soil properties to some degree (Bonatutzky et al., 2019).

Among the majority of volcanic soils worldwide, Icelandic soils show special characteristics: They were formed during the Holocene when glaciers retreated (Arnalds, 2010; Arnalds and Kimble, 2001), receive large inputs of inorganic aeolian sediments and occur in low temperatures with a wide range of precipitation. In such a dynamic environment, the soil surface is constantly recharged with fresh parent material (consolidated rock and tephra), while subsoils are preserved and continue to develop after burial (e.g. Bonatutzky et al., 2019; Gísladóttir et al., 2010).

Iceland has extensive unstable sandy surfaces which are subject to frequent high-velocity winds. Aeolian transport of tephra over long distances, re-deposition and re-suspension are very common. This results in intense wind erosion events. Erosion has removed much of the soils that formed in the aeolian and tephra sediments (e.g. Arnalds et al., 2001; Dugmore et al., 2009; Gísladóttir et al., 2011; 2010; Möckel et al., 2017). Arnalds et al. (2016) have estimated that up to 80% of the aeolian dust in Iceland is amorphous basaltic volcanic glass, rich in heavy metals.

Similar to other volcanic regions worldwide, chemical weathering of basaltic material is a fundamental process in soil formation in Iceland (Kardjilov et al., 2006). Volcanic glass shows the least resistance in this process. As a result of its properties (e.g. fine particle size and amorphous nature), tephra enhances weathering and interactions in the soil environment (Dahlgren et al., 1993). Despite the overall rapid weathering of tephra, rhyolitic tephra weathers much more slowly than basaltic (Gíslason, 2005). With increasing age accompanied by increasing silica content, the total chemical weathering rates decrease (Gíslason, 2008). The dissolution rate of glassy rocks (hyaloclastite) is about 10 times faster than those of crystalline basalt (Gíslason and Eugster, 1987).

The most common weathering residuals of basalts are amorphous allophane, a group of amorphous short-range order (SRO) minerals (Parfitt, 1990) and/or imogolite of variable Al/Si ratios and poorly crystalline ferrihydrite (Arnalds, 2004). Their formation in volcanic soils is connected to the properties of tephra (Shoji et al., 1993). Both, allophane and ferrihydrite are abundant in the clay size fraction of Icelandic soils (e.g. Bonatutzky et al., 2021; 2019). Due to their properties (e.g. large specific surface area and high chemical reactivity), they are more sensitive to chemical dissolution than crystalline clay minerals (Wada, 1989). With increasing soil age, the crystalline weathering phases become more abundant (Crovisier et al., 1992).

Clay minerals, also referred to as phyllosilicates or layer silicates, are rare in Icelandic soils (Bonatutzky et al., 2021; 2019). They develop from volcanic ejecta and are formed in subsurface horizons in situ rather than by translocation or leaching and precipitation

(Arnalds, 2008; Dahlgren et al., 2004). Due to their unique structures and distinctive properties (i.e. small particle size, high surface area), clay minerals strongly affect both the chemical and physical soil properties (Schulze, 1989). They are sensitive to changes in the soil environment and are, thus, useful indicators providing ample information on weathering and the quality of soil development (e.g. Griffin et al., 1968; Jacobs and Hays, 1972; Rateev et al., 1969; Środoń, 2013; 2002).

All Icelandic soils are in their initial state of soil development, but because of the nature of the parent material, they exhibit considerably high weathering rates despite the prevalent cool climate (Gislason et al., 2009; Gíslason et al., 1996).

1.3 Aims of the research

The overall aim of the research is to improve understanding on how the processes of weathering and transformation of minerals in tephra and volcanic soils take place in different soil environments following the deposition of basaltic and rhyolitic tephra. While the impacts of explosive volcanic eruptions and consequences of heavy tephra fall on vegetation, soil (e.g. Eddudóttir et al., 2017, 2020; Þorbjarnarson, 2016) and people's livelihood (Thorarinsson, 1958) in Iceland are increasingly understood, information about the direct impact of tephra deposits on pedogenesis, soil weathering processes and soil quality is lacking.

The specific objectives of this PhD study were:

1. To compare the weathering behaviour and alteration of tephra of different chemical composition and to examine their contrasting mineralogy. **(Papers 1 and 2)**
2. To examine the genesis of soils derived from basaltic and rhyolitic tephra parent material in the Icelandic environment and evaluate their physical and chemical properties. **(Papers 1, 2 and 3)**
3. To examine how the investigated soil reflects external environmental influences (erosional processes such as solifluction, slope instability and aeolian soil/tephra reworking and deposition, as well as influence by seawater precipitation and tephra deposition) which characterise the Icelandic environment **(Paper 3)**
4. To investigate the soil clay mineral composition under given conditions to provide a better understanding of weathering processes, mineral alteration and the formation of pedogenic minerals in young soils, under cool climate and influenced by frequent disturbances, as well as the influx of pristine material. **(Papers 1, 2 and 3)**

The investigations consider five soil profiles in the lowlands south of Vatnajökull, southeast Iceland (Fig. 2.1). The volcanically active Vatnajökull area has received numerous tephra deposits of varying thicknesses during the Holocene (Óladóttir et al., 2011b). The study focuses on two well-preserved and distinct tephra layers; a light coloured, rhyolitic tephra from the Öraefajökull eruption in 1362 CE and a black, basaltic Veiðivötn tephra from 1477 CE (Thorarinsson, 1958; Larsen, 1984). Both tephra layers form an important parent material

in the study area. As hydrological conditions are likely to impact the weathering processes and mineral alteration, both wetland (Histosols, **Paper 1**) and dryland (Andosols, **Paper 2**) soils were examined. This allows for the comparison of soil formation under aerobic and anaerobic conditions. Additionally, a highly degraded and disturbed profile, a common feature in Iceland, was investigated (**Paper 3**).

Clay minerals are useful indicators providing information on weathering and the quality of soil development (e.g. Griffin et al., 1968; Rateev et al., 1969; Jacobs and Hays, 1972; Środoń, 2013; 2002). However, clay mineralogy in Icelandic soils is not well studied and available data are thus still scarce. By extensive investigation of bulk and clay mineralogy in different soil environments and soil types, this study built a large novel dataset on the mineralogy in Icelandic soils. Through a combination of physical, chemical, and mineralogical analyses, an extensive investigation of physical and chemical soil properties and clay mineralogy in various soil types and different soil environments, is presented to improve the understanding of changes in soil properties, mineral formation, and alteration in different types of Icelandic soils following tephra deposition.

2. Study sites

The study sites are located in Austur-Skaftafellsýsla (in Suðursveit and Öræfi district), Southeast Iceland (Fig. 2.1). They are situated in a lowland area close to the sea in close proximity to the Öræfajökull volcano. The investigated soils are formed under both dryland and wetland conditions but often appear highly degraded. Soil erosion is a problem in parts of the area due to steep slopes and interactions between glaciers and glacial rivers, volcanism, strong winds and land use. The area in which the study sites are situated are highly affected by soil erosion.

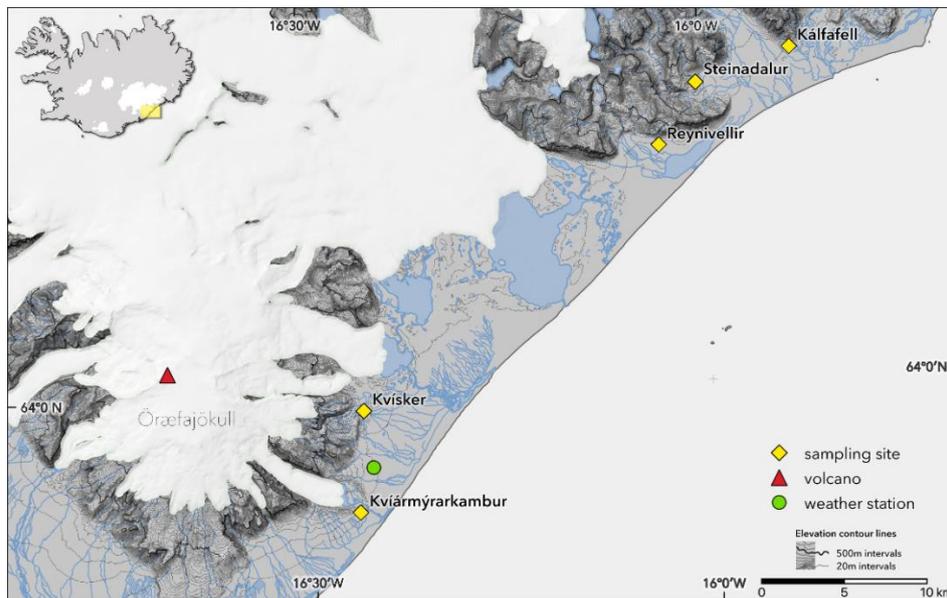


Figure 2.1 Location of the study sites and weather station Kvísker south of Vatnajökull glacier, SE Iceland. (Map produced by Benjamin D. Hennig)

The two investigated wetland sites are located in Reynivellir ($64^{\circ}07.731'N$, $16^{\circ}03.245'W$) and Kálfafell ($64^{\circ}10.749'N$, $15^{\circ}53.236'W$) (**Paper 1**) at the foot of Öræfajökull volcano. The vegetation cover in the research area is mainly comprised of modified grassland and heath utilised for pastoral agriculture. A small conifer plantation is located nearby but has no direct influence upon the sampling area (Fig. 2.2 and 2.3).



Figure 2.2. The study site at Kálfafell (KF; left), soil profile on the right. (Photos taken by Theresa Bonatotsky)



Figure 2.3. The study site at Reynivellir (RV; left), soil profile on the right. (Photos taken by Theresa Bonatotsky)

Kvísker ($63^{\circ}59.443'N$, $16^{\circ}26.029'W$) lies within Öraefi district. Steinadalur ($64^{\circ}09.760'N$, $16^{\circ}0.293'W$) is further east in the Suðursveit district (**Paper 2**). Both are dryland sites with vegetation communities consisting of birch (*Betula*) woodland, grassland, herbs and mosses (Fig. 2.4 and 2.5).

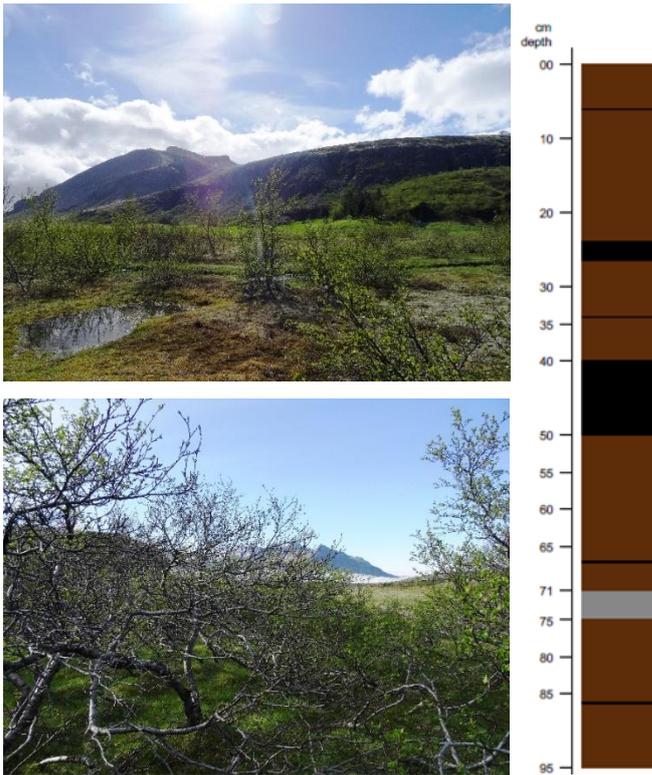


Figure 2.4. The study site at Kvísker (KV; left), schematic soil profile on the right. (Photos taken by Theresa Bonatatzky, soil profile produced by Benedict Rois)



Figure 2.5. The study site at Steinadalur (SD; left), schematic soil profile on the right. (Photo taken by Friðþór S. Sigurmundsson, soil profile produced by Benedict Rois)

Kvíarmýrarkambur (63°56.129'N, 16°26.515'W) is a strongly disturbed site situated within Öraefi district close to a moraine representing the location of the outlet glacier Kvíarjökull by the end of the 19th century (**Paper 3**). Both soil and tephra layers appeared to be disturbed. The sampling site (Fig. 2.6) is situated in a drained wetland, but features different

hydrological conditions compared to the surrounding, i.e. drier and less oxidized, indicated by a less reddish soil colour. The vegetation cover is comprised of grassland, heathland and *Salix* shrubs.



Figure 2.6. The study site at Kvíármýrarkambur (KMK, (left), soil profile on the right. (Photos taken by Theresa Bonatotzky)

The geology of the research area is primarily composed of basaltic lava, hyaloclastite and fluvial and glaciofluvial sediments (Jóhannesson and Sæmundsson, 2009; Thorarinsson, 1958). Even though situated outside the active volcanic zone, the study area is strongly affected by the active central volcanoes of Grímsvötn, Bárðarbunga and Öraefajökull to the North and Katla to the West. All of these systems have erupted on multiple occasions and have produced the majority of the tephra deposits preserved in soils in the region (Óladóttir et al., 2008). Two distinct tephra layers, the light-coloured rhyolitic tephra from the 1362 CE Öraefajökull eruption (Ö1362) and a dark basaltic tephra from the 1477 CE Veiðivötn fissure eruption (V1477), are well preserved at all investigated research sites. After their formation, both tephra were immediately deposited on vegetated land and are thus preserved as important tephra marker layers in the research area. With the aid of the known source volcanic systems, ages obtained from written documents (Höskuldsson, 2019; Óladóttir et al., 2011a; 2011b; Sæmundsson and Larsen, 2019; Þorbjarnarson, 2016) and known geochemical composition (Larsen, 1984; Sharma et al., 2008; Sæmundsson and Larsen, 2019) these tephra layers form an important soil parent material in the study area.

The climate regime in the region is maritime, dominated by cool, moist summers and mild winters with high precipitation and strong winds (Einarsson, 1980), strongly affected by the mountainous landscape (Ólafsson et al., 2007). Mean annual temperature at Kvísker (30 m a.s.l.), the weather station, which is closest to the sampling sites, is 5.9 °C (2009–2016) and annual precipitation (1962–2011) is 3500 mm on average (based on unpublished data from the Icelandic Meteorological Office).

3. Methods

3.1 Sampling and profile description

The sampling sites were selected according to the presence of the two desired tephra layers (detected by test coring with a JMC Backsaver), and to include the main types of developed Icelandic soils (Andosols, Histosols) formed in different environments (wetland, dryland, disturbed). None of the profiles showed a clear horizonation, thus soil samples were taken at 10 cm depth intervals, and at 5 cm intervals to capture the chemical weathering and clay formation for better resolution immediately above and below the two main tephra layers. Where field conditions inhibited the application of this strategy, sampling was adapted slightly. Tephra layers, easily distinguishable from the soil, were sampled separately.

Soil profiles at KF and RV (**Paper 1**) were described according to the Troels-Smith system (Aaby and Berglund, 1986; Troels-Smith, 1955). The Andosols at SD and KV (**Paper 2**) were described in the field according to Schoeneberger et al. (2002). Soil colour was assessed on field-moist soil using a Munsell colour chart (**Paper 1 and 2**). Soil accumulation rates (SAR) (mm yr^{-1}) were calculated by measuring soil thickness between tephra layers of known age (Gísladóttir et al., 2010; Óladóttir et al., 2011a).

3.2 Soil and tephra mineralogy analyses

Soil mineralogy was determined by using X-ray diffraction (XRD), Differential scanning calorimetry (DSC) and Thermogravimetry (TG). XRD of bulk soil samples and the clay fraction were conducted using a PANalytical X'Pert Pro diffractometer with automatic divergent slit, Cu LFF tube 45 kV, 40 mA, with an X'Celerator detector (Malvern Panalytical, Malvern, UK). Bulk soil samples were grinded to analytical fineness and prepared according to the "backloading" procedure (Bish and Post, 1989). Preferential orientation of the clay minerals was obtained by suction through a porous ceramic tile, similar to the method described by Kinter and Diamond (1956). The exchange complex of each sample was saturated with K^+ and Mg^{2+} . Expansion tests using ethylene glycol and dimethyl sulfoxide (DMSO), as well as contraction tests by heating of the clay size fraction up to $550\text{ }^\circ\text{C}$ were done. Analogous to the bulk mineral analysis, the clay minerals were determined by XRD. Bulk samples were X-rayed from 2 to $70^\circ 2\theta$, after each step, clay fraction samples were X-rayed from 2 to $40^\circ 2\theta$. Resultant diffractograms were evaluated by using the software X'Pert HighScorePlus and identified according to Moore and Reynolds (1997), Brindley and Brown (1980) and Wilson (1987). Thermal analyses, consisting of DSC and TG were carried out using a Netzsch STA 409 PC Luxx® Simultaneous Thermal Analyzer (Netzsch GmbH, Germany). Thermal flux and changes in weight were measured simultaneously. Resultant endothermic and exothermic reactions were ascribed according to Smykatz-Kloss (1974) and Barros et al. (2007).

3.3 Physical and chemical soil and tephra analyses

Particle size analyses were carried out in combination with the clay size analysis. Following pre-treatment with H₂O₂, coarse fractions were separated by wet sieving using mesh-sizes ranging from 2000 to 20 µm. The fine particles were analysed by means of sedimentation analysis using a Sedigraph III 5120 (Micromeritics, Georgia, USA). Dry bulk density (DBD) was measured on soil monoliths in the lab as described in Vilmundardóttir et al. (2014). DBD was calculated by dividing the dry weight of a sample by the volume of the undisturbed sample (Brady and Weil, 1996).

Representative bulk soil and tephra samples were air-dried, gently crushed to pass through a 2 mm sieve, ball-milled to pass through a 150 µm sieve, and used for the analyses of physical and chemical properties.

Soil organic matter (SOM) was estimated by loss on ignition (LOI) according to Bengtsson and Enell (1986). Soil pH (H₂O) was obtained in 1:5 water-soil suspension. Andic properties of soil and tephra were estimated by the indirect method of determining soil pH in 1M NaF solution. Phosphate retention (P-ret) was analysed using the method outlined in Blakemore et al. (1987). Concentrations of soil organic carbon (SOC) and total nitrogen (total N) were obtained by the dry combustion method at high temperature (900°C) using a Flash 1112 Elementar Analyzer (Thermo-Scientific, Italy). Since the studied soils did not contain carbonate minerals (determined by HCl test), the values thus obtained were assumed to correspond to organic carbon (OC).

Selective dissolutions were carried out to determine poorly crystalline and amorphous constituents as well as those associated with humus in the soils and tephra samples. Iron (Fe), aluminium (Al) and silica (Si) associated with amorphous constituents (Fe_o, Al_o, Si_o) were extracted with ammonium oxalate in the dark by the shaking method at pH 3.0. Fe and Al associated with OM (Fe_p, Al_p) were extracted with sodium pyrophosphate at pH 10.0 and shaking for 16 h. Both ammonium oxalate and sodium pyrophosphate extraction were carried out according to USDA Soil Survey Laboratory Manual (Burt, 2004). Fe in crystalline and non-crystalline oxides (Fe_d) was extracted by citrate-bicarbonate-dithionite (CBD) as outlined in Sparks et al. (1996). The resultant extracts were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Values obtained were used to estimate the allophane content (%) (Mizota and van Reeuwijk, 1989; Parfitt and Henmi, 1982; Parfitt and Wilson, 1985), and ferrihydrite content (%) according to Childs (1985). Contents of non-crystalline secondary phases of the clay size fraction, hereafter referred to as amorphous secondary clay, were estimated as the total amount of allophane and ferrihydrite (Shang et al., 2008). The molar Al/Si ratios were calculated from (Al_o-Al_p)/Si_o according to Wada (1989). Al_o+0.5Fe_o was used as a taxonomy criterion for andic soil properties (Soil Survey Staff, 2014). Al_p/Al_o ratio was used to differentiate between aluandic and silandic soil properties (IUSS Working group WRB, 2015) and to estimate the presence of allophanic material (Shoji et al., 1993). The molar ratio of metal-humus complexes was estimated by (Al_p+Fe_p)/OC (e.g. Inoue and Higashi, 1988; Takahashi and Dahlgren, 2016). Contents of amorphous Al and Fe were calculated by the formula Al_o-Al_p and Fe_o-Fe_p respectively (e.g. Mizota and van Reeuwijk, 1989).

The effective cation exchange capacity (ECEC) was determined according to USDA Soil Survey Laboratory Manual (Burt, 2004). Exchangeable base cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) were extracted by 1 N pH 7 NH_4OAc , exchangeable Al^{3+} was extracted by 1 N KCl and ECEC was calculated as the sum of these ions. The ion content of the extracts was determined by inductively coupled plasma atomic emission spectrophotometer (ICP-AES).

4. Results

4.1 Selected soil and tephra properties, developed in different soil environments

All investigated soils developed in the lowlands south of Vatnajökull and are representative of the most important soil types and soil environments (Histosols, Andosols, disturbed soils) found in Iceland.

Tephra layers were well preserved at all sites, although at different depths. The basaltic V1477 tephra was found within 35 and 59 cm depth, the rhyolitic tephra (Ö1362) within 48 and 86 cm depth. The thickness of the two distinct tephra layers differed between the sites. In general, V1477 was between 4 cm (KF) and 10 cm (KV) and Ö1362 between 1.5 cm (SD) and 7 cm (KMK) thick. Both, V1477 and Ö1362 were found to be thickest closest to the Öraefajökull volcano, the westernmost part of the research area. Other tephra layers, mainly of basaltic composition, were found in all soil profiles, but were not allocated to a specific volcanic system.

The calculation of the SARs showed differences between the soils formed after the deposition of V1477 tephra to the time of sampling and those formed in 115 years of soil development between Ö1362 and V1477 deposition. Above the basaltic V1477 layer the SAR was between 0.63 mm/yr (SD) and 0.93 mm/yr (KF). At four out of the five investigated sites, the SAR were significantly higher between Ö1362 and V1477 (between 1.48 mm/yr at KF and 2.11 mm/yr at SD). The opposite pattern was only found at site RV, where the rates throughout the profile were generally low, being 0.61 mm/yr between the two tephra layers, but it was slightly higher (0.67 mm/yr) above V1477.

The SOM content was high in the wetland soils, close to 70% in some layers. The content of SOM (expressed by the LOI%) was significantly lower in the Andosols, with a mean content of 8.5%. Soils at site KMK varied in their SOM content between 2.5 and 20%. SOC content ranged between 9 and 38% in the Histosols and between 0.5 and 9% in the soils at site SD, KV and KMK. The soils were acidic, with pH (H₂O) between 3.7 at site KF and 6.7 at site SD.

The particle size distribution was determined for soils and tephra at sites SD, KV and KMK. The soils were dominated by sand and silt. Only the sediment layer in 10 - 30 cm depth at KMK showed a considerable high portion of gravel size constituents (22.3%). Clay contents were between 4.3 - 36.6% in the Andosols and ranged between 2.6% (in the sediment layer) and 33.4% at site KMK. Noticeably high contents were generally found in the soils below both tephra layers.

Both types of tephra were dominated by sand. In V1477 the clay content was similar, around 5% at all sites, whereas it showed differences in Ö1362. While it was 4.2% and 4.8% at KV and KMK, respectively, it was nearly double (7.9%) at site SD.

4.2 Weathering and the amorphous nature of soil and tephra

The ammonium oxalate extractable Al, Fe, and Si, pyrophosphate extractable Al and Fe and Fe_d , varied between the sites. Fe_o and Al_o were higher than those extracted by pyrophosphate (Fe_p , Al_p). Si contents (Si_o) were generally low in the Histosols (mean Si_o 2.6 g/kg), medium (average of 6.2 g/kg) in the soils at site KMK and 16 g/kg in the investigated Andosols (sites SD and KV). In all but one profile the highest Si_o was found in the V1477 and the lowest in Ö1362. The trend was opposite at site KV. Compared to Fe_o values, the content of Fe in crystalline and non-crystalline constituents (Fe_d) were significantly lower in all investigated soils.

The pH values measured in sodium fluoride pH (NaF) were below the limit of 9.5 in the Histosols in all soil layers, while the mean pH (NaF) was 10.9 at sites SD and KV. At site KMK the values for pH in NaF solution were well above the limit of 9.5 in the soils developed from the rhyolitic tephra, while soils above V1477 did not reach the limit.

Al/Si ratios in the Histosols ranged between 0.1 and 2.0, being higher at KF than RV where the ratio was as low as 0.1. The highest Al/Si in the soils were found above the tephra layers. Similar Al/Si ratios, all above 1, were found in the soils at sites SD, KV and KMK. The Al_p/Al_o ratios in the Histosols ranged between 0.3 and 1.0. Low Al_p/Al_o ratios were found at the surface at both sites and in the soils right above the tephra layers. Compared to the remaining layers, the soil just below the tephra showed slightly lower ratios. Except for the top layer at SD and KV, the Al_p/Al_o ratios in all investigated soil layers were 0.1, but even in the uppermost 10 cm, the ratios were close to zero (0.3). The soils at site KMK were all showing Al_p/Al_o ratios below 0.5. The percentage $Al_o+0.5Fe_o$, a criterion for Andosol classification, ranged between 0.1 and 1.9 in the Histosols, between 2.7 and 7.1 at sites SD and KV and between 1.1 and 4.5 in the soils at site KMK, reaching lowest levels in Ö1362 at all sites except for site KV. The Fe_o/Fe_d ratios in the investigated soils rank high, being 1.1 – 2.9 in the Histosols, in a similar range in the soils at site KMK and between 1.3 and even 3.4 at the SD and KV. Increased ratios were often found above Ö1362.

The estimated content of amorphous and poorly crystalline constituents (allophane and ferrihydrite) was 10 - 26% in the Andosols at sites SD and KV, but significantly lower (7 - 9%) at site KMK. A low content of amorphous secondary clay size constituents was found in the investigated Histosols, ranging from 1.5 to 5.0%. The allophane content in the Histosols (KF and RV) was low (0.4 – 2.4%), as well as the estimated content of ferrihydrite (0.9 – 3.2%). Significantly higher contents were found in the Andosols (SD and KV) ranging between 5.5% and 17.4% allophane and between 3.7% and 9.9% ferrihydrite. Allophane (1.9 – 5.5%) and ferrihydrite (1.5 – 4.3%) contents in the soils at site KMK ranged between those from the Histosols and Andosols.

At both wetland sites, the estimated content of non-crystalline constituents in the basaltic V1477 was around 6.0%, but significantly lower in Ö1362 (0.5% at KF and 0.2% at RV). There was a wide range in the amount of amorphous clay size constituents in both types of tephra at sites SD, KV and KMK (4.3 – 14.2% in V1477 and 2.1 – 7.7% in Ö1362). The allophane content in V1477 ranged between 2.6% and 9.4%, in Ö1362 it was 0.2 – 4.8%. Contents of ferrihydrite were found to be lower (0.3 – 4.8% in V1477 and 0.1 – 2.9% in Ö1362). The lowest contents were found in the rhyolitic tephra, irrespective the site.

4.3 Mineralogical composition of soil and tephra

The bulk soil mineralogy was dominated by plagioclase and pyroxene. Additionally, appreciable amounts of quartz and various types of zeolite were found. Volcanic glass was abundant in all samples. A distinct 14 Å reflection was detected in small and trace amounts at SD, KV and KMK, respectively. The bulk mineral composition of the two different tephra was comparable at all sites. Similar to the soils, both types of tephra were dominated by plagioclase, pyroxene and volcanic glass. The rhyolitic Ö1362 was strongly characterized by its amorphous nature.

Investigations of the clay fraction of the soils discerned the presence of layer silicates in the samples. Hydroxy interlayered (HI) minerals were verified at RV but were absent at KF, where smectite was found instead. The latter was also found at site KMK, especially in the soils above the basaltic tephra V1477, but only in traces in some layers below. The investigations of the clay size fraction discerned secondary chlorite as the only type of layer silicates at the dryland sites SD and KV. Traces of plagioclase and zeolite were found even in the clay size fraction in some samples at all sites. According to the clay mineralogy of the soils, the tephra samples showed traces of smectite at KF and small amounts of HI minerals at RV in the basaltic V1477 tephra. Phyllosilicates were not found in Ö1362.

Thermal analyses were performed on soils and tephra from both wetland sites (KF and RV) as well as site KMK. TG curves of the subsoils showed the main average thermogravimetric mass loss of 15% at KMK and even as high as 45% in the Histosols in the temperature range between 200 and 600°C. At low temperatures (< 200°C) the mean mass loss was 6.5%, while it was only marginal at temperatures above 600°C. DSC curves showed a distinct exothermic peak in the temperature around 300°C (occurring at slightly different temperatures) in all samples. A distinct endothermic reaction in the temperature range below 150°C was found in all samples. Dehydration, characterized by a distinct endothermic peak generally occurred at very low temperatures ($\leq 74^\circ\text{C}$) in the wetland soils, but at slightly higher temperatures (133 – 152°C) in the soils at site KMK. Compared to the thermogravimetric mass losses and DSC curves in the subsoils, the surface layers showed differences. Similar trends were visible in the tephra samples, but considerably weaker reactions than those in the soils.

5. Discussion

5.1 Soil development

Irrespective of soil type, Icelandic soils develop from volcanic parent material rich in volcanic glass and receive large amounts of amorphous and inorganic influx (tephra and aeolian material). Even though highly organic soils form from organic plant material they exhibit andic soil properties derived from volcanic material.

The soils in the research area south of Vatnajökull develop in a very dynamic environment. Abundant precipitation, basaltic igneous bedrock and a large amount of volcanic glass present in the soils provide an environment beneficial for chemical weathering in spite of the cool climate (Gislason et al., 2009). Icelandic soils are exposed to a recurrent cycle of tephra addition, incipient soil development and the soil covered by the next tephra deposit and left in its initial state of pedogenesis. The soil surface is constantly recharged with pristine material (tephra and aeolian material), while subsoils are preserved and continue to develop after burial. None of the investigated profiles presented a well-developed pedon but comprised of sequences of buried soils. This process is well known in Iceland (e.g. Bonatutzky et al., 2021; 2019), and similar processes have been found in other volcanic regions on Earth (Takahashi and Dahlgren, 2016).

With an age <650 years, the investigated soils are “young” and reflect an early stage of weathering and soil development (**Paper 1, 2 and 3**). Despite the abundance of weathering-beneficial constituents (basaltic and rhyolitic glass) in the soils, the initial state of weathering does not enable pedogenic minerals to form, i.e. the active Fe is mainly present in form of poorly crystalline ferrihydrite.

The main iron (Fe) source in Icelandic soils is from amorphous basaltic glass, only small amounts originate from crystalline material (e.g. Arnalds et al., 2016; 2014). Compared to Fe in crystalline and non-crystalline constituents (Fe_d), the values for Fe associated with amorphous constituents (Fe_o) in Icelandic soils are high, resulting in a Fe_o/Fe_d ratio > 1 (Arnalds et al., 1995; Bonatutzky et al., 2019; Wada et al., 1992). Fe_o/Fe_d ratios, widely used to indicate the degree of soil development, were generally found quite high, indicating a low degree of pedogenesis in all investigated soils, irrespective of soil type. The ratio ranged between 1.1 and 2.9 in the Histosols and between 1.3 and 3.4 in the Andosols.

A strong influence of Fe in the investigated soils especially above the V1477 tephra, is likely to derive from numerous basaltic tephra layers over a period of about 530 yrs since the Veidivötn eruption in 1477 CE. During approximately 100 yrs of soil development, between the deposition of Ö1362 and V1477, hardly any tephra addition occurred.

OM was the determining factor for soil development and the major factor inhibiting weathering in the investigated Histosols at site Kálfafell and Reynivellir (**Paper 1**). Plant residues were protected from decomposition by the prevailing anaerobic conditions and a

low soil pH (H₂O) (3.7 – 5.1). Most Al_p/Al_o ratios were in the typical range for non-allophanic soils (Nanzyo et al., 1993), exceeding the critical level of 0.5 indicating the dominance of aluminous metal-organic complexes (Kleber et al., 2004). Through thick tephra layers, inorganic material was added to the highly organic soils, leading to lower SOC content (36–54% C averages) in our soils, compared with Loisel et al. (2014) for northern peat soils purely dominated by plant residues. Thus, they can be seen as an outcome of both, organic and volcanic material (Arnalds, 2008; Arnalds and Óskarsson, 2009). According to World Reference Base, both Histosols meet the requirements for histic and andic soil characteristics (IUSS Working Group WRB, 2015). Al_o+0.5Fe_o < 2% and pH (NaF) below the limit of 9.5 suggest a preferred formation of metal-humus complexes. The intermittent deposition of inorganic material as well as the fact that SOM is protected by a build-up of metal-humus complexes, leads to a preservation and further increase of the OM content in the soils. The generally low clay content in the Histosols is driven by the prevailing acidic soil conditions and a high SOM content that limit the weathering process and inhibit formation of pedogenic minerals. The greatest influence of andic material accompanied by low SOM content was found in the layer just above V1477 at Kálfafell.

The influx of aeolian material of unknown origin and the particular site conditions are the driving factors in the development of the investigated Andosols and the alteration of minerals at sites Steinadalur and Kvísker (**Paper 2**). In addition, the high volcanic activity in Iceland constantly adds new tephra to the soils. Parent material, availability of Al and soil pH (H₂O) are important factors contributing to the formation of amorphous SRO minerals and poorly crystalline Fe oxides and hydroxides. A correlation between Al_p/Al_o ratio and SOC and pH (H₂O) above 5 in all but one sample affirmed our assumption that the investigated Andosols are dominated by poorly- and non-crystalline constituents. A high portion of clay size particles, even in the tephra, mainly derives from amorphous constituents (e.g. allophane and ferrihydrite).

Despite the soil type, we observed that particular site conditions (e.g. moisture, SOM), rather than the primary composition of the parent material play an important role in soil development and the formation of different clay minerals (**Paper 1 and 2**). Even though the environmental conditions at the two sites in each environment (wetland and dryland) seemed to be similar, the investigated soils are hardly comparable and have to be considered separately. In the Histosols (**Paper 1**) we demonstrated smectite and hydroxy interlayered minerals as an alteration product in the soils. Secondary chlorite is the only type of layer silicates that could be verified in the Andosols (**Paper 2**) and is supposedly attributed to aeolian influx of material from older, more weathered, more developed eroded surfaces of unknown origin and chemical composition, maybe from sources outside Iceland (Baldo et al., 2020; Bullard et al., 2016). We suppose that with increasing age the chemical composition of the parent material becomes more important in the soil development process.

Higher SARs in the soils originating from Ö1362, compared to those above the basaltic V1477 tephra, reflect a stronger impact of erosion and aeolian activity during 115 yrs of soil development between 1362 and 1477 CE, than in the soils above V1477, in both wetland and dryland soils (**Paper 1, 2 and 3**).

The volcanically active Vatnajökull area has received numerous tephra deposits of varying thickness during the Holocene (Óladóttir et al., 2011a). Beside the chemical composition, the thickness of the tephra layer seems to be a crucial factor in tephra weathering as shown

by Dahlgren (2005). Thick tephra layers are usually more compacted, and thus show lower weathering rates than thinner layers. Thinner layers have greater pore volume and are thus more prone to weathering. While intermittent tephra falls may have a beneficial role in sustaining the productivity of terrestrial ecosystems through soil renewal, large tephra falls can destroy vegetation and separate the underlying strata from the atmosphere, affecting pedogenic processes (e.g. Eddudóttir et al., 2017; 2016; Þorbjarnarson, 2016). Thus, it is a fact that thick tephra deposits may have a significant and lasting effect on ecosystems.

At the time of the Plinian Öraefajökull eruption in 1362 CE, the rhyolitic tephra was deposited as a distinctive layer of up to several tens of centimetres (Thorarinsson, 1958). Even though a large quantity of tephra has been removed by erosion processes subsequent to the eruption event, the initial deposition strongly impacted the terrestrial environment. Based on our results we detected a change in soil properties (e.g. decreased SOM and SOC contents, modified weathering patterns) following the deposition of Ö1362 in all investigated soil profiles, but most notably at site KMK (**Paper 3**).

The results of thermal analysis (**Paper 1 and 3**) led us to the conclusion that mass losses and thermal reactions in our soils are mainly due to the loss of SOM, and possibly hiding changes in the mineral compounds. Decomposition and combustion reactions of organic fractions with slightly different thermal stabilities occurred at all investigated sites.

5.2 Tephra chemistry, weathering processes and pedogenesis

Icelandic soils are characterized by frequent tephra deposition and a steady flux of aeolian material of multiple origins (Arnalds, 2008). While tephra compositions range from basaltic to rhyolitic, up to 80% of the windblown dust is amorphous basaltic volcanic glass (Arnalds et al., 2016).

The fine particle size, glassy nature, high porosity and high permeability of tephra enhance weathering and interaction in the soil environment (Dahlgren et al., 1997; Lowe, 1986). Chemical alteration or even complete dissolution of volcanic glass is controlled by the chemical composition of the parent volcanic material (Pollard et al., 2003; Wolff-Boenisch et al., 2006; 2004). Dissolution rates of “coloured glass” of basaltic andesitic composition are higher than those of rhyolitic “non-coloured glass” (Nanzyo et al., 1993). Temperature and various soil properties, i.e. pH and Al availability have an important impact (Declercq et al., 2013; Gislason and Oelkers, 2003; Wolff-Boenisch et al., 2006; 2004) as well as the thickness of the tephra layer (Dahlgren, 2005) which seems to be a crucial factor in tephra weathering.

Basaltic glass dissolution is one of the main processes in the geochemical weathering of Icelandic soils. At low soil pH conditions, the amorphous basaltic glass dissolves rapidly (Oelkers and Gislason, 2001). The oxalate extracted Fe and Al (Fe_o , Al_o) represented by far the main portion of extractable Fe and Al, verifying the amorphous nature of the tephra (e.g. Oelkers and Gislason, 2001). A difference between the two tephra types is affirmed by a high amount of amorphous Fe and Al in V1477, while their quantity is very low in Ö1362. The average contents of Fe and Al in the tephra showed small differences between the sites.

Under both wetland or dryland conditions, the weathering rates were generally very low in the tephra. According to previous studies on the dissolution rates of volcanic glasses (e.g. Gíslason, 2005; Kirkman and McHardy, 1980; Wolff-Boenisch et al., 2004) the results of our investigations revealed a different state of weathering between the basaltic V1477 and the rhyolitic Ö1362 (Bonatotzky et al., 2021; 2019).

The bulk mineralogy of V1477 mainly consisted of pyroxene and plagioclase, two minerals with a shorter lifetime compared to quartz and thereby, indicative of weathering processes. We found considerably higher contents of clay size material (as high as 36.6% in the Andosols, **Paper 2**) and traces of layer silicates in the basaltic V1477 tephra.

In contrast, the rhyolitic Ö1362 tephra consists of hard and brittle particles and is characterised by a high SiO₂ content (above 70%), but proportionally little Al₂O₃ (e.g. Sharma et al., 2008). Even though the rhyolitic tephra is older, it (especially in the wetland soils) consists almost exclusively of pure volcanic glass and has hardly been altered since its deposition in 1362 CE. In the Andosols we found a slightly more diverse mineralogy in the rhyolitic tephra, suggesting higher weathering in dryland conditions.

While at least traces of layer silicates were found in the basaltic V1477 tephra, we did not find any pedogenic minerals in the rhyolitic tephra in the wetland soils, suggesting that it was hardly altered since its deposition in 1362 CE. In the Andosols we found traces of secondary chlorite in both, V1477 and Ö1362, indicating a slightly higher degree of weathering under dryland conditions.

Our investigations showed that both types of tephra were dominated by inorganic material, rich in amorphous and poorly crystalline SRO minerals and volcanic glass (**Paper 1, 2 and 3**). The OM contents in the tephra layers were low, even in the Histosols, and result in a higher pH (H₂O and NaF) compared to the soils. The majority of the clay size fraction was comprised of poorly crystalline and amorphous constituents (e.g. allophane and ferrihydrite). The predominance of short-range order (SRO) minerals is also confirmed by the Al_p/Al_o ratio, which is close to zero in all tephra samples, but generally slightly higher in Ö1362. The weathering of V1477 is reflected in the lowest Al_p/Al_o value in the layer just above this tephra at KF, suggesting an increase of allophanic properties in the soils due to the precipitation of the basaltic tephra. A similar pattern was visible at site SD (**Paper 2**), but with a significantly lower ratio, reflecting the dominance of inorganic constituents in the Andosol (compared to the Histosols).

At KV the soils formed above the basaltic V1477 tephra show higher ferrihydrite contents than those originated from the rhyolitic Ö1362 tephra. The ferrihydrite content increased suddenly in 20–30 cm depth, presumably due to the presence of a distinct basaltic tephra layer of unknown origin (**Paper 2**).

There is no doubt that tephra has impacted the weathering and properties of the investigated soils, especially at site KMK (**Paper 3**). According to the different weathering state between the tephra layers, the progress of weathering in the soils above V1477 is high, while they tend to be lower between Ö1362 and V1477.

5.3 The source of pedogenic minerals in young Icelandic soils

As would be expected for soils derived from volcanic ejecta of mainly basaltic origin, the examination of the bulk mineralogy revealed a predominance of plagioclase, pyroxene and a large quantity of volcanic glass in all samples. Various types of zeolite (e.g. stilbite, phillipsite, faujasite) were identified. Even though the conditions in volcanic soils are beneficial for layer silicate formation, phyllosilicates are rare in Icelandic soils (e.g. Bonatotzky et al., 2021; 2019). In contrast to previous studies, showing that layer silicates are not present or are just minor components of the clay fraction of Icelandic soils (e.g. Arnalds, 1993; Wada et al., 1992), layer silicates were found to be present in the soils investigated in the study, but only to a limited degree (**Paper 1, 2 and 3**). The major portion of the clay size particles in Icelandic soils mainly derives from amorphous and poorly crystalline constituents (e.g. allophane and ferrihydrite). Therefore, it was generally difficult to identify these crystalline minerals.

The investigations of the Andosols (**Paper 2**) revealed so-called 1.4 nm minerals, a peak showing a 1.4 nm spacing on the bulk XRD pattern. The presence of 1.4 nm minerals provides evidence of clay minerals and is common in Andosols (Kawasaki and Aomine, 1966). In the Histosols we did not find such evidence of clay minerals in the bulk XRD data, and only the investigations of the clay size fraction discerned the presence of layer silicates, with different types found at each location (**Paper 1**).

The clear evidence of smectite in the soils at KF and hydroxy interlayered (HI) minerals at RV were one of the mineralogical characteristics we found in the studied Histosols. Under acid soil conditions, soil vermiculites and smectites act as sinks for Al released to solution by weathering (Chesworth et al., 2008). Al hydroxides incorporate into the interlayer of the 2:1 layer silicates, which leads to the formation of Al-hydroxy interlayered minerals, such as hydroxy interlayered vermiculite (HIV) and smectite (HIS) (Barnhisel and Bertsch, 1989). Smectite was also the most distinct clay mineral found in the soils at KMK (**Paper 3**). It mainly appeared to be abundant in the soils above V1477. Below this basaltic tephra layer, smectite was only found in traces in some of the soil layers. Our findings from the XRD were confirmed by the results from thermal analysis. An endothermic reaction in the low temperature range around 170°C resulted from the dehydration of water in the interlayers and indicates smectite to be present. The results clearly confirmed that smectite “developed” from basaltic tephra, furthermore, indicating an alteration of volcanic glass to smectite. Investigations of the clay size fraction of the soils at both dryland sites discerned secondary chlorite as the only type of layer silicates (**Paper 2**).

Investigations of the soil properties as well as the mineralogy confirm that the investigated soils are young; in their initial state of pedogenesis (**Paper 1, 2 and 3**). It usually takes more time under given environmental conditions for clay minerals to form and alter. For this reason, the question arose, from where do the pedogenic minerals derive?

The chemical and structural characteristics of the parent material (Lowe, 1986), climate and time since the tephra deposition (e.g. Ugolini and Dahlgren, 2002; Vilmundardóttir et al., 2014) as well as the effective time of weathering are the main factors controlling soil development and composition, type and morphology of the resultant tephra-derived pedogenic clay minerals (Jenny, 1941). Our investigations indicated only a minor influence

of the chemical composition of the inorganic parent material (basaltic and rhyolitic tephra) on these processes. We rather revealed a strong dependence on the local environmental conditions (e.g. moisture, SOM content) for the formation of clay minerals (**Paper 1 and 2**).

Volcanic activity, glacier variations and erosion processes highly impacted and formed the Icelandic environment (Björnsson and Pálsson, 2008; Hannesdóttir et al., 2015; Ingólfsson et al., 2010; Vilmundardóttir et al., 2015). Frequent tephra addition and a steady influx of aeolian material provides an input of more developed and weathered constituents to the (on the whole) young soils. A high amount of allophane and ferrihydrite, both amorphous SRO secondary minerals and Fe-hydroxides respectively, are X-ray amorphous and confirm our assumption of an especially high aeolian input. The layer silicates that were found can probably be attributed to aeolian influx of material from older, more weathered and more developed eroded surfaces of unknown origin, maybe from sources outside Iceland (**Paper 2 and 3**).

6. Conclusion

The development of the investigated soils is an outcome of both organic and volcanic (tephra and aeolian) material. Despite the abundance of a weathering-beneficial constituent (basaltic glass) in the soils, they can be seen to be in their early stage of chemical weathering and development (Fig. 6.1).

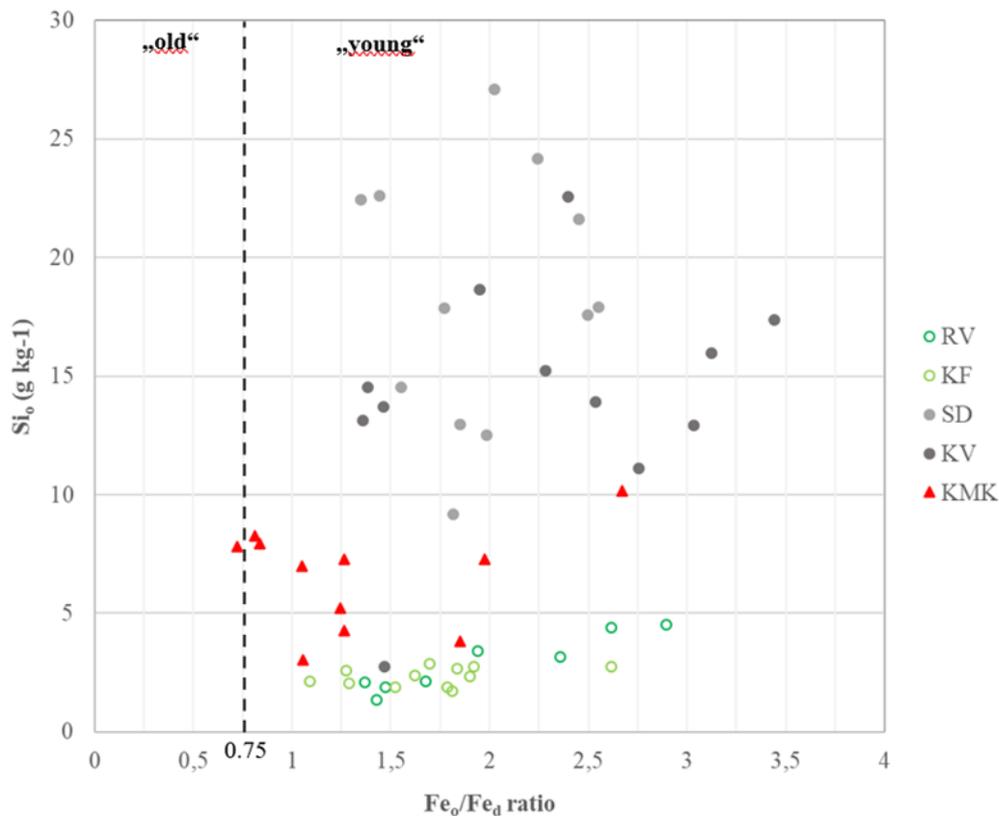


Figure 6.1 Correlation between Fe_0/Fe_a ratio and Si_0 (distinguish the soils between “old” and “young”).

The main findings of the study are:

1. Both types of tephra were dominated by inorganic material, rich in non- and poorly crystalline SRO minerals and Fe-hydroxides (allophane and ferrihydrite) and volcanic glass. The OM contents were low, even in the Histosols, and result in a higher pH (H_2O and NaF) in the tephra compared to the soils. Irrespective of being exposed to wetland or dryland conditions, the weathering rates were generally very low in the tephra. Nevertheless, a different state of weathering between the basaltic V1477 and the rhyolitic Ö1362 tephra was found. In the Histosols (**Paper 1**), traces of layer silicates were found in the basaltic V1477, while we did not find any pedogenic minerals in the rhyolitic tephra, suggesting that it had hardly been altered since its deposition in 1362 CE. In the Andosols (**Paper 2**) we found traces of secondary chlorite in both, V1477 and Ö1362, indicating a slightly higher degree of weathering in the dryland conditions.

2. The parent material (basaltic and rhyolitic tephra) displayed little influence on pedogenesis and the formation of pedogenic minerals in the Histosols. Instead, the OM was the determining driver for soil development and the major factor inhibiting weathering processes. The soils are the result of altered plant residues and volcanic material (tephra and aeolian material). Plant residues, as well as the soil itself, were protected from decomposition by the prevailing anaerobic conditions, a low soil pH and the repeated addition of inorganic matter. Clay formation was low, while metal-humus complexes were predominant. The soils at sites SD, KV and KMK were dominated by SRO minerals. The frequent tephra addition and the influx of aeolian material of unknown origin are the major factors in the Andosol development and the alteration of minerals. A change in soil properties after the deposition of Ö1362 was visible in all investigated profiles, but to varying degrees. In this context, the thickness of the tephra deposition seems to be a crucial factor. Regardless of soil type, we observed that particular site conditions (e.g. moisture, SOM) play an important role in soil development and the formation of different clay minerals. In 115 years of soil development between 1362 CE and 1477 CE, significantly higher SAR's reflect a stronger impact of erosion and aeolian processes on soil development, than in the soils above V1477 at all sites.

3. Icelandic soils develop in a very dynamic environment and signs of external influences were found in the investigated soils. Harsh climate, extensive unstable sandy surfaces which are subject to frequent high-velocity winds, glacier variations, volcanic activity, and not least human occupation over the last centuries, highly impacted and formed the Icelandic environment. Aeolian transport of tephra of basaltic and rhyolitic composition over long distances and re-deposition is very common and characterizes the investigated soils. None of the profiles appeared to be a well-developed pedon but comprised of sequences of buried soils. Furthermore, it is not only the soils that were disturbed over time as disturbance may also have occurred during the deposition of the two tephra layers, especially at site KMK (Fig. 6.2).



Figure 6.2 Visible disturbances at site KMK (detail: Ö1362 tephra layer on the right). (Photos taken by Theresa Bonatatzky)

Tephra deposition impacted and changed soil properties as was observed in the Andosols in general, but most notably at site KMK (**Paper 3**). There, compared to the layers above, soils below Ö1362 showed a finer particle size composition (more clay

and silt than in the layers above), a higher SOM and SOC content, lower pH (H₂O) and in general, a quite low Fe_o/Fe_d ratio, suggesting a more developed soil below Ö1362. Investigations of the mineralogy confirm that the soils are very young, thus in their initial state of soil development. Usually, it takes more time under given environmental conditions for clay minerals to form and alter. Thus, the layer silicates we found are probably attributable to aeolian influx of material from older, more weathered and more developed eroded surfaces of unknown origin, maybe from sources outside Iceland. The distinct sediment layer at site KMK (10 - 30 cm depth) appeared to be very different from the remaining soil layers in the profile. The layer is characterized by a significantly coarser particle size composition, low SOM and SOC content and a more diverse bulk and clay mineralogy. Considering all factors, it is suggested, that the disturbance at 10 - 30 cm depth originated from a landslide coming from the slope of the Kvíármýrarkambur moraine to the north of the site, reflecting the diverse composition of glaciofluvial material.

4. Driven by the prevailing acidic soil conditions and the high SOM content in the Histosols, the weathering processes were limited, resulting in a low clay content and inhibited formation of pedogenic minerals. In contrast, a high portion of clay size particles, even in the tephra, in the investigated profiles at site SD, KV and KMK mainly derives from amorphous constituents (e.g. allophane and ferrihydrite). Even though Icelandic soils are known for their lack of layer silicates, we demonstrate smectite, hydroxy interlayered minerals and secondary chlorite as an alteration product in the soils. Differences in the alteration and formation of pedogenic minerals in the young Icelandic soils investigated in the present study are mainly related to the influx of aeolian material of unknown origin and chemical composition and particular local environmental conditions, rather than the primary composition of the parent material. It is supposed that with increasing age the chemical composition of the parent material becomes more important in the soil development process.

The aim of the research was to improve understanding on how the processes of weathering and transformation of minerals in tephra and volcanic soils take place in different soil environments following the deposition of basaltic and rhyolitic tephra. By extensive investigations of bulk and clay mineralogy in different soil environments and soil types, this study built a comprehensive and novel dataset on the mineralogy in Icelandic soils. The knowledge garnered within this thesis form a basis for further investigations concerning the importance of soil mineralogy in Icelandic soils.

References

- Aaby, B., Berglund, B.E., 1986. Characterisation of lake and peat deposits. in: Berglund, B.E. (Ed.), *Handbook of Holocene Palaeoecology and Paleohydrology*. J. Wiley, Chichester, pp. 231–246.
- Abbott, P. et al., 2021. Cryptotephra from the Icelandic Veiðivötn 1477 CE eruption in a Greenland ice core: confirming the dating of 1450s CE volcanic events and assessing the eruption's climatic impact. *Clim. Past* 17, 565-585.
- Arnalds, O., 2004. Volcanic soils of Iceland. *Catena* 56, 3-20.
- Arnalds, O., 2010. Dust sources and deposition of aeolian materials in Iceland. *Iceland. Agric. Sci.* 23, 3-21.
- Arnalds, O., Dagsson-Waldhauserova, P., Olafsson, H., 2016. The Icelandic volcanic aeolian environment: Processes and impacts - A review. *Aeolian Res.* 20, 176-195.
- Arnalds, O., Gisladottir, F.O., Sigurjonsson, H., 2001. Sandy deserts of Iceland: an overview. *J. Arid Environ.* 47, 359-371.
- Arnalds, O., Hallmark, C.T., Wilding, L.P., 1995. Andisols from Four Different Regions of Iceland. *Soil Sci. Soc. Am. J.* 59, 161-169.
- Arnalds, O., Kimble, J., 2001. Andisols of deserts in Iceland. *Soil Sci. Soc. Am. J.* 65, 1778-1786.
- Arnalds, O., Olafsson, H., Dagsson-Waldhauserova, P., 2014. Quantification of iron-rich volcanogenic dust emissions and deposition over the ocean from Icelandic dust sources. *Biogeosciences* 11, 6623-6632.
- Arnalds, Ó., 1993. Leir í íslenskum jarðvegi. *Náttúrufræðingurinn* 63, 73-85.
- Arnalds, Ó., 2008. Soils of Iceland. *Jökull* 58, 409-421.
- Arnalds, Ó., Óskarsson, H., 2009. Íslenskur jarðvegur. *Náttúrufræðingurinn* 78, 107-121.
- Baldo, C. et al., 2020. Distinct chemical and mineralogical composition of Icelandic dust compared to northern African and Asian dust. *Atmos. Chem. Phys.* 20, 13521-13539.
- Barnhisel, R.I., Bertsch, P.M., 1989. Chlorites and Hydroxy-Interlayered Vermiculite and Smectite, In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*, SSSA, Madison, Wisconsin, pp. 729-788.
- Barros, N., Salgado, J., Feijoo, S., 2007. Calorimetry and soil. *Thermochim. Acta* 458, 11-17.
- Bengtsson, L., Enell, M., 1986. Chemical Analysis. In: Berglund, B.E. (Ed.), *Handbook of Holocene palaeoecology and palaeohydrology*. John Wiley & Sons, Chichester, pp. 423-451.

- Bish, D.L., Post, J.E. (editors) (1989) *Modern Powder Diffraction*. Rev. Mineral. 20, Mineral. Soc. Amer., 369 pp.
- Björnsson, H., Pálsson, F., 2008. Icelandic glaciers. *Jökull* 58, 365-386.
- Blakemore, L.C., Searle, P.L., Daly, B.K., 1987. *Methods for chemical analysis of soils*. NZ Soil Bureau, Dept. of Scientific and Industrial Research, Lower Hutt, N.Z.
- Bonatotzky, T., Ottner, F., Erlendsson, E., Gísladóttir, G., 2019. The weathering of volcanic tephra and how they impact histosol development. An example from South East Iceland. *Catena* 172, 634-646.
- Bonatotzky, T., Ottner, F., Erlendsson, E., Gísladóttir, G., 2021. Weathering of tephra and the formation of pedogenic minerals in young Andosols, South East Iceland. *Catena* 198, 105030.
- Brady, N. C. and Weil, R. R., 2010. *Elements of the nature and properties of soils*. 3rd edition, Pearson AG, Prentice Hall, Boston, U.S.A. 614 pp.
- Brindley, G.W., Brown, G., 1980. *Crystal Structures of Clay Minerals and their X-Ray Identification*. Mineralogical Society, London.
- Bullard, J.E. et al., 2016. High-latitude dust in the Earth system. *Rev. Geophys.* 54, 447-485.
- Burt, R., 2004. *Soil Survey Laboratory Methods Manual*. Natural Resource Conservation Service.
- Chesworth, W., Feldman, S.B., Shang, C., Zelazny, L.W., 2008. Soil mineralogy, *Encyclopedia of Soil Science*, pp. 678-686.
- Childs, C.W., 1985. *Towards Understanding Soil Mineralogy, II. Notes on Ferrihydrite*, N.Z. Soil Bureau, DSIR, New Zealand.
- Compton, K., Bennett, R.A., Hreinsdottir, S., 2015. Climate-driven vertical acceleration of Icelandic crust measured by continuous GPS geodesy. *Geophys. Res. Lett.* 42, 743-750.
- Crovisier, J.L., Honnorez, J., Fritz, B., Petit, J.C., 1992. Dissolution of Subglacial Volcanic Glasses from Iceland - Laboratory Study and Modeling. *Appl. Geochem.* 7, 55-81.
- Dahlgren, R.A., 2005. Early Stage Transformation of 2 : 1 Layer Silicates in Pyroclastic Deposits from the 1980 Eruption of Mt. St. Helens. *JIFS* 2, 5-12.
- Dahlgren, R.A., Shoji, S., Nanzyo, M., 1993. Chapter 5 Mineralogical Characteristics of Volcanic Ash Soils. In: Shoji, S., Nanzyo, M., Dahlgren, R.A. (Eds.), *Developments in Soil Science*. Elsevier, pp. 101-143.
- Dahlgren, R.A., Boettinger, J.L., Huntington, G.L., Amundson, R.G., 1997. Soil development along an elevational transect in the western Sierra Nevada, California. *Geoderma* 78, 207-236.
- Dahlgren, R.A., Saigusa, M., Ugolini, F.C., 2004. The Nature, Properties and Management of Volcanic Soils, *Advances in Agronomy*. Academic Press, pp. 113-182.
- Declercq, J., Diedrich, T., Perrot, M., Gislason, S.R., Oelkers, E.H., 2013. Experimental determination of rhyolitic glass dissolution rates at 40–200°C and 2<pH<10.1. *Geochim. Cosmochim. Acta* 100, 251-263.

- Dugmore, A.J., Gísladóttir, G., Simpson, I.A., Newton, A., 2009. Conceptual Models of 1200 years of Icelandic Soil Erosion Reconstructed Using Tephrochronology. *JONA* 2, 1-18.
- Eddudóttir, S.D., Erlendsson, E., Gísladóttir, G., 2017. Effects of the Hekla 4 tephra on vegetation in Northwest Iceland. *Vegetation History and Archaeobotany* 26, 389-402.
- Eddudóttir, S.D., Erlendsson, E., Gísladóttir, G., 2020. Landscape change in the Icelandic highland: A long-term record of the impacts of land use, climate and volcanism. *Quat. Sci. Rev.* 240, 106363.
- Eddudóttir, S.D., Erlendsson, E., Tinganelli, L., Gísladóttir, G., 2016. Climate change and human impact in a sensitive ecosystem: the Holocene environment of the Northwest Icelandic highland margin. *Boreas* 45, 715-728.
- Einarsson, M.Á., 1980. Climate of Iceland. In: Van Loon, H. (Ed.), *World Survey of Climatology, Climates of the Oceanic*. Elsevier, Amsterdam, pp. 673-697.
- Einarsson, P., 2008. Plate boundaries, rifts and transforms in Iceland. *Jökull* 58, 35-58.
- Gísladóttir, G., Erlendsson, E., Lal, R., 2011. Soil evidence for historical human-induced land degradation in West Iceland. *Appl. Geochem.* 26, S28-S31.
- Gísladóttir, G., Erlendsson, E., Lal, R., Bigham, J., 2010. Erosional effects on terrestrial resources over the last millennium in Reykjanes, southwest Iceland. *Quat. Res.* 73, 20-32.
- Gislason, S.R., Eugster, H.P., 1987. Meteoric water-basalt interactions. I: A laboratory study. *Geochim. Cosmochim. Acta* 51, 2827-2840.
- Gislason, S.R., Oelkers, E.H., 2003. Mechanism, rates, and consequences of basaltic glass dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of pH and temperature. *Geochimica et Cosmochimica Acta*, 67, 3817-3832.
- Gislason, S.R. et al., 2009. Direct evidence of the feedback between climate and weathering. *Earth Planet Sci. Lett.* 277, 213-222.
- Gíslason, S.R., 2005. 12. Chemical weathering, chemical denudation and the CO₂ budget for Iceland. In: Caseldine, C., Russel, A., Harðardóttir, S., Knudsen, Ó (Eds.), *Developments in Quaternary Sciences*. Elsevier, pp. 289-307.
- Gíslason, S.R., 2008. Weathering in Iceland. *Jökull* 58, 387-408.
- Gíslason, S.R., Arnórsson, S., Ármannsson, H., 1996. Chemical weathering of basalt in southwest Iceland: Effects of runoff, age of rocks and vegetative/glacial cover. *Am. J. Sci.* 296, 837-907.
- Griffin, J.J., Windom, H., Goldberg, E.D., 1968. The distribution of clay minerals in the World Ocean. *Deep-Sea Res. Oceanogr. Abstr.* 15, 433-459.
- Gudmundsson, M.T., Larsen, G., Höskuldsson, A., Gylfason, A.G., 2008. Volcanic hazards in Iceland. *Jökull* 58, 251-268.
- Hannsdóttir, H., Björnsson, H., Pálsson, F., Aðalgeirsdóttir, G., Guðmundsson, S., 2015. Changes in the southeast Vatnajökull ice cap, Iceland, between ~ 1890 and 2010. *The Cryosphere* 9, 565-585.

- Höskuldsson, Á., 2019. Öræfajökull. In: Óladóttir, B., Larsen, G., Guðmundsson, M.T. (Eds.), *Catalogue of Icelandic Volcanoes*. IMO, UI and CPD-NCIP. Retrieved from: <http://icelandicvolcanos.is/?volcano=ORA#> (25.3.2020).
- Ingólfsson, Ó., Norðdahl, H., Schomacker, A., 2010. 4 Deglaciation and Holocene Glacial History of Iceland. In: Anders Schomacker, J.K., Kurt, H.K. (Eds.), *Developments in Quaternary Sciences*. Elsevier, pp. 51-68.
- Inoue, K., Higashi, T., 1988. Al- and Fe-humus complexes in Andisols. in: Kinloch, D.I., Shoji, S., Beinroth, F.H., Eswaran, H. (Eds.), *Proc. of the Ninth International Soil Classification Workshop, Properties, Classification, and Utilization of Andisols and Paddy Soils, Japan, 20 July to 1 August 1987., Washington D.C., USA*, pp. 81-96.
- Jacobs, M.B., Hays, J.D., 1972. Paleo-climatic events indicated by mineralogical changes in deep-sea sediments. *JSR* 42, 889-898.
- Jakobsson, S.P., 1979. Petrology of recent basalts of the Eastern Volcanic zone, Iceland. *Acta Naturalia Islandica* 26,1-103.
- Jenny, H., 1941. *Factors of soil formation: a system of quantitative pedology*. McGraw-Hill, New York.
- Jóhannesson, H., Sæmundsson, K., 2009. *Geological map of Iceland, 1:500000*. Icelandic Institute of Natural History.
- Kardjilov, M.I., Gísladóttir, G., Gíslason, S.R., 2006. Land degradation in northeastern Iceland: Present and past carbon fluxes. *Land Degrad. Dev.* 17, 401-417.
- Kawasaki, H., Aomine, S., 1966. So-called 14 Å clay minerals in some Ando soils. *J. Soil Sci. Plant Nutr.*, 12 18-24.
- Kinter, E.B., Diamond, S., 1956. A new Method for Preparation and Treatment of Oriented Aggregate Specimens of Soil Clays for X-Ray Diffraction Analysis. *Soil Sci.* 81 (1), 111-120.
- Kirkman, J.H., McHardy, W.J., 1980. A Comparative-Study of the Morphology, Chemical-Composition and Weathering of Rhyolitic and Andesitic Glass. *Clay Miner.* 15, 165-173.
- Kleber, M., Mikutta, C., Jahn, R., 2004. Andosols in Germany - pedogenesis and properties. *Catena* 56, 67-83.
- Lal, R., 2003. Soil erosion and the global carbon budget. *Environ. Int.* 29, 437-50.
- Lal, R., 2004. Soil carbon sequestration to mitigate climate change. *Geoderma* 123, 1-22.
- Larsen, G., 1984. Recent volcanic history of the Veidivötn fissure swarm, southern Iceland — an approach to volcanic risk assessment. *J. Volcanol. Geotherm. Res.*, 22, 33-58.
- Larsen, G., Dugmore, A., Newton, A., 1999. Geochemistry of historical-age silicic tephra in Iceland. *Holocene* 9, 463-471.
- Larsen, G., Eiriksson, J., 2008. Holocene tephra archives and tephrochronology in Iceland - a brief overview. *Jökull* 58, 229-250.

- Larsen, G., Eiríksson, J., Gudmundsdóttir, E.R., 2014. Last millennium dispersal of air-fall tephra and ocean-rafted pumice towards the north Icelandic shelf and the Nordic seas. *Geological Society, London, Special Publications* 398, 113-140.
- Lawson, I.T. et al., 2007. Environmental impacts of the Norse settlement: palaeoenvironmental data from Myvatnssveit, northern Iceland. *Boreas* 36, 1-19.
- Loisel, J. et al., 2014. A database and synthesis of northern peatland soil properties and Holocene carbon and nitrogen accumulation. *Holocene* 24, 1028-1042.
- Lowe, D.J., 1986. Controls on the rates of weathering and clay mineral genesis in airfall tephra: A review and New Zealand case study, pp. 265-330.
- Mizota, C., van Reeuwijk, L.P., 1989. *Clay Mineralogy and Chemistry of Soils Formed in Volcanic Material in Diverse Climatic Regions*. ISRIC, Wageningen.
- Moore, D.M., Reynolds, R.C., 1997. *X-ray diffraction and the identification and analysis of clay minerals*. Oxford University Press, Oxford.
- Möckel, S.C., Erlendsson, E., Gísladóttir, G., 2017. Holocene environmental change and development of the nutrient budget of histosols in North Iceland. *Plant Soil* 418, 437-457.
- Nanzyo, M., Dahlgren, R.A., Shoji, S., 1993. Chapter 6 Chemical Characteristics of Volcanic Ash Soils. In: Shoji, S., Nanzyo, M., Dahlgren, R.A. (Eds.), *Volcanic Ash Soils - Genesis, properties and utilization*. Elsevier, pp. 145-187.
- Oelkers, E.H., Gislason, S.R., 2001. The mechanism, rates and consequences of basaltic glass dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of aqueous Al, Si and oxalic acid concentration at 25°C and pH 3 and 11. *Geochim. Cosmochim. Acta* 65, 3671-3681.
- Óladóttir, B.A., Larsen, G., Sigmarsson, O., 2011a. Holocene volcanic activity at Grimsvotn, Bardarbunga and Kverkfjoll subglacial centres beneath Vatnajökull, Iceland. *Bull Volcanol*, 73, 1187-1208.
- Óladóttir, B.A., Sigmarsson, O., Larsen, G., Devidal, J.L., 2011b. Provenance of basaltic tephra from Vatnajökull subglacial volcanoes, Iceland, as determined by major- and trace-element analyses. *Holocene*, 21, 1037-1048.
- Óladóttir, B.A., 2009. Holocene eruption history and magmatic evolution of the subglacial volcanoes, Grímsvötn, Bárðarbunga and Kverkfjöll beneath Vatnajökull, Iceland. PhD thesis. Université Blaise Pascal, Clermont-Ferrand and University of Iceland, Reykjavík.
- Óladóttir, B.A., Sigmarsson, O., Larsen, G., Thordarson, T., 2008. Katla volcano, Iceland: magma composition, dynamics and eruption frequency as recorded by Holocene tephra layers. *Bull. Volcanol.* 70, 475-493.
- Ólafsson, H., Furger, M., Brümmer, B., 2007. The weather and climate of Iceland, *Meteorologische Zeitschrift*, pp. 5-8.
- Óskarsson, H., Arnalds, Ó., Gudmundsson, J., Gudbergsson, G., 2004. Organic carbon in Icelandic Andosols: geographical variation and impact of erosion. *Catena* 56, 225-238.
- Pagli, C., Sigmundsson, F., 2008. Will present day glacier retreat increase volcanic activity? Stress induced by recent glacier retreat and its effect on magmatism at the Vatnajökull ice cap, Iceland. *Geophys. Res. Lett.* 35, L09304.

- Palais, J.M., Taylor, K., Mayewski, P.A., Grootes, P., 1991. Volcanic Ash from the 1362 Ad Oraefajokull Eruption (Iceland) in the Greenland Ice-Sheet. *Geophys. Res. Lett.* 18, 1241-1244.
- Parfitt, R.L., 1990. Allophane in New Zealand - a review. *Aus. J. Soil Res.* 28, 343-360.
- Parfitt, R.L., Henmi, T., 1982. Comparison of an oxalate-extraction method and an infrared spectroscopic method for determining allophane in soil clays. *Soil Sci. Plant. Nutr.* 28, 183-190.
- Parfitt, R.L., Wilson, A.D., 1985. Estimation of allophane and halloysite in three sequences of volcanic soils. *Catena* (supplement 7), Braunschweig.
- Pilcher, J., Bradley, R.S., Francus, P., Anderson, L., 2005. A Holocene tephra record from the Lofoten Islands, Arctic Norway. *Boreas* 34, 136-156.
- Pollard, A.M., Blockley, S.P.E., Ward, K.R., 2003. Chemical alteration of tephra in the depositional environment: theoretical stability modelling. *J. Quat. Sci.* 18, 385-394.
- Rateev, M.A., Gorbunova, Z.N., Lisitzyn, A.P., Nosov, G.L., 1969. The Distribution of Clay Minerals in the Oceans. *Sedimentology*, 13 21-43.
- Schoeneberger, P., Wysocki, D., Benham, E., Broderson, W., 2002. *Field Book for Describing and Sampling Soils, Version 2.0*. Natural Resources Conservation Service.
- Schulze, D.G., 1989. An Introduction to Soil Mineralogy. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*, pp. 1-34.
- Shang, C., Zelazny, L.W., Ulery, A.L., Richard Drees, L., 2008. Selective Dissolution Techniques for Mineral Analysis of Soils and Sediments. in: Ulery, A.L., Richard Drees, L. (Eds.), *Methods of Soil Analysis Part 5—Mineralogical Methods*. Soil Science Society of America, Madison, WI, pp. 33-80.
- Sharma, K., Self, S., Blake, S., Thordarson, T., Larsen, G., 2008. The AD 1362 Öræfajökull eruption, S.E. Iceland: Physical volcanology and volatile release. *J. Volcanol. Geoth. Res.* 178, 719-739.
- Shoji, S., Dahlgren, R.A., Nanzyo, M., 1993. Chapter 3 Genesis of Volcanic Ash Soils. Shoji, S., Nanzyo, M., Dahlgren, R.A. (Eds.), *Developments in Soil Science*. Elsevier, pp. 37-71.
- Smykatz-Kloss, W., 1974. *Differential thermal analysis: application and results in mineralogy*. Springer-Verlag.
- Soil Survey Staff, 2014. *Keys to Soil Taxonomy 2014*, 12th ed. USDA - Natural Resources Conservation Service, Washington, DC.
- Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., 1996. *Methods of Soil Analysis Part 3—Chemical Methods*. Soil Science Society of America, American Society of Agronomy, Madison, WI.
- Środoń, J., 2002. Quantitative mineralogy of sedimentary rocks with emphasis on clays and with applications to K-Ar dating. *Mineralogical Magazine* 66(5), 677-687.
- Środoń, J., 2013. Identification and Quantitative Analysis of Clay Minerals, *Handbook of Clay Science*, pp. 25-49.

- Streeter, R., Dugmore, A., 2014. Late-Holocene land surface change in a coupled social-ecological system, southern Iceland: a cross-scale tephrochronology approach. *Quat. Sci. Rev.* 86, 99-114.
- Sæmundsson, K., Larsen, G., 2019. Torfajökull. in: Óladóttir, B., Larsen, G., Guðmundsson, M.T. (Eds.), *Catalogue of Icelandic Volcanoes*. IMO, UI and CPD-NCIP. Retrieved from: <http://icelandicvolcanos.is/?volcano=TOR> (23.5.2020).
- Takahashi, T., Dahlgren, R.A., 2016. Nature, properties and function of aluminum-humus complexes in volcanic soils. *Geoderma* 263, 110-121.
- Thorarinsson, S., 1944. Tefrokronologiska studier på Island : Þjórsárdalur och dess förödelse. PhD thesis, Swedish Society for Anthropology and Geography, Stockholm, 217 pp.
- Thorarinsson, S., 1958. The Örefajökull eruption of 1362. *Acta Natur Islandica* 2, 1-99.
- Thordarson, T., Larsen, G., 2007. Volcanism in Iceland in historical time: Volcano types, eruption styles and eruptive history. *J Geodyn.* 43, 118-152.
- Troels-Smith, J.A., 1955. Karakterisering Af Løse Jordarter. In: *Characterization of Unconsolidated Sediments*. Reitzel, Copenhagen.
- Ugolini, F.C., Dahlgren, R., 2002. Soil Development in Volcanic Ash. *Global J. Environ. Res.* 6, 69-81.
- Vilmundardóttir, O.K., Gísladóttir, G., Lal, R., 2015. Between ice and ocean; soil development along an age chronosequence formed by the retreating Breiðamerkurjökull glacier, SE-Iceland. *Geoderma*, 259, 310-320.
- Vilmundardóttir, O.K., Gísladóttir, G., Lal, R., 2014. Early stage development of selected soil properties along the proglacial moraines of Skaftafellsjökull glacier, SE-Iceland. *Catena* 121, 142-150.
- Vilmundardóttir, O.K., Magnússon, B., Gísladóttir, G., Thorsteinsson, T., 2010. Shoreline erosion and aeolian deposition along a recently formed hydro-electric reservoir, Blöndulón, Iceland. *Geomorphology* 114, 542-555.
- Wada, K., 1989. Allophane and Imogolite. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*. Soil Science Society of America, Madison, WI, pp. 1051-1087.
- Wada, K., Arnalds, O., Kakuto, Y., Wilding, L.P., Hallmark, C.T., 1992. Clay minerals of four soils formed in eolian and tephra materials in Iceland. *Geoderma* 52, 351-365.
- Wilson, M.J., 1987. *A Handbook of Determinative Methods in Clay mineralogy*. Blackie and Sons, Glasgow and London.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2006. The effect of crystallinity on dissolution rates and CO₂ consumption capacity of silicates. *Geochim. Cosmochim. Acta* 70, 858-870.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., Putnis, C.V., 2004. The dissolution rates of natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from 25 to 74 degrees C. *Geochim. Cosmochim. Acta* 68, 4843-4858.

Þorbjarnarson, H., 2016. Soil evolution in the dynamic area south of Vatnajökull. Master's Thesis, University of Iceland.

Paper 1

The Weathering of volcanic tephra and how they impact histosol development. An example from South East Iceland

Author's contribution:

Theresa Bonatutzky (TB), Guðrún Gísladóttir (GG), Egill Erlendsson (EE) and Franz Ottner planned the study. Field work and sampling at sites Kálfafell and Reynivellir were carried out by TB, GG, EE, Höskuldur Þorbjarnarson and Friðþór S. Sigurmundsson. Soil and tephra sample preparation and all analyses (except for ICP-AES analyses of the extracted oxides and hydroxides) were done by TB at BOKU and HÍ. TB did the data analysis and wrote the manuscript. Co-Authors, members of the PhD committee, anonymous reviewers and the journal editor provided useful comments and suggestions on the manuscript. To include the article in the thesis, no permission from the journal was required.



The weathering of volcanic tephra and how they impact histosol development. An example from South East Iceland

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ABSTRACT

Little is known about the impact of tephra deposits from explosive volcanic eruptions on soil formation and weathering processes in organic soils. The weathering of tephra of basaltic and rhyolitic origin and their impact on Icelandic histosols were studied through a combination of physical, chemical and mineralogical analyses. Two sampling sites were selected according to the presence of the light coloured rhyolitic tephra from the Öraefajökull eruption in 1362 CE and a dark-coloured basaltic Veiðivötn tephra from 1477 CE in the volcanically active area south of Vatnajökull in South East Iceland.

The determining factor of pedogenesis in the investigated histosols is the OM, but the influence of tephra and aeolian material from external sources must be taken into consideration. The soils are the result of altered plant residues and volcanic material (tephra and aeolian material). Plant remnants, as well as the soil itself, are protected from decomposition by the prevailing anaerobic conditions, a low soil pH and the repeated addition of inorganic matter. Clay formation is low, while metal-humus complexes are predominant. Fe_e/Fe_d ratios indicated a generally low degree of weathering, being higher close to the basaltic tephra.

The mineralogy was dominated by plagioclase and pyroxene, with quartz and zeolite as minor components. In contrast to previous research on Icelandic soils, our investigations revealed layer silicates at both sites. While we found evidence of smectite in the soils at Kálfafell, hydroxy interlayered minerals were found at Reynivellir. In the basaltic tephra, traces of layer silicates could be verified. In contrast, the rhyolitic tephra did not show any pedogenic minerals, suggesting that it had hardly altered since its deposition in 1362 CE. It is not the chemical composition of the inorganic parent material, but the location that may be an influencing factor on the formation of clay minerals in the investigated histosols.

1. Introduction

Iceland is one of the most active and productive volcanic region in the world with eruptions expected to occur every two years on average (Compton et al., 2015; Pagli and Sigmundsson, 2008), forming consolidated rocks and tephra. The bedrock is mainly of basaltic origin while tephra composition ranges from basaltic to rhyolitic (Thordarson and Larsen, 2007).

Many surfaces have been disturbed by erosion and cryoturbation processes, modifying the surface and the soil environment (Gísladóttir et al., 2011; Möckel et al., 2017; Þorbjarnarson, 2016). Frequent tephra deposition and a steady flux of aeolian material from unstable sandy deserts and eroded soils constantly recharge the surface with new material while subsoils are preserved and continue to develop after burial

(Arnalds et al., 1995). Thus the weathering of tephra is reflected in the soil layers above, although it may also infiltrate the soil immediately below.

Icelandic soils were formed during the Holocene when glaciers retreated (Arnalds, 2010; Arnalds and Kimble, 2001). A cool period between 1250 CE and 1900, referred to as Little Ice Age (LIA) (Ogilvie and Jónsson, 2001) resulted in advancing glaciers (Björnsson and Pálsson, 2008; Hannesdóttir et al., 2015; Ingólfsson et al., 2010). Due to climate warming since the end of the LIA, new land has emerged with subsequent soil formation (Vilmundardóttir et al., 2014; Vilmundardóttir et al., 2015a; Vilmundardóttir et al., 2015b), with time and climate as the key factors controlling weathering and soil development (Ugolini and Dahlgren, 2002; Vilmundardóttir et al., 2014).

A young weathering state is common for all Icelandic soils,

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attributed to the parent material and the prevailing climatic conditions (Arnalds, 2015). Andosols are the predominant soil order, covering 86% of the island, while histosols cover only 1% of the Icelandic surface (Arnalds and Óskarsson, 2009).

Soil is the largest terrestrial pool of organic carbon (OC) (Batjes, 1996), being an important sink of carbon over a long term scale (Loisel et al., 2014). Histosols of the Northern hemisphere are organic soils, dominated by peat, thus often referred to as peat soils. The development in waterlogged, anaerobic conditions (Bridgman et al., 1995; Clymo, 1987; FAO, 2014) and cold climate lead to reduced decomposition rates and an accumulation of poorly decomposed soil organic matter (SOM) and soil organic carbon (SOC). Despite covering only c. 1% of ice-free land globally, histosols contain the highest portion of SOM (up to 50% or even higher) and SOC (20–40%) in all soil types. Therefore, they play an important role in the global carbon cycle. As the climate gets warmer, the extent of peatland may decrease (IPCC, 2015). Prominent wetland areas with histosols in Iceland are in the west and northwest of the island. Other important areas of histosols are in south Iceland (Arnalds and Óskarsson, 2009).

Even though Icelandic histosols show similar rates of organic accumulation ($0.1\text{--}0.45\text{ mm yr}^{-1}$) as reported for peaty soils in neighbouring countries (Gudmundsson, 1978), they exhibit features that separate them from most other histosols on the globe. The parent material is mainly comprised of poorly decomposed plant remains but contains considerable quantities of inorganic material originating from volcanic ejecta and aeolian activity. Despite very limited research, it has been shown that Icelandic histosols exhibit a unique combination of histic and andic soil properties. They are characterized by a considerable amount of metal-humus complexes (Arnalds, 2008; Arnalds and Óskarsson, 2009) and variable SOM content (Möckel et al., 2017). A study on peatland soils in west and north Iceland by Gudmundsson (1978) showed that properties are controlled by the quantity and form of mineral material present.

SOC content and the amount of clay minerals in organic soils are influenced by drainage conditions and the addition of fresh parent material (Möckel et al., 2017). High OM content and low dry bulk density (DBD) ($0.17\text{--}0.4\text{ g cm}^{-3}$) lead to a high water holding capacity (Gísladóttir et al., 2010; Gísladóttir et al., 2011; Möckel et al., 2017) in Icelandic histosols. A prevailing low pH and the presence of large quantities of SOM tend to result in an inhibited formation of amorphous secondary minerals (Stefánsson and Gíslason, 2001).

Ammonium oxalate extractable Al and Fe (Al_o , Fe_o) in Icelandic histosols are commonly found to be in the range of 0.7–1.6% Al_o and 0.5–1.2% Fe_o , while the Si_o content is low (Arnalds, 2004). Icelandic soils are highly affected by windblown dust. Up to 80% of the aeolian dust has a volcanogenic origin of basalt composition, rich in heavy metals (Arnalds et al., 2016). The main source of Fe in the soils is basaltic glass but not crystalline material (Arnalds et al., 2014; Arnalds et al., 2016). At low pH conditions in the soil, the amorphous basaltic glass dissolves rapidly (Oelkers and Gíslason, 2001), leading to high Fe_o values. Arnalds and Kimble (2001) suggested that high Fe_o , compared to Al_o and Si_o , are further caused by ferrihydrite as a common component of the clay fraction. They also stated dithionite-citrate extractable Fe (Fe_d) values to be generally about half of the Fe_o values.

Histic andosols generally show very similar properties to histosols. They cover about 5.5% of the Icelandic surface area and develop in poorly drained areas where aeolian input, especially from volcanic areas, is considerable. SOC content is high (12–20%) but, due to aeolian input, it is too low to meet the criteria for histosols and therefore, the SOC and andic properties of these soils define it as andosols with histic properties (Arnalds, 2004). García-Rodeja et al. (2004) found low Al_p contents in histic andosols from northwest Iceland to be due to low humification caused by temperature regime and poor drainage.

Chemical weathering of basaltic rocks is a fundamental process in soil formation in volcanic regions (Kardjilov et al., 2006). Gíslason (2008) found chemical denudation rates in Iceland being 1.3 times

higher than the world average; despite the cold climate. Linked to the importance of climatic factors on weathering, Eiríksdóttir et al. (2013) showed that chemical denudation in Iceland increased by 13% with each 1°C increase in temperature. Nonetheless, in the southern regions of Iceland, runoff and the age of rocks are the primary factors controlling the chemical denudation rate (e.g. Gíslason, 2008; Gíslason et al., 1994; Gíslason et al., 1996; Stefánsson and Gíslason, 2001). The annual mean surface runoff in Iceland is at a maximum on the south and south eastern fringe of the Vatnajökull ice cap (Jónsdóttir, 2007; Jónsdóttir, 2008). The dissolution rate of glassy rocks (hyaloclastite) is about 10 times faster than those of crystalline basalt (Gíslason and Eugster, 1987).

Total chemical weathering rates decrease with increasing age of rocks (Gíslason, 2008). Volcanic glass shows the least resistance to chemical weathering in soils developed from volcanic ejecta. As a result of its properties (e.g. fine particle size and amorphous nature), tephra enhances weathering and interactions in the soil environment (Dahlgren et al., 1993). Despite the overall rapid weathering of tephra, rhyolitic tephra weathers much more slowly than basaltic (Gíslason, 2005) and dissolution rates of “coloured glass” of basaltic andesitic composition are higher than those of rhyolitic “non-coloured glass” (Nanzyo et al., 1993). Furthermore, with increasing silica content, glass dissolution rates decrease. Studies on dissolution rates of natural glasses by Wolff-Boenisch et al. (2004) showed a lifetime of 4500 yrs for natural glass of rhyolitic composition, whereas it is only 500 yrs for natural basaltic glass.

Clay minerals in Icelandic soils developed from volcanic ejecta are formed in subsurface horizons *in situ* rather than by translocation or leaching and precipitation (Arnalds, 2008; Dahlgren et al., 2004). Amorphous secondary minerals are predominant. With increasing soil age the crystalline weathering phases become more abundant (Crovissier et al., 1992). Crystalline plagioclase and pyroxene are major primary minerals of Icelandic basalt (Arnalds, 2005). Allophane, imogolite and poorly crystalline ferrihydrite are the dominant phases for the clay size fraction of Icelandic soils (Stefánsson and Gíslason, 2001) while layer silicates are rare (Arnalds, 1993).

A recent study by Möckel et al. (2017) showed that aeolian material had an impact on soil properties of histosols in North Iceland. Furthermore, it has been verified that heavy tephra falls influence vegetation and soil (Eddudóttir et al., 2016; Þorbjarnarson, 2016). Nevertheless, the impact of tephra deposits from big explosive eruptions on soil formation and soil weathering processes in histosols is not well studied in Iceland. The island offers unique opportunity to conduct such research, specifically in regions that have been inundated with thick tephra deposits of different chemical composition.

In this paper we present the results from a comprehensive study on histosols in the lowlands south of Vatnajökull glacier, SE Iceland. The volcanically active Vatnajökull area has received numerous tephra deposits of varying thicknesses during the Holocene (Óladóttir et al., 2011). The presence of the light coloured rhyolitic tephra from the Óræfajökull eruption in 1362 CE and a black basaltic Veidivötn tephra from 1477 CE in this region enables comparison between the weathering behaviour of tephra of different composition and to examine their contrasting mineralogy. The present research will improve the understanding of changes in soil properties and mineralogy in histosols after tephra deposition and will add significant knowledge about the impact of volcanism on weathering processes and histosol development globally. The main purpose is to examine the following research questions:

- 1) How do different tephra weather?
- 2) How do tephra influence the weathering processes and development of histosols?

The weathering behaviour of tephra deposits of basaltic and rhyolitic origin and their impact on Icelandic histosols were studied through a combination of physical, chemical and mineralogical methods. As far

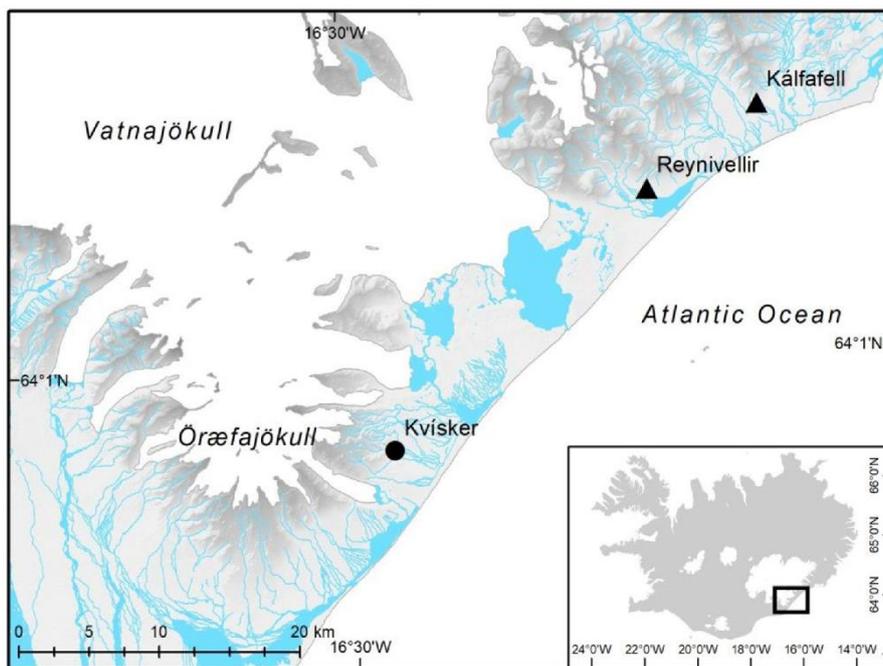


Fig. 1. The research area south of Vatnajökull glacier, SE Iceland. Triangles show the position of the two sampling sites at Kálfafell to the east and Reynivellir further to the west. The location of the weather station Kvísker is shown as circle.

as we are aware of, no research on this matter has been published previously.

2. Study sites and material

The study area lies in a lowland area close to the sea, south of Vatnajökull, in southeast Iceland (Fig. 1). The two investigated sites are located in Reynivellir (64°07.731'N, 16°03.245'W) and Kálfafell (64°10.749'N, 15°53.236'W) (Fig. 2 and Fig. 3). Both sites sustain wetland soils at the foot of Örfajökull volcano.

The climate in the research area is maritime, dominated by cool, moist summers and relatively warm winters with high precipitation (Einarsson, 1980). The climate is strongly affected by the mountainous landscape (Ólafsson et al., 2007). Mean annual temperature at Kvísker, the weather station which is closest to the sampling sites, is 5.9 °C (2009–2016) and annual precipitation (1962–2011) is 3500 mm on average (based on unpublished data from the Icelandic Meteorological Office).

The geology of the research area is primarily composed of basaltic lava and hyaloclastite (Jóhannesson and Sæmundsson, 2009; Thorarinnsson, 1958). The research sites are in an area influenced by the active central volcanoes of Grímsvötn, Bárðarbunga and Örfajökull (north) and Katla (west). All of these systems have erupted on multiple occasions in historic times and have produced the majority of the tephra deposits preserved in soils in the region (Óladóttir et al., 2008). Two distinct tephra layers, the light coloured rhyolitic tephra from the 1362 CE Örfajökull eruption (Ö1362) and a dark basaltic tephra from the 1477 CE Veiðivötn fissure eruption (V1477), are well preserved at both research sites.

The 1362 CE Plinian Örfajökull eruption is thought to be the largest rhyolitic eruption in Iceland in historic times and produced huge amounts of tephra (Sharma et al., 2008) which can easily be identified by its light grey colour and major element composition. According to Sharma et al. (2008) the Ö1362 is characterized by a high content of Na₂O (average 4.95%) and a very low MgO content (close to zero). The range in SiO₂ (average 72.71%) is similar to some historical Hekla



Fig. 2. The study site at Kálfafell (left), soil profile on the right. View north towards the edge of Vatnajökull National Park.



Fig. 3. The study site at Reynivellir (left), soil profile on the right. View west towards Örafajökull in the background.

tephra layers, but a higher FeO (average 3.30%) and lower MgO content enable Ö1362 to be distinguished (Larsen et al., 1999). The basaltic 1477 CE tephra is characterized by its black colour and originates from an eruption in the Veiðivötn fissure swarm, which belongs to the Bárðarbunga volcanic system. This eruption produced one of the most voluminous tephra layers of its kind in Iceland (Larsen, 1984). Compared to the rhyolitic tephra, V1477 has a lower SiO₂ content of c. 50%, about half of Na₂O (approx. 2.5%), but a multiple of the MgO (6–7%) and FeO content (around 13%) (e.g. Streeter and Dugmore, 2014; Lawson et al., 2007). Iron-enrichment typifies the basaltic magmatism in Iceland (Jennings et al., 2014). Other tephra layers, mainly of basaltic composition, were found in both soil profiles, e.g. a coarse basaltic tephra right below Ö1362 which is presumed to belong to the Grímsvötn volcanic system. Other basaltic tephra layers were detected but not allocated to a specific volcanic system.

The vegetation cover in the research area is mainly comprised of modified grassland and heath utilised for pastoral agriculture. A small conifer plantation is located nearby, but has no direct influence upon the sampling area. Soils are formed under both dryland and wetland conditions but often appear highly degraded. A detailed description of the soil samples is given in Table 1.

3. Methods

3.1. Sampling and profile description

Both sampling sites (Figs. 2 and 3) were selected according to the occurrence of wetland condition in conjunction with the two desired tephra layers detected by test coring with a JMC Backsaver. A soil pit was dug and samples were taken at 10 cm depth intervals, and at 5 cm intervals immediately above and below the two main tephra layers. Where field conditions inhibited the application of the preferred strategy, sampling had to be adapted slightly. Tephra layers were sampled separately. Additionally, soil monoliths of each profile were taken. Prior to analyses, soil and tephra samples were marked, kept in sealed plastic bags, and stored at 4 °C. Soil profiles were described according to the Troels-Smith system (Aaby and Berglund, 1986; Troels-Smith, 1955). Soil colour was assessed on field-moist soil using a Munsell colour chart (Table 1).

3.2. Soil sample analyses

Soil and tephra samples were analysed at the University of Natural Resources and Life Sciences, Vienna and at the University of Iceland. Ammonium oxalate, sodium pyrophosphate and

citrate–bicarbonate–dithionite (CBD) extractions were operated at the Innovation Centre Iceland (Nýsköpunarmiðstöð Íslands).

3.3. Soil and tephra mineralogical analyses

To determine soil mineralogy we used X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetry (TG) methods. For bulk mineral analyses the samples were oven-dried at 70 °C and ground to analytical fineness. To obtain the clay fraction (< 2 µm), the OM of the samples was removed by 10% hydrogen peroxide (H₂O₂) treatment. After this pre-treatment it was separated from the soil by a combination of sieving and centrifugation after initial dispersion with ultrasonic vibration. XRD of bulk soil samples was conducted by using a Panalytical XPert Pro MPD diffractometer with automatic divergent slit, Cu LFF tube 45 kV, 40 mA, with an X'Celerator detector. The measuring time was 250 s, with a stepsize of 0.017°. Analogous to the bulk mineral analysis, the clay minerals were determined by X-ray diffraction and identified according to Moore and Reynolds (1997), Brindley and Brown (1980) and Wilson (1987). Afterwards, expansion tests using ethylglycol, as well contraction tests heating of the clay size fraction up to 550 °C were done. After each step the samples were X-rayed from 2 to 40°2θ. A semiquantitative mineral composition of both, bulk and clay size fraction was estimated from the resultant diffractograms according to Riedmüller (1978) by using the Panalytical software X'Pert HighScorePlus.

DSC and TG were conducted on 15 mg of air-dry and ground bulk soil samples and 50 mg of tephra respectively, using a Netzsch STA 409 PC Luxx® Simultaneous thermal analyzer, which monitored the heat flow of a sample relative to a reference as a function of temperature, while the sample was heated up from 25 to 1000 °C at a rate of 10 °C min⁻¹ in a reaction atmosphere of synthetic air (flow rate: 50 ml min⁻¹). Thermal flux and changes in weight were measured simultaneously. The resulting endothermic and exothermic reactions were ascribed according to Smykatz-Kloss (1974) and Barros et al. (2007).

3.4. Physical and chemical soil and tephra sample analyses

Representative bulk soil and tephra samples were air-dried, gently crushed to pass through a 2 mm sieve and used for the analyses of physical and chemical properties. SOM content was estimated by loss on ignition (LOI) method at 550 °C (Heiri et al., 2001). Contents of SOC and total nitrogen (total N) were obtained on oven-dried fine earth by the dry combustion method at high temperature (900 °C) using a Thermo Fisher Scientific Flash EA 112 CN elemental analyzer. The

Table 1

Selected morphological, physical and chemical characteristics of the studied pedons at Kálfafell (KF) and Reynivellir (RV) (values marked with * term the OM and OC in the tephra). Abbreviations in the sediment description follow the Troels-Smith system (Aaby and Berglund, 1986; Troels-Smith, 1955). The description of the organic compound of the samples is abbreviated as follows: Th (*Turfia herbacea*), Dh (*Detritus herbosus*) and Sh (*Substantia humosa*). Mineral particles are abbreviated as follows: As (*Argilla steatodes*) consists of colloids or grains < 0.002 mm, Ag (*Argilla granosa*) consists of grains the size of which ranges from 0.06–0.002 mm, Ga (*Grana arenosa*) consists of grains from 0.06 to 0.6 mm. All estimated on a 5 class scale: (+) very slight quantities of a given element. (1) 25% and (2) 50% proportion of the component of the individual deposit.

Sample	Depth cm	Munsell colour code (moist)	Sediment description built upon Troels-Smith	SOM	SOC	Total N	DBD g cm ⁻³	pH(H ₂ O)	pH(NaF)
				%	%	%			
Soil KF1	0–10	7.5YR 3/3 (dark brown)	Ag2, Th1, Sh1, Dh+, Ga+	24.41	10.31	0.630	0.38	4.7	9.0
Soil KF2	10–20	7.5YR 2.5/2 (very dark brown)	Dh1, Th1, Ag1, Sh1, As+	53.07	28.66	1.500	0.21	4.8	8.2
Soil KF3	20–30	10YR 2/2 (very dark brown)	Dh1, Th1, Ag1, Sh1, As+	57.39	24.55	1.060	0.25	4.7	7.8
Soil KF4	30–40	7.5YR 2.5/3 (very dark brown)	Th1, Ga1, Ag1, Sh1, Dh+, As+	56.91	28.43	1.590	0.25	4.3	7.9
Soil KF5	40–45	7.5YR 2.5/2 (very dark brown)	Th2, Ag1, Sh1, Dh+, As+	39.08	20.31	1.112	0.15	4.2	8.5
Soil KF6	45–50	10YR 3/3 (dark brown)	Th1, Ga1, Ag1, Sh1, Dh+, As+	23.96	17.76	0.910	0.36	4.3	8.6
Tephra KF V1477	50–54	–	–	2.87 *	0.74 *	0.010	–	4.9	9.3
Soil KF7	54–59	10YR 2/2 (very dark brown)	Dh1, Th1, Ag1, Sh1, As+	45.67	21.44	0.860	0.21	3.7	8.1
Soil KF8	60–65	10YR 2/1 (black)	Dh1, Th1, Ga1, Ag1, As+, Sh+	63.61	34.79	1.460	0.13	3.9	7.8
Soil KF9	65–70	10YR 2/2 (very dark brown)	Dh1, Th1, Ag1, Sh1, Ga+, As+	56.90	30.77	1.531	0.12	4.1	7.9
Tephra KF Ö1362	71–74	–	–	3.01 *	0.70 *	0.010	–	5.2	8.7
Soil KF10	75–80	10YR 2/1 (black)	Th1, Ga1, Ag1, Sh1, Dh+, As+	55.64	26.37	0.980	0.45	4.6	8.3
Soil KF11	80–85	10YR 2/2 (very dark brown)	Dh1, Th1, Ag1, As1, Ga+, Sh+	54.80	31.83	1.510	0.15	4.9	8.1
Soil KF12	85–92	10YR 2/2 (very dark brown)	Dh1, Th1, Ag1, Sh1, Ga+, As+	55.23	28.92	1.560	0.14	5.1	8.1
Soil RV1	0–10	7.5YR 2.5/3 (very dark brown)	Ag2, Th1, Sh1, Ga+, As+	24.76	15.05	1.024	0.43	4.0	9.7
Soil RV2 + 3	10–18	7.5YR 3/3 (dark brown)	Th2, Ag1, Dh1, Dh+, Sh+	55.48	25.69	1.465	0.26	4.2	8.8
Soil RV4 + 5	19–30	10YR 2/2 (very dark brown)	Th1, Ga1, Ag1, Sh1, Dh+, As+	55.60	29.68	1.633	0.29	4.4	8.5
Soil RV6	30–36	7.5YR 3/3 (dark brown)	Dh1, Th1, Ag1, Sh1, Ga+, As+	47.10	23.35	1.262	0.21	4.3	9.2
Tephra RV V1477	36–41	–	–	3.57 *	1.45 *	0.050	–	5.3	10.4
Soil RV7	41–42	10YR 2/2 (very dark brown)	Th2, Dh1, Ag1, Ga+, As+, Sh+	41.81	23.31	1.060	0.23	4.5	9.3
Soil RV8	43–48	10YR 2/2 (very dark brown)	Dh1, Th1, Ag1, Sh1, As+	50.08	25.56	1.180	0.20	4.4	8.7
Tephra RV Ö1362	48–52	–	–	3.96 *	1.01 *	0.030	–	5.4	9.7
Soil RV9	53–63	10YR 2/1 (black)	Th2, Ag1, Sh1, Dh+, Ga+	61.68	28.41	1.029	0.18	4.5	8.6
Soil RV10	63–75	10YR 2/2 (very dark brown)	Dh2, Th1, Ag1, Ga+, As+	69.20	37.60	1.656	0.18	4.4	7.9

values thus obtained were assumed to correspond to organic carbon, since the studied soils did not contain carbonate minerals. Soil pH was determined in water-soil suspension according to ÖNORM L1083 (Austrian Standard Institute, 2006) and in 1 M NaF solution for estimation of the andic properties of the soil following the method of Fields and Perrott as outlined in Blakemore et al. (1987). Dry bulk density (DBD) was measured on soil monoliths in the lab. For this purpose we used small cubical cores of known volume (7.9 cm³) as described in Vilmundardóttir et al. (2014). Due to the small size of cores, three replicates (n) for each DBD sample were collected to obtain an average value. The samples were dried and sieved through a 2 mm sieve. The top layer of site Reynivellir contained coarse fragments (> 2 mm). Their volume was determined by the water displacement technique. The DBD of the fine earth fraction was calculated after subtracting the weight and volume of the coarse fraction from the weight and volume of the total bulk density sample.

To determine poorly crystalline and amorphous materials (e.g. allophane, ferrihydrite, iron and aluminium-humus complexes), extractions of pedogenic oxides and hydroxides were implemented (Blakemore et al., 1987). Therefore, air-dry tephra and soil samples were ground to pass through a 150 µm sieve. Iron (Fe), aluminium (Al) and silica (Si) associated with amorphous constituents (Fe_o, Al_o, Si_o) were extracted with acid ammonium oxalate in the dark by the shaking method at pH 3.0 (Schwertmann, 1964). Fe and Al associated with OM (Fe_p, Al_p) were extracted with sodium pyrophosphate at pH 10.0 (McKeague, 1967). Fe in crystalline and non-crystalline oxides (Fe_d) was extracted by the citrate-bicarbonate-dithionite procedure (Mehra and Jackson, 1960). Al, Fe and Si from dissolution analyses were determined by inductively coupled plasma optical emission spectroscopy (ICP-AES). The molar Al/Si ratios of allophane in the soil and tephra samples were calculated from (Al_o - Al_p)/Si_o (e.g. Wada, 1989). Allophane content (%) was estimated by the formula: 100 × % Si_o/[23.4–5.1x] with x = (Al_o - Al_p)/Si_o (e.g. Mizota and van Reeuwijk, 1989; Parfitt and Henmi, 1982; Parfitt and Wilson, 1985). The amount

of ferrihydrite (%) was estimated by multiplying the %Fe_o by a factor of 1.7 (Childs et al., 1991). Contents of non-crystalline secondary clay minerals, herein after referred to as clay content, was estimated as the total amount of allophane and ferrihydrite (e.g. Shang and Zelazny, 2008). Ammonium oxalate extractable Al_o plus 0.5 Fe_o was used as a taxonomic criterion for andic soil properties (Soil Survey Staff, 2014). The contents of amorphous Al and Fe were calculated by the formula Al_o - Al_p and Fe_o - Fe_p respectively (e.g. Mizota and van Reeuwijk, 1989). The molar ratio of metal-humus complexes was estimated by (Al_p + Fe_p)/OC (e.g. Takahashi and Dahlgren, 2016; Inoue and Higashi, 1988).

3.5. Statistical analysis

Descriptive statistics and correlations were performed using the JMP software (JMP, 2013).

4. Results

4.1. Selected soil properties

Soils from both sample sites developed in wetland habitats in the lowlands to the south of Vatnajökull. Tephra layers are well preserved although those at Reynivellir occur at a shallower depth (Fig. 4). SOM content was generally high, 25–69% at Reynivellir and 24–64% at Kálfafell (Table 1). SOC was high and ranged between 9 and 38% at the two sites. There is a strong correlation between SOC and SOM (r² = 0.76, P < 0.0001).

The DBD was low at both sites, but varied more at Kálfafell than at Reynivellir. DBD above the tephra layers varied according to site and tephra. The amount of total N was above 1% at Reynivellir and varied more at Kálfafell, but was generally close to 1% in all soil layers (Table 1).

The soils were acidic with pH(H₂O) ranging from 4.0 to 4.5 at

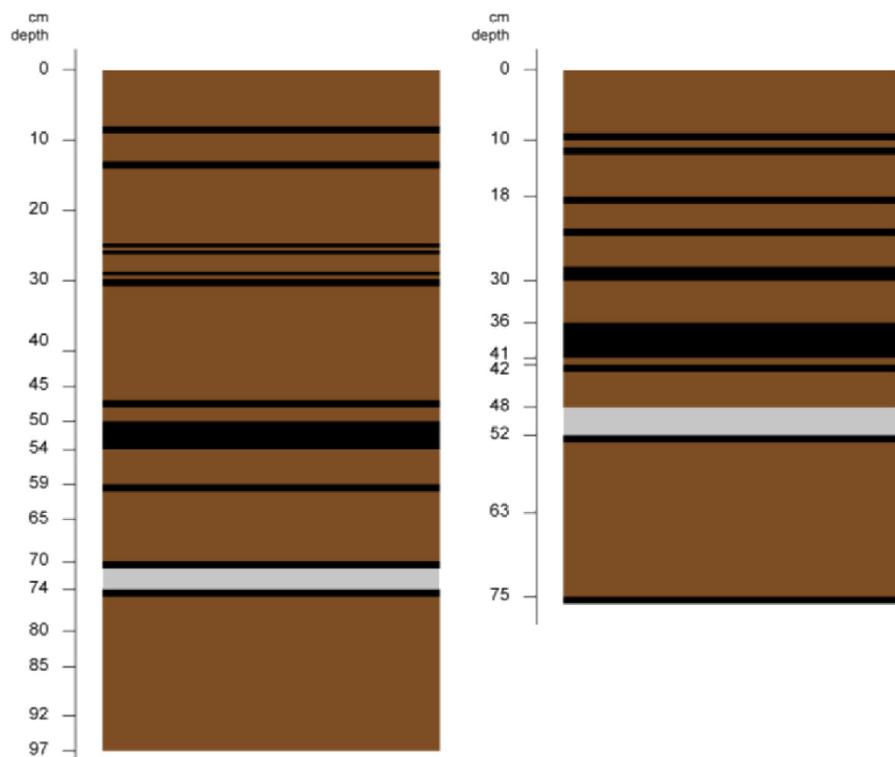


Fig. 4. Schematic soil profiles at Kálfafell (left) and Reynivellir (right). Soils are illustrated in brown, basaltic tephra in black and rhyolitic tephra layers in light grey. At Kálfafell V1477 was found in 50–54 cm depth, at site Reynivellir in 36–41 cm depth. Ö1362 was found in 71–74 cm and 48–52 cm depth at Kálfafell and Reynivellir, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Reynivellir and between 3.7 and 5.1 at Kálfafell. The pH(H₂O and NaF) were higher in the tephra than in the soil at both sites (Table 1).

4.2. Weathering of soil and tephra

The ammonium oxalate extractable Al, Fe, and Si, pyrophosphate extractable Al and Fe and Fe_d, varied between the two sites. Fe_o and Al_o were higher than those extracted by pyrophosphate (Fe_p, Al_p). Si contents (Si_o) were generally low with highest values in V1477 and lowest in Ö1362. Citrate–bicarbonate–dithionite extractable Fe (Fe_d) was higher at Kálfafell, but fluctuated in both sites.

There was a significant correlation between Al_o and pH(NaF) (Fig. 5), but no correlation between Fe_o and pH(NaF) (Fig. 6), Al/Si ratios in the soils were below 2, being higher at Kálfafell than Reynivellir where Al/Si was as low as 0.1. Highest ratios in soils were found above the tephra layers. Clay contents in the soils ranged between 2.6 and 5.0% at Kálfafell and between 1.5 and 4.9% at Reynivellir. In V1477 the clay content was around 6.0% at both sites, but significantly lower in Ö1362 (0.5% at Kálfafell and 0.2% at Reynivellir).

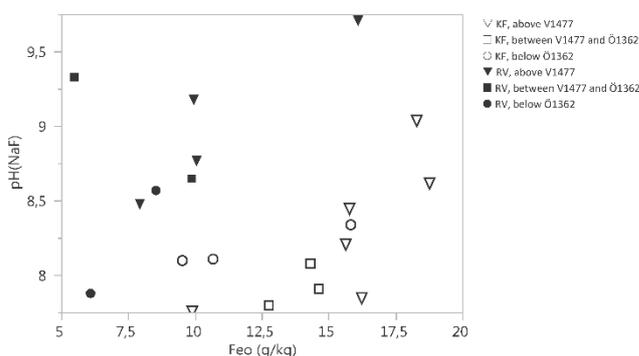


Fig. 6. No correlation between Fe_o and pH(NaF).

Al_o + 0.5Fe_o ranged between 0.1 and 1.9, reaching lowest levels in Ö1362.

The Al_p/Al_o ratios were between 0.5 and 1.0 in the soils at Reynivellir and generally lower at Kálfafell, ranging between 0.3 and 0.7 (Table 2). Low Al_p/Al_o ratios were found in the surface layer at both sites and in the soils above the tephra layers. Compared to the remaining layers, the soil just below the tephra layers showed slightly lower ratios.

Fe_o/Fe_d ratios in the soils were higher at Reynivellir than Kálfafell, the highest ratio was above Ö1362 at Reynivellir.

4.3. Mineralogy of soil and tephra

The bulk XRD data (Table 3) showed the dominance of pyroxene and plagioclase in all soils. Additionally, appreciable amounts of quartz and traces or greater amounts of zeolite were found in most samples. While stilbite and faujasite were the main types of zeolite at Kálfafell, the soils at Reynivellir were dominated by laumontite.

There is a difference in the bulk mineralogy of the two different types of tephra. V1477 mainly consisted of pyroxene and plagioclase

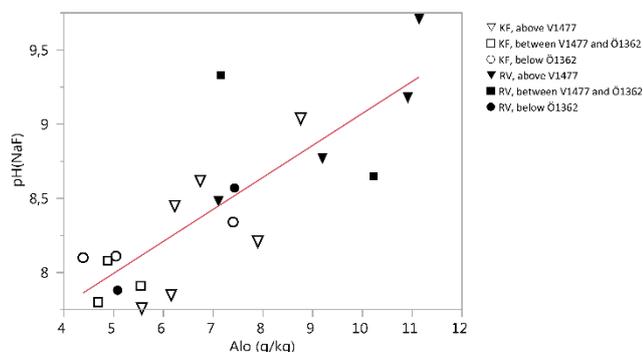


Fig. 5. Correlation between Al_o and pH(NaF) ($r^2 = 0.66$, $y = 6.9157406 + 0.2157065x$, $P < 0.0001$).

Table 2
Results of selective dissolution analyses and properties related to amorphous material in the studied pedons at Kálfafell (KF) and Reynivellir (RV).

Sample	Depth cm	g kg ⁻¹										Molar ratio	Ratio	Fe _d	Fe _p	Fe _o /Fe _d	Al _o + 0.5*Fe _o	Allophane	Ferrihydrite	Clay	Amorphous Al g kg ⁻¹	Amorphous Fe g kg ⁻¹	Metal-humus complexes Molar ratio
		Al _o	Fe _o	Si _o	Al _p	Fe _p	Fe _d	(Al _o - Al _p)/Si _o	Al _p /Al _o	Ratio	%												
Soil KF1	0–10	8.8	18.3	2.7	3.7	6.9	7.0	1.8	0.4	2.6	1.8	0.4	2.6	1.8	1.86	3.11	4.97	5.06	11.41	0.08			
Soil KF2	10–20	7.9	15.6	2.8	4.3	6.9	8.1	1.3	0.5	1.9	1.6	0.5	1.9	1.6	1.55	2.66	4.21	3.57	8.71	0.03			
Soil KF3	20–30	5.6	9.9	1.9	3.5	6.0	5.5	1.1	0.6	1.8	1.1	0.6	1.8	1.1	0.98	1.68	2.66	2.02	3.93	0.02			
Soil KF4	30–40	6.2	16.2	2.3	3.5	10.6	8.5	1.1	0.6	1.9	1.4	0.6	1.9	1.4	1.24	2.76	4.00	2.68	5.64	0.03			
Soil KF5	40–45	6.2	15.8	2.4	2.9	8.8	9.7	1.4	0.5	1.6	1.4	0.5	1.6	1.4	1.39	2.68	4.07	3.32	6.95	0.07			
Soil KF6	45–50	6.7	18.8	2.9	2.1	6.9	11.1	1.6	0.3	1.7	1.6	0.3	1.7	1.6	1.80	3.19	4.99	4.59	11.91	0.04			
Tephra KF V1477	50–54	9.8	15.3	5.9	0.6	1.1	3.4	1.6	0.1	-	1.7	0.1	-	1.7	3.66	2.61	6.26	9.22	14.25	-			
Soil KF7	54–59	4.9	14.3	2.1	3.3	11.7	11.1	0.7	0.7	1.3	1.2	0.7	1.3	1.2	0.92	2.43	3.35	1.53	2.60	0.02			
Soil KF8	60–65	4.7	12.7	1.9	3.5	11.3	8.4	0.6	0.6	1.5	1.1	0.81	2.17	1.1	0.81	2.17	2.97	1.22	1.49	0.02			
Soil KF9	65–70	5.5	14.6	1.7	3.2	9.5	8.1	1.3	0.6	1.8	1.3	0.6	1.8	1.3	1.00	2.49	3.48	2.34	5.13	0.02			
Tephra KF Ö1362	71–74	1.0	1.5	0.4	0.3	0.5	0.6	2.0	0.3	-	0.2	0.25	0.25	0.2	0.25	0.25	0.50	0.70	1.01	-			
Soil KF10	75–80	7.4	15.8	2.7	3.1	8.4	8.6	1.6	0.4	1.8	1.5	0.4	1.8	1.5	1.67	2.69	4.36	4.27	7.40	0.02			
Soil KF11	80–85	5.0	10.7	2.6	2.7	7.3	8.4	0.9	0.5	1.3	1.0	0.5	1.3	1.0	1.24	1.81	3.05	2.34	3.36	0.02			
Soil KF12	85–92	4.4	9.5	2.2	2.9	7.5	8.7	0.7	0.7	1.1	0.9	0.7	1.1	0.9	0.93	1.62	2.55	1.45	1.96	0.01			
Soil RV1	0–10	11.1	16.1	4.4	6.7	7.1	6.1	1.0	0.6	2.6	1.9	0.6	2.6	1.9	2.20	2.73	4.94	4.44	8.98	0.06			
Soil RV2 + 3	10–18	9.2	10.0	2.1	7.6	3.7	6.0	0.8	0.8	1.7	1.4	0.8	1.7	1.4	0.96	1.71	2.67	1.61	6.34	0.02			
Soil RV4 + 5	19–30	7.1	7.9	1.9	6.4	4.8	5.4	0.4	0.9	1.5	1.1	0.9	1.5	1.1	0.70	1.35	2.05	0.72	3.11	0.02			
Soil RV6	30–36	10.9	9.9	3.2	7.5	4.1	4.2	1.1	0.7	2.4	1.6	0.7	2.4	1.6	1.64	1.69	3.33	3.43	5.80	0.03			
Tephra RV V1477	36–41	11.7	13.6	6.6	1.7	0.6	0.9	1.5	0.1	-	1.8	0.1	-	1.8	4.00	2.30	6.31	9.94	12.99	-			
Soil RV7	41–42	7.2	5.5	2.1	6.5	3.8	4.0	0.3	0.9	1.4	1.0	0.9	1.4	1.0	0.74	0.93	1.67	0.64	1.71	0.02			
Soil RV8	43–48	10.2	9.9	4.5	5.3	3.5	3.4	1.1	0.5	2.9	1.5	0.5	2.9	1.5	2.34	1.68	4.02	4.92	6.32	0.03			
Tephra RV Ö1362	48–52	1.0	0.4	0.3	0.6	0.2	0.2	1.4	0.6	-	0.1	0.6	-	0.1	0.16	0.06	0.22	0.38	0.19	-			
Soil RV9	53–63	7.4	8.5	3.4	5.2	5.3	4.4	0.7	0.7	1.9	1.2	0.7	1.9	1.2	1.46	1.45	2.91	2.23	3.25	0.02			
Soil RV10	63–75	5.1	6.1	1.3	4.9	5.8	4.2	0.1	1.0	1.4	0.8	1.0	1.4	0.8	0.42	1.03	1.46	0.17	0.23	0.01			

Table 3
Bulk mineralogy of the studied pedons and tephra samples at Kálfafell (KF) and Reynivellir (RV).

Sample	Depth cm	Quartz	Plagioclase	Pyroxene	Zeolite
Soil KF1	0–10	*	**	**	*
Soil KF2	10–20	*	**	**	*
Soil KF3	20–30	*	**	**	tr
Soil KF4	30–40	*	**	**	tr
Soil KF5	40–45	*	**	**	tr
Soil KF6	45–50	*	**	**	tr
Tephra KF V1477	50–54	tr	**	**	-
Soil KF7	54–59	*	**	**	*
Soil KF8	60–65	*	**	**	tr
Soil KF9	65–70	*	**	**	tr
Tephra KF Ö1362	71–74	-	tr	-	-
Soil KF10	75–80	*	**	**	tr
Soil KF11	80–85	*	**	**	tr
Soil KF12	85–92	*	**	**	tr
Soil RV1	0–10	*	**	**	tr
Soil RV2 + 3	10–18	*	**	**	tr
Soil RV4 + 5	19–30	*	**	**	*
Soil RV6	30–36	*	**	**	tr
Tephra RV V1477	36–41	*	**	**	-
Soil RV7	41–42	*	**	**	tr
Soil RV8	43–48	*	**	**	tr
Tephra RV Ö1362	48–52	*	tr	-	-
Soil RV9	53–63	-	**	**	tr
Soil RV10	63–75	*	**	**	**

tr = trace amounts, * = low, ** = medium, - = not detected.

with a small amount of quartz. The rhyolitic Ö1362 was strongly affected by its amorphous nature. Based on our investigations we found traces of plagioclase, but additionally incorporated a small amount of quartz at Reynivellir.

Investigations of the clay fraction (presented in Table 4) of the soils at both sites discerned the presence of layer silicates, with different types found at each location. Smectite was found to be present at Kálfafell (Fig. 7), but was absent at Reynivellir where hydroxy interlayered

Table 4
Layer silicates found in the clay size fraction of the studied pedons and tephra samples at Kálfafell (KF) and Reynivellir (RV).

Sample	Depth cm	Smectite	HI minerals
Soil KF1	0–10	**	-
Soil KF2	10–20	**	-
Soil KF3	20–30	*	-
Soil KF4	30–40	*	-
Soil KF5	40–45	**	-
Soil KF6	45–50	*	-
Tephra KF V1477	50–54	tr	-
Soil KF7	54–59	*	-
Soil KF8	60–65	tr	-
Soil KF9	65–70	*	-
Tephra KF Ö1362	71–74	-	-
Soil KF10	75–80	*	-
Soil KF11	80–85	*	-
Soil KF12	85–92	tr	-
Soil RV1	0–10	-	*
Soil RV2 + 3	10–18	-	*
Soil RV4 + 5	19–30	-	*
Soil RV6	30–36	-	*
Tephra RV V1477	36–41	-	*
Soil RV7	41–42	-	*
Soil RV8	43–48	-	*
Tephra RV Ö1362	48–52	-	-
Soil RV9	53–63	-	*
Soil RV10	63–75	-	tr

tr = trace amounts, * = low, ** = medium, - = not detected.

(HI) minerals were found instead (Fig. 8). Traces of plagioclase and zeolite were found in some samples at both sites, but in insignificant quantities and are therefore not shown in the tables.

The clay fraction of the tephra samples showed traces of smectite at Kálfafell and small amounts of HI minerals at Reynivellir in the basaltic V1477 tephra. Phyllosilicates were not found in Ö1362.

TG curves of the soils showed an average thermogravimetric mass loss of 6% at low temperatures (< 200 °C). The main mass loss of 45% average occurred in the temperature range between 200 and 600 °C. At temperatures above 600 °C only a marginal mass loss was recorded. DSC curves showed a sharp exothermic peak in the temperature range between 200 °C and 600 °C (Fig. 9a and b). In some samples a shoulder at the higher temperature side of the reaction peak was visible at Reynivellir. One distinct exothermic peak around 300 °C was visible for the soils of Kálfafell, but hardly any shoulder was detected. We also detected a distinct but small exothermic peak in two of the Kálfafell samples above 500 °C (521 °C and 540 °C). All reactions (endothermic and exothermic) above 200 °C occurred at slightly higher temperatures at Reynivellir. No reaction was detected above 550 °C. Dehydration generally occurred at low temperatures ≤ 41 °C in the subsoil at Kálfafell and ≤ 74 °C at Reynivellir.

The mass loss in the tephra samples below 200 °C was 2.56% average in V1477 and slightly higher (2.57% average) in Ö1362. In the temperature range 200–600 °C the average mass loss was 2.72% and 3.27% for V1477 and Ö1362 respectively. As shown in Fig. 10, an exothermic peak around 300 °C was detected in the DSC curves of the tephra samples, but this was considerably weaker than those in the soils.

5. Discussion

5.1. Tephra weathering or: how do different tephra weather?

Our investigations showed that both types of tephra were dominated by inorganic material. The OM contents were low and result in a higher pH (H₂O and NaF) compared to the soils (Table 1). Except for the top soil layer at Kálfafell, the highest Al/Si ratios (> 1.0 and even as high as 2.0 in Ö1362 at Kálfafell) in each profile were found in the tephra indicating the amorphous nature of both, V1477 and Ö1362. The predominance of short-range order (SRO) minerals is also confirmed by the Al_p/Al_o ratio which is close to zero in all tephra samples, but slightly higher in Ö1362 at Reynivellir. The weathering rates were generally very low in the tephra. Clay contents in V1477 (around 6%) were considerably higher than in Ö1362 (≤ 0.5). The investigation of the mineralogy showed differences between the two main tephra layers. Rhyolitic tephra consists of hard and brittle particles. They are composed of high amounts of SiO₂, but proportionally little Al₂O₃. Even though the rhyolitic tephra is older, no pedogenic minerals were found. This leads to the conclusion that the rhyolitic tephra consists almost exclusively of pure, volcanic glass and has hardly been altered since its deposition in 1362 CE. In contrast, the bulk mineralogy of V1477 mainly consisted of pyroxene and plagioclase, two minerals with a shorter lifetime compared to quartz and thereby indicative of weathering processes. In the clay fraction we found traces of layer silicates (smectite at Kálfafell and HI minerals at Reynivellir) showing small signs of weathering in the basaltic tephra. In line with previous studies (e.g. Kirkman and McHardy, 1980; Gislason, 2005; Wolff-Boenisch et al., 2004), we suggest a different state of weathering between basaltic and rhyolitic tephra.

The average contents of Fe and Al in the tephra showed small differences between the sites. Nonetheless (Fe, Al)_o at both sites represented by far the main portion of extractable Fe and Al, verifying the amorphous nature of the tephra (e.g. Oelkers and Gislason, 2001). A difference between the two tephra types is affirmed by a high amount of amorphous Fe and Al in V1477, while their presence is very low in Ö1362 (Table 2).

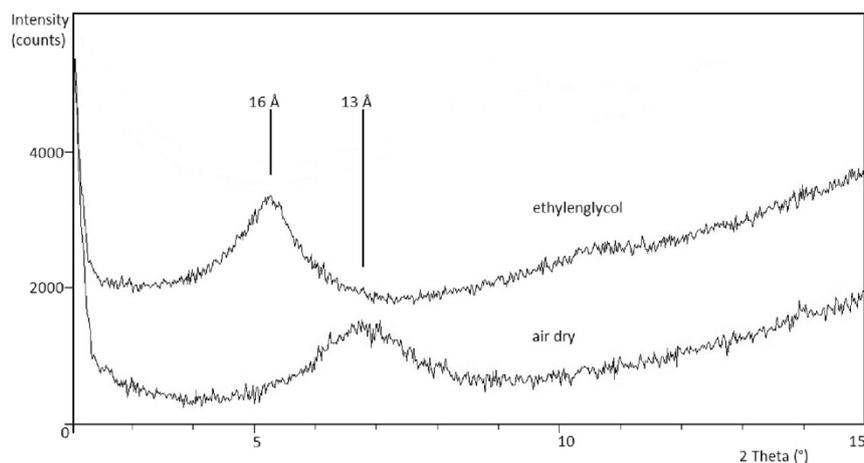


Fig. 7. X-ray diffraction patterns of the clay size fraction of the soil in 40–45 cm depth at Kálfafell (KF5), showing evidence of smectite.

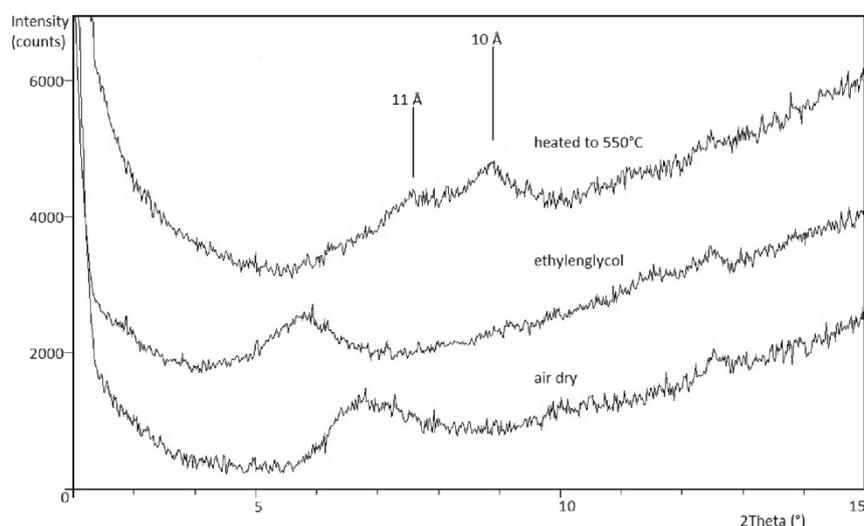


Fig. 8. X-ray diffraction patterns of the clay size fraction of the representative soil in 19–30 cm depth at Reynivellir (RV4 + 5), showing evidence of hydroxy interlayered (HI) minerals.

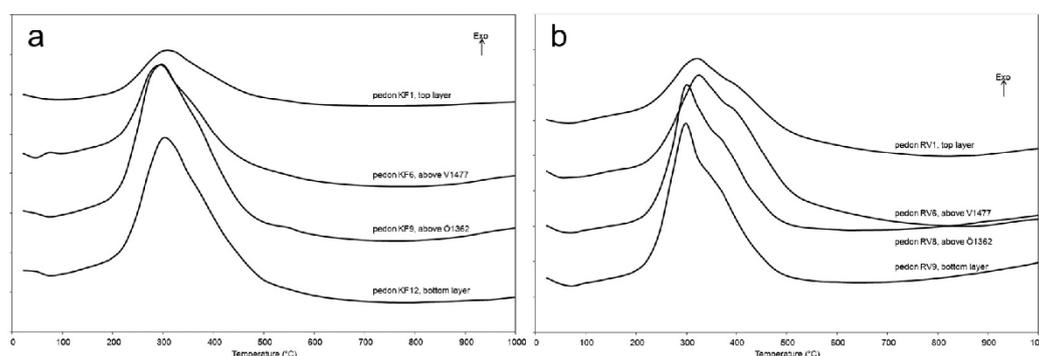


Fig. 9. a and b. Differential scanning calorimetry of selected soil layers at Kálfafell on the left and Reynivellir on the right; one increment on the y-axis corresponds to a heat flow of 0.2 W g^{-1} .

5.2. The impact of tephra on weathering processes and the development of histosols

OM is the determining factor in soil development and weathering behaviour of the investigated soils. The > 20% SOC in the subsoils at both sites meet the criteria for histosol (FAO, 2014). As already observed in other areas of Iceland (Möckel et al., 2017), the steady input

of amorphous and inorganic material (tephra and aeolian material) plays a major role in the genesis of Icelandic histosols. Whenever organically rich soil layers were covered by thick tephra deposits, soil development was returned to a new starting point. Similar processes have been found in other volcanic regions (e.g. Takahashi and Dahlgren, 2016).

None of the histosol sections show evidence of pedon development;

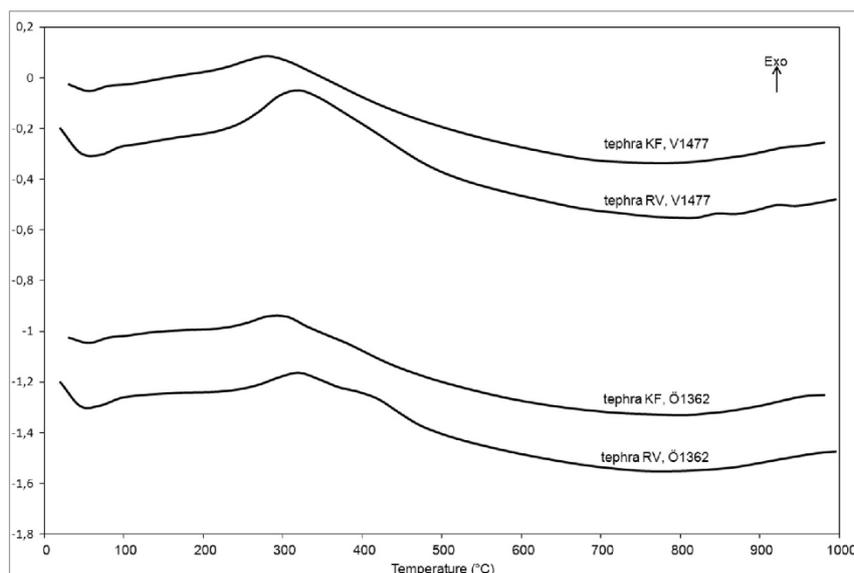


Fig. 10. Differential scanning calorimetry of tephra samples. V1477 above, Ö1362 below; one increment on the y-axis correspond to a heat flow of 0.2 W g^{-1} .

both were comprised of a sequence of buried soils. Over a period of > 530 yrs since the *Veidivötn* eruption in 1477 CE, developing soil was frequently buried by numerous tephra deposits (Fig. 4) and pedogenesis recurrently rejuvenated. During approx. 100 yrs of soil development between the deposition of Ö1362 and V1477, the soils at the two sites hardly received any tephra addition. The intermittent deposition of inorganic material as well as the fact that SOM is protected by build-up of metal-humus complexes, leads to a preservation and further increase of the OM content in the soils. Therefore, the investigated soils are an alteration outcome of both plant residues and volcanic material. Plant residues were protected from decomposition by the prevailing anaerobic conditions and a low soil pH. A repeated addition of tephra and aeolian material may explain the considerably lower carbon content in our soils, compared with the 36–54% C averages in soils purely dominated by plant residues as reported by Loisel et al. (2014) for northern peat soils.

The addition of base-poor, silica-rich, volcanic deposits (such as rhyolitic tephra) in areas with high precipitation contribute to soil acidification, a process further enhanced by cold climate. Organic acids are capable of reducing soil pH and forming metal-humus complexes (Renella et al., 2004). With increasing acidity, the increasing formation of Al-humus complexes protects OM against biodegradation by micro-organisms. Humus competes for dissolved aluminium and leaves only a small portion available to form aluminosilicate minerals (Ugolini and Dahlgren, 2002). Through the formation of organo-metal complexes the SOM is bound and stabilized in the soils (Inoue and Higashi, 1988). A weak correlation between SOC and Al_p/Al_o ratio ($r^2 = 0.30$, $P = 0.0128$) supports the influence of SOM on Al in humus complexes, showing slightly increasing Al_p/Al_o ratio with increasing SOC.

Studies on andosols in Japan by Takahashi and Dahlgren (2016) showed a decrease in allophanic materials with a concomitant increase in Al-humus complexes, indicating the conversion of allophanic to non-allophanic upon prolonged acidification. In contrast to their studies, we found a significant correlation ($r^2 = 0.70$, $P < 0.0001$) between the amount of metal-humus complexes and the clay content. Most soil layers fell short of Al/Si ratios range of 1.7–2 as reported in Arnalds (2004) for organic rich horizons in Icelandic soils. However, Icelandic soils are generally characterized by a wide range of Al/Si ratios, but show considerably lower values than indicated by Parfitt and Kimble (1989) for volcanic soils around the world. Low ratios in our soils are most likely attributed to the ability of ferrihydrite to adsorb Si to the surface, but may also reflect the basaltic origin of the volcanic parent

material (Arnalds et al., 1995; Dahlgren, 1994; Parfitt, 1990).

The generally low clay content in our soils is driven by the prevailing low pH and the high SOM content, that limit the weathering process and inhibit formation of amorphous secondary clay minerals. Ferrihydrite is more abundant than allophane (Table 2).

Our investigations of the mineralogy indicated only a minor influence on the weathering processes by the chemical composition of the inorganic parent material (basaltic and rhyolitic tephra). We rather revealed a strong dependence on the location for the formation of clay minerals. The soils at Kálfafell showed more signs of soil development than those at Reynivellir. Non-allophanic volcanic soils dominated by Al-humus complexes worldwide often contain 2:1 layer silicates (Shoji, 1985). In contrast to previous research, which show that layer silicates are not present or are just minor components of the clay fraction of Icelandic soils (e.g. Arnalds, 2005; Wada et al., 1992), our investigations revealed phyllosilicate at both sites. The clear evidence of smectite in the soils at Kálfafell and HI minerals at Reynivellir were one of the perplexing mineralogical characteristics we found in the studied soils (Table 4). Under acid soil conditions, soil vermiculites and smectites act as sinks for Al released to solution by weathering (Feldman et al., 2008). Aluminium hydroxides incorporate into the interlayer of the 2:1 layer silicates, which leads to the formation of Al-hydroxy interlayered minerals, such as hydroxy interlayered vermiculite (HIV) and smectite (HIS) (Barnhisel and Bertsch, 1989). While at least traces of layer silicates were found in the basaltic V1477 tephra, we did not find any pedogenic minerals in the rhyolitic tephra, suggesting that it was hardly altered since its deposition in 1362 CE.

The results of thermal analysis lead us to the conclusion that mass losses and thermal reactions in our soils are mainly due to the loss of OM, while hiding possible changes in the mineral compounds. Decomposition and combustion reactions of organic fractions with slightly different thermal stabilities occurred at both investigated sites. SOM at Kálfafell seems to be made up of more thermolabile components than those at Reynivellir. The distinct exothermic reaction around 300 °C indicate a thermal degradation of less condensed compounds, for example hemicelluloses and celluloses (e.g. Grisi et al., 1998; Guo et al., 2016; Yang et al., 2007). The shoulders at the higher temperature side of the reaction peaks in DSC-curves of some soils at Reynivellir refer to the degradation of more stable compounds of the OM.

Despite the inorganic material, none of the soil layers reached the criteria $\text{Al}_o + 0.5\text{Fe}_o \geq 2.0$ for andic properties (FAO, 2014; Soil Survey Staff, 2014). Nonetheless, the values of some layers in both profiles

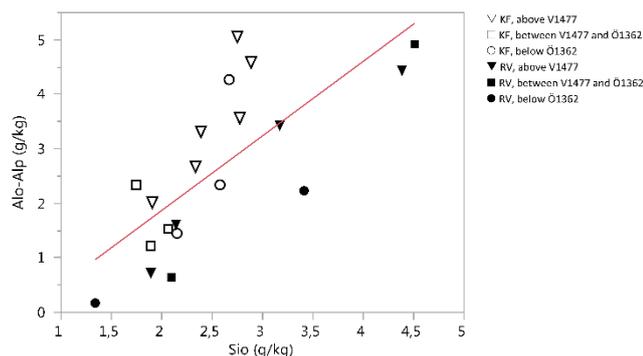


Fig. 11. Correlation between Si_o and $Al_o - Al_p$ ($r^2 = 0.56$, $y = -0.86663 + 1.3680669x$, $P = 0.0002$).

were close to the defined limit. Amorphous Al, Fe and their oxides were the major fractions in the soils but there were also considerable amounts of organically bound Al and Fe. Indicated by the fact that there was no significant correlation between SOM and Al_p ($r^2 = 0.22$, $P = 0.0366$), but visibly more Al_p in the soils at Reynivellir, the SOM was more likely to be Al bound there. The amorphous Al ($Al_o - Al_p$) were highest in the top layers and in the soil above V1477. Similar to the research by García-Rodeja et al. (2004) on different European volcanic soils, the histosols in our research showed increasing Si_o with increasing content of amorphous Al (Fig. 11). The correlation was found to be weaker than the average in their studies, presumably due to higher content of OM in our soils. High amounts of Al are bound in OM while Fe is linked to amorphous constituents. Compared to the amorphous Al, the content of amorphous Fe ($Fe_o - Fe_p$) was significantly higher. It is likely that the strong influence of Fe in the investigated soils result from numerous basaltic tephra layers throughout the profiles.

Most Al_p/Al_o ratios were in the typical range for non-allophanic soils (Nanzyo et al., 1993). All soil samples from Reynivellir exceed the critical level of 0.5, indicating the dominance of aluminous metal-organic complexes (Kleber et al., 2004). However, Al_p/Al_o ratios below 0.5 indicate the influence of inorganic constituents in some soil layers at Kálfafell. The greatest influence of andic material accompanied by low SOM content was found in the layer just above V1477 at Kálfafell. Nanzyo et al. (1993) reported a decrease of Al_p/Al_o ratio in volcanic ash soils (mainly andosols) with increasing depth. There is no such trend visible in our research due to the steady input of volcanic material. The weathering of V1477 is reflected in the lowest Al_p/Al_o value in the layer just above this tephra at Kálfafell, suggesting an increase of allophanic properties in the soils due to the precipitation of the basaltic tephra. There is no doubt that tephra has appreciably impacted the soil weathering and properties of the investigated soils.

As opposed to the different state of weathering in the tephra, soils originated from basaltic and rhyolitic tephra hardly showed differences in the mineralogy, but did so in terms of chemical characteristics. The Fe_o/Fe_d ratio has widely been used to indicate the degree of crystallinity or “age” of Fe oxides (Mizota and van Reeuwijk, 1989) and has

been found to be a sensitive index of soil weathering and soil development (Malucelli et al., 1999). Fe_o/Fe_d ratios in our soils were in the range between 1.1 and 2.9 and therefore rank very high, indicating a low degree of weathering. Similar studies on andosols in Taiwan by Tsai et al. (2010) show much lower ratios between 0.2 and 0.9 at similar pH conditions and basaltic parent material. While the most influential factor in their study was the climate, which was predominantly subtropical and therefore beneficial for weathering, the OM and anaerobic conditions were the determining factors contributing to the low weathering rates in our histosols.

Fig. 12a and b shows the changing degree of weathering by depth in both profiles. By means of the Fe_o/Fe_d ratios, the weathering rates were higher close to the basaltic tephra. While alteration of soils formed in V1477 started soon after tephra deposition and showed a decreasing degree of weathering by the age of soil, there were hardly any signs of weathering in the soils developed from Ö1362. The discussed trend is more obvious at Kálfafell, but exists at both sites. Nonetheless our investigations suggest that the chemical composition of the tephra as parent material has just a minor influence on the alteration of the minerals in the histosols. Moreover, the main factor of pedogenesis in the investigated soils is the OM, but the influence of tephra and aeolian material from external sources must be taken in consideration.

6. Conclusion

The development of the investigated soils is an outcome of both organic and volcanic (tephra and aeolian) material. OM was the determining driver for soil development and the major factor inhibiting weathering in the investigated histosols. Through thick tephra layers, inorganic material was added to the highly organic soils. As a result, plant residues, as well as the soil itself, were protected by the prevailing anaerobic conditions.

The chemical composition of inorganic parent material has an insignificant influence on minerals formed during pedogenesis. In fact, local conditions may contribute to formation of different clay minerals. Icelandic histosols are known for their lack of layer silicates, however we demonstrate smectite and hydroxy interlayered minerals as an alteration product in the soils.

This study improves our understanding of soil forming processes in histosols following tephra deposition. The findings are important for Iceland in particular, but may have wide-ranging influence on the management of volcanic soils worldwide.

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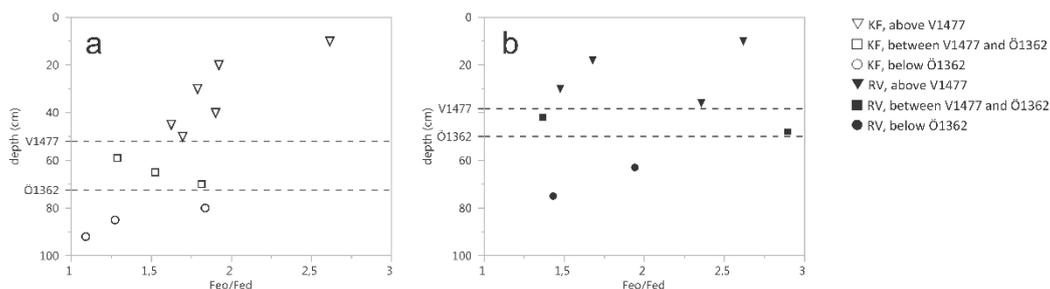


Fig. 12. a and b. Changing degree of weathering (Fe_o/Fe_d) by depth, Kálfafell on the left and Reynivellir on the right.

research.

References

- Aaby, B., Berglund, B.E., 1986. Characterisation of lake and peat deposits. In: Berglund, B.E. (Ed.), *Handbook of Holocene Palaeoecology and Paleohydrology*. J. Wiley, Chichester, pp. 231–246.
- Arnalds, Ó., 1993. Leir í íslenskum jarðvegi. *Náttúrufræðingurinn* 63, 73–85.
- Arnalds, Ó., 2004. Volcanic soils of Iceland. *Catena* 56, 3–20.
- Arnalds, Ó., 2005. Icelandic soils. *Dev. Quat. Sci.* 5, 309–318.
- Arnalds, Ó., 2008. Soils of Iceland. *Jökull* 58, 409–421.
- Arnalds, Ó., 2010. Dust sources and deposition of Aeolian materials in Iceland. *Icel. Agric. Sci.* 23, 3–21.
- Arnalds, Ó., 2015. *The Soils of Iceland*. Springer, Netherlands.
- Arnalds, Ó., Kimble, J., 2001. Andisols of deserts in Iceland. *Soil Sci. Soc. Am. J.* 65, 1778–1786.
- Arnalds, Ó., Óskarsson, H., 2009. Íslenskur jarðvegur. *Náttúrufræðingurinn* 78, 107–121.
- Arnalds, Ó., Hallmark, C.T., Wilding, L.P., 1995. Andisols from 4 different regions of Iceland. *Soil Sci. Soc. Am. J.* 59, 161–169.
- Arnalds, Ó., Olafsson, H., Dagsson-Waldhauserova, P., 2014. Quantification of iron-rich volcanogenic dust emissions and deposition over ocean from Icelandic dust sources. *Biogeosciences* 11, 5941–5967.
- Arnalds, Ó., Dagsson-Waldhauserova, P., Olafsson, H., 2016. The Icelandic volcanic Aeolian environment: processes and impacts - a review. *Aeolian Res.* 20, 176–195.
- Austrian Standard Institute, 2006. ÖNORM L 1083, *Chemische Bodenuntersuchungen - Bestimmung der Acidität (pH-Wert)*. Vienna.
- Barnhisel, R.M., Bertsch, 1989. Chlorites and hydroxy-interlayered vermiculite and smectite. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environment*. SSSA, Madison, Wisconsin, pp. 729–788.
- Barros, N., Salgado, J., Feijoo, S., 2007. Calorimetry and soil. *Thermochim. Acta* 458, 11–17.
- Batjes, N.H., 1996. Total carbon and nitrogen in the soils of the world. *Eur. J. Soil Sci.* 47, 151–163.
- Björnsson, H., Pálsson, F., 2008. Icelandic glaciers. *Jökull* 58, 365–386.
- Blakemore, L.C., Searle, P.L., Daly, B.K., 1987. *Methods for Chemical Analysis of Soils*. NZ Soil Bureau, Dept. of Scientific and Industrial Research, Lower Hutt, N.Z.
- Bridgman, S.D., Johnston, C.A., Pastor, J., Updegraff, K., 1995. Potential feedbacks of northern wetlands on climate-change - an outline of an approach to predict climate-change impact. *Bioscience* 45, 262–274.
- Brindley, G.W., Brown, G., 1980. *Crystal Structures of Clay Minerals and Their X-Ray Identification*. Mineralogical Society, London.
- Childs, C.W., Matsue, N., Yoshinaga, N., 1991. Ferrihydrite in volcanic ash soils of Japan. *Soil Sci. Plant Nutr.* 37, 299–311.
- Clymo, R.S., 1987. The ecology of peatlands. *Sci. Prog. Oxf.* 71, 593–614.
- Compton, K., Bennett, R.A., Hreinsdóttir, S., 2015. Climate-driven vertical acceleration of Icelandic crust measured by continuous GPS geodesy. *Geophys. Res. Lett.* 42, 743–750.
- Crovisier, J.L., Honnorez, J., Fritz, B., Petit, J.C., 1992. Dissolution of subglacial volcanic glasses from Iceland - laboratory study and modeling. *Appl. Geochem.* 7, 55–81.
- Dahlgren, R.A., 1994. Quantification of allophane and imogolite. In: Amonette, J.E., Zelazny, L.W. (Eds.), *Quantitative Methods in Soil Mineralogy*. Soil Sci. Soc. Am, Madison, WI, pp. 430–451.
- Dahlgren, R., Shoji, S., Nanzyo, M., 1993. Chapter 5 mineralogical characteristics of volcanic ash soils. In: Shoji, S., Nanzyo, M., Dahlgren, R. (Eds.), *Developments in Soil Science*. Elsevier, pp. 101–143.
- Dahlgren, R.A., Saigusa, M., Ugolini, F.C., 2004. The Nature, Properties and Management of Volcanic Soils, *Advances in Agronomy*. Academic Press, pp. 113–182.
- Eddudóttir, S.D., Erlendsson, E., Tinganelli, L., Gísladóttir, G., 2016. Climate change and human impact in a sensitive ecosystem: the Holocene environment of the Northwest Icelandic highland margin. *Boreas* 45, 715–728.
- Einarsson, M.Á., 1980. Climate of Iceland. In: Van Loon, H. (Ed.), *World Survey of Climatology, Climates of the Oceans*, vol. 15. Elsevier, Amsterdam, pp. 673–697.
- Eiríksdóttir, E.S., Gíslason, S.R., Oelkers, E.H., 2013. Does temperature or runoff control the feedback between chemical denudation and climate? Insights from NE Iceland. *Geochim. Cosmochim. Acta* 107, 65–81.
- FAO, 2014. *World Reference Base for Soil Resources 2014, International Soil Classification System for Naming Soils and Creating Legends for Soil Maps, Update 2015*. Food and Agriculture Organization of the UN.
- Feldman, S.B., Shang, C., Zelazny, L.W., 2008. Soil mineralogy. In: Chestworth, W. (Ed.), *Encyclopedia of Soil Sciences*. Springer, Dordrecht, Netherlands, pp. 678–686.
- García-Rodeja, E., Nóvoa, J.C., Pontevedra, X., Martínez-Cortizas, A., Buurman, P., 2004. Aluminium fractionation of European volcanic soils by selective dissolution techniques. *Catena* 56, 155–183.
- Gísladóttir, G., Erlendsson, E., Lal, R., Bigham, J., 2010. Erosional effects on terrestrial resources over the last millennium in Reykjanes, southwest Iceland. *Quat. Res.* 73, 20–32.
- Gísladóttir, G., Erlendsson, E., Lal, R., 2011. Soil evidence for historical human-induced land degradation in West Iceland. *Appl. Geochem.* 26, S28–S31.
- Gíslason, S.R., 2005. 12. Chemical weathering, chemical denudation and the CO₂ budget for Iceland. In: Caseldine, C., Russel, A., Harðardóttir, S., Knudsen, Ó. (Eds.), *Developments in Quaternary Sciences*. Elsevier, pp. 289–307.
- Gíslason, S.R., 2008. Weathering in Iceland. *Jökull* 58, 387–408.
- Gíslason, S.R., Eugster, H.P., 1987. Meteoric water-basalt interactions. I: a laboratory study. *Geochim. Cosmochim. Acta* 51, 2827–2840.
- Gíslason, S.R., Arnórsson, S., Ármannsson, H., 1994. Present Chemical Weathering of Basalt Goldschmidt Conference, Edinburgh. pp. 333–334.
- Gíslason, S.R., Arnórsson, S., Ármannsson, H., 1996. Chemical weathering of basalt in southwest Iceland: effects of runoff, age of rocks and vegetative/glacial cover. *Am. J. Sci.* 296, 837–907.
- Grisi, B., Grace, C., Brookes, P.C., Benedetti, A., Dell'Abate, M.T., 1998. Temperature effects on organic matter and microbial biomass dynamics in temperate and tropical soils. *Soil Biol. Biochem.* 30, 1309–1315.
- Gudmundsson, T., 1978. *Pedological Studies of Icelandic Peat Soils*. Doctoral Thesis. University of Aberdeen.
- Guo, F., Wu, F., Mu, Y., Hu, Y., Zhao, X., Meng, W., Giesy, J.P., Lin, Y., 2016. Characterization of organic matter of plants from lakes by thermal analysis in a N₂ atmosphere. *Sci. Rep.* 6, 22877.
- Hannesdóttir, H., Björnsson, H., Pálsson, F., Aðalgeirsdóttir, G., Guðmundsson, S., 2015. Changes in the southeast Vatnajökull ice cap, Iceland, between ~1890 and 2010. *Cryosphere* 9, 565–585.
- Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *J. Paleolimnol.* 25, 101–110.
- Ingólfsson, Ó., Norðdahl, H., Schomacker, A., 2010. 4 deglaciation and holocene glacial history of Iceland. In: Anders Schomacker, J.K., Kurt, H.K. (Eds.), *Developments in Quaternary Sciences*. Elsevier, pp. 51–68.
- Inoue, K., Higashi, T., 1988. Al- and Fe-humus complexes in Andisols. In: Kinloch, D.I., Shoji, S., Beinroth, F.H., Eswaran, H. (Eds.), *Proc. of the Ninth International Soil Classification Workshop, Properties, Classification, and Utilization of Andisols and Paddy Soils*, Japan, 20 July to 1 August 1987, Washington D.C., USA, pp. 81–96.
- IPCC, 2015. *IPCC Climate Change 2014: Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel of Climate Change*.
- Jennings, A., et al., 2014. Holocene tephra from Iceland and Alaska in SE Greenland Shelf Sediments. *Geol. Soc. Lond., Spec. Publ.* 398, 157–193.
- JMP, 2013. *A business unit of SAS. In: JMP User Guide*. SAS Institute Inc., SAS Campus Drive, Cary.
- Jóhannesson, H., Sæmundsson, K., 2009. *Geological Map of Iceland, 1:500000*. Icelandic Institute of Natural History.
- Jónsdóttir, J.F., 2007. *Water Resources in Iceland-Impacts of Climate Variability and Climate Change*. Doctoral Thesis. Lund University (148 pp).
- Jónsdóttir, J.F., 2008. A runoff map based on numerically simulated precipitation and a projection of future runoff in Iceland/Une carte d'écoulement basée sur la précipitation numériquement simulée et un scénario du futur écoulement en Islande. *Hydrol. Sci. J.* 53, 100–111.
- Kardjilov, M.I., Gísladóttir, G., Gíslason, S.R., 2006. Land degradation in northeastern Iceland: present and past carbon fluxes. *Land Degrad. Dev.* 17, 401–417.
- Kirkman, J.H., McHardy, W.J., 1980. A comparative-study of the morphology, chemical composition and weathering of rhyolitic and andesitic glass. *Clay Miner.* 15, 165–173.
- Kleber, M., Mikutta, C., Jahn, R., 2004. Andosols in Germany - pedogenesis and properties. *Catena* 56, 67–83.
- Larsen, G., 1984. Recent volcanic history of the Veidivötn fissure swarm, southern Iceland — an approach to volcanic risk assessment. *J. Volcanol. Geotherm. Res.* 22, 33–58.
- Larsen, G., Dugmore, A., Newton, A., 1999. Geochemistry of historical-age silicic tephras in Iceland. *The Holocene* 9, 463–471.
- Lawson, I.T., Gathorne-Hardy, F.J., Church, M.J., Newton, A.J., Edwards, K.J., Dugmore, A.J., Einarsson, A., 2007. Environmental impacts of the Norse settlement: palaeoenvironmental data from Myvatnssveit, northern Iceland. *Boreas* 36, 1–19.
- Loisel, J., et al., 2014. A database and synthesis of northern peatland soil properties and Holocene carbon and nitrogen accumulation. *The Holocene* 24, 1028–1042.
- Malucelli, F., Terribile, F., Colombo, C., 1999. Mineralogy, micromorphology and chemical analysis of andosols on the Island of São Miguel (Azores). *Geoderma* 88, 73–98.
- McKeague, J.A., 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in Podzols and some other soils. *Can. J. Soil Sci.* 47, 95–99.
- Mehra, O.P., Jackson, M.L., 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. In: *Clays and Clay Minerals*. Pergamon, pp. 317–327.
- Mizota, C., van Reeuwijk, L.P., 1989. *Clay Mineralogy and Chemistry of Soils Formed in Volcanic Material in Diverse Climatic Regions*. 90-6672-035-2. ISRIC - World Soil Information, Wageningen.
- Möckel, S.C., Erlendsson, E., Gísladóttir, G., 2017. Holocene environmental change and development of the nutrient budget of histosols in North Iceland. *Plant Soil* 418, 437–457.
- Moore, D.M., Reynolds, R.C., 1997. *X-ray Diffraction and the Identification and Analysis of Clay Minerals*. Oxford University Press, Oxford.
- Nanzyo, M., Dahlgren, R., Shoji, S., 1993. Chapter 6 chemical characteristics of volcanic ash soils. In: Shoji, S., Nanzyo, M., Dahlgren, R. (Eds.), *Volcanic Ash Soils - Genesis, Properties and Utilization*. Elsevier, pp. 145–187.
- Oelkers, E.H., Gíslason, S.R., 2001. The mechanism, rates and consequences of basaltic glass dissolution: I. an experimental study of the dissolution rates of basaltic glass as a function of aqueous Al, Si and oxalic acid concentration at 25 °C and pH 3 and 11. *Geochim. Cosmochim. Acta* 65, 3671–3681.
- Ogilvie, A.E.J., Jónsson, T., 2001. "Little Ice Age" research: a perspective from Iceland. *Clim. Chang.* 48, 9–52.
- Óladóttir, B.A., Sigmarrson, O., Larsen, G., Thordarson, T., 2008. Katla volcano, Iceland: magma composition, dynamics and eruption frequency as recorded by Holocene tephra layers. *Bull. Volcanol.* 70, 475–493.
- Óladóttir, B.A., Larsen, G., Sigmarrson, O., 2011. Holocene volcanic activity at Grimsvötn, Bárðarbunga and Kverkfjöll subglacial centres beneath Vatnajökull, Iceland. *Bull. Volcanol.* 73, 1187–1208.

- Ólafsson, H., Furger, M., Brümmer, B., 2007. The weather and climate of Iceland. *Meteorol. Z.* 5–8.
- Pagli, C., Sigmundsson, F., 2008. Will present day glacier retreat increase volcanic activity? Stress induced by recent glacier retreat and its effect on magmatism at the Vatnajökull ice cap, Iceland. *Geophys. Res. Lett.* 35, L09304.
- Parfitt, R.L., 1990. Allophane in New Zealand - a review. *Aust. J. Soil Res.* 28, 343–360.
- Parfitt, R.L., Henmi, T., 1982. Comparison of an oxalate-extraction method and an infrared spectroscopic method for determining allophane in soil clays. *J. Soil Sci. Plant Nutr.* 28, 183–190.
- Parfitt, R.L., Kimble, J.M., 1989. Conditions for formation of allophane in soils. *Soil Sci. Soc. Am. J.* 53, 971–977.
- Parfitt, R.L., Wilson, A.D., 1985. Estimation of allophane and halloysite in three sequences of volcanic soils, New Zealand. *Catena*(supplement 7) (Braunschweig).
- Renella, G., Landi, L., Nannipieri, P., 2004. Degradation of low molecular weight organic acids complexed with heavy metals in soil. *Geoderma* 122, 311–315.
- Riedmüller, G., 1978. Neofomations and transformations of clay minerals in tectonic shear zones. *Tschermaks Mineral. Petrogr. Mitt.* 25, 219–242.
- Schwertmann, U., 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. *Z. Pflanzenernähr. Dung. Bodenkd.* 105, 194–202.
- Shang, C., Zelazny, L.W., 2008. Selective dissolution techniques for mineral analysis of soils and sediments. In: Ulery, A.L., Drees, I.R. (Eds.), *Methods of Soil Analysis. Part 5. Mineralogical Methods*. Soil Sci. Soc. Am, Madison, WI, pp. 33–80.
- Sharma, K., Self, S., Blake, S., Thordarson, T., Larsen, G., 2008. The AD 1362 Öræfajökull eruption, S.E. Iceland: physical volcanology and volatile release. *J. Volcanol. Geotherm. Res.* 178, 719–739.
- Shoji, S., 1985. Genesis and properties of non-allophanic andisols in Japan. *Appl. Clay Sci.* 1, 83–88.
- Smykatz-Kloss, W., 1974. *Differential Thermal Analysis: Application and Results in Mineralogy*. Springer-Verlag.
- Soil Survey Staff, 2014. *Keys to Soil Taxonomy 2014*, 12th ed. USDA - Natural Resources Conservation Service, Washington, DC.
- Stefánsson, A., Gíslason, S.R., 2001. Chemical weathering of basalts, Southwest Iceland: effect of rock crystallinity and secondary minerals on chemical fluxes to the ocean. *Am. J. Sci.* 301, 513–556.
- Streeter, R., Dugmore, A., 2014. Late-Holocene land surface change in a coupled social-ecological system, southern Iceland: a cross-scale tephrochronology approach. *Quat. Sci. Rev.* 86, 99–114.
- Takahashi, T., Dahlgren, R.A., 2016. Nature, properties and function of aluminum-humus complexes in volcanic soils. *Geoderma* 263, 110–121.
- Thorarinnsson, S., 1958. The Öræfajökull eruption of 1362. *Acta Natur. Islandica* 2, 1–99.
- Þorbjarnarson, H., 2016. *Soil Evolution in the Dynamic Area South of Vatnajökull*. Master's Thesis. University of Iceland.
- Thordarson, T., Larsen, G., 2007. Volcanism in Iceland in historical time: volcano types, eruption styles and eruptive history. *J. Geodyn.* 43, 118–152.
- Troels-Smith, J.A., 1955. Karakterisering Af Løse Jordarter. In: *Characterization of Unconsolidated Sediments*. Reitzel, Copenhagen.
- Tsai, C.C., Chen, Z.S., Kao, C.I., Ottner, F., Kao, S.J., Zehetner, F., 2010. Pedogenic development of volcanic ash soils along a climosequence in Northern Taiwan. *Geoderma* 156, 48–59.
- Ugolini, F.C., Dahlgren, R., 2002. Soil development in volcanic ash. *Global J. Environ. Res.* 6, 69–81.
- Vilmundardóttir, O.K., Gísladóttir, G., Lal, R., 2014. Early stage development of selected soil properties along the proglacial moraines of Skaftafellsjökull glacier, SE-Iceland. *Catena* 121, 142–150.
- Vilmundardóttir, O.K., Gísladóttir, G., Lal, R., 2015a. Between ice and ocean; soil development along an age chronosequence formed by the retreating Breiðamerkurjökull glacier, SE-Iceland. *Geoderma* 259, 310–320.
- Vilmundardóttir, O.K., Gísladóttir, G., Lal, R., 2015b. Soil carbon accretion along an age chronosequence formed by the retreat of the Skaftafellsjökull glacier, SE-Iceland. *Geomorphology* 228, 124–133.
- Wada, K., 1989. Allophane and imogolite. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environment*. Soil Sci. Soc. Am, Madison, WI, pp. 1051–1087.
- Wada, K., Arnalds, O., Kakuto, Y., Wilding, L.P., Hallmark, C.T., 1992. Clay minerals of four soils formed in eolian and tephra materials in Iceland. *Geoderma* 52, 351–365.
- Wilson, M.J., 1987. *A Handbook of Determinative Methods in Clay Mineralogy*. Blackie and Sons, Glasgow and London.
- Wolff-Boenisch, D., Gíslason, S.R., Oelkers, E.H., Putnis, C.V., 2004. The dissolution rates of natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from 25 to 74 degrees C. *Geochim. Cosmochim. Acta* 68, 4843–4858.
- Yang, H.P., Yan, R., Chen, H.P., Lee, D.H., Zheng, C.G., 2007. Characteristics of hemi-cellulose, cellulose and lignin pyrolysis. *Fuel* 86, 1781–1788.

Paper 2

Weathering of tephra and the formation of pedogenic minerals in young Andosols, South East Iceland

Author's contribution:

Theresa Bonatutzky (TB), Guðrún Gísladóttir, Egill Erlendsson and Franz Ottner planned the study. Friðþór S. Sigurmundsson, María Svavarsdóttir and Páll V. Kólka conducted fieldwork and sampling at the dryland sites Steinadalur and Kvísker. Preparation of the soil and tephra samples and all analyses (except for analyses of Total C and N and ICEP-AES analyses of the extracted oxides and hydroxides) were done by TB at BOKU and HÍ. The data analysis and writing of the manuscript were done by TB. Co-Authors, members of the PhD committee, anonymous reviewers and the journal editors provided useful comments and suggestions on the manuscript. To include the article in the thesis, no permission from the journal was required



Weathering of tephra and the formation of pedogenic minerals in young Andosols, South East Iceland

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ABSTRACT

Frequent tephra deposition and a steady influx of aeolian material of multiple origins, dominate soil formation in Iceland. Little is known about the weathering behaviour, mineral formation and alteration of tephra and Icelandic Andosols after tephra deposition.

Two sampling sites in the volcanically active area south of Vatnajökull in South East Iceland were selected according to the presence of two distinctive tephra layers; a light coloured, rhyolitic, tephra from the Óræfajökull eruption in 1362 CE and a black, basaltic, Veiðivötn tephra from 1477 CE. Through a combination of physical, chemical and mineralogical analyses, the present research improves the understanding of changes in properties, weathering processes and mineralogy in Andosols after the deposition of tephra and aeolian material. It adds significant knowledge about the impact of explosive volcanic eruptions and consequences of heavy tephra fall and erosion on soil development in Iceland in particular, but may have wide-ranging influence on the management of volcanic soils worldwide.

Both pedons can be classified as Andosols, showing silandic and vitric soil properties. The soils were acidic and dominated by sand. Fe_0/Fe_d ratios above 0.75 in all soils indicated a low degree of soil development. The major portion of the clay size particles mainly derived from poorly crystalline and amorphous constituents (e.g. allophane and ferrihydrite). In spite of the low soil age (less than 650 years) and the prevailing cool climatic conditions, we observed signs of pedogenesis and the presence of secondary clay minerals in both, soils and tephra. It was mainly secondary chlorite, which could be verified. Usually it takes more time under given environmental conditions for clay minerals to form and alter. The phyllosilicates we found are supposedly attributed to aeolian influx of material from older, more weathered, more developed eroded surfaces of unknown origin and chemical composition, maybe from sources outside Iceland. This and the particular local site conditions (e.g. moisture, soil temperature, SOM), rather than the primary composition of the parent material, are the driving factors in the development of the investigated Andosols and the alteration of minerals. Additionally, the high volcanic activity in Iceland constantly provides new tephra to the soils.

1. Introduction

Soils developed from volcanic ejecta cover about 1% of the Earth's terrestrial surface (e.g. Dahlgren et al., 2004; Takahashi and Shoji, 2002). They show special characteristics and properties, which separate them from other soil types, mainly attributed to two dominant pedogenic processes: the accumulation of organic carbon (OC) and the formation of poorly-crystalline and non-crystalline material (Dahlgren et al., 2004; Ugolini and Dahlgren, 2002).

Situated on the Mid-Atlantic Ridge and above the Iceland mantle plume, Iceland is characterized by high volcanic activity (Einarsson, 2008). On average, every two years an eruption occurs (Compton et al., 2015; Pagli and Sigmundsson, 2008). The bedrock consists mostly of basaltic igneous rocks, while tephra composition ranges from basaltic to rhyolitic (Thordarson and Larsen, 2007). In such a dynamic environment, soil surface is constantly recharged with fresh parent material (consolidated rock and tephra), while subsoils are preserved and continue to develop after burial (e.g. Bonatotzky et al., 2019; Gísladóttir

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et al., 2010). All Icelandic soils, even highly organic Histosols, exhibit andic soil properties to some degree (Bonatotzky et al., 2019).

86% of Iceland is covered by Andosols (Arnalds and Óskarsson, 2009), a Reference Soil Group (according to World Reference Base, WRB; IUSS Working Group WRB, 2015) developed from volcanic ejecta. Their distinct properties, e.g. low bulk density and high OC, arise largely from the formation of amorphous and poorly-crystalline short-range order (SRO) secondary minerals and hydroxides, e.g. allophane, ferrihydrite and metal-humus complexes (Dahlgren et al., 2004; Nanzyo et al., 1993). These transformations play an important role in soil development as the clay minerals in Andosols are formed in situ, and not by translocation or leaching and precipitation in subsurface horizons (Dahlgren et al., 2004). However, layer silicates in Icelandic Andosols are rare (Bonatotzky et al., 2019).

Among the majority of volcanic soils worldwide, Icelandic soils show special characteristics: their formation started about 10,000 years ago, when Pleistocene glaciers retreated due to a warming climate. Thus, they are of Holocene age and can be considered “young” (Arnalds and Kimble, 2001). Further, they receive large inputs of inorganic aeolian sediments and occur in low temperatures with a wide range of precipitation. Similar conditions can only be found in a few other locations on Earth, e.g. Kamchatka (Kuznetsova and Motenko, 2018; Zakharikhina, 2006).

Iceland has extensive unstable sandy surfaces which are subject to frequent high-velocity winds. Aeolian transport of tephra over long distances and re-deposition is very common. This results in intense wind erosion events. Erosion has removed much of the soils that formed in the aeolian and tephra sediments (e.g. Arnalds et al., 2001; Dugmore et al., 2009; Gísladóttir et al., 2011; Gísladóttir et al., 2010; Möckel et al., 2017). Up to 80% of the windblown dust is amorphous basaltic volcanic glass (Arnalds et al., 2016). Frequent tephra deposition and a steady flux of aeolian material of multiple origins, which normally exhibit characteristics dissimilar to the material above and below, dominate soil formation in Iceland (Arnalds, 2008).

With the intermittent deposition of volcanic ash (Óladóttir, 2009), each addition of new material rejuvenates soil development processes so that Andosols may be maintained as a relatively stable soil conditions (Dahlgren et al., 2004). The fine particle size, glassy nature, high porosity and high permeability of tephra enhance weathering and interaction in the soil environment (Dahlgren et al., 1997; Lowe, 1986). Not least due to the nature of the parent material, Icelandic soils exhibit high weathering rates despite the prevalent cool climate (Gíslason et al., 1996; Gíslason et al., 2009).

The most common weathering residuals of basalts comprise of mostly amorphous allophane and/or imogolite of variable Al/Si ratios and poorly crystalline ferrihydrite (Arnalds, 2004), all of them showing large specific surface area and high chemical reactivity. Thus, they are more sensitive to chemical dissolution than crystalline clay minerals (Wada, 1989). Despite the overall rapid weathering of tephra, rhyolitic tephra weathers much more slowly than basaltic (Bonatotzky et al., 2019; Gíslason, 2005; Wolff-Boenisch et al., 2004).

The least mobile elements released during chemical weathering of basalt are aluminium (Al) and iron (Fe) (Gíslason, 2008). Their active forms hold an important role in Andosols, since they determine physical and chemical soil properties (Nanzyo et al., 1993), e.g. the formation and stabilization of soil aggregates.

The availability of Al appears to be a critical factor for the formation of allophane. Investigations on volcanic soils in Japan (e.g. Shoji and Fujiwara, 1984), New Zealand (e.g. Parfitt et al., 1983; Russell et al., 1981) but also Mediterranean regions (e.g. Vacca et al., 2003) report that the formation of Al-humus complexes inhibits the formation of allophane through competition for Al released by the weathering of volcanic ejecta. Shoji et al. (1982) and Shoji and Fujiwara (1984) found that soil pH(H₂O) is another important factor in allophane formation.

The impact of explosive volcanic eruptions and consequences of heavy tephra fall on vegetation and soil in Iceland are increasingly

understood (e.g. Eddudóttir et al., 2017; úorbjarnarson, 2016), as is the impact upon human’s livelihood (e.g. Thorarinsson, 1958; regarding the historical eruption of Örafajökull in 1362 CE). To date, there has been little research on weathering behaviour, mineral formation and the alteration of tephra and Andosols after tephra deposition in Iceland.

By investigating the physical and chemical properties of soil and tephra and obtaining a deeper insight in their mineralogy, the primary objectives of this study are described as follows:

- 1) How much time does Andosol development require and how fast is “rapid weathering” in Icelandic Andosols?
- 2) Does the high content of amorphous and poorly-crystalline constituents in Andosols decrease with time?
- 3) Do crystalline clay minerals form in young Icelandic Andosols?

Our investigations consider two Andosol profiles in a volcanically active area south of Vatnajökull, southeast Iceland (Fig. 1). The focus is upon two well preserved, most distinct tephra layers; a light coloured, rhyolitic tephra from the Örafajökull eruption in 1362 CE and a black, basaltic Veiðivötn tephra from 1477 CE (Larsen, 1984; Thorarinsson, 1958).

It is hypothesized that the chemical composition of the parent material and the hydrological site conditions are the major factors in soil development and the formation of different layer silicates.

The second hypothesis is that the formation of crystalline pedogenic minerals is possible even in very young soils and prevailing cool climate.

2. Material and methods

2.1. Study sites and material

The two study sites are situated in a lowland area close to the sea in south east Iceland. Kvísker (63°59.443’N, 16°26.029’W; Fig. 1; KV) lies within Öraefi district, in close proximity to the Örafajökull volcano. Steinadalur (64°09.760’N, 16°0.293’W; Fig. 1; SD) is further east in the Suðursveit district. Both sites are free draining (dryland) with vegetation communities comprising of birch (*Betula*) woodland, grasslands, herbs and mosses.

The prevailing climate regime in the region is maritime with cool summers and mild winters. Based on unpublished data from the Icelandic Meteorological Office the mean annual temperature is 5.9 °C (2009–2016), the annual precipitation (1962–2011) is 3500 mm on average. The latter is one of the greatest annual precipitation values recorded in Iceland. Both, temperature and precipitation values are derived from the Kvísker weather station (63°57.576’N, 16°25.465’W, 30 m a.s.l.).

Previous research (úorbjarnarson, 2016) has shown that a former wetland soil at SD converted to a dryland soil following a tephra deposition. This change probably occurred as a consequence of increased soil drainage after the tephra deposition and shows evidence of the drastic impact of volcanic eruptions on soils. Soil erosion is a problem in parts of the area due to steep slopes and interactions between glaciers and glacial rivers, volcanism and land use. Both sites investigated are highly affected by erosion.

The study area is situated outside the active volcanic zone, but strongly affected by the active central volcanoes to the north and west. The bedrock is therefore composed of basaltic lava and hyaloclastite (glassy rocks) (Jóhannesson and Sæmundsson, 2009; Thorarinsson, 1958).

Explosive hydro-magmatic basaltic eruptions were the most common volcanic activity in Iceland during the Holocene (e.g. Larsen and Eiríksson, 2008). Eruptions producing rhyolitic tephra are less common, but at least 24 eruptions have produced silicic tephra since the settlement of Iceland in the late 9th century (Gudmundsson et al., 2008; Larsen et al., 1999).

The eruption of Örafajökull central volcano in 1362 CE is the most

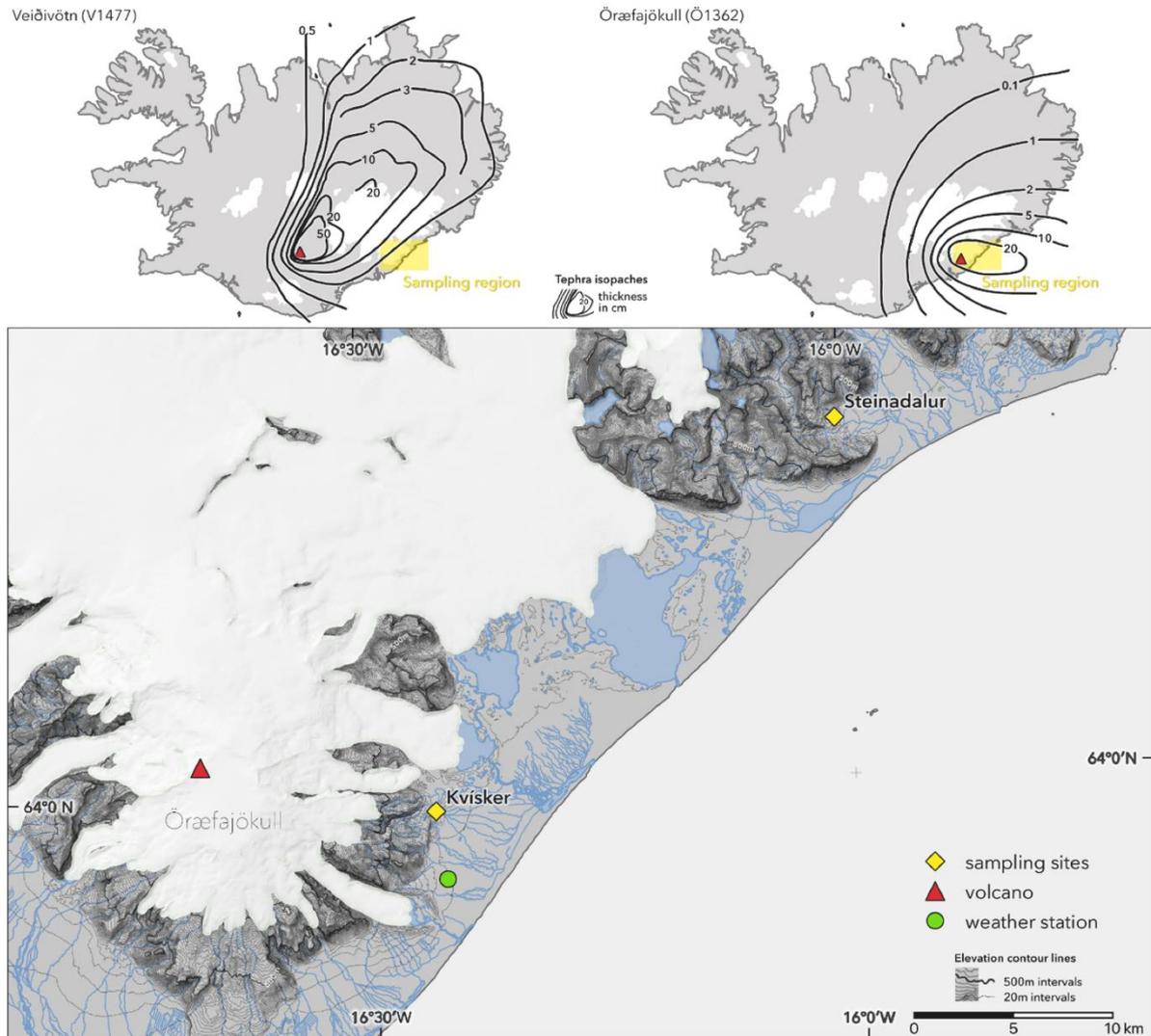


Fig. 1. The research area south of Vatnajökull glacier, SE Iceland. Representative for the great Öræfajökull massif, the red triangle marks Hvannadalshnjúkur at 2110 m a.s.l., the highest peak of Iceland beneath the Vatnajökull glacier. Rectangles show the position of the two sampling sites Kvísker at the foot of Öræfajökull and Steinadalur further to the east. The location of the weather station Kvísker is shown as circle. Isopach maps of the distinctive tephra layers from Veidivötn eruption in 1477 CE (left) and the Öræfajökull eruption in 1362 CE (right) are presented above the map of the research area. On both maps the respective source volcano is marked by a red triangle. Isopach maps have been modified from Thorarinsson (1958) and Larsen (1984). The particular research area is marked by a yellow rectangle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

voluminous explosive silicic eruptions to have occurred in Iceland in historical times, producing at least 10 km^3 of acidic, uncompacted tephra (Gudmundsson et al., 2008; Larsen et al., 1999). According to Thorarinsson (1958) the vast quantity of the erupted ejecta was carried southeast. On the basis of the chemical composition, the rhyolitic Ö1362 tephra can be distinguished from other Icelandic tephra deposits with a similar SiO_2 content of 72.71% on average (e.g. historical Hekla tephra) by its high FeO (average 3.30%), low MgO (close to zero), low CaO content (<1.2%) and high Na_2O (around 5%) values (e.g. Larsen et al., 1999; Wolff-Boenisch et al., 2004).

The 1477 CE a Veidivötn fissure eruption is thought to be the largest explosive basaltic eruption in Iceland during the last 1200 years. More than 10 km^3 of tephra was dispersed towards east, northeast and north, depositing a layer of tephra up to 12 m thick in some places (Larsen, 1984).

Both tephra were formed, immediately deposited on vegetated land and are thus preserved as important tephra marker layers in the research area (Fig. 1). With the aid of the known source volcanic systems, ages

obtained from written documents (Bonatotzky et al., 2019; Höskuldsson, 2019; Óladóttir, 2009; Óladóttir et al., 2011; úorbjarnarson, 2016, Sæmundsson and Larsen, 2019) and known geochemical composition (Larsen, 1984; Sæmundsson and Larsen, 2019; Sharma et al., 2008) these tephra layers form an important parent material in the study area.

2.2. Sampling, profile description

Both sampling sites were selected according to the occurrence the two desired tephra layers detected by test coring with a JMC Backsaver in conjunction with dryland conditions. Due to the absence of a clear horizonation, soil samples were taken at 10 cm depth interval and at 5 cm intervals immediately above and below the two main tephra layers. Where field conditions inhibited the application of this strategy, sampling had to be adapted slightly. Tephra layers, easily distinguishable from the soil, were sampled separately. The samples were kept in sealed plastic bags and stored at $4 \text{ }^\circ\text{C}$ pending analyses. Soil profiles were described in the field according to Schoeneberger et al. (2002). Soil

colour was assessed on field moist soil using a Munsell colour chart.

2.3. Soil sample analyses

Soil and tephra samples were analysed at the University of Natural Resources and Life Science, Vienna and at the University of Iceland. Ammonium oxalate, sodium pyrophosphate and citrate-bicarbonate-dithionite (CBD) were extracted at the Innovation Centre Iceland (Nýsköpunarmiðstöð Íslands). Total carbon (C) and nitrogen (N) were analysed at the Forest Research Laboratory, Farnham, Surrey, UK.

2.4. Physical and chemical soil and tephra sample analyses

Particle size analyses were carried out in combination with the clay size analysis. Following pre-treatment with H₂O₂ coarse fractions were separated by wet sieving using mesh-sizes ranging from 2000 to 20 µm. The fine particles (<20 µm) were analysed by means of sedimentation analysis using a Sedigraph III 5120 (Micromeritics, Georgia, USA).

Bulk soil and tephra samples were air-dried, passed through a 2 mm sieve and used for analyses of physical and chemical properties. According to Bengtsson and Enell (1986) the loss on ignition (LOI) was measured by combusting 1.2 cm³ of sample at 550 °C for 5 h. Concentrations of soil organic carbon (SOC) and total nitrogen (total N) were determined on oven-dried fine earth by dry combustion using a Flash 1112 Elementar Analyzer (Thermo-Scientific, Italy) with ball-milled soil and tephra samples passed through a 150 µm sieve and dried at 50 °C. Since the studied soils did not contain carbonate minerals (determined by HCl test), the values thus obtained were assumed to correspond to OC. Soil pH (H₂O) was obtained in water-soil suspension (1:5) according to ÖNORM L1083 (Austrian Standard Institute, 2006), pH determined in 1 M NaF solution was determined following the method of Fieldes and Perrott (1966). Bulk density data was acquired from Þorbjarnarson (2016). Phosphate retention was analysed using the method outlined in Blakemore et al. (1987). Soil accumulation rates (SAR) (mm yr⁻¹) were calculated by measuring soil thickness between tephra layers of known age (Gísladóttir et al., 2010).

Selective dissolutions were carried out to determine poorly crystalline and amorphous constituents as well as those associated with humus in the soils and tephra samples. Air-dried, ball-milled samples were passed through a 150 µm sieve. Iron (Fe), aluminium (Al) and silica (Si) associated with amorphous constituents (Fe_o, Al_o, Si_o) were extracted with ammonium oxalate in the dark by the shaking method at pH 3.0. Fe and Al associated with OM (Fe_p, Al_p) were extracted with sodium pyrophosphate at pH 10.0 and shaking for 16 h. Both ammonium oxalate and sodium pyrophosphate extraction were carried out according to USDA Soil Survey Laboratory Manual (Burt, 2004). Fe in crystalline and non-crystalline oxides (Fe_d) was extracted by citrate-bicarbonate-dithionite (CBD) as outlined in Sparks et al. (1996). The resultant extracts were stored at 4 °C until analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

The molar Al/Si ratios of allophane in the soil and tephra samples were calculated from (Al_o-Al_p)/Si_o according to e.g. Wada (1989). Al_o + 0.5Fe_o was used as a taxonomy criterion for andic soil properties (Soil Survey Staff, 2014). The Al_p/Al_o ratio has been used to differentiate between aluandic and silandic Andosols (IUSS Working group WRB, 2015) and to estimate the presence of allophanic material (Shoji et al., 1993). Allophane content (%) was estimated by the formula 100x%Si_o/[23.4-5.1x] with x = (Al_o-Al_p)/Si_o (e.g. Mizota and van Reeuwijk, 1989; Parfitt and Henmi, 1982; Parfitt and Wilson, 1985). Ferrihydrite content (%) was estimated by multiplying the %Fe_o by a factor of 1.7 (Childs, 1985). Contents of non-crystalline secondary phases of the clay size fraction, hereafter referred to as amorphous secondary clay, were estimated as the total amount of allophane and ferrihydrite (e.g. Shang and Zelazny, 2008).

2.5. Soil and tephra mineralogical analyses

Prior to mineralogical analyses bulk soil and tephra samples were oven-dried at 70 °C and ground to analytical fineness. The clay size fraction (<2 µm) was separated by a combination of sieving and centrifugation after OM removal using 10% hydrogen peroxide (H₂O₂) pre-treatment. To determine soil mineralogy, we used X-ray diffraction (XRD).

XRD of bulk samples was conducted by using a Panalytical XPert Pro MPD diffractometer equipped with automatic divergent slit, Cu LFF tube (45 kV, 40 mA) and an X'Celerator detector. The measuring time was 250 s, with a step size of 0.017° 2θ. Analogous to the bulk mineral analysis, the clay minerals were determined by X-ray diffraction and identified according to Moore and Reynolds (1997), Brindley and Brown (1980) and Wilson (1987). Sample preparation for clay mineral analysis followed methods described by Whittig (1965) and Tributh (1989). Preferential orientation of the clay minerals was obtained by suction through a porous ceramic tile, similar to the method described by Kinter and Diamond (1956). Afterwards, expansion tests using ethylene glycol and dimethyl sulfoxide (DMSO), as well contraction tests heating of the clay size fraction up to 550 °C were done. Bulk samples were X-rayed from 2 to 70° 2θ, after each step clay fraction samples were X-rayed from 2 to 40° 2θ. A semiquantitative mineral composition of both, bulk and clay size fraction were estimated from the resultant diffractograms according to Riedmüller (1978) by using the Panalytical software X'Pert HighScorePlus.

2.6. Statistical analysis

Descriptive statistics and correlations were performed using the software JMP 14 (JMP, 2018).

3. Results

3.1. Selected soil properties

Soils at both sampling sites developed in dryland habitats.

Well-preserved tephra layers can be found at comparable depths at both sites (Fig. 2).

A summary of selected soil properties is presented in Table 1.

The mean LOI was 9.5% at SD and 7.6% at KV. SOC content ranged between 0.5 and 5.8% at SD and between 1.1 and 8.4% at KV. Highest SOC content is the uppermost 10 cm depth at both sites.

The soils were acidic with pH(H₂O) ranging from 5.3 to 6.7 at SD and lower values between 4.7 and 5.6 at KV.

The particle size distribution at both sites was dominated by sand with fine sand as the main portion of the sand size fraction (not shown) and appreciable amounts of silt (Table 3). The distribution of the sand content at KV followed the same trend in the soils above V1477, as well as above and below Ö1362. Sand content was lowest in the upper layers of the profile but increased with depth. Above the V1477 tephra layer the soils at SD followed a similar trend but became more irregular downwards. The influence of tephra layers on the soils at SD seems to be stronger than at KV.

SAR in the soils after the deposition of the basaltic V1477 to the time of sampling (2012) was 0.63 mm yr⁻¹ at SD and 0.69 mm yr⁻¹ at site KV. The SAR were significantly higher between Ö1362 and V1477 at both sites, 2.11 mm yr⁻¹ and 1.78 mm yr⁻¹ at SD and KV, respectively.

3.2. Amorphous nature of soils and tephra

Data of selective dissolution analysis are shown in Table 2.

The amorphous Al (Al_o - Al_p) in the soils ranged between 13 and 37%, being lowest in the top layers at both sites. The content of amorphous Fe (Fe_o - Fe_p) was higher, between 21 and 56% (Table 2). Fig. 3 and Fig. 4 show an increasing Si_o with increasing content of amorphous

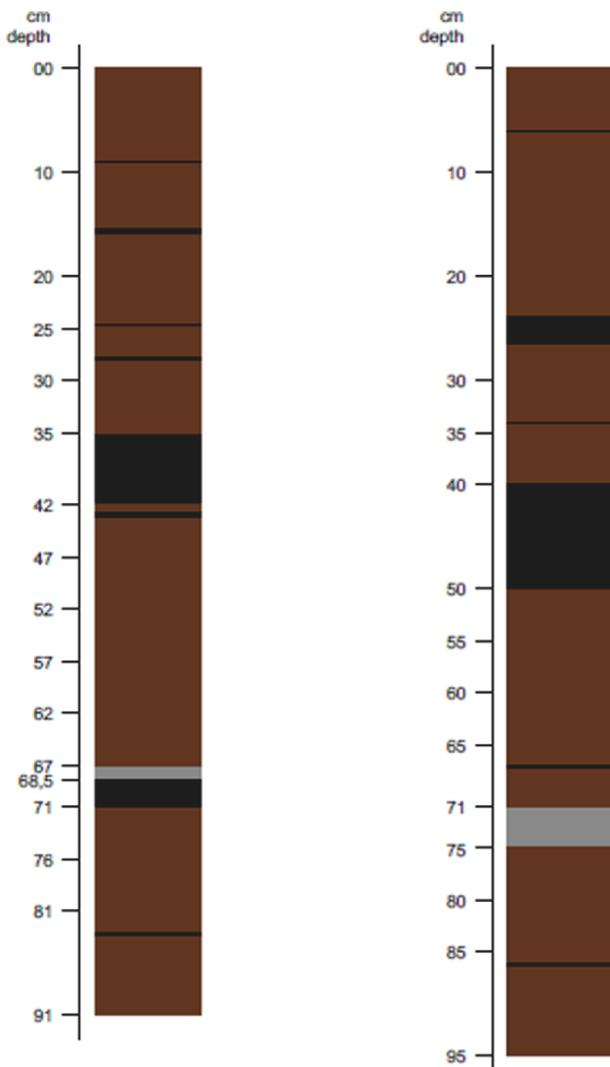


Fig. 2. Schematic soil profiles at Steinadalur (left) and Kvísker (right). Soils are illustrated in brown, basaltic tephra in black and rhyolitic tephra layers in light grey. At Steinadalur V1477 was found in 35–41 cm depth, at site Kvísker in 40–50 cm depth. Ö1362 was found in 67–68.5 cm and 71–75 cm depth at Steinadalur and Kvísker, respectively.

Al and Fe, respectively.

The mean pH measured in sodium fluoride pH(NaF) was 10.9 at both sites. Except for the top layer at both sites, the Al_p/Al_o ratios in all investigated soil layers were 0.1, but even in the uppermost 10 cm, the ratios were close to zero (0.3). The Al/Si ratio was above 1 at both sites, from 1.4 to 1.7 at SD and 1.3 to 1.8 at KV. The percentage ratio $Al_o + 0.5Fe_o$, a criterion for Andosol classification, ranged between 2.7 and 7.1 in the soils. Fe_o/Fe_d ratios in the soils were slightly higher at KV than SD.

Clay content is between 4.3% and 34.6% in the soils at SD and between 7.8% and 36.6% at KV. In V1477 the clay content was similar around 5% at both sites, whereas the clay contents in Ö1362 showed differences. While it was 4.2% at KV, it was nearly double (7.9%) at site SD. The estimated content of amorphous constituents (allophane and ferrihydrite) was 10.1–26.0% at SD and 12.5–22.7% at KV.

At both sites, the estimated allophane content ranged between 5.5 and 17.4%, the estimated ferrihydrite content ranged between 3.7 and 9.9%. The highest amounts of ferrihydrite were found in the oldest soils (those below Ö1362). The soils at SD showed a different, less consistent pattern. The highest amounts of ferrihydrite were found in the soils above Ö1362 but decrease by about the half in the layer right below

V1477. The soils above the basaltic V1477 exhibited lower contents, but without any trend.

3.3. Mineralogical composition of tephra and soils

Evaluation of the bulk XRD data (Table 4, Fig. 5 and Fig. 6) revealed that volcanic glass is abundant in all samples, both tephra and soil. Besides that, the bulk mineralogy was dominated by plagioclase and pyroxene. Small amounts of stilbite and phillipsite were observed in the soils at SD, while the only type of zeolite found in most of the soils at KV was stilbite. Appreciable amounts of quartz were found in all soil samples. A distinct 14 Å reflection was detected in small and trace amounts at SD and KV, respectively.

The bulk mineral composition (Table 4) of the two different types of tephra was comparable at both sites. Similar to the soils, both types of tephra were dominated by plagioclase, pyroxene and volcanic glass. While the pyroxene content was found to be higher in the basaltic V1477 tephra, the Ö1362 showed a larger amount of volcanic glass. Furthermore, the latter gives a very amorphous impression of the rhyolitic tephra. Traces of zeolite were only found in V1477 at KV.

The identification of the XRD patterns for the clay size fraction are presented in Table 5. As illustrated in Fig. 7, a clear reflection at $6.2^\circ 2\theta$ (1.4 nm) appeared in the air-dried clay fraction and remained after ethylene glycol treatment as well as treatment with DMSO. This pattern indicates the absence of smectite and vermiculite. After heating the samples to 550 °C the distinct 1.4 nm at $6.2^\circ 2\theta$ disappeared. Consequently, investigations of the clay size fraction of the soils at both sites discerned secondary chlorite (at least in trace amounts) as only type of layer silicates (Fig. 8 and Fig. 9).

4. Discussion

4.1. Pedogenesis in Icelandic Andosols – A question of parent material and time

The investigated soils at both sites developed from tephra and aeolian deposits rich in volcanic glass. Values for pH in NaF solution clearly above the limit of 9.5, $Al_o + 0.5Fe_o > 2.0\%$ and the presence of significant amounts of amorphous and poorly crystalline constituents give an indication of andic soil properties, common in soils derived from volcanic ejecta (Shoji et al., 1993). According to World Reference Base both pedons meet the requirements for silandic and vitric soil properties in all layers (Table 1) and can be classified as Andosols (IUSS Working Group WRB, 2015).

A regular burial of soil by tephra and aeolian material impedes an undisturbed soil development. For this reason, both profiles are comprised of sequences of buried soils. This process is well known in Iceland (e.g. Bonatatzky et al., 2019), but similar processes are reported for soils in Japan, New Zealand and other volcanic regions (e.g. Takahashi and Dahlgren, 2016). We found a strong correlation between SOC and Al_p (Fig. 10), showing the important role of Al-humus complexes on SOC stocks in Andosols. The correlation between SOC and Fe_o , representing the adsorption of SOC on mineral surfaces, was weaker, but still significant, especially at site KV (Fig. 11). Except for the surface layer at both sites, the highest SOC contents were found below the Ö1362 tephra layer.

Similar to the findings by Chevallier et al. (2019), most of the active Al pertained to Al-humus complexes. Al_p/Al_o ratios < 0.5 in all investigated soils suggest that the reactive Al pool is dominated by inorganic constituent. Consistent with García-Rodeja et al. (2004), we observed the highest ratios in the top layers, decreasing with depth. Al_p/Al_o ratios in the soils above V1477 showed a decreasing trend, with soil depth from 0.31 to 0.06 at SD and from 0.28 to 0.09 at KV but was relatively consistent in the soils developed after the deposition of Ö1362 tephra at both sites.

Aside from the parent material, previous studies reported two other

Table 1

Selected morphological, physical and chemical characteristics of the studied pedons at Steinadalur (SD) and Kvísker (KV). Profile description terminology is from Schoenberger et al. (2002). Abbreviations: Roots, quantity – 1, few; 2, common; 3, many. Roots, size – f, fine; m, medium; co, coarse. Boundary, distinctness – a, abrupt; c, clear. Boundary, topography – s, smooth; w, wavy. Structure, grade – 1, weak; 2, moderate. Structure, size – f, fine; m, medium. Structure, type – gr, granular; sbk, subangular blocky. Texture – l, loam; sil, silt loam; sicl, silty clay; sl, sandy loam. * Texture was estimated by feel on the fine earth fraction, gravel content not estimated.

Sample	Depth	Munsell color code (moist)	Roots	Boundary	Structure	Texture	LOI	SOC	total N	Phosphate retention	pH (H ₂ O)	pH (NaF)
	cm		(quantity, size)	(distinctness, topography)	(grade, size, type)		%	%	%	%		
Soil SD1	0–10	10YR 3/2 (very dark greyish brown), 10YR 3/3 (dark brown)	3,f; 1,m; 1,co	c, s	2, f, gr; 1, f, sbk	sil	13,86	5,79	0,362	83	5,3	11,0
Soil SD2	10–20	10YR 3/6 (dark yellowish brown)	2,f, 1 m	c, s	1, sbk	sil	10,86	3,69	0,255	88	5,9	11,2
Soil SD3	20–25	10YR 3/6 (dark yellowish brown)	2,f; 1,m	c, s	1, sbk	sil	6,55	2,35	0,164	77	6,3	11,1
Soil SD4	25–30	7.5YR 2.5/3 (very dark brown)	1,f	c, s	1, f, sbk	sl	8,81	3,06	0,217	82	6,2	11,2
Soil SD5	30–35	highly impacted by tephra V1477	–	–	–	–	1,66	0,60	0,038	54	6,7	10,6
Tephra SD V1477	35–42	–	–	–	–	–	1,93	0,65	0,044	–	6,6	10,7
Soil SD6	42–47	7.5YR 2.5/3 (very dark brown)	1,f	a, s	1, f, sbk	sil	1,51	0,47	0,030	60	6,6	10,6
Soil SD7	47–52	7.5YR 4/6 (strong brown)	1,f; 1,m	a, s	1, m, sbk	sicl	7,73	2,49	0,196	85	6,5	10,9
Soil SD8	52–57	7.5YR 4/6 (strong brown)	1,f; 1,m	a, s	1, m, sbk	sicl	11,99	3,48	0,272	97	6,4	11,0
Soil SD9	57–62	7.5YR 4/6 (strong brown)	1,f; 1,m	a, s	1, m, sbk	sicl	13,52	3,15	0,238	98	6,5	11,0
Soil SD10	62–67	7.5YR 4/6 (strong brown)	1,f; 1,m	a, s	1, m, sbk	sicl	11,41	2,64	0,191	94	6,5	11,0
Tephra SD Ö1362	67–68.5	–	–	–	–	–	2,82	0,54	0,036	–	6,4	10,5
Soil SD11	71–76	7.5YR 3/3 (dark brown)	1,f; 1,m	c, s	1, sbk	sicl	11,06	3,29	0,259	93	6,4	10,9
Soil SD12	76–81	7.5YR 2.5/3 (very dark brown)	1,f	c, s	1, f, sbk	sic	11,52	4,19	0,341	95	6,2	11,0
Soil SD13	81–91	7.5YR 2.5/3 (very dark brown)	1,f	c, s	1, f, sbk	sic	13,45	4,85	0,416	98	6,3	11,0
Soil KV1	0–10	10YR 3/3 (dark brown)	3, f; 1, m; 1,co	c, s	2, f, sbk	sil	18,50	8,43	0,447	82	4,7	10,6
Soil KV2	10–20	10YR 3/4 (dark yellowish brown)	3, f; 1, m	c, s	1, f, sbk	l	9,48	3,89	0,235	77	5,0	11,2
Soil KV3	20–30	10YR 3/4 (dark yellowish brown)	3, f; 1, m	c, s	1, f, sbk	l	6,62	2,32	0,147	85	5,1	11,1
Soil KV4	30–35	10YR 4/4 (dark yellowish brown)	2, f	a	1, f, sbk	l	5,88	2,05	0,123	85	5,3	11,1
Soil KV5	35–40	10YR 4/4 (dark yellowish brown)	2, f	a	1, f, sbk	l	4,98	1,65	0,099	75	5,4	11,0
Tephra KV V1477	40–50	–	–	–	–	–	1,83	0,48	0,030	–	5,2	10,5
Soil KV7	50–55	10YR 4/4 (dark yellowish brown)	1, f	c, s	1, sbk	sl	6,34	1,68	0,124	89	5,3	11,0
Soil KV8	55–60	10YR 5/4 (yellowish brown)	no roots	c, w	1, sbk	sl	5,04	1,19	0,085	71	5,2	10,9
Soil KV9	60–65	10YR 5/4 (yellowish brown)	no roots	c, w	1, sbk	sl	4,93	1,22	0,090	66	5,1	10,9
Soil KV10	65–71	10YR 3/3 (dark brown)	1, f	c, w	1, sbk	l	4,57	1,13	0,079	65	5,2	10,9
Tephra KV Ö1362	71–75	–	–	–	–	–	2,21	0,27	0,019	–	5,4	10,4
Soil KV11	75–80	10YR 3/4 (dark yellowish brown)	no roots	c, s	1, sbk	sicl	9,11	3,25	0,224	94	5,5	11,0
Soil KV12	80–85	10YR 3/4 (dark yellowish brown)	no roots	c, s	1, sbk	sicl	8,08	2,69	0,172	96	5,3	11,0
Soil KV13	85–95	10YR 3/3 (dark brown)	1, f	c, s	1, sbk	sicl	7,28	2,24	0,142	96	5,6	10,9

Table 2

Selected selective dissolution analyses and properties related to the amorphous material in the studied pedons and tephra at Steinadalur (SD) and Kvísker (KV).

Sample	Depth cm	Al _o g kg ⁻¹	Fe _o g kg ⁻¹	Si _o g kg ⁻¹	Fe _d g kg ⁻¹	Al _p g kg ⁻¹	Fe _p g kg ⁻¹	Fe _d / Fe _p Ratio	(Al _o -Al _p)/ Si _o Molar ratio	Al _p / Al _o Ratio	Amorphous Al g kg ⁻¹	Amorphous Fe g kg ⁻¹	Al _o + 0.5*Fe _o %
Soil SD1	0–10	19,3	27,3	9,2	15,0	5,9	5,9	1,8	1,5	0,31	13,34	21,42	3,3
Soil SD2	10–20	33,1	48,5	17,9	19,0	4,3	3,1	2,6	1,6	0,13	28,79	45,37	5,7
Soil SD3	20–25	22,7	32,7	12,5	16,4	2,8	1,7	2,0	1,6	0,12	19,92	30,98	3,9
Soil SD4	25–30	31,6	46,2	17,6	18,5	3,5	2,6	2,5	1,6	0,11	28,08	43,55	5,5
Soil SD5	30–35	15,9	22,0	13,0	11,9	1,0	0,7	1,8	1,2	0,06	14,92	21,32	2,7
Tephra SD V1477	35–42	20,9	28,3	18,1	14,5	1,0	0,8	–	1,1	0,05	19,88	27,54	3,5
Soil SD6	42–47	20,9	28,3	18,5	14,7	0,9	0,7	1,9	1,1	0,04	20,03	27,59	3,5
Soil SD7	47–52	33,3	48,4	21,6	19,7	2,4	1,5	2,5	1,4	0,07	30,93	46,90	5,8
Soil SD8	52–57	41,1	47,3	22,4	35,1	3,4	1,6	1,3	1,7	0,08	37,65	45,77	6,5
Soil SD9	57–62	39,8	47,3	22,6	32,8	3,0	1,4	1,4	1,6	0,07	36,85	45,91	6,3
Soil SD10	62–67	43,0	56,7	27,1	28,0	2,6	1,3	2,0	1,5	0,06	40,37	55,43	7,1
Tephra SD Ö1362	67–68.5	11,8	17,0	8,6	12,4	0,9	0,5	–	1,3	0,08	10,89	16,45	2,0
Soil SD11	71–76	30,4	40,5	17,9	22,9	3,1	2,3	1,8	1,5	0,10	27,21	38,22	5,1
Soil SD12	76–81	26,8	36,5	14,5	23,6	4,0	3,5	1,5	1,6	0,15	22,74	33,02	4,5
Soil SD13	81–91	40,9	55,1	24,1	24,6	4,1	3,3	2,2	1,5	0,10	36,76	51,85	6,8
Soil KV1	0–10	22,4	39,7	11,1	14,4	6,2	7,0	2,8	1,5	0,28	16,17	32,68	4,2
Soil KV2	10–20	34,9	55,1	17,4	16,0	4,3	3,3	3,4	1,8	0,12	30,53	51,77	6,2
Soil KV3	20–30	25,8	42,2	13,9	16,6	2,9	1,6	2,5	1,6	0,11	22,90	40,58	4,7
Soil KV4	30–35	24,8	41,8	14,5	30,2	2,5	1,3	1,4	1,5	0,10	22,33	40,48	4,6
Soil KV5	35–40	22,8	36,0	13,7	24,6	2,0	1,1	1,5	1,5	0,09	20,76	34,94	4,1
Tephra KV V1477	40–50	5,9	9,9	5,4	16,3	0,9	0,6	–	0,9	0,16	4,98	9,30	1,1
Soil KV7	50–55	26,7	38,1	15,2	16,7	2,1	0,9	2,3	1,6	0,08	24,59	37,18	4,6
Soil KV8	55–60	20,5	29,4	12,9	9,7	1,7	0,7	3,0	1,5	0,08	18,77	28,62	3,5
Soil KV9	60–65	19,8	28,6	13,1	21,1	1,6	0,7	1,4	1,4	0,08	18,27	27,91	3,4
Soil KV10	65–71	22,1	33,9	16,0	10,9	1,6	0,8	3,1	1,3	0,07	20,51	33,16	3,9
Tephra KV Ö1362	71–75	3,9	5,6	2,8	3,8	0,7	0,2	–	1,2	0,17	3,19	5,37	0,7
Soil KV11	75–80	33,7	58,5	21,7	20,8	2,9	2,2	2,8	1,4	0,09	30,81	56,28	6,3
Soil KV12	80–85	35,3	52,9	22,6	22,1	2,6	1,6	2,4	1,4	0,07	32,72	51,36	6,2
Soil KV13	85–95	29,0	41,4	18,7	21,2	2,2	1,5	2,0	1,4	0,08	26,80	39,89	5,0

Table 3

Particle size distribution and estimated content of the amorphous constituents in the studied pedons and tephra at Steinadalur (SD) and Kvísker (KV).

Sample	Depth cm	Sand %	Silt %	Clay %	Ferrihydrite %	Allophane %	Amorphous secondary clay %
Soil SD1	0–10	51,5	31,7	16,7	4,6	5,5	10,1
Soil SD2	10–20	51,4	29,6	19,0	8,2	11,2	19,5
Soil SD3	20–25	61,6	20,3	18,1	5,6	7,8	13,4
Soil SD4	25–30	52,7	24,9	22,3	7,8	11,0	18,8
Soil SD5	30–35	84,2	11,4	4,3	3,7	6,9	10,6
Tephra SD V1477	35–42	74,4	20,8	4,8	4,8	9,4	14,2
Soil SD6	42–47	67,0	26,8	6,3	4,8	9,6	14,4
Soil SD7	47–52	45,9	35,5	18,6	8,2	12,8	21,0
Soil SD8	52–57	32,7	32,7	34,6	8,0	14,4	22,5
Soil SD9	57–62	33,8	36,1	30,1	8,0	14,3	22,3
Soil SD10	62–67	45,7	32,0	22,3	9,6	16,3	26,0
Tephra SD Ö1362	67–68.5	68,0	24,1	7,9	2,9	4,8	7,7
Soil SD11	71–76	58,9	23,3	17,7	6,9	10,9	17,8
Soil SD12	76–81	44,0	25,6	30,4	6,2	9,0	15,2
Soil SD13	81–91	40,0	28,7	31,3	9,4	14,7	24,1
Soil KV1	0–10	40,6	36,7	22,5	6,7	6,6	13,4
Soil KV2	10–20	50,8	28,5	19,9	9,4	11,4	20,8
Soil KV3	20–30	51,6	29,4	18,6	7,2	8,8	16,0
Soil KV4	30–35	56,2	28,2	15,1	7,1	8,9	16,0
Soil KV5	35–40	56,2	31,8	11,9	6,1	8,3	14,5
Tephra KV V1477	40–50	67,7	26,9	5,2	1,7	2,6	4,3
Soil KV7	50–55	44,9	39,2	15,8	6,5	9,6	16,1
Soil KV8	55–60	50,7	40,1	9,2	5,0	7,7	12,7
Soil KV9	60–65	52,6	37,2	10,1	4,9	7,6	12,5
Soil KV10	65–71	55,2	25,9	7,8	5,8	8,9	14,7
Tephra KV Ö1362	71–75	42,2	30,4	4,2	1,0	1,5	2,4
Soil KV11	75–80	34,8	28,5	36,6	9,9	12,8	22,7
Soil KV12	80–85	44,7	35,0	20,2	9,0	13,4	22,4
Soil KV13	85–95	46,6	36,5	16,9	7,0	11,0	18,1

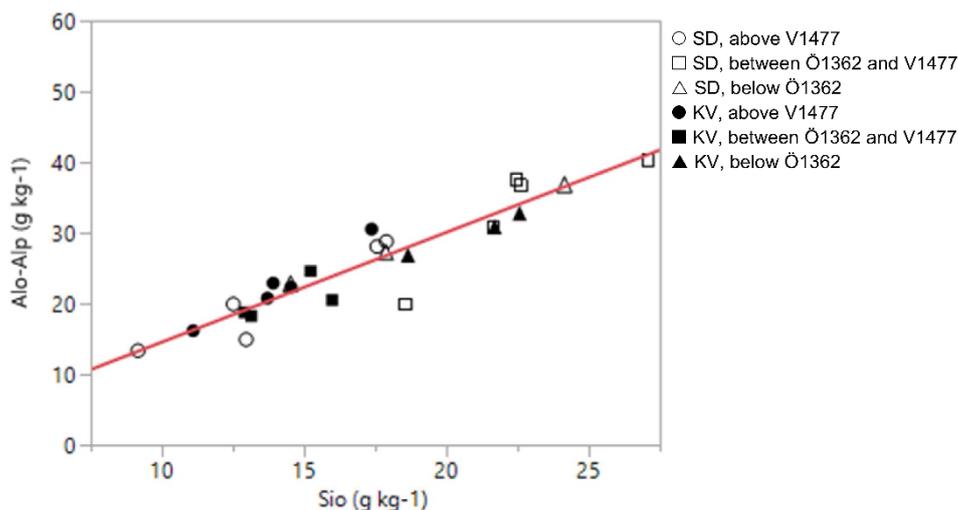


Fig. 3. Correlation between Si_o and amorphous Al, $r^2 = 0.88$, $y = -0,992103 + 1,5536402x$, $P < 0.0001$.

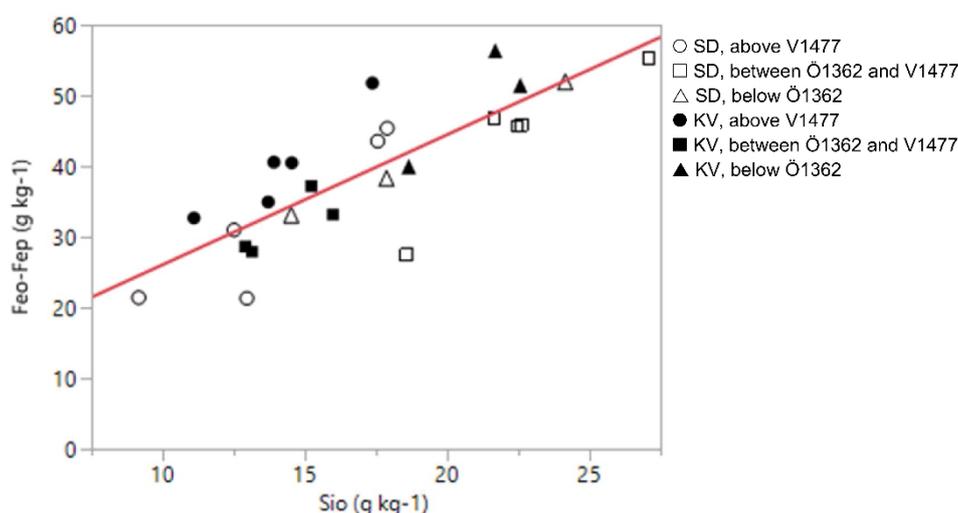


Fig. 4. Correlation between Si_o and amorphous Fe, $r^2 = 0.68$, $y = 7,6645445 + 1,8399385x$, $P < 0.0001$.

important factors contributing to the formation of allophanes: soil pH (H_2O) and availability of Al. A pH(H_2O) above 5 in all but one sample in our study supports the formation of allophane. A correlation between Al_p/Al_o ratio and SOC, shown in Fig. 12, indicates that the investigated soils are dominated by poorly- and non-crystalline constituents.

The Fe_o/Fe_d ratio has widely been used to indicate the degree of soil development (Malucelli et al., 1999). The main Fe source in Icelandic soils is from amorphous basaltic glass, only small amounts originate from crystalline material (e.g. Arnalds et al., 2016; Arnalds et al., 2014). Therefore, compared to Fe in crystalline and amorphous constituents (Fe_d), the Fe_o values in Icelandic soils are high, resulting in a Fe_o/Fe_d ratio > 1 (Arnalds et al., 1995; Bonatovsky et al., 2019; Wada et al., 1992). In the investigated soils it ranged between 1.3 and 3.4, indicating a low degree of pedogenesis. Compared to the Icelandic Histosols in the study by Bonatovsky et al. (2019), we found lower ratios in the Andosols. Acidic soil conditions, moisture and parent material are important factors to promote weathering processes. A lower %LOI and higher soil pH explain the lower weathering in the Andosols of the present study.

A correlation between Fe_o/Fe_d ratio and the content of amorphous Si (Si_o) indicate that the soils are “young” (Fig. 13). With an age < 650 years, the investigated soils are considered to be in their early stage of

development. The initial state of weathering does not enable goethite or similar minerals to form, i.e. the active Fe is mainly present in form of ferrihydrite.

At site SD we observed higher Si_o contents above Ö1362 tephra than in the soils developed from V1477, concluding that inorganic constituents are more abundant in the soils developed from Ö1362. This trend was not identifiable in the soils at KV.

A consistent SAR through the soil profile is assumed to represent a stable environment, while SAR is expected to vary with time during erosion phases (Gísladóttir et al., 2010). Our investigations showed differences between the soils formed after the deposition of V1477 tephra and those developed between Ö1362 and V1477 deposition. In 115 years of soil development between 1362 and 1477 CE, significantly higher SAR reflect a stronger impact of erosion and aeolian processes on soil development, than in the soils above V1477 at both sites. The impact of aeolian activity during this period of time was higher at SD, than at KV, illustrated by higher SAR. A decrease in SAR by a factor of 3.3 (0.63 mm yr^{-1}) at SD and 2.6 (0.69 mm yr^{-1}) at KV after V1477 CE suggest a reduced aeolian impact (and/or less erosion respectively) on the investigated soils since the deposition of the basaltic V1477 tephra.

The frequent addition of tephra and aeolian material is a crucial

Table 4

Bulk mineralogy of the studied pedons and tephra samples at Steinadalur (SD) and Kvísker (KV), d-values (nm) of the main peaks for identification included.

Sample	Depth cm	Quartz	14 Å	Plagioclase	Pyroxene	Zeolite Stilbite	Phillipsite	Volcanic glass
	d-values:	0.3 nm	1.4 nm	0.3 nm	0.3 nm	0.9 nm	0.7 nm	
Soil SD1	0–10	*	*	**	**	tr	tr	**
Soil SD2	10–20	*	*	**	**	tr	tr	**
Soil SD3	20–25	*	*	**	**	tr	tr	**
Soil SD4	25–30	*	*	**	**	tr	tr	**
Soil SD5	30–35	*	–	**	**	–	–	**
Tephra SD V1477	35–42	*	–	**	**	–	–	**
Soil SD6	42–47	*	tr	**	**	–	–	**
Soil SD7	47–52	*	*	**	**	tr	tr	**
Soil SD8	52–57	*	*	**	**	tr	tr	**
Soil SD9	57–62	*	*	**	**	tr	tr	**
Soil SD10	62–67	*	*	**	**	tr	tr	**
Tephra SD Ö1362	67–68.5	tr	–	*	*	–	–	***
Soil SD11	71–76	*	*	**	**	tr	tr	**
Soil SD12	76–81	*	*	**	**	tr	tr	**
Soil SD13	81–91	tr	*	**	*	tr	tr	**
Soil KV1	0–10	tr	tr	***	**	tr	–	**
Soil KV2	10–20	tr	tr	**	**	tr	–	**
Soil KV3	20–30	tr	tr	***	**	tr	–	**
Soil KV4	30–35	tr	tr	***	**	tr	–	**
Soil KV5	35–40	tr	tr	**	**	tr	–	**
Tephra KV V1477	40–50	tr	–	**	*	–	–	**
Soil KV7	50–55	tr	–	**	**	–	–	**
Soil KV8	55–60	tr	tr	**	**	–	–	**
Soil KV9	60–65	tr	–	**	**	tr	–	**
Soil KV10	65–71	tr	tr	**	**	tr	–	**
Tephra KV Ö1362	71–75	tr	–	**	tr	–	–	***
Soil KV11	75–80	tr	tr	**	**	tr	–	**
Soil KV12	80–85	tr	tr	**	**	–	–	**
Soil KV13	85–95	–	tr	**	**	–	–	**

tr = trace amounts, * = low, ** = medium, *** = high, - = not detected.

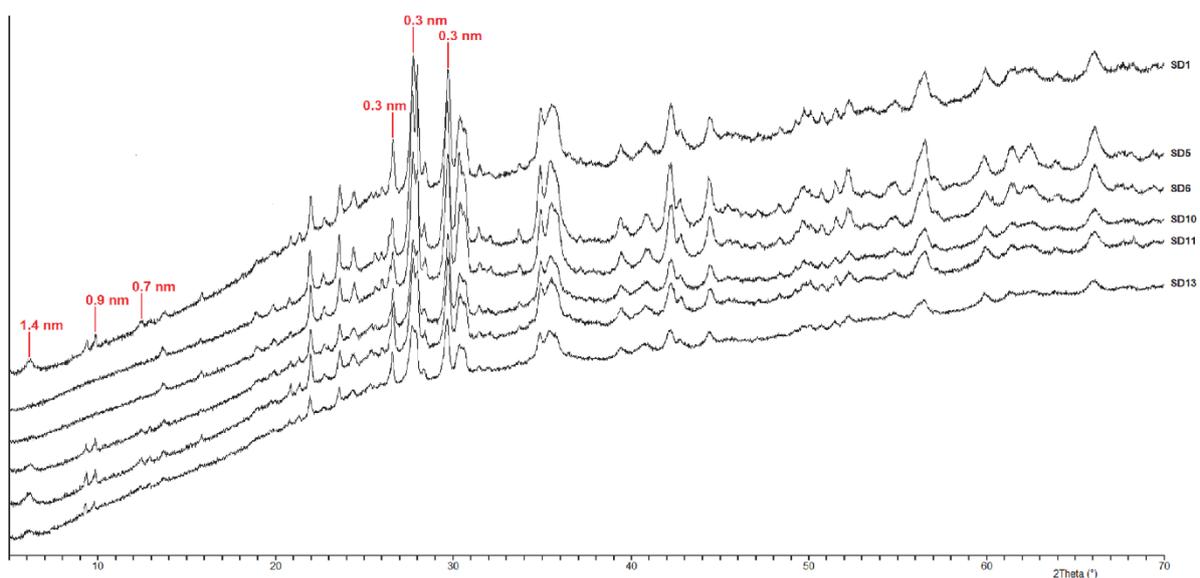


Fig. 5. Bulk mineral composition of selected soil samples (top and bottom layer as well as those above and below the two tephra layers V1477 and Ö1362) site SD; main peaks for identification are labelled (please find the explanation in Table 4).

factor in the development of the investigated soils. It does not only effect the soil above, but also the soil layer immediately below (Bonatovsky et al., 2019). On the basis of an increased sand content in the soil above both tephra layers at site KV and above the basaltic V1477 layer at SD we can see the influence of tephra on the soils above. The sand content in the layer below Ö1362 at SD was much higher, pointing at a higher intermixture of the rhyolitic tephra with the soil below during the eruption event. The input of aeolian material of unknown origin and chemical composition provides an influx of more developed, more

weathered materials to the otherwise young soils. Thus, in spite of the low soil age and the prevailing cool climatic conditions, we observed signs of pedogenesis and the presence of clay minerals.

4.2. Tephra – Source of the amorphous nature

Icelandic Andosols are characterized by frequent tephra addition. Volcanic glass of various chemical composition (basaltic to rhyolitic) weather to allophane, but at widely different rates (Kirkman and

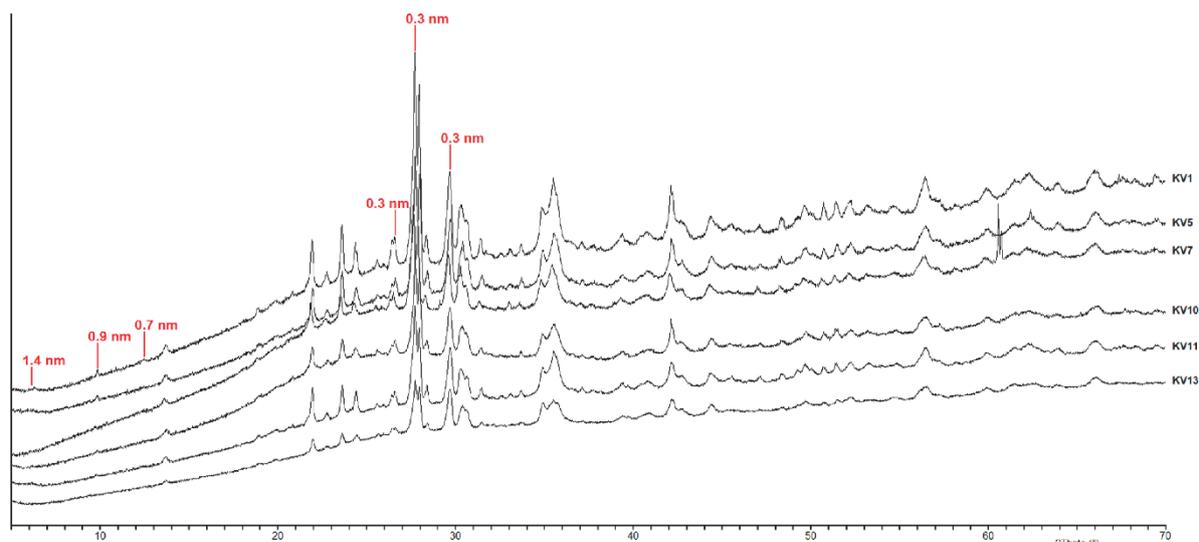


Fig. 6. Bulk mineral composition of selected soil samples (top and bottom layer as well as those above and below the two tephra layers V1477 and Ö1362) site KV; main peaks for identification are labelled (please find the explanation in Table 4).

Table 5
Layer silicates found in the clay size fraction of the studied pedons and tephra samples at Steinadalur (SD) and Kvísker (KV).

Sample	Depth cm	Secondary chlorite	Zeolite Phillipsite
Soil SD1	0–10	*	tr
Soil SD2	10–20	*	tr
Soil SD3	20–25	*	tr
Soil SD4	25–30	*	tr
Soil SD5	30–35	–	tr
Tephra SD V1477	35–42	tr	–
Soil SD6	42–47	tr	tr
Soil SD7	47–52	tr	*
Soil SD8	52–57	tr	tr
Soil SD9	57–62	–	tr
Soil SD10	62–67	–	tr
Tephra SD Ö1362	67–68.5	tr	–
Soil SD11	71–76	tr	*
Soil SD12	76–81	tr	*
Soil SD13	81–91	–	*
Soil KV1	0–10	–	–
Soil KV2	10–20	–	–
Soil KV3	20–30	–	–
Soil KV4	30–35	–	–
Soil KV5	35–40	tr	–
Tephra KV V1477	40–50	tr	–
Soil KV7	50–55	–	–
Soil KV8	55–60	tr	–
Soil KV9	60–65	tr	–
Soil KV10	65–71	–	–
Tephra KV Ö1362	71–75	tr	–
Soil KV11	75–80	tr	–
Soil KV12	80–85	tr	–
Soil KV13	85–95	–	–

tr = trace amounts, * = low, - = not detected.

McHardy, 1980; Wada and Harward, 1974). It is one of the most important constituents of Andosols (Shoji et al., 1993) and takes an important role in the cycling of numerous elements and chemical species at the Earth’s surface (Wolff-Boenisch et al., 2004). Dissolution rates of “coloured glass” of basaltic andesitic composition are higher than those of rhyolitic “non-coloured glass” (Nanzyo et al., 1993), but the difference between the crystalline and glassy material is greater for rhyolitic than basaltic material (Wolff-Boenisch et al., 2006; Wolff-Boenisch et al., 2004).

Chemical alteration or even complete dissolution of volcanic glass is

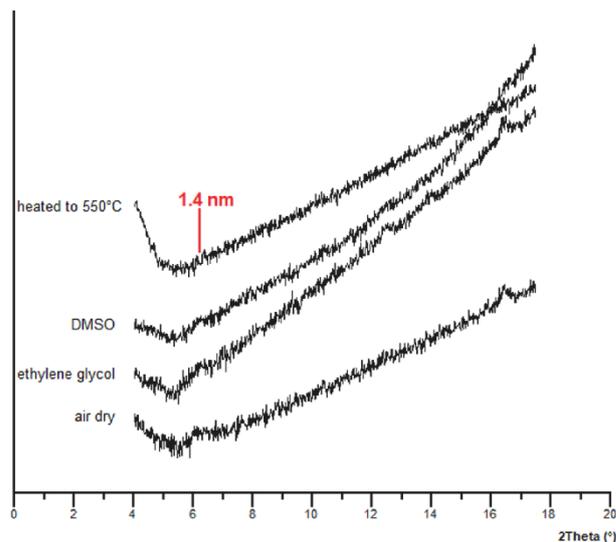


Fig. 7. XRD patterns of a selected 2 µm sample (SD2) showing treatments for identification of secondary chlorite.

controlled by the chemical composition of the parent volcanic glass (Pollard et al., 2003). Kirkman and McHardy (1980) investigated volcanic soils in New Zealand and have shown that basaltic glasses weather 10 times faster than glasses of rhyolitic composition (silica-rich), releasing elements to the surrounding soil, which are further transported away from weathering site by water (Gíslason, 2005). The dissolution rate of volcanic glasses normalized to specific surface are dependent on 1) the glass composition; ultramafic to basaltic dissolving fastest, andesitic at intermediate rates and rhyolitic at slowest rates (Wolff-Boenisch et al., 2006; Wolff-Boenisch et al., 2004); 2) temperature; the higher the temperature the faster the rates; 3) soil solution composition including pH, Al-complexing agents such as oxalate, Al concentration and overall saturation stage of the glass with respect to the solution (Declercq et al., 2013; Gíslason and Oelkers, 2003; Wolff-Boenisch et al., 2006; Wolff-Boenisch et al., 2004)

As expected, a different state of weathering existed between the basaltic V1477 and the rhyolitic Ö1362 tephra (e.g. Bonatovsky et al., 2019; Gíslason, 2005; Kirkman and McHardy, 1980; Wolff-Boenisch

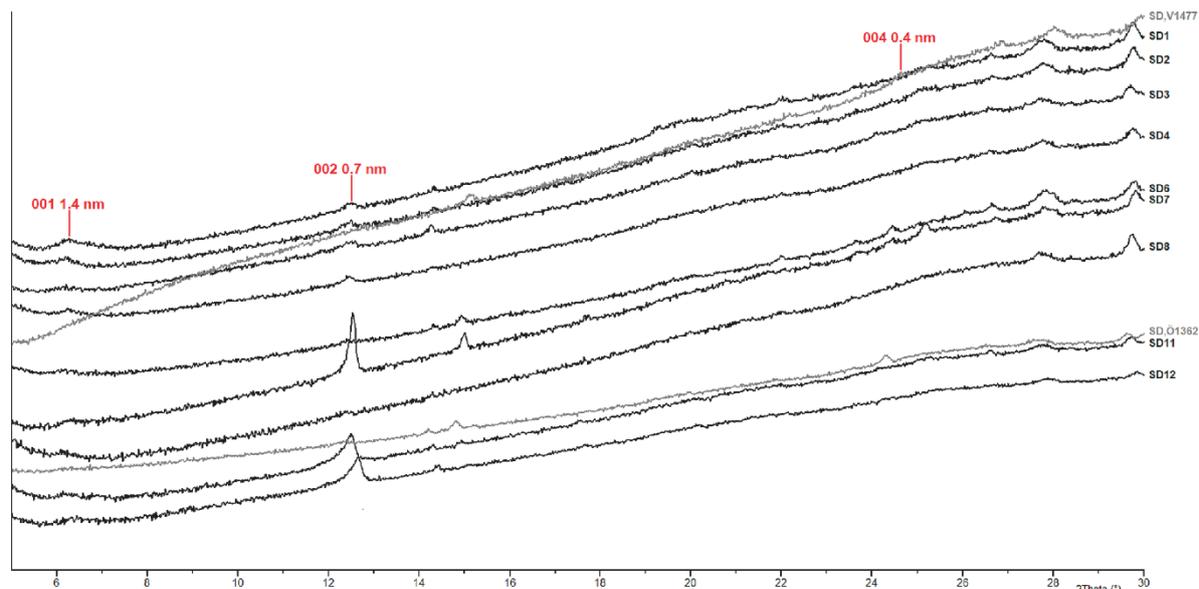


Fig. 8. X-ray diffraction patterns of the clay size fraction of selected soils at site SD, showing evidence of secondary (“pedogenic”) chlorite (soils are illustrated in black, tephra in grey).

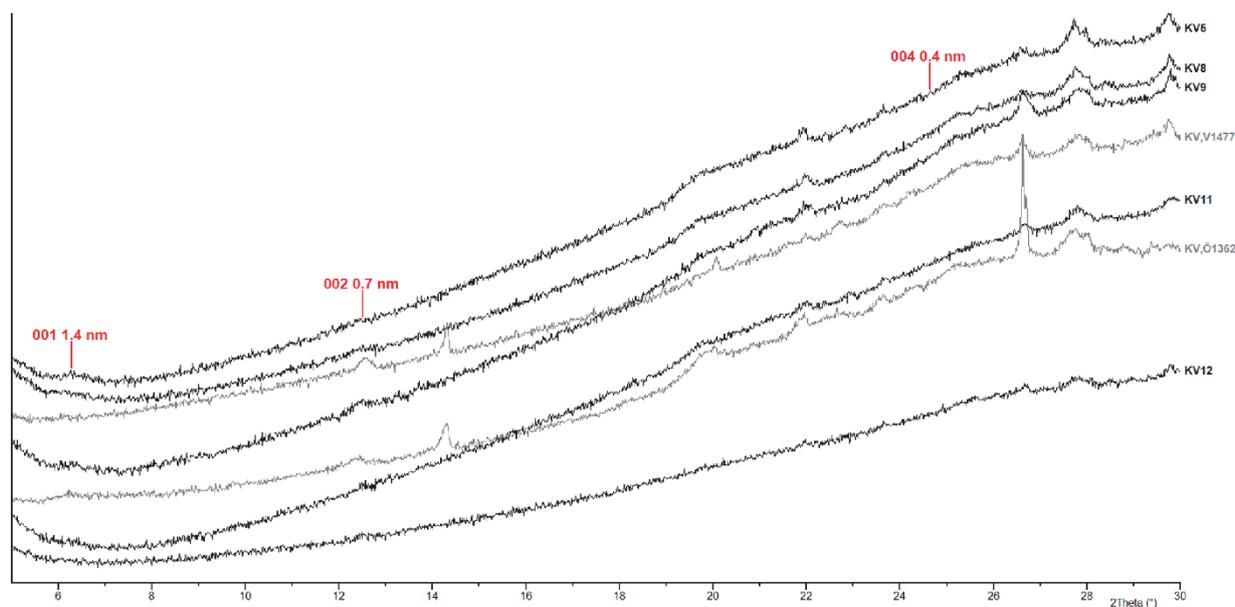


Fig. 9. X-ray diffraction patterns of the clay size fraction of selected soils at site KV, showing evidence of secondary (“pedogenic”) chlorite (soils are illustrated in black, tephra in grey).

et al., 2004). Indeed, the influence of the tephra on the soils was quite visible in our samples. According to the different weathering state between the tephra layers, the progress of weathering in the soils above V1477 were high, while they tend to be lower between Ö1362 and V1477. Beside the chemical composition, the thickness of the tephra layer seems to be a crucial factor in tephra weathering as shown by Dahlgren (2005). The thicker the layer, the more compacted it is, showing lower weathering rates than thinner layers, which have greater pore volume, thus are more prone to weathering.

The strong influence of Fe (Fe_o exceeding Al_o) in the investigated soils presumably results from the numerous basaltic tephra layers present throughout the profile. Poorly drained soils rich in OM are able to mobilize large amounts of Fe, which precipitates rapidly when exposed to oxygen rich waters (unpublished data). The area south of Vatnajökull

is known for high precipitation (Ólafsson et al., 2007). Developed in predominant aerobic dryland conditions and from mainly basaltic parent material, these requirements are given for both investigated soil profiles. At KV the soils formed above the basaltic V1477 tephra show higher ferrihydrite contents than those originated from the rhyolitic Ö1362 tephra. The ferrihydrite content increased suddenly in 20–30 cm depth, presumably due to a distinct basaltic tephra layer of unknown origin.

Icelandic Andosols are exposed to a recurrent cycle of tephra addition, incipient soil development and the soil covered by the next tephra deposit and left in its initial state of pedogenesis. Thus, we cannot make a statement about changes of the amorphous constituents with time and advancing pedogenesis.

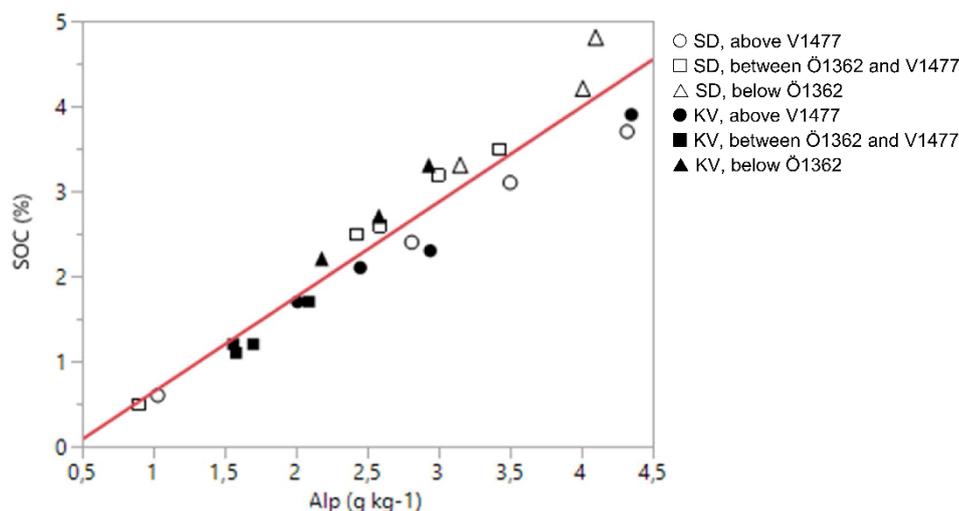


Fig. 10. Correlation between Al_p (representing Al-humus complexes) and SOC $r^2 = 0,92$, $y = -0,477855 + 1,116913x$, $P < 0.0001$ (top layers at both sites excluded).

4.3. Aeolian deposition and the crux of pedogenic minerals in young Icelandic Andosols

Even though the clay contents in the soils at SD and KV were as high as 36.6%, the majority of the clay size fraction was comprised of poorly crystalline and amorphous constituents (e.g. allophane and ferrihydrite).

The examination of the bulk XRD samples revealed a predominance of plagioclase, pyroxene and large quantity of volcanic glass in all samples, as would be expected for soils derived from volcanic ejecta, mainly of basaltic origin. Furthermore, all soils at SD and some of the soils at site KV contained so-called 1.4 nm minerals, a peak showing a 1.4 nm spacing on the X-ray diffraction pattern. The presence of 1.4 nm minerals provides evidence of clay minerals and is common in Andosols (e.g. Kawasaki and Aomine, 1966). However, the identification of the species of these minerals was generally difficult, mainly due to the predominance of amorphous constituents. Even though the conditions in Andosols are beneficial for layer silicate formation, phyllosilicates are rare in Icelandic Andosols (e.g. Arnalds, 2005; Bonatotzky et al., 2019; Wada et al., 1992). Layer silicates were found to be present in the soils investigated in the study, but only to a limited degree.

In general, the type and morphology of tephra-derived clay minerals are said to be determined by the chemical and structural characteristics of the parent material (Lowe, 1986). According to e.g. Ugolini and Dahlgren (2002) and Vilmundardóttir et al. (2014) climate and time since the tephra deposition, as well as the effective time of weathering are the main factors controlling soil development and composition, type and morphology of the resultant pedogenic clay minerals. A study of Icelandic Histosols by Bonatotzky et al. (2019) demonstrated the importance of local environmental conditions (e.g. moisture, soil temperature, SOM content) in this context.

It was mainly secondary chlorite, which could be verified clearly. The main peaks of secondary or “pedogenic” chlorite (001 (1.4 nm), 002 (0.7 nm) and 004 (0.4 nm), see Fig. 8 and Fig. 9) were present in the clay size fraction. A definitive statement about the assemblage of the present layer silicate species was not possible to make from the soils at site KV, but traces of secondary chlorite were found in some samples at this site (Fig. 8 and Fig. 9).

Regarding the clay mineralogy of the investigated soils we propose that the soils at both sites are young; in their initial state of pedogenesis. It usually takes more time under given environmental conditions for clay minerals to form and alter. The layer silicates we found are supposedly

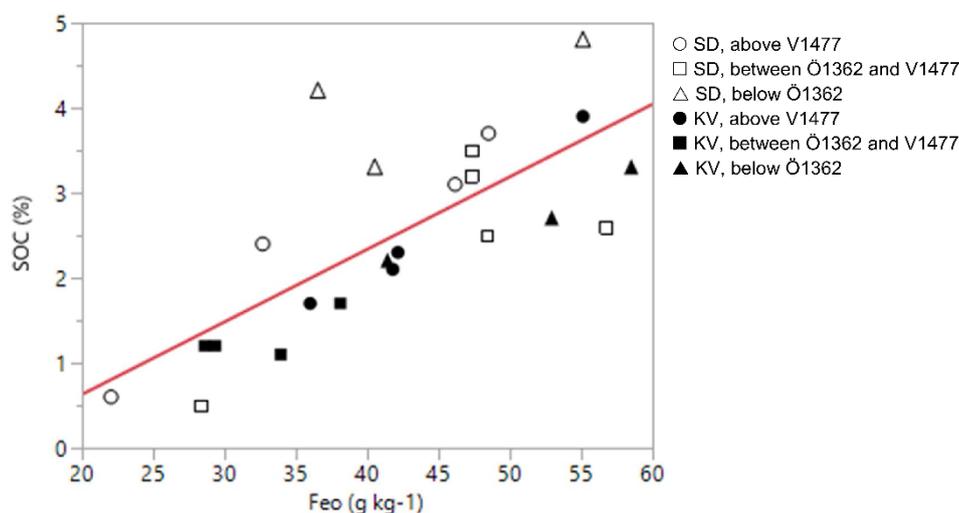


Fig. 11. Correlation between Fe_o (representing SRO minerals) and SOC $r^2 = 0.57$, $y = -1,077642 + 0,0853564x$, $P < 0.0001$ (top layers at both sites excluded).

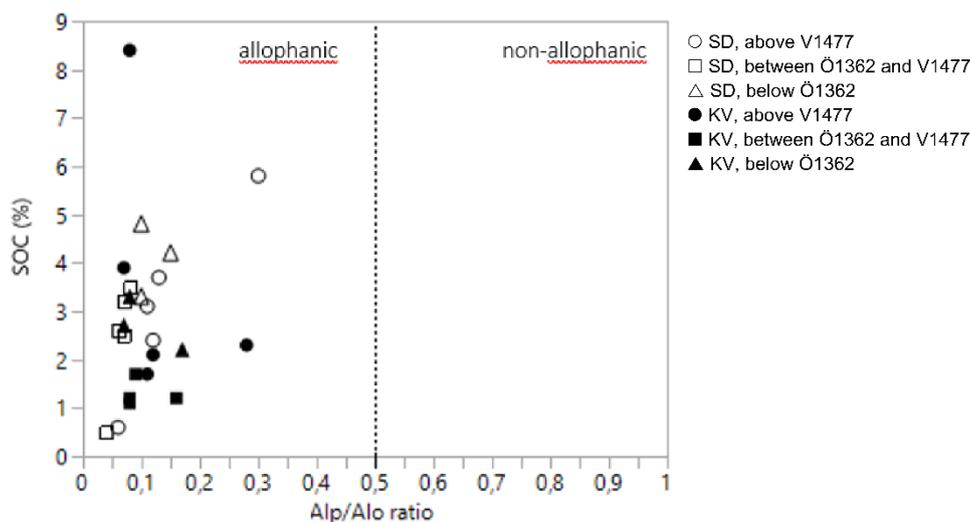


Fig. 12. Correlation between Al_p/Al_o ratio and SOC (distinguish the soils between allophanic and non-allophanic).

attributed to aeolian influx of material from older, more weathered, more developed eroded surfaces of unknown origin, maybe from sources outside Iceland. As reported by numerous previous studies (e.g. Arnalds et al., 2016; Bullard et al., 2016; Butwin et al., 2019; Đorđević et al., 2019) a transport of dust over long distances is common. According to the generally lower degree of soil development compared to the Icelandic Histosols studied by Bonatutzky et al. (2019), less clay minerals were formed in the present Andosols.

The soil layer at 52–57 cm depth stands out at site SD. The high clay content in this layer goes well with the highest weathering rate of all investigated soils. The XRD pattern of the clay size fraction samples looked very amorphous. Hardly any peak has been verified. There is no distinct tephra layer in this depth that would explain the sample striking within the profile at SD. A high estimated amount of allophane and ferrihydrite, both amorphous SRO secondary minerals and Fe-hydroxides respectively, are X-ray amorphous, thus not visible, and confirm our assumption of an especially high aeolian input.

Not just the frequent tephra addition, but a steady influx of aeolian material provides an input of more developed and weathered constituents to the, on the whole, very young Andosols.

5. Conclusion

The influx of aeolian material of unknown origin and the particular site conditions are the driving factors in the development of the investigated Andosols and the alteration of minerals. In addition, the high volcanic activity in Iceland constantly provides new tephra to the soils.

A high portion of clay size particles, even in the tephra, mainly derives from amorphous constituents (e.g. allophane and ferrihydrite). Secondary chlorite is the only type of layer silicates that could be verified and is supposedly attributed to aeolian influx of material from older, more weathered, more developed eroded surfaces of unknown origin and chemical composition, maybe from sources outside Iceland. Even though the environmental conditions at the two sites seemed to be similar, the investigated soils are hardly comparable and have to be considered separately. Similar to the findings of Lowe (1986) and what has been found in a previous study on Icelandic Histosols (Bonatutzky et al., 2019), the contrasts in mineralogy between the two sites in the present study is mainly related to the particular local environmental conditions (e.g. moisture, soil temperature, SOM), rather than the primary composition of the parent material. Both investigated Andosols are very young, thus in their initial state of soil development. We suppose

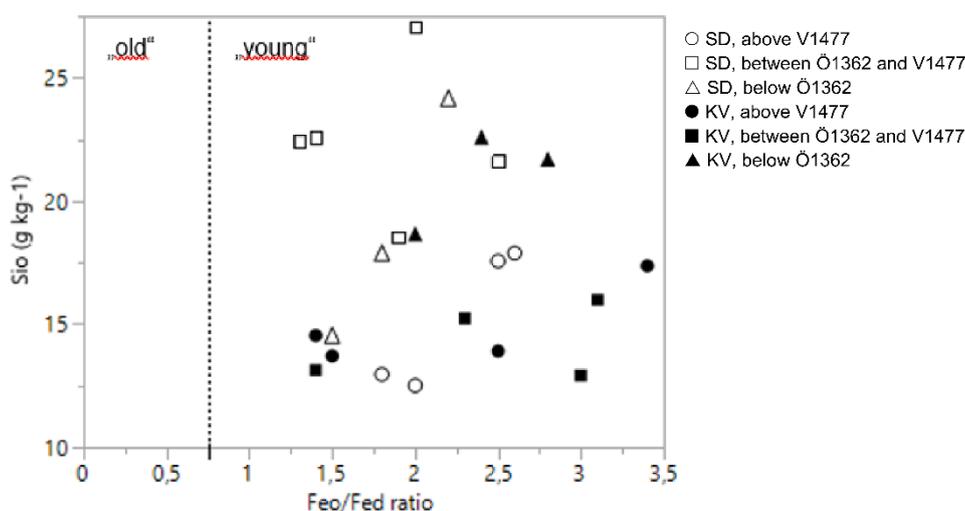


Fig. 13. Correlation between Fe_o/Fe_d ratio and Si_o (distinguish the soils between “old” and “young”).

that with increasing age the chemical composition of the parent material becomes more important in the soil development process, but therefore we would have to wait another (at least) 1000 years.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Arnalds, O., 2004. Volcanic soils of Iceland. *Catena* 56 (1–3), 3–20. <https://doi.org/10.1016/j.catena.2003.10.002>.
- Arnalds, Ó., 2008. Soils of Iceland. *Jökull* 58, 409–421.
- Arnalds, Ó., 2005. 13. Icelandic soils. In: Caseldine, C., Russell, A., Hardardóttir, J., Knudsen, Ó (Eds.), *Iceland — Modern Processes and Past Environments*. Dev. Quat. Sci. Elsevier, pp. 309–318.
- Arnalds, O., Dagsson-Waldhauserova, P., Olafsson, H., 2016. The Icelandic volcanic aeolian environment: Processes and impacts — A review. *Aeolian Res.* 20, 176–195. <https://doi.org/10.1016/j.aeolia.2016.01.004>.
- Arnalds, O., Gísladóttir, F.O., Sigurjonsson, H., 2001. Sandy deserts of Iceland: an overview. *J. Arid Environ.* 47 (3), 359–371. <https://doi.org/10.1006/jare.2000.0680>.
- Arnalds, O., Hallmark, C.T., Wilding, L.P., 1995. Andisols from Four Different Regions of Iceland. *Soil Sci. Soc. Am. J.* 59 (1), 161–169. <https://doi.org/10.2136/sssaj1995.03615995005900010025x>.
- Arnalds, O., Kimble, J., 2001. Andisols of deserts in Iceland. *Soil Sci. Soc. Am. J.* 65 (6), 1778–1786. <https://doi.org/10.2136/sssaj2001.1778>.
- Arnalds, O., Olafsson, H., Dagsson-Waldhauserova, P., 2014. Quantification of iron-rich volcanogenic dust emissions and deposition over the ocean from Icelandic dust sources. *Biogeosciences* 11 (23), 6623–6632. <https://doi.org/10.5194/bgd-11-5941-2014>.
- Arnalds, Ó., Óskarsson, H., 2009. Íslenskt Jarðvegskort. Náttúrufræðingurinn 78, 107–121.
- Austrian Standard Institute, 2006. ÖNORM I 1083, Chemische Bodenuntersuchungen - Bestimmung der Acidität (pH-Wert), Vienna.
- Bengtsson, L., Enell, M., 1986. Chemical analysis. In: Berglund, B.E. (Ed.), *Handbook of Holocene Palaeoecology and Palaeohydrology*: Chichester. John Wiley & Sons, pp. 423–451.
- Blakemore, L.C., Searle, P.L., Daly, B.K., 1987. *Methods for Chemical Analysis of Soils*. NZ Soil Bureau, Dept. of Scientific and Industrial Research, Lower Hutt, N.Z.
- Bonatzky, T., Ottner, F., Erlendsson, E., Gísladóttir, G., 2019. The weathering of volcanic tephra and how they impact histosol development. An example from South East Iceland. *Catena* 172, 634–646. <https://doi.org/10.1016/j.catena.2018.09.022>.
- Brindley, G.W., Brown, G., 1980. *Crystal Structures of Clay Minerals and Their x-Ray Identification*. Mineralogical Society, London.
- Bullard, J.E., Baddock, M., Bradwell, T., Crusius, J., Darlington, E., Gaiero, D., Gasso, S., Gísladóttir, G., Hodgkins, R., McCulloch, R., McKenna-Neuman, C., Mockford, T., Stewart, H., Thorsteinsson, T., 2016. High-latitude dust in the Earth system. *Rev. Geophys.* 54 (2), 447–485. <https://doi.org/10.1002/2016RG000518>.
- Burt, R., 2004. *Soil Survey Laboratory Methods Manual*. Nat. Resour. Conserv. Serv.
- Butwin, M.K., von Lewis, S., Pfeffer, M.A., Thorsteinsson, T., 2019. The effects of volcanic eruptions on the frequency of particulate matter suspension events in Iceland. *J. Aerosol. Sci.* 128, 99–113. <https://doi.org/10.1016/j.jaerosci.2018.12.004>.
- Chevallier, T., Fujisaki, K., Rounsard, O., Guidat, F., Kinoshita, R., de melo Viginio Filho, E., Lehner, P., Albrecht, A., 2019. Short-range-order minerals as powerful factors explaining deep soil organic carbon stock distribution: the case of a coffee agroforestry plantation on Andosols in Costa Rica. *SOIL* 5 (2), 315–332. <https://doi.org/10.5194/soil-5-315-2019>.
- Childs, C.W., 1985. *Towards Understanding Soil Mineralogy*, II. N.Z. Soil Bureau, DSIR, Notes on Ferrihydrite.
- Compton, K., Bennett, R.A., Hreinsdóttir, S., 2015. Climate-driven vertical acceleration of Icelandic crust measured by continuous GPS geodesy. *Geophys. Res. Lett.* 42 (3), 743–750. <https://doi.org/10.1002/2014GL062446>.
- Dahlgren, R., 2005. Early Stage Transformation of 2:1 Layer Silicates in Pyroclastic Deposits from the 1980 Eruption of Mt. St. Helens. *JIFS* 2, 5–12.
- Dahlgren, R.A., Boettinger, J.L., Huntington, G.L., Amundson, R.G., 1997. Soil development along an elevational transect in the western Sierra Nevada, California. *Geoderma* 78 (3–4), 207–236. [https://doi.org/10.1016/S0016-7061\(97\)00034-7](https://doi.org/10.1016/S0016-7061(97)00034-7).
- Dahlgren, R.A., Saigusa, M., Ugolini, F.C., 2004. *The Nature, Properties and Management of Volcanic Soils*. Advances in Agronomy. Academic Press, pp. 113–182.
- Declercq, J., Diedrich, T., Perrot, M., Gíslason, S.R., Oelkers, E.H., 2013. Experimental determination of rhyolitic glass dissolution rates at 40–200°C and 2<pH<10.1. *Geochim. Cosmochim. Acta* 100, 251–263. <https://doi.org/10.1016/j.gca.2012.10.006>.
- Đorđević, D., Tošić, I., Sakan, S., Petrović, S., Đuričić-Milanković, J., Finger, D.C., Dagsson-Waldhauserová, P., 2019. Can Volcanic Dust Suspended From Surface Soil and Deserts of Iceland Be Transferred to Central Balkan Similarly to African Dust (Sahara)? *Front. Earth Sci.* 7 (142) <https://doi.org/10.3389/feart.2019.00142>.
- Dugmore, A.J., Gísladóttir, G., Simpson, I.A., Newton, A., 2009. Conceptual Models of 1200 Years of Icelandic Soil Erosion Reconstructed Using Tephrochronology. *J. North Atlantic* 2, 1–18. <https://doi.org/10.3721/037.002.0103>.
- Eddudóttir, S.D., Erlendsson, E., Gísladóttir, G., 2017. Effects of the Hekla 4 tephra on vegetation in Northwest Iceland. *Veg. Hist. Archaeobot.* 26 (4), 389–402. <https://doi.org/10.1007/s00334-017-0603-5>.
- Einarsson, P., 2008. Plate boundaries, rifts and transforms in Iceland. *Jökull* 58, 35–58.
- Fieldes, M., Perrott, K.W., 1966. The nature of allophane in soils: part 3. Rapid field and laboratory test for allophane. *N.Z.J. Soil Sci.* 9, 623–629.
- García-Rodeja, E., Nóvoa, J.C., Pontevedra, X., Martínez-Cortizas, A., Buurman, P., 2004. Aluminium fractionation of European volcanic soils by selective dissolution techniques. *Catena* 56 (1–3), 155–183. <https://doi.org/10.1016/j.catena.2003.10.009>.
- Gísladóttir, G., Erlendsson, E., Lal, R., 2011. Soil evidence for historical human-induced land degradation in West Iceland. *Appl. Geochem.* 26, S28–S31. <https://doi.org/10.1016/j.apgeochem.2011.03.021>.
- Gísladóttir, G., Erlendsson, E., Lal, R., Bigham, J., 2010. Erosional effects on terrestrial resources over the last millennium in Reykjanes, southwest Iceland. *Quat. Res.* 73 (1), 20–32. <https://doi.org/10.1016/j.yqres.2009.09.007>.
- Gíslason, S.R., 2008. Weathering in Iceland. *Jökull* 58, 387–408.
- Gíslason, S.R., 2005. Chemical weathering, chemical denudation and the CO2 budget for Iceland. In: Caseldine, C., Russell, A., Hardardóttir, J., Knudsen, Ó (Eds.), *Iceland — Modern Processes and Past Environments*. Developments in Quaternary Sciences, 12. Elsevier, pp. 289–307. [https://doi.org/10.1016/S1571-0866\(05\)80014-4](https://doi.org/10.1016/S1571-0866(05)80014-4).
- Gíslason, S.R., Arnórsson, S., Ármannsson, H., 1996. Chemical weathering of basalt in southwest Iceland: Effects of runoff, age of rocks and vegetative/glacial cover. *Am. J. Sci.* 296 (8), 837–907. <https://doi.org/10.2475/ajs.296.8.837>.
- Gíslason, S.R., Oelkers, E.H., 2003. Mechanism, rates, and consequences of basaltic glass dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of pH and temperature. *Geochim. Cosmochim. Acta* 67 (20), 3817–3832. [https://doi.org/10.1016/S0016-7037\(03\)00176-5](https://doi.org/10.1016/S0016-7037(03)00176-5).
- Gíslason, S.R., Oelkers, E.H., Eiriksdóttir, E.S., Kardjilov, M.I., Gísladóttir, G., Sigfusson, B., Snorrason, A., Elefsen, S., Hardardóttir, J., Torssander, P., Óskarsson, N., 2009. Direct evidence of the feedback between climate and weathering. *Earth Planet. Sci. Lett.* 277 (1–2), 213–222. <https://doi.org/10.1016/j.epsl.2008.10.018>.
- Gudmundsson, M.T., Larsen, G., Höskuldsson, A., Gylfason, A.G., 2008. Volcanic hazards in Iceland.
- Höskuldsson, Á., 2019. Órafajökull. In: Óladóttir, B., Larsen, G., Guðmundsson, M. T., Catalogue of Icelandic Volcanoes. IMO, UI and CPD-NCIP. Retrieved from <http://icelandicvolcanoes.is/?volcano=ORA#> (25.3.2020).
- IUSS Working Group WRB, 2015. World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps. Update 2015. World Soil Resources Report No. 106. FAO, Rome, pp.192.
- JMP, 2018. A Business Unit of SAS, JMP user guide. SAS Institute Inc., Cary, NC.
- Jóhannesson, H., Sæmundsson, K., 2009. *Geological Map of Iceland*. Icelandic Institute of Natural History, p. 1:500 000.
- Kawasaki, H., Aomine, S., 1966. So-called 14 Å clay minerals in some Ando soils. *J. Soil Sci. Plant Nut.* 12 (4), 18–24. <https://doi.org/10.1080/00380768.1966.10431949>.
- Kinter, E.B., Diamond, S., 1956. A new Method for Preparation and Treatment of Oriented Aggregate Specimens of Soil Clays for X-Ray Diffraction Analysis. *Soil Sci.* 81 (1), 111–120. <https://doi.org/10.1097/00010694-195602000-00003>.
- Kirkman, J.H., McHardy, W.J., 1980. A Comparative Study of the Morphology, Chemical-Composition and Weathering of Rhyolitic and Andesitic Glass. *Clay Miner.* 15 (2), 165–173. <https://doi.org/10.1180/claymin.1980.015.2.07>.
- Kuznetsova, E., Motenko, R., 2018. Weathering of volcanic ash in the cryogenic zone of Kamchatka, eastern Russia. *Clay Miner.* 49 (2), 195–212.
- Larsen, G., 1984. Recent volcanic history of the Veidivötn fissure swarm, southern Iceland — an approach to volcanic risk assessment. *J. Volcanol. Geotherm. Res.* 22 (1–2), 33–58. [https://doi.org/10.1016/0377-0273\(84\)90034-9](https://doi.org/10.1016/0377-0273(84)90034-9).
- Larsen, G., Dugmore, A., Newton, A., 1999. Geochemistry of historical-age silicic tephras in Iceland. *Holocene* 9 (4), 463–471.
- Larsen, G., Eiriksson, J., 2008. Holocene tephra archives and tephrochronology in Iceland - a brief overview. *Jökull* 58, 229–250.
- Lowe, D., 1986. Controls on the rates of weathering and clay mineral genesis in airfall tephras: A review and New Zealand case study, 265–330.
- Malucelli, F., Terribile, F., Colombo, C., 1999. Mineralogy, micromorphology and chemical analysis of andosols on the Island of São Miguel (Azores). *Geoderma* 88, 73–98.
- Mizota, C., van Reeuwijk, L.P., 1989. *Clay Mineralogy and Chemistry of Soils Formed in Volcanic Material in Diverse Climatic Regions*. 90-6672-035-2. ISRIC, World Soil Information, Wageningen.

- Möckel, S.C., Eriksen, E., Gísladóttir, G., 2017. Holocene environmental change and development of the nutrient budget of histosols in North Iceland. *Plant Soil* 418 (1–2), 437–457. <https://doi.org/10.1007/s11104-017-3305-y>.
- Moore, D.M., Reynolds Jr., R.C., 1997. X-ray diffraction and the identification and analysis of clay minerals, Second Edition. Oxford University Press (OUP), Oxford.
- Nanzyo, M., Dahlgren, R., Shoji, S., 1993. Chapter 6: Chemical Characteristics of Volcanic Ash Soils. In: Shoji, S., Nanzyo, M., Dahlgren, R. (Eds.), *Volcanic Ash Soils - Genesis, Properties and Utilization*. Elsevier, pp. 145–187. [https://doi.org/10.1016/S0166-2481\(08\)70267-8](https://doi.org/10.1016/S0166-2481(08)70267-8).
- Óladóttir, B.A., 2009. Holocene eruption history and magmatic evolution of the subglacial volcanoes, Grímsvötn, Bárðarbunga and Kverkfjöll beneath Vatnajökull, Iceland. PhD thesis. Université Blaise Pascal, Clermont-Ferrand and University of Iceland, Reykjavík.
- Óladóttir, B.A., Larsen, G., Sigmarsson, O., 2011. Holocene volcanic activity at Grímsvötn, Bárðarbunga and Kverkfjöll subglacial centres beneath Vatnajökull, Iceland. *Bull. Volcanol.* 73 (9), 1187–1208. <https://doi.org/10.1007/s00445-011-0461-4>.
- Ólafsson, H., Furger, M., Brummer, B., 2007. The weather and climate of Iceland. *Meteorol. Z.* 16 (1), 5–8. <https://doi.org/10.1127/0941-2948/2007/0185>.
- Pagli, C., Sigmundsson, F., 2008. Will present day glacier retreat increase volcanic activity? Stress induced by recent glacier retreat and its effect on magmatism at the Vatnajökull ice cap. *Iceland. Geophys. Res. Lett.* 35 (9) <https://doi.org/10.1029/2008GL033510>.
- Parfitt, R.L., Henmi, T., 1982. Comparison of an oxalate-extraction method and an infrared spectroscopic method for determining allophane in soil clays. *J. Soil Sci. Plant Nut.* 28 (2), 183–190. <https://doi.org/10.1080/00380768.1982.10432435>.
- Parfitt, R.L., Russell, M., Orbell, G.E., 1983. Weathering Sequence of Soils from Volcanic Ash Involving Allophane and Halloysite. *New-Zealand. Geoderma* 29 (1), 41–57. [https://doi.org/10.1016/0016-7061\(83\)90029-0](https://doi.org/10.1016/0016-7061(83)90029-0).
- Parfitt, R.L., Wilson, A.D., 1985. Estimation of allophane and halloysite in three sequences of volcanic soils. *Catena supplement* 7, 1.
- Pollard, A.M., Blockley, S.P.E., Ward, K.R., 2003. Chemical alteration of tephra in the depositional environment: theoretical stability modelling. *J. Quat. Sci.* 18 (5), 385–394. <https://doi.org/10.1002/jqs.760>.
- Riedmüller, G., 1978. Neoformations and transformations of clay minerals in tectonic shear zones. *Tschermak's Mineral. Petrogr. Mitt.* 25 (3), 219–242.
- Russell, M., Parfitt, R.L., Claridge, G.G.C., 1981. Estimation of the Amounts of Allophane and Other Materials in the Clay Fraction of an Egmont Loam Profile and Other Volcanic Ash Soils. *New-Zealand. Aust. J. Soil Res.* 19 (3), 185–195. <https://doi.org/10.1071/SR9810185>.
- Sæmundsson, K., Larsen, G., 2019. Torfajökull. In: Óladóttir, B., Larsen, G. & Guðmundsson, M. T. *Catalogue of Icelandic Volcanoes*. IMO, UI and CPD-NCIP. Retrieved from <http://icelandicvolcanos.is/?volcano=TOR> (25.3.2020).
- Schoeneberger, P., Wysocki, D., Benham, E., Broderick, W., 2002. Field Book for Describing and Sampling Soils, Version 2.0. Natural Resources Conservation Service.
- Shang, C., Zelazny, L.W., 2008. Selective dissolution techniques for mineral analysis of soils and sediments. In: Uleriy, A.L., Drees, L.R. (Eds.), *Methods of Soil Analysis*. Part 5 - Mineralogical Methods. Soil. Sci. Soc. Am., Madison, WI, pp. 33–80.
- Sharma, K., Self, S., Blake, S., Thordarson, T., Larsen, G., 2008. The AD 1362 Öræfajökull eruption, S.E. Iceland: physical volcanology and volatile release. *J. Volcanol. Geotherm. Res.* 178, 719–739.
- Shoji, S., Dahlgren, R., Nanzyo, M., 1993. Chapter 3 Genesis of Volcanic Ash Soils. In: S. Shoji, M. Nanzyo, R. Dahlgren (Eds.), *Dev. Soil Sci.* Elsevier, pp. 37–71. [https://doi.org/10.1016/S0166-2481\(08\)70264-2](https://doi.org/10.1016/S0166-2481(08)70264-2).
- Shoji, S., Fujiwara, Y., 1984. Active Aluminum and Iron in the Humus Horizons of Andosols from Northeastern Japan - Their Forms, Properties, and Significance in Clay Weathering. *Soil Sci.* 137 (4), 216–226.
- Shoji, S., Fujiwara, Y., Yamada, I., Saigusa, M., 1982. Chemistry and Clay Mineralogy of Ando Soils, Brown Forest Soils, and Podzolic Soils Formed from Recent Towada Ashes. *Northeastern Japan. Soil Sci.* 133 (2), 69–86.
- Soil Survey Staff, 2014. *Keys to Soil Taxonomy 2014*, 12th ed. USDA - Natural Resources Conservation Service, Washington, DC.
- Sparks, D.L., Page, A.L., Helmke, P.A., Loepfert, R.H., 1996. *Methods of Soil Analysis Part 3—Chemical Methods*. Soil Science Society of America, American Society of Agronomy, Madison, WI, SSSA Book Series.
- Takahashi, T., Dahlgren, R.A., 2016. Nature, properties and function of aluminum–humus complexes in volcanic soils. *Geoderma* 263, 110–121. <https://doi.org/10.1016/j.geoderma.2015.08.032>.
- Takahashi, T., Shoji, S., 2002. Distribution and classification of volcanic ash soil. *Global Environ. Res.* 6 (2), 83–97.
- Thorarinnsson, S., 1958. The Öræfajökull eruption in 1362. *Acta Natur. Islandica* 2, 1–99.
- úorbjarnarson, H., 2016. Soil evolution in the dynamic area south of Vatnajökull. Master's Thesis. University of Iceland.
- Thordarson, T., Larsen, G., 2007. Volcanism in Iceland in historical time: Volcano types, eruption styles and eruptive history. *J. Geodyn.* 43 (1), 118–152. <https://doi.org/10.1016/j.jog.2006.09.005>.
- Tributh, H., 1989. Notwendigkeit und Vorteil der Aufbereitung von Boden- und Lagerstättentönen. In: Tributh, H., Lagaly, G. (Eds.), *Identifizierung und Charakterisierung von Tonmineralen. Berichte der Deutschen Ton- und Tonmineralsgruppe*, Giessen, Germany, pp. 29–33.
- Ugolini, F.C., Dahlgren, R.A., 2002. Soil development in volcanic ash. *Global Environ. Res.* 6, 69–81.
- Vacca, A., Adamo, P., Pigna, M., Violante, P., 2003. Genesis of tephra-derived soils from the Roccamonfina Volcano, South Central Italy. *Soil Sci. Soc. Am. J.* 67, 198–207.
- Vilmundardóttir, O.K., Gísladóttir, G., Lal, R., 2014. Early stage development of selected soil properties along the proglacial moraines of Skaftafellsjökull glacier, SE-Iceland. *Catena* 121, 142–150. <https://doi.org/10.1016/j.catena.2014.04.020>.
- Wada, K., 1989. Allophane and Imogolite. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*. Soil Science Society of America, Madison, WI, SSSA Book Series, pp. 1051–1087.
- Wada, K., Arnalds, O., Kakuto, Y., Wilding, L.P., Hallmark, C.T., 1992. Clay minerals of four soils formed in eolian and tephra materials in Iceland. *Geoderma* 52 (3–4), 351–365. [https://doi.org/10.1016/0016-7061\(92\)90046-A](https://doi.org/10.1016/0016-7061(92)90046-A).
- Wada, K., Harward, M.E., 1974. Amorphous Clay Constituents of Soils. In: Brady, N.C. (Ed.), *Advances in Agronomy*. Academic Press, pp. 211–260. [https://doi.org/10.1016/S0065-2113\(08\)60872-X](https://doi.org/10.1016/S0065-2113(08)60872-X).
- Whittig, L.D., 1965. X-ray diffraction techniques for mineral identification and mineralogical identification. In: Black, C.A. (Ed.), *Methods of Soil Analysis*, Vol. 1. American Society of Agronomists, Madison, WI, pp. 671–698.
- Wilson, M.J., 1987. *A Handbook of Determinative Methods in Clay Mineralogy*. Blackie and Sons, Glasgow and London.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2006. The effect of crystallinity on dissolution rates and CO₂ consumption capacity of silicates. *Geochim. Cosmochim. Acta* 70 (4), 858–870. <https://doi.org/10.1016/j.gca.2005.10.016>.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., Putnis, C.V., 2004. The dissolution rates of natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from 25 to 74°C. *Geochim. Cosmochim. Acta* 68 (23), 4843–4858. <https://doi.org/10.1016/j.gca.2004.05.027>.
- Zakharikhina, L.V., 2006. Soil formation on acid and basic volcanic ashes of different ages in Kamchatka. *Eurasian Soil Sci.* 39 (9), 938–952.

Paper 3

The impact of environmental factors on early stage Andosol development south of Vatnajökull, Iceland.

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Author's contribution:

Theresa Bonatitzky (TB), Guðrún Gísladóttir (GG), Egill Erlendsson (EE) and Franz Ottner planned the study. Fieldwork and sampling at site Kvíármýrarkambur were carried out by TB, GG and EE. Soil and tephra sample preparation and all analyses (except for analyses of Total C and N and ICEP-AES analyses of the extracted oxides and hydroxides) were done by TB at BOKU and HÍ. TB did the data analysis and wrote the manuscript. Co-Authors and members of the PhD committee provided useful comments and suggestions on the manuscript.

The impact of environmental factors on early stage Andosol development south of Vatnajökull, Iceland.

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ABSTRACT

Icelandic soils develop in a dynamic environment affected by both natural processes and anthropogenic impacts. We present an extensive investigation of soil mineralogy and pedogenesis in a disturbed (i.e. by solifluction) pedon under such conditions. The study focuses on two distinct tephra layers; a rhyolitic tephra from the Öräfajökull eruption in 1362 CE (Ö1362) and a basaltic Veiðivötn tephra from 1477 CE (V1477). Both tephra layers form an important parent material in the study area south of Vatnajökull, Iceland.

The Andosol developed from tephra and aeolian material, rich in volcanic glass. The pH (H₂O) values were between 5.5 and 6.6 and clay mineralogy displayed a predominance of allophanic material in both soil and tephra. The pedon can be seen in its early stage of chemical weathering and soil development. Despite the overall predominance of non- and poorly-crystalline SRO secondary materials and Fe (hydr)oxides in the clay-size fraction, we found indication of smectite.

High exchangeable Ca²⁺ and Mg²⁺ concentrations reflect enhanced aeolian input of volcanic material, while elevated exchangeable Na⁺ concentrations are most likely caused by the oceanic composition of precipitation. The impact of erosion and aeolian processes on pedogenesis seemed to be higher between the deposition of Ö1362 and V1477, than in the soils above.

Both, soil and tephra layers appeared disturbed by erosion/deposition processes over time. Characterized by a significantly coarser particle size composition, low SOC content, and a more diverse mineralogy, a distinct fluvial sediment layer at 10 – 30 cm depth appeared sharply contrasting to the other soil layers in the profile. This possibly reflects the diverse composition of glaciofluvial material from a landslide originating from a Kvíárjökull moraine in the North. Changed weathering patterns and properties in the soils above the Ö1362 tephra indicated soil degradation following the deposition of the rhyolitic tephra.

Keywords: Aeolian influx, erosion, Iceland, pedogenic minerals, soil development, tephra, volcanic soil

1. INTRODUCTION

1.1. Soil development within a naturally dynamic environment

Iceland is characterized by a harsh, subpolar oceanic climate and frequent volcanic eruptions. Its location in the middle of the North Atlantic Ocean, near both oceanic and atmospheric fronts, makes it highly sensitive to climate changes (e.g. Hannesdóttir et al., 2015). All Icelandic soils are of Holocene age (Arnalds et al., 2001) and develop in this dynamic environment. The majority of them can be classified as Andosols (Arnalds and Óskarsson, 2009), rich in volcanic glass. The soils are strongly affected by frequent tephra deposition and influx of aeolian material from proximal and distal sources, even from outside Iceland. Soil surfaces are constantly recharged with pristine material (dust, tephra and lava flows), while subsoils are preserved and continue to develop after burial (e.g. Bonatutzky et al., 2019; Gísladóttir et al., 2010).

The fine particle size, glassy nature, high porosity and high permeability of tephra enhance weathering and interaction in the soil environment (Dahlgren et al., 1997; Lowe, 1986). Attributed to the parent material, Icelandic soils exhibit high weathering rates despite a prevalent cool climate (Gíslason et al., 2009; 1996) but in general, a young weathering state is characteristic for all Icelandic soils (e.g. Bonatutzky et al., 2021). The formation of non-crystalline materials in soils formed from volcanic parent material is connected to the properties of tephra (Shoji et al., 1993). The rate of weathering and the formation, type and morphology of tephra-derived pedogenic clay minerals are said to be determined by the chemical and structural characteristics (such as the amount, size, porosity and chemical and mineralogical composition) of the parent material (Lowe, 1986; Shoji et al., 1993; Van Ranst et al., 1993), climate and time (Ugolini and Dahlgren, 2002; Vilmundardóttir et al., 2014), and local environmental conditions (Bonatutzky et al., 2021; 2019). Studying the dissolution of natural glasses, Wolff-Boenisch et al. (2004) showed that the lifetime of “coloured glass” of basaltic andesitic composition can be nine times lower than those of rhyolitic “non-coloured glass”. Despite the overall rapid weathering of tephra, volcanic material of rhyolitic composition weathers much more slowly than basaltic (Bonatutzky et al., 2021; Gíslason, 2005; Nanzyo et al., 1993a).

Clay minerals hold a major role in many pedons, but are rare in Icelandic soils (Bonatutzky et al., 2021; 2019). Because of their distinctive characteristics (i.e. small particle size, high surface area) they influence both chemical and physical soil properties (Schulze, 1989). They are sensitive to changes in the soil environment and are useful indicators that provide abundant information on weathering and the degree of soil development (e.g. Griffin et al., 1968; Jacobs and Hays, 1972; Rateev et al., 1969; Środoń, 2013; 2002). In Icelandic soils, clay minerals develop from volcanic ejecta and are formed in subsurface horizons *in situ* rather than by translocation or leaching and precipitation (Arnalds, 2008; Dahlgren et al., 2004). Allophane, a group of short-range order (SRO) materials (Parfitt, 1990) and poorly crystalline ferrihydrite are generally abundant in the clay-size fraction (e.g. Bonatutzky et

al., 2021; 2019; Stefánsson and Gíslason, 2001). With increasing soil age, the crystalline weathering phases become more abundant (Crovisier et al., 1992).

1.2 Anthropogenic influence on soil development

In Iceland, prior to human settlement in the late 9th century, climate was the main driver of ecosystem change (Gísladóttir et al., 2011). Human occupation and associated pastoral farming facilitated a crucial change of the Icelandic terrestrial environment. Based on written documents (Íslendingabók and Landnámabók, Benediktsson, 1986a; Benediktsson, 1986b) and studies simulating the vegetation cover over the Holocene (e.g. Eddudóttir et al., 2020; Erlendsson and Edwards, 2010; Erlendsson et al., 2014; Haraldsson and Ólafsdóttir, 2003; Ólafsdóttir et al., 2001), it is suggested that Iceland was covered by dense and widespread birch woodlands until the time of settlement.

With the decline of vegetation cover due to land-use, soil exposure proceeded. Large areas became prone to wind and water erosion processes, forming vast areas of dust and sandy deserts. Severe increased soil erosion/deposition further facilitated by the harsh climate and frequent volcanic eruptions resulted in drastically decreased soil quality and depletion of soil organic carbon (Dugmore et al., 2009; Gísladóttir et al., 2010; Kardjilov et al., 2006; Lal, 2004; Óskarsson et al., 2004), reflected by e.g. increased soil accumulation and bulk density, changed particle size composition (becoming coarser) and altered mineralogy. Up to 80% of the aeolian dust has a volcanic origin of basalt composition, the remainder being of intermediate to silicic composition originating from sources in- and outside of Iceland (Arnalds et al., 2016; Gíslason, 2008). The main source areas for dust in Iceland nowadays are the Highlands in central Iceland and the sandur plains along the South coast, where the surface is made up of loose sediment (Arnalds et al., 2016).

Given the dynamic environmental context arising from both climatological and anthropological drivers, it is important to investigate how soils develop under such conditions. In this paper we present the results from an extensive study on soil mineralogy and pedogenesis in a disturbed soil profile in the lowlands south of Vatnajökull, SE Iceland (Fig. 1). Environmental factors that are taken for consideration are erosional processes such as solifluction, slope instability and aeolian soil/tephra reworking and deposition, as well as influence by seawater precipitation and tephra deposition.

Our research questions addressed two major factors:

Soil development and mineral alteration

How is the mineral parent material of volcanic origin (tephra) reflected in variations in soil properties (i.e. andic/vitric properties) and in the formation and alteration of minerals?

Erosion

How do the investigated soils reflect external environmental processes as factors in soil development?

By investigating selected physical, chemical and mineralogical properties of soil and tephra, the primary objectives of this study were to examine the genesis of soils derived from basaltic and rhyolitic (tephra) parent material under the prevailing environmental conditions of Iceland. Further we investigated the clay mineral composition under given conditions to provide a better understanding of weathering processes, pedogenesis and the formation of pedogenic minerals in young soils, under a cool climate and influenced by frequent external environmental disturbances and influx of pristine material.

2. MATERIAL and METHODS

2.1. Study site and material

The area south of Vatnajökull is characterized by maritime climate with cool, moist summers and relatively warm winters. Mean annual temperature at Kvísker weather station (63°57.576'N, 16°25.465'W, 30 m a.s.l.), the weather station closest (about 3 km) to the sampling site, is 5.9 °C (2009–2016) and annual precipitation (1962–2011) is 3500 mm on average (unpublished data from the Icelandic Meteorological Office). Precipitation values in the region are among the highest observed in Iceland (Einarsson, 1980). Soils in the research area developed under frigid and udic conditions (Soil Survey Staff, 2014).

The sampling site Kvíármýrarkambur (63°56.129'N, 16°26.515'W; Fig. 1) is situated within Öraefi district, located in the lowland at the foot of Öraefajökull volcano, and is strongly influenced by glacial and volcanic activity. It is also affected by its close proximity to the North Atlantic Ocean to the south, and the steep and high mountain range beneath the Vatnajökull glacier to the north (Olafsson et al., 2007; Sigurmundsson et al., 2020). Soil erosion is a problem in the area due to morphology and interactions between glaciers and glacial rivers, volcanism, land use and the influence of the sea. Even though the area is glacier-free nowadays, it has been highly influenced by advance and retreat of several Vatnajökull outlet glaciers during the Holocene (Hannesdóttir, 2014). The end moraine of Kvíárjökull, the largest of its kind in front of Vatnajökull, is located just a short distance north of the sampling site.

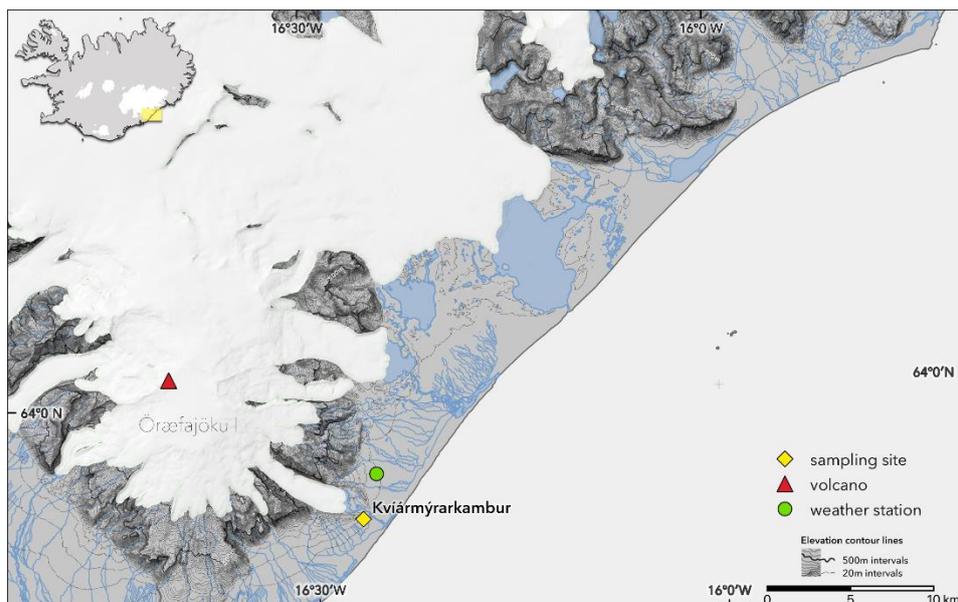


Figure 1. The research area south of Vatnajökull glacier, SE Iceland. Set within the Öraefajökull massif, the triangle marks Hvannadalshnjúkur at 2110 m a.s.l., the highest peak of Iceland. The diamond shows the position of the sampling site Kviármýrarkambur at the foot of Öraefajökull. The location of the weather station Kviósker is shown as circle. (Map produced by Benjamin D. Hennig)

Both, soil and tephra layers show signs of disturbance (i.e. by erosion/deposition processes). The sampling site is situated in a for decades drained wetland (Fig. 2), used for sheep grazing. The vegetation cover is comprised of grass- and heathland with *Salix spp.* shrubs.



Figure 2. The study site at Kviármýrarkambur (KMK) on the left, soil profile on the right. V1477 tephra was found at 50 - 59 cm depth, Ö1362 at 79 - 86 cm depth.

The geology of the research area is primarily composed of basaltic lava and hyaloclastite (glassy rocks) (Jóhannesson and Sæmundsson, 2009; Thorarinsson, 1958). Although situated outside the active volcanic zone, the study area is strongly affected by active central volcanoes nearby. Two distinct tephra layers, the light colored rhyolitic tephra from the 1362

CE Öräfajökull eruption (Ö1362) and a dark basaltic tephra from the 1477 CE Veiðivötn fissure eruption (V1477), are well preserved in the soil (Fig. 2).

The eruption of the Öräfajökull central volcano in 1362 CE was the most voluminous explosive silicic eruption to have occurred in Iceland in historical times. It produced at least 10 km³ of acidic, uncompacted, light grey tephra (Gudmundsson et al., 2008; Larsen et al., 1999), mainly dispersed to the southeast (Thorarinsson, 1958). The Ö1362 is characterized by a high content of Na₂O (average 4.95%) and low CaO content (< 1.2%) (e.g. Larsen et al., 1999; Wolff-Boenisch et al., 2004). The range in SiO₂ (average 72.71%) is similar to some historical Hekla tephra layers, but a higher FeO (average 3.30%) and a very low MgO content (close to zero) enable the Ö1362 to be distinguished from other rhyolitic tephra deposits (Larsen et al., 1999).

In 1477 CE an eruption in the Veiðivötn fissure swarm, which belongs to the Bárðarbunga volcanic system, produced more than 10 km³ of basaltic tephra that was dispersed towards east, northeast and north (Larsen, 1984). The eruption is thought to be the largest explosive basaltic eruption in Iceland during the last 1200 years. Compared to the rhyolitic Ö1362 tephra, V1477 has a lower SiO₂ content of c. 50%, about half of Na₂O (approx. 2.5%), but a multiple of the MgO (6 – 7%) and FeO (approx. 13%) content (e.g. Lawson et al., 2007; Streeter and Dugmore, 2014).

During both eruptions, the tephra was deposited on vegetated land. Thus, they are preserved as important tephra marker layers in the research area. Other tephra layers of basaltic composition were found in the soil profile but not distinguished as a specific volcanic system or eruption event.

2.2. Sampling and preparation

The sampling site was selected according to the occurrence of the two distinctive tephra layers which were detected by test coring with a JMC Backsaver. The pedon stratigraphy did not allow for a distinction between soil horizons. Thus, we followed a sampling strategy appropriate to our research questions. Soil samples were taken at a 10-cm depth interval and at 5-cm intervals immediately above and below the two main tephra layers. We slightly adapted the strategy (see sediment layer from 10 to 30 cm depth) where field conditions inhibited the pre-defined strategy. Tephra layers, easily distinguishable from the soil, were sampled separately. Both, V1477 and Ö1362 did not appear as single layer, but were split into two and three sublayers respectively within the particular tephra deposit (hereafter referred to as V1477, A and B and Ö1362, A, B and C). Each sublayer was sampled separately. Additionally, a soil monolith was taken. After collection, all samples were kept in sealed plastic bags and stored at 4°C pending analyses. Prior to the analyses of physical and chemical properties, representative bulk soil and tephra samples were air-dried and gently crushed to pass through a 2-mm sieve.

2.3. Soil and tephra sample analyses

2.3.1. Mineralogical soil and tephra analyses

Representative samples for bulk mineral analyses were oven-dried at 70 °C and ground to analytical fineness. To obtain the clay fraction (< 2 µm), the OM of the samples was removed by 10% hydrogen peroxide (H₂O₂) treatment. After this pre-treatment, clay was separated from the soil by a combination of wet-sieving (mesh: 2000 to 20 µm) and centrifugation (after initial dispersion with ultrasonic vibration). Similar to the method described by Kinter and Diamond (1956), the preferential orientation of the clay minerals was obtained by suction through a porous ceramic tile.

X-ray diffraction (XRD) analyses were performed using a PANalytical X'Pert Pro diffractometer with automatic divergent slit, Cu LFF tube 45 kV, 40 mA, with an X'Celerator detector. The measuring time was 250 s per step, with a stepsize of 0.017°. Bulk powder samples were X-rayed from 2 to 70° 2θ. The exchange complex of each sample was saturated with K⁺ and Mg²⁺. Expansion tests on the clay-size fraction samples, using ethylene glycol (EG), dimethyl sulfoxide (DMSO) as well as contraction tests heating of the < 2 µm fraction up to 550 °C were performed. After each treatment, the samples were X-rayed from 2 to 40° 2θ. Resultant diffractograms were evaluated using X'Pert HighScorePlus software and identified according to Moore and Reynolds (1997), Brindley and Brown (1980) and Wilson (1987). A semiquantitative mineral composition of the clay-size fraction was estimated from the resultant diffractograms according to Riedmüller (1978).

Differential scanning calorimetry (DSC) and thermogravimetry (TG) were conducted on 50 mg of clay-size fraction powder sample (pre-dried at 65°C) using a Netzsch STA 409 PC Luxx® Simultaneous thermal analyzer. While heating the sample from 25 to 1000 °C at a rate of 10 °C min⁻¹ in a reaction atmosphere of synthetic air (flow rate: 50 ml min⁻¹), the heat flow to or from the sample as a function of energy was monitored. Thermal flux and weight changes were measured simultaneously. The resulting endothermic and exothermic reactions were ascribed according to Smykatz-Kloss (1974) and Barros et al. (2007).

2.3.2. Physicochemical soil and tephra analyses

Particle-size analyses were carried out in combination with the clay-size analysis. The fine particles (< 20 µm) were obtained by means of sedimentation using a Sedigraph III 5120 (Micromeritics, Georgia, USA). Dry bulk density (DBD) was measured on a soil monolith in the lab. For this purpose, we used small cubical cores of known volume (7.9 cm³) as described in Vilmundardóttir et al. (2014). Due to the small size of cores, three replicates (n) for each DBD sample were collected to obtain an average value. According to Bengtsson and Enell (1986), the SOM was measured by the loss on ignition (LOI) by combusting 1.2 cm³ of soil/tephra at 550°C for 5 hours. Soil pH (H₂O) was obtained in soil:water (1:5) suspension according to ÖNORM L1083 (Austrian Standard Institute, 2006), pH determined in 1M NaF solution for estimation of the andic properties of the soil was determined

following the method of Fieldes and Perrott (1966) as outlined in Blakemore et al. (1987). Concentrations of soil organic carbon (SOC) and total nitrogen (total N) were determined by dry combustion at 900°C using a Flash 1112 Elementar Analyzer (Thermo-Scientific, Italy) with ball-milled soil and tephra samples passed through a 150- μm sieve and dried at 50°C. Since the studied soils did not contain carbonate minerals (determined by HCl test and XRD), the values thus obtained were assumed to correspond to organic carbon (OC). Phosphate retention (P-retention or P-ret) was analysed using the method outlined in Blakemore et al. (1987).

Non-sequential, selective dissolutions were carried out to determine poorly crystalline and amorphous constituents as well as those associated with humus in the soil and tephra samples. In preparation for analyses, samples were air-dried, ball-milled and passed through a 150- μm sieve. Iron (Fe), aluminium (Al) and silica (Si) associated with amorphous constituents (Fe_o , Al_o , Si_o) were extracted with ammonium oxalate (pH 3.0) in the dark using a mechanical extractor (SampleTek mechanical vacuum, Mavco Industries). Fe and Al associated with OM (Fe_p , Al_p) were extracted with sodium pyrophosphate at pH 10.0 and shaking for 16 h. Both ammonium oxalate and sodium pyrophosphate extraction were carried out according to USDA Soil Survey Laboratory Manual (Burt, 2004). Fe in crystalline and non-crystalline (hydr)oxides (Fe_d) was extracted by citrate-bicarbonate-dithionite (CBD) as outlined in Sparks et al. (1996). The resultant extracts were stored at 4°C until analysed by inductively coupled plasma atomic emission spectrophotometer (ICP-AES).

The effective cation exchange capacity (ECEC) was determined according to USDA Soil Survey Laboratory Manual (Burt, 2004). Exchangeable Ca^{2+} , Mg^{2+} , Na^+ and K^+ were extracted by 1 M pH 7 NH_4OAc , exchangeable Al^{3+} was extracted by 1 M KCl and ECEC was calculated as the sum of these ions. The ion content of the extracts was determined by ICP-AES.

Soil accumulation rates (SAR) (mm/yr) were calculated by measuring soil thickness between the tephra layers of known age (Gísladóttir et al., 2010; Óladóttir et al., 2011).

2.4. Calculation of relevant geochemical indices

Allophane content (%) was estimated by the formula $100x\% \text{Si}_o / [23.4 - 5.1x]$ with $x = (\text{Al}_o - \text{Al}_p) / \text{Si}_o$ (e.g. Mizota and van Reeuwijk, 1989; Parfitt and Henmi, 1982; Parfitt and Wilson, 1985). Ferrihydrite content (%) was estimated by multiplying the $\% \text{Fe}_o$ by a factor of 1.7 (Childs, 1985). Contents of non-crystalline secondary phases of the clay size fraction, hereafter referred to as amorphous secondary clay, were estimated as the total amount of allophane and ferrihydrite (Shang et al., 2008). The molar Al/Si ratios of allophane in the soil and tephra were calculated from $(\text{Al}_o - \text{Al}_p) / \text{Si}_o$ according to e.g. Wada (1989). $\text{Al}_o + 0.5\text{Fe}_o$ was used as a taxonomy criterion for andic soil properties (Soil Survey Staff, 2014). To differentiate between aluandic and silandic soil properties (IUSS Working Group WRB,

2015) and to estimate the presence of allophanic material (Shoji et al., 1993), the Al_p/Al_o ratio was used.

3. RESULTS

3.1. Selected soil and tephra properties

A summary of selected soil properties is presented in Table 1. The basaltic V1477 tephra was found at 50 - 59 cm depth and the rhyolitic Ö1362 was found at 79 - 86 cm depth. Instead of a single, distinct tephra layer, both V1477 and Ö1362 appeared disturbed and split into two and three sublayers respectively within the particular tephra.

Table 1. Selected morphological, physical and chemical characteristics of the studied pedon at Kvíármýrarkambur (KMK).

Sample	Depth cm	pH(H ₂ O)	pH(NaF)	SOM	total N %	SOC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Al ³⁺	ECEC	P-ret %	DBD ² g/cm ³	SAR mm/yr
							cmolc/kg								
KMK1	0-10	5.8	8.4	20.0	0.66	9.05	1.05	0.40	0.44	0.05	0.02	2.0	90	0.287	0.89
KMK2	10-30	6.4	8.8	2.5	0.04	0.60	0.40	0.18	0.54	0.06	0.05	1.2	49	0.997	
KMK3	30-40	5.8	8.9	14.3	0.45	6.29	1.01	0.36	0.63	0.09	0.39	2.5	78	0.651	
KMK4	40-45	6.0	8.9	8.9	0.21	3.07	0.72	0.29	0.85	0.10	0.38	2.3	64	0.862	
KMK5	45-50	5.8	9.3	10.4	0.28	3.87	0.36	0.07	0.31	0.05	0.30	1.1	82	0.813	
V1477,A	50-52	6.3	10.2	4.8	0.13	2.08	-	-	-	-	-	-	-	-	1.74
V1477,B	52-59	5.7	9.6	1.6	0.12	4.83	-	-	-	-	-	-	-	-	
KMK6	59-64	6.2	10.5	9.5	0.27	3.74	0.63	0.28	0.33	0.05	0.15	1.4	93	0.916	
KMK7	64-69	6.3	10.5	6.8	0.16	2.29	0.41	0.16	0.31	0.04	0.13	1.0	82	0.783	
KMK8	69-74	6.6	10.1	3.6	0.06	1.00	0.24	0.10	0.28	0.03	0.11	0.8	54	0.983	
KMK9	74-79	6.1	10.1	3.5	0.07	1.04	0.28	0.10	0.25	0.03	0.18	0.8	61	0.955	
Ö1362,A	79-84	6.6	7.9	2.0	0.01	0.13	-	-	-	-	-	-	-	-	
Ö1362,B	84-85	8.6	8.7	1.8	0.02	0.30	-	-	-	-	-	-	-	-	
Ö1362,C	85-86	8.6	8.2	2.1	0.01	0.22	-	-	-	-	-	-	-	-	
KMK10	86-91	5.5	9.7	18.7	0.49	8.72	1.11	0.47	0.39	0.05	0.33	2.3	93	0.567	-
KMK11	91-96	5.6	9.6	14.3	0.33	6.07	0.68	0.34	0.30	0.05	0.35	1.7	81	0.647	-

* DBD: standard deviation \pm 0.216 g/cm³

The pH (H₂O) was found to be slightly acidic (5.5 - 6.6) in the soils. The mean pH (H₂O) in V1477 was 6.0, but higher (7.9) in Ö1362. Soil and tephra pH measured in sodium fluoride (pH (NaF)) ranged between 7.9 (in the rhyolitic Ö1362 tephra) and 10.5 (in the soil below the basaltic V1477 tephra layer). The SOM in the soils ranged between 20% in the surface layer and 2.5% in the sediment layer at 10 - 30 cm depth. SOC ranged between 0.6% and 9.0%, being highest in the surface layer and rather high below Ö1362 tephra, while low between the two tephra layers. The mean DBD in the soils was 0.8 g/cm³. P-retention was between 61% and 93%, except in the sediment layer (10 - 30 cm depth) where P-retention decreased below 50%. Highest values were found immediately below both tephra layers. SAR in the soils after the deposition of the basaltic V1477 to the time of sampling (2012) was 0.89 mm/yr, much lower than the 1.74 mm/yr measured between Ö1362 and V1477. The soils were dominated by sand and silt (Table 2). While the sand fraction in soil layers above V1477 (except the sediment layer) exceeded the silt portion, the opposite was found in the soils between Ö1362 and V1477 tephra layer. Only the sediment layer at 10 - 30 cm depth showed a considerably high portion of gravel-sized constituents (22.3%).

Table 2. Particle size distribution and estimated content of the amorphous constituents in the studied pedon and tephra at Kviármyrarkambur (KMK).

Sample	Depth cm	Gravel	Sand	Silt %	Clay	Ferrihydrite	Allophane %	Amorphous secondary clay-size material %
KMK1	0-10	0.6	21.4	44.5	33.4	13.19	3.31	16.5
KMK2	10-30	22.3	62.3	12.8	2.6	2.73	2.07	4.8
KMK3	30-40	0.7	37.3	46.2	15.8	3.01	2.97	6.0
KMK4	40-45	0.6	36.0	55.3	8.1	1.59	1.85	3.4
KMK5	45-50	0.1	35.2	56.1	8.7	1.91	2.48	4.4
V1477,A	50-52	0.4	64.9	27.5	7.3	2.03	3.47	5.5
V1477,B	52-59	0.0	79.4	17.1	3.5	3.23	6.30	9.5
KMK6	59-64	2.1	48.7	34.2	15.0	2.42	4.85	7.3
KMK7	64-69	1.8	55.7	34.1	8.4	1.52	4.10	5.6
KMK8	69-74	3.3	75.3	16.6	4.7	1.87	3.84	5.7
KMK9	74-79	1.5	72.8	21.1	4.6	2.71	5.45	8.2
Ö1362,A	79-84	6.9	60.6	31.0	1.4	0.16	0.29	0.5
Ö1362,B	84-85	6.7	79.7	10.1	3.5	1.58	2.46	4.0
Ö1362,C	85-86	2.7	38.9	48.9	9.5	0.91	0.83	1.7
KMK10	86-91	0.5	25.9	46.6	27.0	4.33	4.57	8.9
KMK11	91-96	2.1	47.1	34.2	16.6	3.59	3.88	7.5

Above the basaltic V1477 tephra layers, the availability of exchangeable cations varied over time (Table 1). The development of selected exchangeable cations along the profile KMK is presented in Fig. 3. Between Ö1362 and V1477 they followed a declining trend with depth, with the exception of Al^{3+} . Both, Ca^{2+} and Mg^{2+} presented the highest contents below the Ö1362 layer, while highest Na^+ contents were found above V1477. K^+ contents were close to zero in all but one layer. A similar trend, varying above V1477, but decreasing with depth between V1477 and Ö1362, was present in ECEC. The ECEC was lowest (mean 1.0) in the soils above the rhyolitic Ö1362.

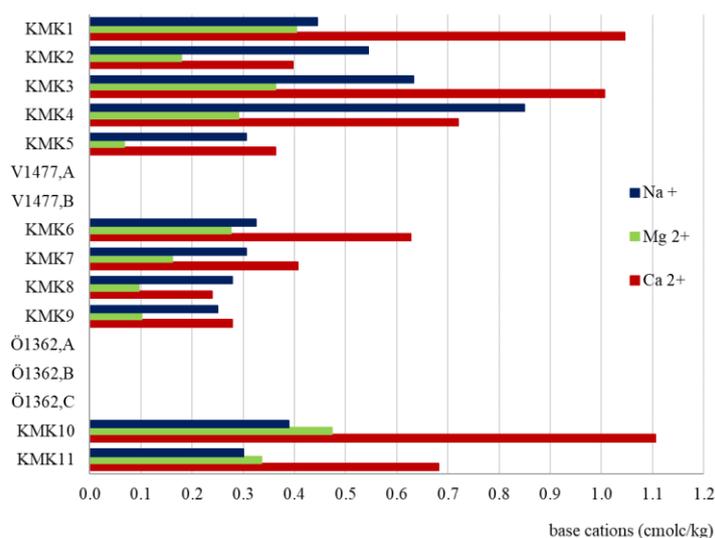


Figure 3. Profile development of selected base cations Na^+ , Mg^{2+} and Ca^{2+} .

3.2. Mineralogy of the clay-size fraction

The clay-size content in the soil samples ranged between 2.6% in the sediment layer (10 - 30 cm depth) and 33.4% in the surface layer. Noticeably high contents of clay-size material were found in the soils below both tephra layers. The allophane content in the soils ranged between 1.85 and 3.31% above the basaltic V1477, but 3.84 – 5.45% in the soils below. Ferrihydrite contents were found in the range 1.51 – 4.33% (except 13.19% in surface layer). The content in V1477 fits into this range, but in the Ö1362 tephra the ferrihydrite content was lower.

The investigation of the bulk mineral composition (Table 3) revealed a dominance of plagioclase and pyroxene and the occurrence of quartz in all samples, both soils and tephra.

Table 3. Bulk mineralogy of the studied pedon and tephra samples at Kvíármýrarkambur (KMK).

Sample	Depth cm					Zeolite			Volcanic	
		14Å	Quartz	Plagioclase	Pyroxene	Phillipsite	Stilbite	Analcime	glass	Olivine
KMK1	0-10	-	tr	*	*	-	tr	-	**	-
KMK2	10-30	*	*	**	**	-	tr	tr	**	tr
KMK3	30-40	*	*	**	**	tr	tr	tr	**	-
KMK4	40-45	*	*	**	**	tr	tr	*	**	-
KMK5	45-50	*	*	**	**	tr	tr	*	**	-
V1477,A	50-52	-	tr	*	**	-	-	tr	**	-
V1477,B	52-59	-	tr	*	**	-	-	-	**	-
KMK6	59-64	tr	*	**	**	-	tr	-	**	-
KMK7	64-69	tr	*	**	**	-	tr	-	**	-
KMK8	69-74	-	*	**	**	-	-	-	**	-
KMK9	74-79	-	*	**	**	-	tr	tr	**	-
Ö1362,A	79-84	-	tr	*	tr	-	-	-	***	-
Ö1362,B	84-85	-	*	**	*	-	-	-	**	-
Ö1362,C	85-86	tr	tr	*	tr	-	tr	-	***	-
KMK10	86-91	tr	tr	*	**	-	tr	-	**	-
KMK11	91-96	tr	tr	*	**	-	tr	-	**	-

tr = trace amounts, * = low, ** = medium, *** = high, - = not detected.

Volcanic glass was abundant in all samples, both tephra and soil. A distinct 14Å peak was visible especially in the soils above the basaltic V1477 tephra and some traces below (Table 4). Volcanic glass was abundant in all investigated samples and zeolites were found in all soil samples (Table 3). The three zeolite types detected were phillipsite, stilbite and analcime. Phillipsite was only found in traces in the soils above V1477, while traces of stilbite were found in most soil layers along the profile and in the lowest Ö1362 sublayer. Analcime was found in traces in some soil layers and in the V1477 tephra, but in higher quantity right above said tephra layer. Similar to the soils, both types of tephra were dominated by plagioclase, pyroxene and volcanic glass. When comparing the two tephra deposits, the pyroxene content was found to be higher in the basaltic V1477 tephra. The rhyolitic Ö1362,B layer showed a higher quantity of mineral, but lesser amount of volcanic glass than in the other sublayers of Ö1362. The identification of the XRD patterns for the clay-size fraction is presented in Table 4. A distinct reflection at 6.2° 2Θ (1.4 nm) appeared

in the Mg and K treated sample but shifted after further treatment to 1.7 and 1.9 nm with ethylene glycol and DMSO, respectively. After heating the samples to 550 °C the distinct reflection contracted to 1.0 nm. This pattern is consistent with the presence of smectite (Fig. 4).

Table 4. Mineral composition of the clay size fraction of the studied pedon and tephra samples at Kvíármýrarkambur (KMK).

Sample	Depth		Smectite	Goethite	Zeolite
	cm				
KMK1	0-10		-	*	tr
KMK2	10-30		*	-	*
KMK3	30-40		*	-	*
KMK4	40-45		*	-	*
KMK5	45-50		*	-	*
V1477,A	50-52		-	-	tr
V1477,B	52-59		tr	tr	tr
KMK6	59-64		tr	tr	tr
KMK7	64-69		tr	-	*
KMK8	69-74		-	-	tr
KMK9	74-79		-	-	tr
Ö1362,A	79-84		-	-	-
Ö1362,B	84-85		-	-	-
Ö1362,C	85-86		tr	-	tr
KMK10	86-91		-	-	*
KMK11	91-96		tr	tr	tr

tr = trace amounts, * = low, - = not detected.

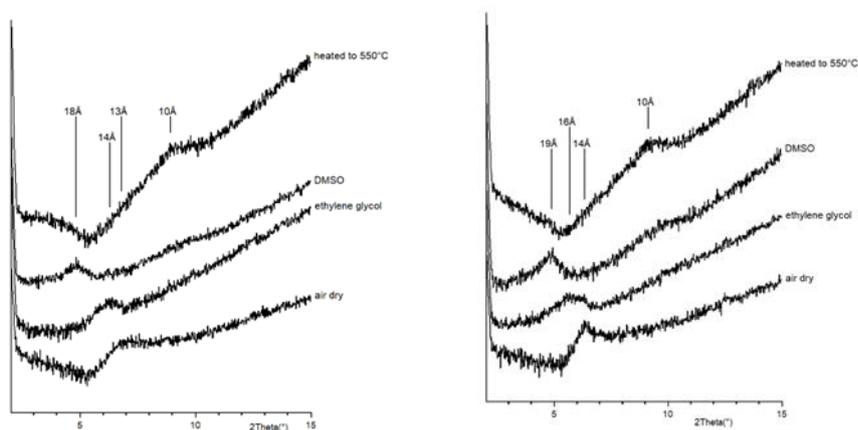


Figure 4. X-ray diffraction pattern of sample KMK5; 45 - 50 cm depth, clay-size fraction K-saturated (left) and Mg-saturated (right), showing evidence of smectite.

TG curves of the subsoils showed the main average thermogravimetric mass loss of 15% in the temperature range between 200 and 600°C. At low temperatures (< 200°C) the mean mass loss was 7.3%, while only marginal at temperatures above 600°C. Compared to the thermogravimetric mass losses in the subsoils, the surface layer (0 – 10 cm) showed differences. As presented in Fig. 5a and b, DSC curves showed a distinct exothermic peak around 300°C. A distinct endothermic reaction in the temperature range between 133 and 152°C was found in all samples.

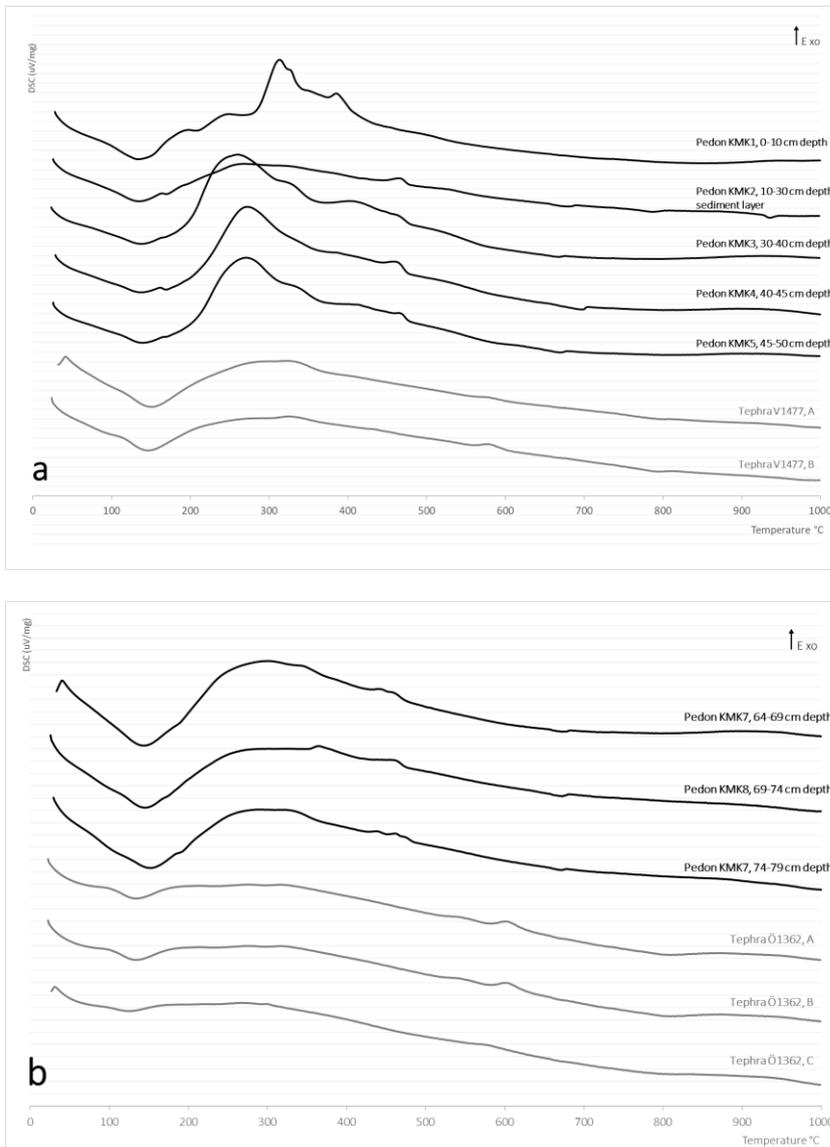


Figure 5a and b. Differential scanning calorimetry VI477 tephra layers (grey) and soils (black) above (a) and Ö1362 tephra layers (grey) and soils (black) above; one increment on the y-axis corresponds to a heat flow of 0.2 W g^{-1} .

3.3. Weathering and amorphous nature of soils and tephra

Data of selective dissolution analysis are given in Table 5.

Table 5. Selected non-sequential, selective dissolution analyses and properties related to the amorphous material in the studied pedon and tephra at Kvíarmýrarkambur (KMK).

Sample	Depth cm	Al _o	Fe _o	Si _o	Fe _d	Al _p	Fe _p	Fe _o /Fe _d ratio	(Al _o -Al _p)/Si _o ratio	Al _p /Al _o ratio	Al _o +0.5Fe _o %	Amorphous Al g/kg	Amorphous Fe g/kg
KMK1	0-10	6.6	77.6	8.3	95.4	2.3	13.8	0.8	0.5	0.35	4.5	4.32	63.78
KMK2	10-30	5.4	16.0	3.8	8.7	0.9	1.3	1.9	1.2	0.16	1.3	4.57	14.70
KMK3	30-40	9.7	17.7	5.2	14.2	2.8	4.3	1.2	1.3	0.29	1.9	6.92	13.37
KMK4	40-45	6.1	9.4	3.0	8.9	1.5	2.0	1.1	1.5	0.24	1.1	4.59	7.39
KMK5	45-50	8.1	11.2	4.3	8.9	2.2	2.5	1.3	1.4	0.27	1.4	5.92	8.71
V1477.A	50-52	9.9	12.0	6.7	7.5	2.6	2.7	-	1.1	0.27	1.6	7.31	9.24
V1477.B	52-59	14.1	19.0	12.7	4.5	1.7	1.6	-	1.0	0.12	2.4	12.43	17.38
KMK6	59-64	16.0	14.3	7.9	17.0	3.9	3.2	0.8	1.5	0.24	2.3	12.13	11.03
KMK7	64-69	12.5	9.0	7.3	7.1	3.1	1.5	1.3	1.3	0.24	1.7	9.48	7.48
KMK8	69-74	10.1	11.0	7.3	5.6	1.9	1.1	2.0	1.1	0.18	1.6	8.24	9.95
KMK9	74-79	14.1	15.9	10.2	6.0	2.2	1.4	2.7	1.2	0.16	2.2	11.89	14.58
Ö1362.A	79-84	0.9	0.9	0.6	0.7	0.3	0.2	-	0.9	0.38	0.1	0.53	0.70
Ö1362.B	84-85	5.6	9.3	5.0	4.3	0.9	0.7	-	0.9	0.16	1.0	4.74	8.57
Ö1362.C	85-86	2.5	5.4	1.4	3.7	0.4	0.6	-	1.5	0.17	0.5	2.04	4.75
KMK10	86-91	15.0	25.5	7.8	35.3	4.0	5.0	0.7	1.4	0.27	2.8	10.99	20.49
KMK11	91-96	12.1	21.1	7.0	20.1	3.3	4.5	1.0	1.3	0.27	2.3	8.84	16.66

Compared to Fe_o values, the content of Fe in crystalline and non-crystalline constituents (Fe_d) were significantly lower. Si contents (Si_o) were 6.2 g/kg on average. The highest Si_o was found in the V1477 and the lowest in Ö1362.

Estimated contents of amorphous and poorly crystalline clay size constituents were 7 - 9%. The amount of allophane content ranged between 1.9 and 5.5%, the ferrihydrite content ranged between 1.5 and 4.3%. The lowest contents were found in the rhyolitic Ö1362 tephra. There was a significant difference in the amount of amorphous clay size constituents in both tephra layers at KMK (mean 7.5% in V1477 and mean 2.1% in Ö1362). The mean allophane content in V1477 was 4.9%, in Ö1362 it was 1.2%. Contents of ferrihydrite were 2.63% in V1477 and 0.9% in Ö1362 on average.

The amorphous Al (Al_o-Al_p) ranged between 0.5 and 12.1 g/kg, being lowest in the Ö1362 tephra. The contents of amorphous Fe (Fe_o-Fe_p) were found in a wide range between 0.7 and 63.8 g/kg. Similar to amorphous Al, the lowest content was found in the Ö1362 tephra, the highest in the surface layer. The pH values measured in sodium fluoride (pH (NaF)) were well above the limit of 9.5 in the soils developed after the deposition of Ö1362, while soils above V1477 did not reach the limit. All soils at site KMK showed Al_p/Al_o ratios below 0.5, and (Al_o-Al_p)/Si_o ratios above 1 (except for the surface layer). The percentage Al_o+0.5Fe_o ranged between 1.1 and 4.5 in the profile, with lowest values in Ö1362. The Fe_o/Fe_d ratios ranked high, between 0.7 (in the surface layer and below the two tephra layers) and 2.7. Increased ratios were found above Ö1362.

4. DISCUSSION

4.1. Tephra composition reflected in soil properties and mineral alteration

Öræfajökull volcano is known for rhyolitic volcanism. These kinds of eruptions are rare but extremely violent. Nevertheless, the main volcanic ejecta in Iceland is of basaltic composition and basaltic glass dissolution is one of the main processes in the weathering of Icelandic soils. Under low pH (H₂O) conditions, the amorphous basaltic glass dissolves rapidly (Oelkers and Gislason, 2001), leading to high Fe_o values. The oxalate extracted Fe and Al (Fe_o, Al_o) represented by far the greatest portion of extractable Fe and Al (Table 5), verifying the amorphous nature of the tephra (e.g. Oelkers and Gislason, 2001).

A higher pH (H₂O) in the rhyolitic tephra was reflected in the soils developed from Ö1362. Values for pH (NaF), well above the limit of 9.5 in the soils developed above the rhyolitic tephra, pointed to a dominance of amorphous and poorly crystalline constituents. Soils above V1477 did not reach the 9.5 limit.

Studies on volcanic soils in other parts of the world (e.g. Parfitt et al., 1983; Shoji and Fujiwara, 1984; Vacca et al., 2003) reported that Al-humus complexes, as well as allophanes are competing for Al released by the weathering of volcanic ejecta. The crucial factor to determine between the formation of Al-humus complexes and allophane is the soil pH (H₂O) (Shoji and Fujiwara, 1984; Shoji et al., 1982). Nearly all varieties of volcanic ash (whole range from basaltic to rhyolitic) weather to allophane (Wada and Harward, 1974). The major portion of the clay size particles of the investigated soils was mainly derived from allophane and ferrihydrite, both X-ray amorphous SRO secondary materials and Fe (hydr)oxides. Nevertheless, we provided evidence of crystalline pedogenic minerals. The most distinct clay mineral found was smectite. The evidence of zeolites was proved in all samples, except for two sublayers of the rhyolitic Ö1362 tephra. Investigations of the soil properties, as well as the mineralogy, confirmed that the investigated pedon is in the initial state of pedogenesis. The presence of smectite and zeolite is widespread in soils developed from volcanic parent materials and possibly formed during an early stage of hydrothermal weathering (De Rosa et al., 2016; Mirabella et al., 2005; Wada, 1989). At KMK, smectite mainly appeared to be abundant in the soils above V1477 (Tab. 4). Below this tephra deposit, it was only found in traces in some of the soil layers. Our findings from the XRD were confirmed by the results from thermal analysis (Fig. 5a and b). An endothermic reaction in the low temperature range around 170°C resulted from the dehydration of water in the interlayers and indicates smectite to be present. In situ formation of smectite in the investigated soils, possibly as an alteration product of volcanic glass, cannot be ruled out. Considering the high aeolian activity in Iceland and the location of the sampling site just outside a geothermal area and active volcanic zone, we rather suggest that smectite, as well as zeolites, originate from hydrothermal alteration of volcanic material (e.g. tephra), inherited from glacial out-wash plains within the country, or sources even from outside Iceland by aeolian transport. According to the origin of the clay minerals, quartz may also have derived from aeolian transport from Icelandic and/or external sources.

The distinct endothermic reaction around 140°C in DSC patterns (Fig. 5a and b) of all samples can be linked to dehydration of water associated with allophane. This reaction occurred at slightly higher temperatures in the soils above the rhyolitic tephra layer, indicating a degradation of more stable compounds of OM and accompanied by higher allophane content in the soils above Ö1362 than those above the basaltic V1477. The reaction occurred at a higher temperature, suggesting the OM being more stable close to the tephra layer, getting looser bound further up the profile.

4.2 Pedogenesis in unstable conditions

4.2.1 Soil development in a dynamic environment

The soils at KMK developed from tephra and aeolian material. A distinct sediment layer was found in 10 - 30 cm depth, while aeolian material was mixed throughout the whole profile. Volcanic glass was abundant in both tephra and soil. According to the World Reference Base (IUSS Working Group WRB, 2015) the investigated pedon meet the requirements for andic and vitric soil properties in all layers and can be classified as Andosol.

Physical and chemical properties of volcanic soils are largely regulated by the amount of active Al and Fe present (Nanzyo et al., 1993a), the least mobile elements released during chemical weathering of basalt (Gíslason, 2008). In contrast with the general understanding, the acid oxalate extractable (amorphous) Fe_o values in Icelandic soils are usually high compared to Fe in crystalline and amorphous constituents (Fe_d), which is said to result from the influence of amorphous basaltic glass (e.g. Arnalds et al., 2016). Thus, Fe_o/Fe_d ratios, reflecting the crystallinity or “age” of Fe (hydr)oxides (e.g. Malucelli et al., 1999), in Icelandic soils often exceed 1 (Arnalds et al., 1995; Bonatutzky et al., 2019; Wada et al., 1992). The ratios in the investigated soils rank very high, even as high as 2.7, indicating a dominance by amorphous and poorly-crystalline Fe compounds (Tab. 5). Nevertheless, the reason for Fe_o exceeding Fe_d and consequentially Fe_o/Fe_d ratio > 1 in the present study may be attributed to an over-estimation of acid oxalate extractable Fe (hydr)oxides. According to previous studies (e.g. Algoe et al., 2012; Borggard, 1982; Fine and Singer, 1989; Rennert, 2019), ammonium oxalate solution not only extracts Fe (hydr)oxides from the amorphous and poorly-crystalline material, it may also dissolve crystalline Fe compounds (esp. magnetite/maghemite, lepidocrocite). The process of basaltic glass dissolution is very sensitive to the pH (H_2O). Oelkers and Gíslason (2001) found the lowest dissolution rates at (approximately) pH 6. The prevailing (low) pH and the influence of the ammonium oxalate, which is known to affect the process in the range around between pH 2 and pH 7, may also contribute to the high Fe_o values in the investigated soils. On the other hand, several studies (e.g. Rennert, 2019; Varadachari et al., 2006;) reported that magnetite/maghemite may not completely be dissolved by dithionite-citrate-bicarbonate solution, leading to an under-estimation of Fe_d .

The predominance of SRO constituents is confirmed by the Al_p/Al_o ratio, which is widely used to separate allophanic (< 0.5) from non-allophanic (≥ 0.5) Andosols (Saigusa et al.,

1991). In the present study all samples were showing Al_p/Al_o ratios below 0.5 indicating that both soils and tephra are allophanic (Tab. 5). The predominance of allophane was also indicated by $(Al_o - Al_p)/Si_o$ ratios above 1. Overall, the pH (H_2O) in the investigated soils were slightly acidic (Tab. 1), but well above the described threshold of 5 and indicate the preferential formation of allophane rather than Al-humus complexes (Shoji and Fujiwara, 1984; Shoji et al., 1982).

Thermal analysis showed that the main mass losses and thermal reactions in the investigated soils occurred due to the loss of OM (Fig. 5a and b). With increasing depth, decomposition and combustion reactions of organic fractions with slightly different thermal stabilities took place. A distinct exothermic reaction around $300^\circ C$ indicated the thermal degradation of less condensed organic compounds (e.g. Grisi et al., 1998; Guo et al., 2016; Yang et al., 2007). The highest SOM content in the surface layer is also reflected by DSC pattern. The sharp exothermic peak at $313^\circ C$ indicates the presence of thermally labile OM. Compared to the soils below, the peak occurs at a slightly higher temperature at the surface. With increasing depth, the “organic” reaction shifted to the right (occurring at higher temperature), suggesting the content of more thermally stable compounds of the OM closer to the tephra layer and at the surface.

Our investigations revealed elevated exchangeable- Na^+ contents, especially in the soils above V1477 (Tab. 1, Fig. 3). These relatively high Na^+ concentrations presumably do not originate from the parent material but are most likely caused by the sea salt composition of precipitation, reflecting the study sites' proximity to the sea (Damman, 1988; Gíslason, 1993; Möckel et al., 2017; Nanzyo et al., 1993b). Similar to studies by Tomita et al. (1993) on volcanic glass in Japan, we found a correlation between elevated Na^+ contents and smectite occurrence, suggesting a reaction of volcanic material (ash, glass) with seawater to form smectite minerals.

4.2.2 Erosion reflected in soil properties

Human occupation, introduced grazing livestock and other land-use practices induced a significant change in the terrestrial environment of Iceland from the late 9th century. With the decline of vegetation cover, much of the previously pristine, well vegetated land is now deforested and barren and subject to frequent high-velocity winds. As a result, intense wind erosion events with aeolian transport of tephra and loose sediment over long distances and re-deposition are very common. Up to 80% of the windblown dust is amorphous basaltic glass which dissolves rapidly (Arnalds et al., 2016). Despite the abundance of weathering-beneficial constituent (basaltic glass) in the soils, they can be seen to be in their early stage of chemical weathering and soil development (Bonatotzky et al., 2021; 2019; Gíslason et al., 1996). Older, more weathered, more developed material may be sourced by aeolian transport from easily erodible areas in Iceland (these include extensive unstable sandy surfaces in the Highlands and glacial out-wash plains on the south coast), or even further afar, such as Mongolia or Sahara.

The investigation of the bulk mineralogy, mainly comprised of plagioclase and pyroxene (Tab. 3), reflected the mainly basaltic composition of the Icelandic bedrock, which contains relatively high concentrations of CaO and MgO (Jakobsson et al., 2008). High exchangeable Ca²⁺ and Mg²⁺ concentrations close to the surface and in the soils below Ö1362, however, reflect enhanced aeolian input of material of volcanic origin. The calculation of the SAR showed differences between the soils formed after the deposition of V1477 tephra and those formed over 115 years of soil development between Ö1362 and V1477 deposition. According to Gísladóttir et al. (2011), a consistent SAR through a soil profile implies a stable environment, while SAR is altered by erosion phases. Hence, as suggested by SARs (Tab. 1), the impact of erosion and aeolian processes was higher in 115 yrs of soil development between the deposition of Ö1362 and V1477 (1.74 mm/yr), than in 540 yrs of pedogenesis since the deposition of the basaltic tephra V1477 (0.89 mm/yr). Similar results were found in a study by Bonatutzky et al. (2021) on Andosols south of Vatnajökull. The trend of SOM between tephra layers confirmed signs of unstable environmental conditions as indicated by the high SARs. Below the basaltic V1477, it decreased from 9.5 % SOM closest to the basaltic tephra down to 3.5 % SOM right above the rhyolitic Ö1362. Likewise, total SOC and ECEC are conspicuously low between tephra layers, while BD is comparatively high, as is the pH (NaF) (e.g. Gísladóttir et al., 2011; 2010; Möckel et al., 2017; Óskarsson et al., 2004). All these factors are an indication of enhanced aeolian impact between the deposition of Ö1362 and V1477 (e.g. Axford et al., 2009; Blakemore et al., 1987; Vilmundardóttir et al., 2015; 2014).

When deposited on vegetated land, tephra and loose aeolian material will be (at least partly) sheltered from the wind (e.g. Óladóttir, 2009). Thick tephra deposits can destroy vegetation and detach the underlying strata from the atmosphere, affecting pedogenic processes (e.g. Eddudóttir et al., 2017; 2016; Þorbjarnarson, 2016). Thus, thick tephra deposits may have a significant and lasting effect on ecosystem. A change in weathering patterns and soil properties can be seen after the Öræfajökull eruption in 1362 CE. The deposition of the rhyolitic Ö1362 tephra layer impacted soil formation and soil weathering processes. Compared to the layers above, soils below Ö1362 showed a finer particle size composition, a higher SOM and lower pH (H₂O) (Tab. 1, 2 and 5). The SOC content below Ö1362 was comparable to the surface layer and to the soil right below the sediment layer, but significantly higher (a multiple) than the soils above. Al_o+0.5Fe_o > 2 in the soils below Ö1362 were clearly reflecting andic soil properties, while the soils above Ö1362 display mainly vitric soil properties. Overall, our results reflect a change in soil properties following the deposition of Ö1362.

We saw an irregular pattern in SOM content in the soils above V1477, which may be caused by erosion/deposition disturbances during pedogenesis. Such disturbances are further confirmed by a conspicuous sediment layer at 10 - 30 cm depth. Particle size composition in this layer was significantly coarser with considerable gravel content, while the SOM was very low and SOC content below 1%. Bulk mineralogy was more diverse than in the surface

layer above, suggesting that external material became deposited. A similar pattern was found with respect to the clay mineralogy.

KMK is named after a large frontal moraine, originating from Kvíárjökull, a southern outlet glacier of the Öræfajökull icecap. The Kvíármýrarkambur moraine on the western side of the Kvíárjökull was formed during the Holocene (Gudmundsson, 1997; Spedding and Evans, 2002; Thórarinnsson, 1956). It extends for a distance of approximately 3 km south of the glacier, reaching a height of up to 150 m a.s.l., and is characterized by steep slopes. Glacier variations of Kvíárjökull over the last few centuries have had a significant impact on the geomorphological development of the region (Hannesdóttir, 2014; Iturrizaga, 2008). As a consequence of deglaciation, the valley flanks became unstable and collapsed, spreading glaciofluvial material at the side of the Kvíárjökull (Iturrizaga, 2008). Considering said factors, we suggested that the disturbance at 10 - 30 cm depth originated from a landslide coming from the slope of the Kvíármýrarkambur moraine in the North, reflecting the diverse composition of glaciofluvial material.

Not just the soils appeared disturbed over time, disturbance may also have occurred during the deposition of the two tephra layers. Both, V1477 and Ö1362 did not appear as single layers but were split. While the V1477 tephra layer was split into two sublayers with a thin peat layer in between, the Ö1362 was split into three layers of different particle size composition and colour. From previous research (e.g. Sharma et al., 2008) we know that the main phreatomagmatic and Plinian phase of the 1362 Öræfajökull eruption occurred in three phases, each phase producing slightly different material. Based on our results we observed that the middle layer of Ö1362 seems to be more related to the soils above the tephra layer, than to the tephra itself. Not only was its mineralogy composition similar to the soils, it also harboured considerably higher oxalate and dithionite extractable Al, Fe and Si values. Thus, we suggest that the disturbances observed within the Ö1362 tephra layer are attributed to disturbances (i.e. solifluction) during soil formation, rather than linked to the nature of the Öræfajökull eruption in 1362 CE.

CONCLUSION

The investigated Andosol developed from tephra and aeolian material, rich in volcanic glass. Despite the abundance of weathering-beneficial constituents in the soils, they can be seen in their early stage of chemical weathering and soil development. The overall predominance of non- and poorly crystalline SRO secondary materials and Fe (hydr)oxides (allophane and ferrihydrite) was higher in the soils developed from the rhyolitic tephra than those above basaltic V1477. Based on our results we found evidence of smectite, most likely inherited from glacial out-wash plains within the country, or sources even from outside Iceland by aeolian transport.

Evidence of external environmental processes that may have impacted the soil development were found throughout the profile:

- Elevated exchangeable- Na^+ concentrations are most likely caused by the oceanic composition of precipitation and reflect the close proximity to the sea, while high Ca^{2+} and Mg^{2+} concentrations close to the surface and in the soils below Ö1362 are linked to enhanced aeolian input of volcanic material. Over 115 years of soil development, between 1362 CE and 1477 CE, significantly higher SARs reflect a stronger impact of erosion and aeolian processes on pedogenesis, than in the soils above V1477. Disturbances may also have occurred during the deposition of the two tephra layers.
- Tephra deposition impacted and changed soil properties, as it was visible after the deposition of Ö1362. A finer particle size composition, higher SOM and SOC content, lower pH (H_2O) and in general, a low Fe_o/Fe_d ratio in the soils below Ö1362 suggested soil degradation (erosion) following the deposition of Ö1362.
- A distinct fluvial sediment layer in 10 - 30 cm depth appeared to be sharply contrasting with the surrounding soil layers in the profile. Characterized by a significantly coarser particle size composition including gravels, low SOC content and a more diverse bulk and clay mineralogy, the sediment layer reflects the diverse composition of glaciofluvial material from a landslide coming from a Kvíárjökull moraine in the North.

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REFERENCES

- Algoe, C., Stoops, G., Vandenberghe, R.E. and Van Ranst, E.: Selective dissolution of Fe-Ti oxides - Extractable iron as a criterion for andic properties revisited. *Catena* 92, 49-54, 2012.
- Arnalds, O., Dagsson-Waldhauserova, P., and Olafsson, H.: The Icelandic volcanic aeolian environment: Processes and impacts - A review. *Aeolian Res.* 20, 176-195, 2016.
- Arnalds, O., Gísladóttir, F.O., and Sigurjonsson, H.: Sandy deserts of Iceland: an overview. *J. Arid Environ.* 47, 359-371, 2001.
- Arnalds, O., Hallmark, C.T., and Wilding, L.P.: Andisols from Four Different Regions of Iceland. *Soil Sci. Soc. Am. J.* 59, 161-169, 1995.
- Arnalds, O. and Óskarsson, H.: Íslenskt Jarðvegskort. *Náttúrufræðingurinn*, 78, 107-121, 2009.
- Arnalds, Ó.: Soils of Iceland. *Jökull* 58, 409-421, 2008.
- Austrian Standard Institute: ÖNORM L 1083, Chemische Bodenuntersuchungen - Bestimmung der Acidität (pH-Wert), Vienna, 2006.
- Axford, Y., Geirsdóttir, Á., Miller, G., and Langdon, P.: Climate of the Little Ice Age and the past 2000 years in northeast Iceland inferred from chironomids and other lake sediment proxies. *J. Paleolimnol.* 41, 7-24, 2009.
- Barros, N., Salgado, J., and Feijoo, S.: Calorimetry and Soil. *Thermochim. Acta* 458, 11-17, 2007.
- Benediktsson, J.: Íslenks fornrit I - Landnámabók. Hið íslenka fornritafélag. Reykjavík, 1986a.
- Benediktsson, J.: Íslenk fornrit I - Íslendingabók. Hið íslenka fornritafélag. Reykjavík. 1986b.
- Bengtsson, L. and Enell, M.: Chemical Analysis. in: Berglund, B.E. (Ed.), *Handbook of Holocene palaeoecology and palaeohydrology*. John Wiley & Sons, Chichester, pp. 423-451, 1986.
- Blakemore, L.C., Searle, P.L., and Daly, B.K.: *Methods for chemical analysis of soils*. NZ Soil Bureau, Dept. of Scientific and Industrial Research, Lower Hutt, N.Z., 1987.
- Bonatotzky, T., Ottner, F., Erlendsson, E., and Gísladóttir, G.: The weathering of volcanic tephra and how they impact histosol development. An example from South East Iceland. *Catena* 172, 634-646, 2019.
- Bonatotzky, T., Ottner, F., Erlendsson, E., and Gísladóttir, G.: Weathering of tephra and the formation of pedogenic minerals in young Andosols, South East Iceland. *Catena* 198, 105030, 2021.
- Borggaard, O.K.: Selective extraction of amorphous iron oxides by EDTA from selected silicates and mixtures of amorphous and crystalline iron oxides. *Clay Miner.* 17, 365-368, 1982.
- Brindley, G.W. and Brown, G.: *Crystal Structures of Clay Minerals and their X-ray Identification*. Mineralogical Society, London, 1980.
- Burt, R.: *Soil Survey Laboratory Methods Manual*. Natural Resource Conservation Service, 2004.

- Childs, C.W.: Towards Understanding Soil Mineralogy, II. Notes on Ferrihydrite, N.Z. Soil Bureau, DSIR, New Zealand, 1985.
- Crovisier, J.L., Honnorez, J., Fritz, B., and Petit, J.C.: Dissolution of subglacial volcanic glasses from Iceland: laboratory study and modelling. *Appl. Geochem.* 7, 55-81, 1992.
- Dahlgren, R.A., Boettinger, J.L., Huntington, G.L., and Amundson, R.G.: Soil development along an elevational transect in the western Sierra Nevada, California. *Geoderma* 78, 207-236, 1997.
- Dahlgren, R.A., Saigusa, M., and Ugolini, F.C.: The Nature, Properties and Management of Volcanic Soils, *Advances in Agronomy*. Academic Press, pp. 113-182, 2004.
- Damman, A.W.H.: Japanese raised bogs: their special position within the Holarctic with respect to vegetation, nutrient status and development. *Veröff. Geobot. Inst. ETH, Stiftung Rübel*, 330-353, 1988.
- De Rosa, R., Donato, P., and Scarciglia, F.: On the origin and post-depositional history of widespread massive ash deposits: The case of Intermediate Brown Tuffs (IBT) of Lipari (Aeolian Islands, Italy). *J. Volcanol. Geotherm. Res.* 327, 135-151, 2016.
- Eddudóttir, S.D., Erlendsson, E., Tinganelli, L., and Gísladóttir, G.: Climate change and human impact in a sensitive ecosystem: the Holocene environment of the Northwest Icelandic highland margin. *Boreas* 45, 715-728, 2016.
- Eddudóttir, S.D., Erlendsson, E., and Gísladóttir, G.: Effects of the Hekla 4 tephra on vegetation in Northwest Iceland. *Vegetation History and Archaeobotany* 26, 389-402, 2017.
- Eddudóttir, S.D., Erlendsson, E., and Gísladóttir, G.: Landscape change in the Icelandic highland: A long-term record of the impacts of land use, climate and volcanism. *Quat. Sci. Rev.* 240, 106363, 2020.
- Einarsson, M.Á.: Climate of Iceland. in: Van Loon, H. (Ed.), *World Survey of Climatology, Climates of the Oceans*, vol. 15. Elsevier, Amsterdam, 673-697, 1980.
- Erlendsson, E., and Edwards, K.J.: *Gróðurfarsbreytingar á Íslandi við landnám*. Árbók hins íslenska fornleifafélags, 29-55, 2010.
- Erlendsson, E., Edwards, K.J., and Gísladóttir, G.: Landscape Change, Land Use, and Occupation Patterns Inferred from Two Palaeoenvironmental Datasets from the Mosfell Valley, SW Iceland, *Viking Archaeology in Iceland*, pp. 181-192, 2014.
- Fieldes, M. and Perrott, K.W.: The nature of allophane in soils: part 3. Rapid field and laboratory test for allophane. *N.Z.J. Soil Sci.* 9, 623-629, 1966.
- Fine, P. and Singer, M.J.: Contribution of Ferrimagnetic Minerals to Oxalate- and Dithionite-Extractable Iron. *SSSAJ* 53, 191-196, 1989.
- Gísladóttir, G., Erlendsson, E., and Lal, R.: Soil evidence for historical human-induced land degradation in West Iceland. *Appl. Geochem.* 26, S28-S31, 2011.
- Gísladóttir, G., Erlendsson, E., Lal, R., and Bigham, J.: Erosional effects on terrestrial resources over the last millennium in Reykjanes, southwest Iceland. *Quat. Res.* 73, 20-32, 2010.

- Gíslason, S.R., Oelkers, E.h., Eiríksdóttir, E.S., Kardjilov, M.I., Gísladóttir, G., Sigfusson, B., Snorrason, A., Elefsen, S., Hardardóttir, J., Torssander, P. and Oskarsson, N.: Direct evidence of the feedback between climate and weathering. *Earth Planet Sci. Lett.* 277, 213-222, 2009.
- Gíslason, S.R.: Efnifræði úrkomu, jökla, árvatns, stöðuvatna og grunnvatns á Íslandi. *Náttúrufræðingurinn* 63 219-236, 1993.
- Gíslason, S.R.: 12. Chemical weathering, chemical denudation and the CO₂ budget for Iceland. in: Caseldine, C., Russel, A., Harðardóttir, S., Knudsen, Ó (Eds.), *Developments in Quaternary Sciences*. Elsevier, pp. 289-307, 2005.
- Gíslason, S.R.: Weathering in Iceland. *Jökull* 58, 387-408, 2008.
- Gíslason, S.R., Arnórsson, S., and Ármannsson, H.: Chemical weathering of basalt in southwest Iceland: Effects of runoff, age of rocks and vegetative/glacial cover. *Am J Sci*, 296, 837-907, 1996.
- Griffin, J.J., Windom, H., and Goldberg, E.D.: The distribution of clay minerals in the World Ocean. *Deep-Sea Res. Oceanogr. Abstr.* 15, 433-459, 1968.
- Grisi, B., Grace, C., Brookes, P.C., Benedetti, A., and Dell'Abate, M.T.: Temperature effects on organic matter and microbial biomass dynamics in temperate and tropical soils. *Soil Biol. Biochem.* 30, 1309-1315, 1998.
- Gudmundsson, H.J.: A review of the holocene environmental history of Iceland. *Quat. Sci. Rev.* 16, 81-92, 1997.
- Gudmundsson, M.T., Larsen, G., Höskuldsson, A., and Gylfason, A.G.: Volcanic hazards in Iceland. *Jökull* 58, 251-268, 2008.
- Guo, F., Wu, F., Mu, Y., Hu, Y., Zhao, X., Meng, W., Giesy, J.P., and Lin, Y.: Characterization of organic matter of plants from lakes by thermal analysis in a N₂ atmosphere. *Sci. Rep.* 6, 22877, 2016.
- Hannadóttir, H.: Variations of southeast Vatnajökull, past, present and future. PhD Thesis, University of Iceland, Reykjavík, 197 pp., 2014.
- Hannadóttir, H., Björnsson, H., Pálsson, F., Aðalgeirsdóttir, G., and Guðmundsson, S.: Changes in the southeast Vatnajökull ice cap, Iceland, between ~ 1890 and 2010. *The Cryosphere* 9, 565-585, 2015.
- Haraldsson, H. and Ólafsdóttir, R.: Simulating vegetation cover dynamics with regards to long-term climatic variations in sub-arctic landscapes. *Glob. Planet. Change* 38, 313-325, 2003.
- Inoue, K. and Higashi, T.: Al- and Fe-humus complexes in Andisols. in: Kinloch, D.I., Shoji, S., Beinroth, F.H., Eswaran, H. (Eds.), *Proc. of the Ninth International Soil Classification Workshop, Properties, Classification, and Utilization of Andisols and Paddy Soils, Japan, 20 July to 1 August 1987.*, Washington D.C., USA, pp. 81-96, 1988.
- Iturrizaga, L.: Post-sedimentary transformation of lateral moraines. *J. Mt. Sci.* 5, 1-16, 2008.
- IUSS Working Group WRB: World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps. Update 2015. *World Soil Resources Report No. 106*. FAO, Rome, pp.192, 2015.
- Jacobs, M.B. and Hays, J.D.: Paleo-climatic events indicated by mineralogical changes in deep-sea sediments. *JSR* 42, 889-898, 1972.

- Jakobsson, S., Jónasson, K., and Sigurdsson, I.: The three igneous rock series of Iceland. *Jökull* 58, 117-138, 2008.
- Jóhannesson, H. and Sæmundsson, K.: Geological Map of Iceland, 1:500 000. Icelandic Institute of Natural History, 2009.
- Kardjilov, M.I., Gísladóttir, G., and Gíslason, S.R.: Land degradation in northeastern Iceland: Present and past carbon fluxes. *Land Degrad. Dev.* 17, 401-417, 2006.
- Kinter, E.B. and Diamond, S.: A new Method for Preparation and Treatment of Oriented Aggregate Specimens of Soil Clays for X-Ray Diffraction Analysis. *Soil Sci.* 81, 111-120, 1956.
- Lal, R.: Soil carbon sequestration to mitigate climate change. *Geoderma* 123, 1-22, 2004.
- Larsen, G.: Recent volcanic history of the Veidivötn fissure swarm, southern Iceland — an approach to volcanic risk assessment. *J. Volcanol. Geotherm. Res.* 22, 33-58, 1984.
- Larsen, G., Dugmore, A., and Newton, A.: Geochemistry of historical-age silicic tephras in Iceland. *Holocene* 9, 463-471, 1999.
- Lawson, I.T., Gathorne-Hardy, F.J., Church, M.J., Newton, A.J., Edwards, K.J., Dugmore, A.J. and Einarsson, Á.: Environmental impacts of the Norse settlement: palaeoenvironmental data from Myvatnssveit, northern Iceland. *Boreas* 36, 1-19, 2007.
- Lowe, D.J.: Controls on the rates of weathering and clay mineral genesis in airfall tephras: A review and New Zealand case study, pp. 265-330, 1986.
- Malucelli, F., Terribile, F., and Colombo, C.: Mineralogy, micromorphology and chemical analysis of andosols on the Island of São Miguel (Azores). *Geoderma* 88, 73-98, 1999.
- Mirabella, A., Egli, M., Raimondi, S., and Giaccari, D.: Origin of clay minerals in soils on pyroclastic deposits in the island of Lipari (Italy). *Clays Clay Miner.* 53, 409-421, 2005.
- Mizota, C. and van Reeuwijk, L.P.: Clay Mineralogy and Chemistry of Soils Formed in Volcanic Material in Diverse Climatic Regions. ISRIC, Wageningen, 1989.
- Moore, D.M. and Reynolds, R.C., Jr.: X-ray diffraction and the identification and analysis of clay minerals. Second Edition. Oxford University Press, Oxford, 1997.
- Möckel, S.C., Erlendsson, E., and Gísladóttir, G.: Holocene environmental change and development of the nutrient budget of histosols in North Iceland. *Plant Soil* 418, 437-457, 2017.
- Nanzyo, M., Dahlgren, R., and Shoji, S.: Chapter 6 Chemical Characteristics of Volcanic Ash Soils. in: Shoji, S., Nanzyo, M., Dahlgren, R.A. (Eds.), *Volcanic Ash Soils - Genesis, properties and utilization*. Elsevier, pp. 145-187, 1993a.
- Nanzyo, M., Shoji, S., and Dahlgren, R.: Chapter 7 Physical Characteristics of Volcanic Ash Soils. in: Shoji, S., Nanzyo, M., Dahlgren, R.A. (Eds.), *Developments in Soil Science*. Elsevier, pp. 189-207, 1993b.
- Oelkers, E.H. and Gíslason, S.R.: The mechanism, rates and consequences of basaltic glass dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of aqueous Al, Si and oxalic acid concentration at 25°C and pH 3 and 11. *Geochim. Cosmochim. Acta* 65, 3671-3681, 2001.
- Olafsson, H., Furger, M., and Brummer, B.: The weather and climate of Iceland. *Meteorologische Zeitschrift*, 16, 5-8, 2007.

- Óladóttir, B.A.: Holocene eruption history and magmatic evolution of the subglacial volcanoes, Grímsvötn, Bárðarbunga and Kverkfjöll beneath Vatnajökull, Iceland. PhD Thesis, Université Blaise Pascal, Clermont-Ferrand and University of Iceland, Reykjavík, 2009.
- Óladóttir, B.A., Larsen, G., and Sigmarsson, O.: Holocene volcanic activity at Grímsvötn, Bárðarbunga and Kverkfjöll subglacial centres beneath Vatnajökull, Iceland. *Bull Volcanol.* 73, 1187-1208, 2011.
- Ólafsdóttir, R., Schlyter, P., and Haraldsson, H.: Simulating Icelandic vegetation cover during the Holocene Implications for long-term land degradation. *Geografiska Annaler: Series A, Phys. Geogr.* 83, 203-215, 2001.
- Óskarsson, H., Arnalds, Ó., Gudmundsson, J., and Gudbergsson, G.: Organic carbon in Icelandic Andosols: geographical variation and impact of erosion. *Catena* 56, 225-238, 2004.
- Parfitt, R.L.: Allophane in New Zealand - a review. *Aus.J. Soil Res.* 28, 343-360, 1990.
- Parfitt, R.L. and Henmi, T.: Comparison of an oxalate-extraction method and an infrared spectroscopic method for determining allophane in soil clays. *Soil Sci. Plant Nutr.* 28, 183-190, 1982.
- Parfitt, R.L., Russell, M., and Orbell, G.E.: Weathering sequence of soils from volcanic ash involving allophane and halloysite, New Zealand. *Geoderma* 29, 41-57, 1983.
- Parfitt, R.L. and Wilson, A.D.: Estimation of allophane and halloysite in three sequences of volcanic soils. *Catena supplement* 7, 1, 1985.
- Rateev, M.A., Gorbunova, Z.N., Lisitzyn, A.P., and Nosov, G.L.: The Distribution of Clay Minerals in the Oceans. *Sedimentology* 13, 21-43, 1969.
- Rennert, T.: Wet-chemical extractions to characterise pedogenic Al and Fe species – a critical review. *Soil Res.* 57, 1-16, 2019.
- Riedmüller, G.: Neof ormations and transformations of clay minerals in tectonic shear zones. *Tschermaks Mineral. Petrogr. Mitt.* 25, 219-242, 1978.
- Saigusa, M., Shoji, S., and Otowa, M.: Clay Mineralogy of Two Andisols Showing a Hydrosequence and Its Relationships to Their Physical and Chemical Properties. *Pedologist* 35, 21-33, 1991.
- Schulze, D.G.: An Introduction to Soil Mineralogy. in: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*, pp. 1-34, 1989.
- Shang, C., Zelazny, L.W., Ulery, A.L., and Richard Drees, L.: Selective Dissolution Techniques for Mineral Analysis of Soils and Sediments. in: Ulery, A.L., Richard Drees, L. (Eds.), *Methods of Soil Analysis Part 5—Mineralogical Methods*. Soil Science Society of America, Madison, WI, pp. 33-80, 2008.
- Shoji, S., Dahlgren, R.A., and Nanzyo, M.: Chapter 3 Genesis of Volcanic Ash Soils. Shoji, S., Nanzyo, M., Dahlgren, R.A. (Eds.), *Developments in Soil Science*. Elsevier, pp. 37-71, 1993.
- Shoji, S. and Fujiwara, Y.: Active Al and Fe in the humus horizons of andosols from northeastern Japan: Their forms, properties and significance in clay weathering. *Soil Sci.* 137, 21V 226, 1984.

- Shoji, S., Fujiwara, Y., Yamada, I., and Saigusa, M.: Chemistry and clay mineralogy of Ando soils, Brown forest soils and Podzolic soils formed from recent Towada ashes, Northeastern Japan. *Soil Sci.* 133, 69-86, 1982.
- Sigurmundsson, F.S., Gísladóttir, G., and Erlendsson, E.: The roles of agriculture and climate in land degradation in southeast Iceland AD 1700–1900. *Geografiska Annaler: Series A, Phys. Geogr.* 1-19, 2020.
- Smykatz-Kloss, W.: *Differential thermal analysis: application and results in mineralogy.* Springer-Verlag.
- Soil Survey Staff: *Keys to Soil Taxonomy 2014*, 12th ed. USDA - Natural Resources Conservation Service, Washington, DC, 1974, 2014.
- Sparks, D.L., Page, A.L., Helmke, P.A., and Loeppert, R.H.: *Methods of Soil Analysis Part 3—Chemical Methods.* Soil Science Society of America, American Society of Agronomy, Madison, WI, 1996.
- Spedding, N. and Evans, D.J.A.: Sediments and landforms at Kvíárjökull, southeast Iceland: a reappraisal of the glaciated valley landsystem. *Sediment. Geol.* 149, 21-42, 2002.
- Środoń, J.: Quantitative mineralogy of sedimentary rocks with emphasis on clays and with applications to K-Ar dating. *Mineralogical Magazine* 66(5), 677-687, 2002.
- Środoń, J.: Identification and Quantitative Analysis of Clay Minerals, *Handbook of Clay Science*, 25-49, 2013.
- Stefánsson, A. and Gíslason, S.R.: Chemical weathering of basalts, southwest Iceland: effect of rock crystallinity and secondary minerals on chemical fluxes to the ocean. *Am. J. Sci.* 301, 513-556, 2001.
- Stonehouse, H.B. and St. Arnaud, R.J.: Distribution of Iron, Clay and Extractable Iron and Aluminum in Some Saskatchewan Soils. *CJSS* 51, 283-292, 1971.
- Streeter, R. and Dugmore, A.: Late-Holocene land surface change in a coupled social–ecological system, southern Iceland: a cross-scale tephrochronology approach. *Quat. Sci. Rev.* 86, 99-114, 2014.
- Takahashi, T. and Dahlgren, R.A.: Nature, properties and function of aluminum-humus complexes in volcanic soils. *Geoderma* 263, 110-121, 2016.
- Thorarinsson, S.: The Öraefajökull eruption in 1362. *Acta Natur. Islandica*, 2, 1-99, 1958.
- Thórarinnsson, S.: On the variations of Svínafellsjökull, Skaftafellsjökull and Kvíárjökull in Öraefi. *Jökull* 6, 1-15, 1956.
- Tomita, K., Yamane, H., and Kawano, M.: Synthesis of Smectite from Volcanic Glass at Low Temperature. *Clays Clay Miner.* 41, 655-661, 1993.
- Ugolini, F.C. and Dahlgren, R.: Soil Development in Volcanic Ash. *Global J. Environ. Res.*, 6, 69-81, 2002.
- Vacca, A., Adamo, P., Pigna, M., and Violante, P.: Genesis of Tephra-derived Soils from the Roccamonfina Volcano, South Central Italy. *SSSAJ* 67, 198–207, 2003.
- Van Ranst, E., Coninck, F., and Debaveye, J.: Implication of charge properties and chemical management in volcanic ash soils from West Cameroon. *Sols Africains*, XXVI, 64-76, 1993.
- Varadachari, C., Goswami, G. and Ghosh, K.: Dissolution of Iron Oxides. *Clay Research* 25, 1-19, 2006.

- Vilmundardóttir, O.K., Gísladóttir, G., and Lal, R.: Early stage development of selected soil properties along the proglacial moraines of Skaftafellsjökull glacier, SE-Iceland. *Catena* 121, 142-150, 2014.
- Vilmundardóttir, O.K., Gísladóttir, G., and Lal, R.: Between ice and ocean; soil development along an age chronosequence formed by the retreating Breiðamerkurjökull glacier, SE-Iceland. *Geoderma* 259, 310-320, 2015.
- Wada, K.: Allophane and Imogolite. in: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*. Soil Science Society of America, Madison, WI, pp. 1051-1087, 1989.
- Wada, K., Arnalds, O., Kakuto, Y., Wilding, L.P., and Hallmark, C.T.: Clay minerals of four soils formed in eolian and tephra materials in Iceland. *Geoderma* 52, 351-365, 1992.
- Wada, K. and Harward, M.E.: Amorphous Clay Constituents of Soils. *Adv. Agron.* 26, 211-260, 1974.
- Wilson, M.J.: *A Handbook of Determinative Methods in Clay mineralogy*. Blackie and Sons, Glasgow and London, 1987.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., and Putnis, C.V.: The dissolution rates of natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from 25 to 74°C. *Geochim. Cosmochim. Acta* 68, 4843-4858, 2004.
- Yang, H.P., Yan, R., Chen, H.P., Lee, D.H., and Zheng, C.G.: Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 86, 1781-1788, 2007.
- Þorbjarnarson, H.: Soil evolution in the dynamic area south of Vatnajökull. Master's Thesis, University of Iceland, 2016.