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PEATLANDS

Depth trends of δ^{13}C and δ^{15}N values in peatlands in aeolian environments of Iceland

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Abstract
Depth patterns of δ^{13}C and δ^{15}N values in peatlands are used to reconstruct their environmental history, e.g. their hydrology, temperature changes and degradation. However, the suitability of δ^{13}C and δ^{15}N as proxies for environmental reconstructions needs to be verified by studies in a diverse range of environments. We present a study on the influence of aeolian deposits on δ^{13}C and δ^{15}N values in peatlands in Iceland. Large areas in Iceland comprise highly active aeolian environments due to tephra from volcanic eruptions, and material from eroding drylands. The study is a first step toward assessing if depth profiles of δ^{13}C and δ^{15}N values can provide insight into the environmental history of peatlands in aeolian environments. We compare δ^{13}C and δ^{15}N values with several conventional proxies of decomposition (dry bulk density, C/N ratio and two ratios derived from ^{13}C NMR spectra). We also interpret variations in δ^{13}C and δ^{15}N values in relation to the pedogenic minerals allophane and ferrihydrite and total mineral content. The complexity of depth trends of δ^{13}C and δ^{15}N values increases with proximity to source areas of windborne material. Particularly, there are turning points adjacent to major tephra layers. These patterns appear to be related to the influence of the volcanic deposits on factors like hydrology and fertility of the peatlands, microbial activity and vegetation composition. Depth trends of δ^{13}C and δ^{15}N values in peatlands of aeolian environments need to be interpreted in relation to other proxies reflecting the organic matter chemistry, and mineral soil constituents.

Keywords δ^{13}C · δ^{15}N · Peatlands · Aeolian deposits · Carbon characteristics

Introduction

Depth patterns of stable carbon (δ^{13}C) and nitrogen (δ^{15}N) isotope values in peat profiles can provide information about the environmental history of peatlands, e.g. their hydrologic regimes, temperature changes (Jędrysek & Skrzypek 2005) and shifts in vegetation (Zeh et al. 2020), and about their state of decomposition or degradation (e.g. Alewell et al. 2011; Drollinger et al. 2019; Groß-Schmölders et al. 2020). An interplay of various mechanisms often shapes the depth pattern of δ^{13}C and δ^{15}N values in peatlands. Metabolic processes by microbes lead to distinct isotopic fractionation. Increasing δ^{13}C and δ^{15}N values are often a result of aerobic conditions, as the lighter isotopes ^{12}C and ^{14}N are preferentially used during microbial organic matter decomposition (Alewell et al. 2011; Krüger et al. 2014; Zeh et al. 2020). Stable or slightly decreasing δ^{13}C values and stable δ^{15}N values with depth in peatlands indicate anaerobic conditions and slow decomposition. Therefore, climate changes leading to changes in precipitation and the hydrology of peatlands, may be reflected by the isotopic fingerprint and the decomposition state of the peat substrate. Warming climate may also shape the depth patterns of δ^{13}C and δ^{15}N values. According to e.g. Skrzypek et al. (2008), the δ^{13}C values of plants decrease as air temperature increases and Jędrysek and Skrzypek (2005) found temperature to be the dominant factor controlling variations in δ^{13}C values in peat profiles of a raised *Sphagnum* peat bog in northeast Poland. Differences

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in vegetation composition between sites, or shifts in vegetation through time, can also contribute to variations in $\delta^{13}C$ and $\delta^{15}N$ values of the initial substrate in peatlands (Asada et al. 2005; Zeh et al. 2020). For instance, recalcitrant carbon compounds such as lignin, are usually relatively depleted in ^{13}C and ^{15}N compared to more labile carbon compounds such as polysaccharides (Benner et al. 1987; Feyissa et al. 2020). Importantly however, there is still a lack of understanding how isotopic signatures of carbon and nitrogen reflect changes in the chemical characteristics of the organic matter (Serk et al. 2022), not least in interaction with hydrological fluctuations and temperature.

The interpretation of $\delta^{13}C$ and $\delta^{15}N$ values in peatlands can be challenging. This is particularly true for the bulk peat of the older catotelm, where a complicated interplay between historic vegetation effects, climate fluctuations, and decomposition processes of several thousand years is imprinted in the biochemistry of the organic material (Hobbie et al. 2017). To better understand the environmental factors shaping $\delta^{13}C$ and $\delta^{15}N$ values, and in order to estimate the suitability of $\delta^{13}C$ and $\delta^{15}N$ values as proxies of peat decomposition, more studies on peat cores in a diverse range of environments are needed (Drzymulska 2016; Esmeijer-Liu et al. 2012; Hobbie et al. 2017). Normally, the cycling of elements in peatlands is considered to be governed by biohydrochemical processes (Vitt and Wieder 2006). In peatlands of active aeolian environments, however, the surrounding geology and windborne mineral soil constituents can play a role for element cycling (Arnalds et al. 2016a, b; Broder et al. 2012; Möckel 2022). Examples of peatlands, which receive considerable amounts of windborne mineral material and have tephra deposits embedded in their strata, are peatlands of volcanic regions such as in Alaska, Patagonia, Indonesia, Kamchatka, New Zealand, Japan and Iceland (Ayris and Delmelle 2012; Broder et al. 2012; Chimner and Karberg 2008; Hotes et al. 2006; Hughes et al. 2013; Möckel 2022; Ratcliffe et al. 2020).

Tephra contributes elements to the peat solution, which influence the characteristics and pathways of the organic material. Nutrient supply from weathering of tephra may enhance microbial activity and decomposition (Broder et al. 2012; Hughes et al. 2013). Some particles deposited during volcanic eruptions, such as sulphate aerosols (Rose et al. 2004), or minerals precipitated during the weathering of tephra, such as secondary Fe-phases (Klaes et al. 2023), can serve as alternative electron acceptors. Under anoxic conditions, some organisms can use alternative electron acceptors instead of O_2 for their metabolism, resulting in enhanced anaerobic decomposition of organic material (Broder et al. 2012; Strawn et al. 2015b). This could lead to increases of $\delta^{13}C$ and $\delta^{15}N$ values (Bernstein et al. 2008; Mancini et al. 2003), like would be predicted under aerobic conditions. Furthermore, tephra deposits can induce temporary or long-term shifts in vegetation characteristics (Blackford et al. 2014; Eddudóttir et al. 2017, 2020; Hughes et al. 2013; Loisel and Bunsen 2020), which can alter the isotopic fingerprint of the peat substrate (Asada et al. 2005; Zeh et al. 2020). Overall, research evidence of $\delta^{13}C$ and $\delta^{15}N$ values in peatlands affected by tephra deposits is scarce (but see Broder et al. 2012), and more research is needed in order to understand their depth patterns. It is possible for example, that particularly fine grained and compacted tephra layers could hamper, rather than enhance, decomposition in parts of the peat column. Fine grained and compacted tephra layers sometimes serve as impermeable strata within the peat column (De Vleeschouwer et al. 2008; Möckel et al. 2021). Such strata can hinder the vertical movement of water, dissolved organic material and nutrients, and reduce microbial activities and decomposition processes (Broder et al. 2012). The result could be alterations in $\delta^{13}C$ and $\delta^{15}N$ values.

In Iceland, element cycling in peatlands is complicated by another source of windborne material than tephra from volcanic eruptions. The island belongs to the most active aeolian environments worldwide. This is not only owing to frequent explosive volcanic eruptions (Thordarson and Hoskuldsson 2008), but also to widespread volcaniclastic deserts (Arnalds et al. 2016a, b), whose extent increased rapidly due to anthropogenic activities after the settlement in ca. 870 CE (Dugmore et al. 2009; Eddudóttir et al. 2020). Therefore, many peatlands in Iceland contain not only distinct tephra layers, but generally more inorganic material within their peat substrate than other northern peatlands (Bonatotzky et al. 2019; Loisel et al. 2014; Möckel et al. 2021; Möckel et al. 2021a, b). Novel research on peatlands in northwest Iceland indicates that both distinct tephra layers (Möckel, Erlendsson, and Gísladóttir 2021a) and redeposited dryland material (Möckel et al. 2023) influence the chemistry of the peat organic matter. The studies show an increased accumulation of labile carbon compounds such as carbohydrates below compacted tephra layers, and in soils affected by redeposited dryland soil material. This is probably a result of changes in hydrology and vertical fluid movement around compacted tephra layers, and preferential stabilization of certain organic matter compounds by complexation with pedogenic minerals common in soils of volcanic regions like allophane and ferrihydrite, and by metal ions like Fe^{3+} and Al^{3+} (see also Matus et al. 2014; Möckel 2022). Summarized, peat in these environments can be dominated by carbon compounds which are characteristic of relatively undecomposed organic material. Due to differences in stable isotope compositions between carbon groups (Benner et al. 1987; Feyissa et al. 2020), the influence of windborne material of various origin on the organic matter composition could well be reflected in the depth pattern of $\delta^{13}C$ and $\delta^{15}N$ values.

To our knowledge, no research on the influence of tephra deposits and windborne mineral material from the volcaniclastic deserts on $\delta^{13}C$ and $\delta^{15}N$ values in Icelandic peatlands has been conducted. Skrzypek et al. (2008) investigated the suitability of $\delta^{13}C$ ratios for paleaoenvironmental reconstructions in one peatland. However, the investigated peatland was not representative of the majority of Icelandic peatlands due to the site's remoteness from the active volcanic zones (Arnalds et al. 2016a, b).

The aim of this study is to evaluate what controls depth patterns of $\delta^{13}C$ and $\delta^{15}N$ values in three Icelandic peatlands along a climatic and depositional transect. We particularly focus on (i) differences in depth patterns of $\delta^{13}C$ and $\delta^{15}N$ values between sites which may be caused by differences in environmental constraints, and (ii) on pattern and variations in $\delta^{13}C$ and $\delta^{15}N$ values around prominent tephra layers within the peat profiles. To interpret depth patterns of $\delta^{13}C$ and $\delta^{15}N$ values, we use common proxies of peat decomposition such as C/N ratios and dry bulk density (DBD; g cm^{-3}) (Drollinger et al. 2020, 2019; Groß-Schmölders et al. 2020), the ratio of alkyl carbon to O/N alkyl carbon (A:O/N) and the (70–75)/(52–57) ratio, which reflects the ratio of O-alkyl carbon of carbohydrates to methoxyl carbon of lignin (Bonanomi et al. 2013; Möckel et al. 2021; Preston et al. 1987) derived by ^{13}C NMR spectroscopy. We also interpret depth trends of $\delta^{13}C$ and $\delta^{15}N$ values in relation to aeolian indicators, such as total mineral content (%Ash), and pedogenic minerals formed from mineral volcanic material, i.e. allophane and ferrihydrite (Bonatotzky et al. 2019; Möckel et al. 2023).

Methods

Site characteristics and soil sampling

Soil samples were collected from three relatively undisturbed sloping fen peatlands from the Austur Húnavatnssýsla district in northwest Iceland (Fig. 1a). The northernmost site, Torfdalsmýri, is located in the north of the Skagi peninsula, very close to the open sea and ~ 55 m a.s.l. The lowland site, Tindar, is located ~ 10 km from the sea and ~ 98 m a.s.l. A third site, Hrafnabjörg is located at the fringe of the highlands, ~ 334 m a.s.l. and ~ 25 km from the sea. The research area reflects a climatic and dust-depositional transect. Generally, mineral aeolian deposition increases southwards with decreasing distance to eroded drylands in the interior of the country and the active volcanic zones (Arnalds et al. 2016a, b; Arnalds 2010). Average annual precipitation in the area is relatively low (400–500 mm; Table 1; Icelandic Met Office n.d.-a), with higher amounts at the coast than further inland. Likewise, average air temperatures decrease toward the highlands, with mean annual temperatures of ca. 3 °C at the coast and in the lowlands and around 0.6 °C in the highlands. A summary of main climate characteristics at weather stations within the research area is shown in Table 1.

At each site, composite soil samples were taken at 10 cm intervals down to a depth of 20 cm below the prominent tephra deposit from the Hekla 4 eruption (ca. 4.25 ka BP; Dugmore et al. 1995; Larsen and Thorarinsson 1977). Above and below tephra deposits of Hekla 3 (ca. 3.06 ka BP; Dugmore et al. 1995) and Hekla 4, the sampling interval was reduced to 5 cm (Fig. 1b; see also Möckel et al. 2021b). The Hekla 3 tephra deposit was at 40 cm depth at Torfdalsmýri, at 82–84 cm depth at Tindar, and at 89–91 cm depth at Hrafnabjörg. The Hekla 4 tephra deposit was at 50–59 cm depth at Torfdalsmýri, at 113–120 cm depth at Tindar, and at 121–124 cm depth at Hrafnabjörg. Composite samples were not taken from tephra layers.

Vegetation analysis was conducted at nine quadrats (0.25 m^2) along three parallel transects from the margin to the centre of each peatland. Vegetation assessment was conducted by the Relevé Method by Braun-Blanquet (Mueller-Dombois and Ellenberg 1974). Plant species were identified using Kristinsson (2010). Following the European Nature Information System (EUNIS; European Environment Agency 2019; Ottóson et al. 2016), vegetation characteristics at Torfdalsmýri resemble the habitat type of D2.26 Common cotton-grass fens (see also Möckel et al. 2023). Vegetation at Tindar is similar to two habitat types, i.e. D3.162 Boreal black sedge-brown moss fens and D4.163 Icelandic black sedge-brown moss fens. Vegetation characteristics at Hrafnabjörg are similar to D2.332 Basicline bottle sedge quaking mires. A list of species identified at the quadrats next to the sampling spots at each site is provided in Table 2.

Determination of decomposition proxies

Determination of $\delta^{13}C$ and $\delta^{15}N$ values and total carbon (%C) and nitrogen (%N) was performed on a Thermo Delta V isotope ratio mass spectrometer (IRMS) interfaced to a NC2500 elemental analyzer at the Cornell Isotope Laboratory in the USA. $\delta^{13}C$ values are expressed relative to Vienna Pee-Dee Belemnite standard and reported in delta notation (‰), $\delta^{15}N$ values are expressed relative to the atmospheric N standard and reported in delta notation (‰). Internal Buffalo standard was used to ensure instrument accuracy and precision, with a standard deviation of 0.13‰ for $\delta^{15}N$ values and 0.17‰ for $\delta^{13}C$ values. To quantify the ability of the instrument to accurately measure the range of isotope values in our peatlands, chemical Methionine standard was used. Delta values between the amplitudes of 17 mV and 15000 mV for $\delta^{15}N$ had an error of 0.36‰ and delta values between 70 and 15000 mV for $\delta^{13}C$ had an error of 0.40‰. Previous research (e.g. Bonatotzky et al. 2021; Mankasingh and Gísladóttir 2019; Vilmundardóttir et al.

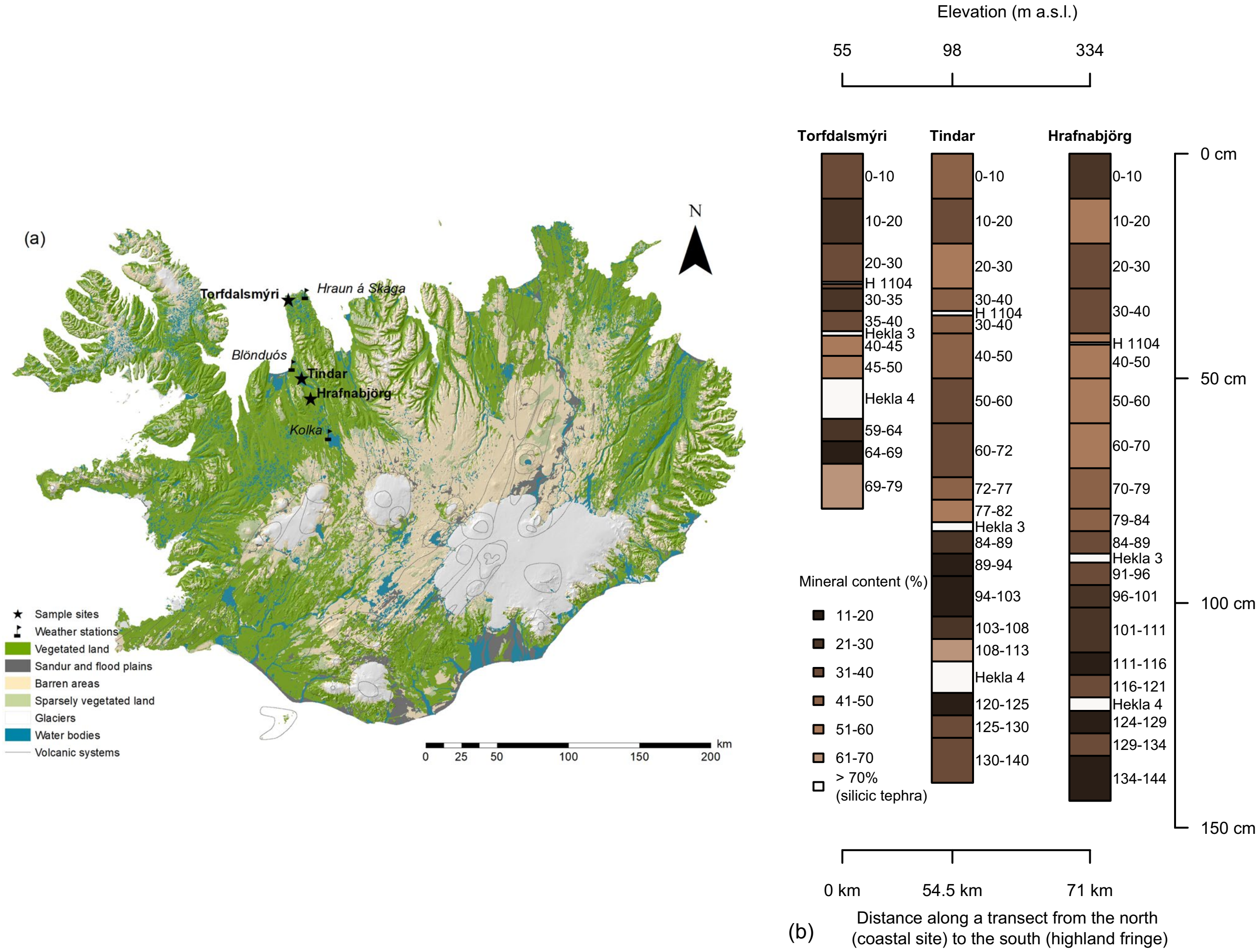

Fig. 1 (a) The map shows the location of the sample sites in Northwest Iceland. (b) Soil cores from each peatland show the sampled depth intervals. Lighter colours reflect a higher mineral content. White layers represent prominent tephra deposits within the soil column: two layers from pre-settlement eruptions of the volcano Hekla, the so-called Hekla 4 (ca. 4.25 ka BP; Dugmore et al. 1995) and Hekla 3 (ca. 3.06 ka BP; Dugmore et al. 1995), and a deposit from an eruption of the volcano Hekla in 1104 CE (H 1104; Larsen and Thorarinsson 1977). This latter eruption occurred ca. 230 years after the settlement of Iceland and serves as an approximate demarcation line between soil formation pre- and post-human settlement

Table 1 Main climate characteristics at weather stations within the research area. Data are available for the following time spans: Hraun á Skaga: 1956 – 2015; Blönduós: 1949 – 2001; Kolka: 1994 –2015 (Icelandic Met Office n.d.-a, b). The summer tritherm in Iceland comprises the months June – August, the autumn tritherm comprises September – October. The winter tritherm lasts from December to February and spring tritherm lasts from March to May. For information about the sampling locations in relation to the position of each weather station compare Fig. 1a

Weather station	Hraun á Skaga	Blönduós	Kolka
Elevation (m a.s.l.)	3	8	506
Mean annual temperature (°C)	2.94	3.05	0.64
Mean summer tritherm temperature (°C)	7.9	9.1	7.8
Minimum summer tritherm temperature (°C)	6.3	7.4	6.3
Maximum summer tritherm temperature (°C)	10.2	10.4	9.3
Mean winter tritherm temperature (°C)	-1.0	-1.6	-4.7
Mean autumn tritherm temperature (°C)	3.6	3.4	0.6
Mean spring tritherm temperature (°C)	1.3	1.7	-1.3
Mean annual precipitation (mm)	512	480	352
Mean annual windspeeds (m s^{-1})	5.7	3.8	7.4

Table 2 Major plant functional groups and species identified at the quadrats next to the sampling spots. Abbreviations denote the occurrence at the respective sites: TDM = Torfdalsmýri, TIN = Tindar and HRAFN = Hrafnabjörg. When marked bold, the species are prominent at the site (i.e. they reach at least cover scale category "3"). The nomenclature follows Kristinsson (2010) and the Panarctic Flora (PAF n.d.)

	Occurrence		Occurrence
Sedges/Rushes		**Deciduous woody plants**	
Carex nigra	TDM, **TIN,** HRAFN	*Betula nana*	**TDM, TIN,** HRAFN
Carex rariflora	TDM, HRAFN	*Salix arctica*	HRAFN
Carex rostrata	**HRAFN**	*Salix herbacea*	TDM
Eriophorum angustifolium	**TDM**, HRAFN	*Salix phylicifolia*	TDM, HRAFN
		Vaccinium uliginosum	TDM, TIN, HRAFN
Grasses			
Anthoxanthum odoratum	TIN	**Evergreen woody plants**	
Calamagrostis neglecta	TDM	*Empetrum nigrum*	**TDM,** TIN, **HRAFN**
Forbs		**Pterydophytes**	
Bistorta vivipara	TDM, HRAFN	*Equisetum palustre*	TDM, TIN, HRAFN
Cardamine pratensis ssp. *angustifolia*	TIN, HRAFN		
Comarum palustre	TDM, TIN	***Bryophyta***	TDM, TIN, HRAFN
Galium verum	TIN		
Thalictrum alpinum	TIN		

2014) demonstrates absence of carbonate minerals from Icelandic soils. Hence, %C is assumed to reflect total soil organic carbon (SOC). The molar C/N ratio as a common peat decomposition proxy was calculated based on %C and %N. The total soil organic matter content (SOM) and total soil inorganic content (%Ash) was determined via mass loss upon ignition at 550 °C (Heiri et al. 2001). The SOM/SOC ratio was also calculated, as a function of substrate and substrate changes (Klingenfuß et al. 2014; Pribyl 2010). The DBD of the peat as another common proxy of decomposition was determined based on dry mass per volume of soil, after drying known volumes of soil for 24 h at 105 °C.

The structure of the carbon was determined based upon Solid-state Cross-Polarization Magic Angle Spinning ^{13}C nuclear magnetic resonance spectroscopy (CPMAS ^{13}C NMR spectroscopy) at the Chair of Soil Science at the Technical University of Munich. Analyses were conducted with a Bruker DSX 200 spectrometer (Billerica/USA) with a proton resonance frequency of 50.32 MHz and a spinning speed of 6.8 kHz. A ramped 1 H-pulse was used during a contact time of 1 ms. Pulse delays of 0.8 s were used to circumvent spin modulation during the Hartmann-Hahn contact. A line broadening of 25 Hz was applied. The ^{13}C chemical shifts were calibrated relative to tetramethylsilane, equalized to 0 ppm. Signal intensities for the chemical shift regions 75–70 ppm (O-alkyl C of carbohydrates) and 57–52 ppm (methoxyl C of lignin) were used to calculate the (70–75)/(52–57) ratio, which correlate positively with decay rates (Bonanomi et al. 2013; Möckel et al. 2021a, b). As a proxy for the state of decomposition, the alkyl C (chemical shift region of 45–0 ppm) to O/N-alkyl C (chemical shift region of 110–45 ppm) (A:O/N) ratio was calculated (Baldock et al. 1997).

Pedogenic minerals allophane and ferrihydrite

Selective dissolution of Al, Fe and Si with ammonium oxalate (0.2 M, pH 3.0), was carried out following Soil Survey Staff (2014; method 4G2). The Al, Fe and Si thus extracted (Al_o, Fe_o, Si_o) is indicative of the active forms of Al and Fe of organic complexes (Al/F-humus complexes), nanocrystalline hydrous oxides of Fe and Al, and nanocrystalline aluminosilicates like allophane (Nanzyo et al. 1993; Wada 1989). Ferrihydrite was estimated as $\%ferrihydrite = \%Fe_o \times 1.7$ (Childs 1985). Sodium pyrophosphate was used to extract the part of active Fe and Al (Fe_p, Al_p), which is associated with organic compounds (Al/Fe-humus complexes; Soil Survey Staff 2014; method 4G3). Allophane or allophane-like constituents were estimated by the equation proposed by Mizota and van Reeuwijk (1989), based on Parfitt and Wilson (1985). While Mizota and van Reeuwijk (1989) recommend to use only Al/Si ratios (derived from $[Al_o\text{-}Al_p]/Si_o$) between 1.0 and 2.5 for the calculation of allophane, we also use Al/Si ratios < 1 (see also Parfitt and Kimble 1989).

Data analysis

Kendall rank correlations (R package GGally, function ggpairs; Quinn and Keough 2002; Schloerke 2021) were used to test for correlations between $\delta^{13}C$ and $\delta^{15}N$ values, and other proxies reflecting decomposition and mineral material: C/N ratios and DBD, A:O/N ratios and (70–75)/(52–57) ratios, SOM/SOC, %Ash, and allophane and ferrihydrite. Statistical analyses and graphic design were carried out using the software R, version 4.0.2.

Results

Patterns of $\delta^{13}C$ and $\delta^{15}N$ values and selected variables above Hekla 1104

At Torfdalsmýri, $\delta^{13}C$ values are rather stable in the section above Hekla 1104, while $\delta^{15}N$ values increase downwards (Fig. 2). DBD and A:O/N ratios increase downwards whereas (70–75)/(52–57) ratios decrease. At Tindar, $\delta^{13}C$ values increase, and $\delta^{15}N$ values decrease. DBD, %Ash and C/N ratios increase sharply. At Hrafnabjörg, $\delta^{13}C$ values first increase sharply, then decrease, whereas $\delta^{15}N$ values decrease above Hekla 1104. DBD, %Ash and $\delta^{13}C$ all peak at 10–20 cm. Ferrihydrite contents are comparatively high in this section at Hrafnabjörg.

Patterns of $\delta^{13}C$ and $\delta^{15}N$ values and selected variables between Hekla 1104 and Hekla 3

At Torfdalsmýri, $\delta^{13}C$ values remain stable, while $\delta^{15}N$ values peak between Hekla 1104 and Hekla 3 tephra layers (Fig. 2). DBD and A:O/N ratios continue to increase, while (70–75)/(52–57) ratios stabilize. At Tindar, $\delta^{13}C$ values continue to increase between the two tephra layers and peak close to Hekla 3; $\delta^{15}N$ values peak slightly higher in the profile, then decrease towards Hekla 3. Allophane contents show two peaks, and ferrihydrite contents are also elevated. The A:O/N ratios increase slowly, while (70–75)/(52–57) ratios first decrease sharply before they stabilize. At Hrafnabjörg, both $\delta^{13}C$ and $\delta^{15}N$ values show only minor fluctuations. DBD, %Ash, ferrihydrite and allophane experience a peak, but decrease thereafter.

Patterns of $\delta^{13}C$ and $\delta^{15}N$ values and selected variables between Hekla 3 and Hekla 4

At Torfdalsmýri, $\delta^{13}C$ values decrease between the Hekla 3 and Hekla 4 tephra layers, while $\delta^{15}N$ peak right below

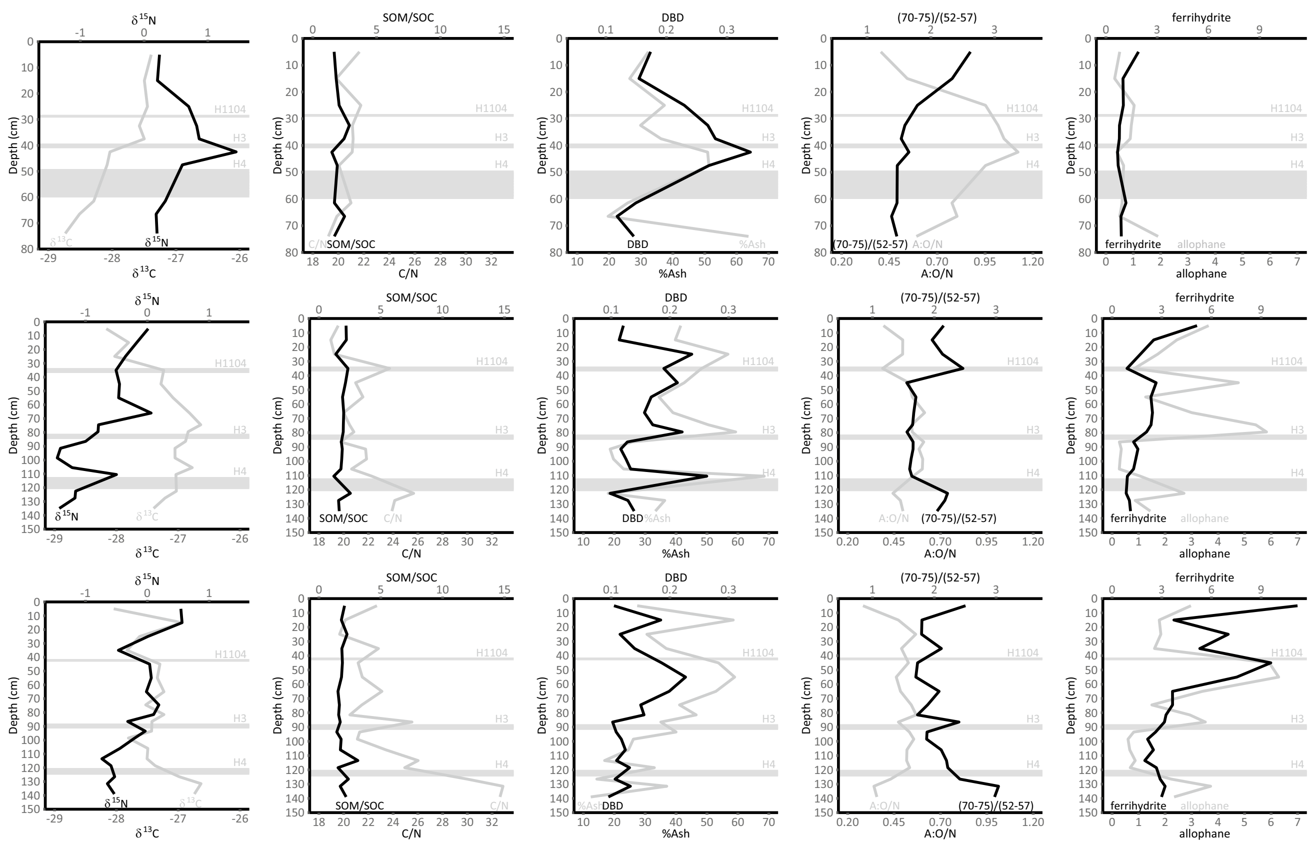

Fig. 2 Depth profiles of $\delta^{13}C$ values (‰) and $\delta^{15}N$ values (‰), SOM/SOC and C/N ratios, %Ash and DBD (g cm^{-3}), A:O/N and (70–75)/(52–57) ratios, and allophane (%) and ferrihydrite (%) at Torfdalsmýri (upper row), Tindar (middle row) and Hrafnabjörg (bottom row). Horizontal grey bars denote prominent silicic tephra layers within the peat profile (H1104 = Hekla 1104, H3 = Hekla 3, H4 = Hekla 4; compare also Fig. 1b)

Hekla 3 and decrease thereafter (Fig. 2). DBD, %Ash and A:O/N ratios peak at the same depth as the δ^{15}N values. At Tindar, both δ^{13}C and δ^{15}N values first decrease, then peak close to Hekla 4 tephra. DBD and %Ash generally decrease between the two tephra layers, but show a peak close to Hekla 4. Ferrihydrite and allophane contents are also noticeably reduced. A:O/N ratios and (70–75)/(52–57) ratios remain fairly stable, while C/N ratios increase. At Hrafnabjörg, δ^{13}C values increase and δ^{15}N values decrease slightly between the two tephra layers. Ferrihydrite and allophane contents, and DBD and %Ash are overall decreased, while C/N ratios and (70–75)(52–57) ratios increase.

Patterns of δ^{13}C and δ^{15}N values and selected variables below Hekla 4

At Torfdalsmyri, δ^{13}C and δ^{15}N values continue to decrease below Hekla 4 (Fig. 2). Allophane content and %Ash rise sharply, while A:O/N ratios decrease and (70–75)(52–57) ratios remain stable. At Tindar, δ^{13}C and δ^{15}N values decrease below the tephra layer. C/N ratios experience a peak, and (70–75)/(52–57) ratios and allophane content also increase. At Hrafnabjörg, δ^{13}C values increase sharply while δ^{15}N values remain rather stable. Allophane and %Ash increase, and C/N ratios and (70–75)(52–57) ratios reveal a peak.

Kendall correlations between δ^{13}C and δ^{15}N values, decomposition proxies, and mineral soil constituents

Mineral material, probably of aeolian origin, (expressed as %Ash) correlates with the C/N ratios and DBD (Fig. 3). It is positively correlated with DBD ($\tau = 0.49$, $p < 0.001$), but exhibits a negative relationship with C/N ratios ($\tau = -0.25$, $p = 0.014$); this pattern is most notable at Tindar and Hrafnabjörg, but less strong or even negligible at Torfdalsmýri. There is no correlation between %Ash and δ^{13}C values ($\tau = -0.03$, $p = 0.76$). Overall, there is only a weak positive correlation between %Ash and δ^{15}N values ($\tau = 0.18$, $p = 0.087$), stronger at Tindar ($\tau = 0.35$, $p = 0.052$) and Hrafnabjörg ($\tau = 0.45$, $p = 0.009$) than Torfdalsmýri. Ferrihydrite shows a positive relationship with δ^{15}N values at Tindar ($\tau = 0.43$, $p = 0.017$) and Hrafnabjörg ($\tau = 0.48$, $p = 0.005$), but no notable correlation with δ^{13}C values ($\tau = 0.1$, $p = 0.34$). At Tindar, there is a strong negative relationship between ferrihydrite and C/N ratios ($\tau = -0.59$, $p < 0.001$). Allophane reveals a positive relationship with δ^{15}N values at Tindar $\tau = 0.40$, $p = 0.027$).

Overall, δ^{13}C values correlate positively with C/N ratios ($\tau = 0.25$, $p = 0.015$; Fig. 3), but the correlation is particularly strong at Torfdalsmýri ($\tau = 0.64$, $p = 0.009$). Also, there is also a strong positive correlation between δ^{15}N values and DBD at Torfdalsmýri ($\tau = 0.82$, $p < 0.001$), but none between δ^{13}C values and DBD ($\tau = 0.24$, $p = 0.325$). Generally, δ^{15}N values correlate negatively with C/N ratios ($\tau = -0.23$, $p = 0.026$), but the correlation is stronger at Tindar ($\tau = -0.43$, $p = 0.017$) and Hrafnabjörg ($\tau = -0.57$, $p < 0.001$). Changes in SOM/SOC are not reflected in changes in δ^{13}C values ($\tau = -0.01$, $p = 0.91$) and δ^{15}N values ($\tau = 0.03$, $p = 0.78$). Overall, the relationship between (70–75)/(52–57) ratios and δ^{13}C ($\tau = 0.07$, $p = 0.51$) and δ^{15}N values ($\tau = -0.14$, $p = 0.18$) is poor. However, at Torfdalsmýri there is a strong positive relationship between δ^{13}C values and (70–75)/(52–57) ratios ($\tau = 0.78$, $p < 0.001$), while there is a moderate negative relationship between these variables at Tindar ($\tau = -0.35$, $p = 0.052$). At Hrafnabjörg, there is a negative relationship between δ^{15}N values and (70–75)/(52–57) ($\tau = -0.50$, $p = 0.003$). Although the overall relationship between A:O/N ratios and δ^{13}C values ($\tau = -0.13$, $p = 0.21$) and A:O/N ratios and δ^{15}N values ($\tau = 0.19$, $p = 0.061$) is poor, there is a positive relationship between δ^{15}N values and A:O/N ratios at Torfdalsmýri ($\tau = 0.69$, $p = 0.005$), a positive relationship between δ^{13}C values and A:O/N ratios at Tindar ($\tau = 0.47$, $p = 0.008$), and a negative relationship between δ^{13}C values and A:O/N ratios at Hrafnabjörg ($\tau = -0.32$, $p = 0.069$). While the overall correlation between δ^{13}C values and δ^{15}N values is negative ($\tau = -0.40$, $p < 0.001$), the correlation is negligible at the individual sites (Torfdalsmýri: $\tau = 0.24$, $p = 0.38$; Tindar: $\tau = -0.22$, $p = 0.24$; Hrafnabjörg: $\tau = -0.09$, $p = 0.60$; compare also Fig. 2).

Discussion

Correlations between δ^{13}C and δ^{15}N values, DBD and C/N ratios

Correlations between δ^{13}C and δ^{15}N values and the other proxies in this study (Fig. 3) signify that δ^{13}C and δ^{15}N values partly reflect the state of decomposition, but are also influenced by other factors. At Tindar and Hrafnabjörg, we observe a negligible positive correlation between δ^{13}C values and the C/N ratios, which compares well with previous studies (Drollinger et al. 2019; Esmeijer-Liu et al. 2012). As lower C/N ratios usually indicate more advanced decomposition (Kuhry and Vitt 1996), the strong positive correlation between the two variables at Torfdalsmýri contradicts the anticipated increase in δ^{13}C values as decomposition proceeds (Alewell et al. 2011; Kuhry and Vitt 1996). However, depth changes in C/N ratios are in fact minor at the site, and we consider the correlation between the variables to be of little significance.

Negative correlation between δ^{15}N values and C/N ratios, and a positive correlation between δ^{15}N values and DBD (Fig. 3), are in line with previous studies (e.g.

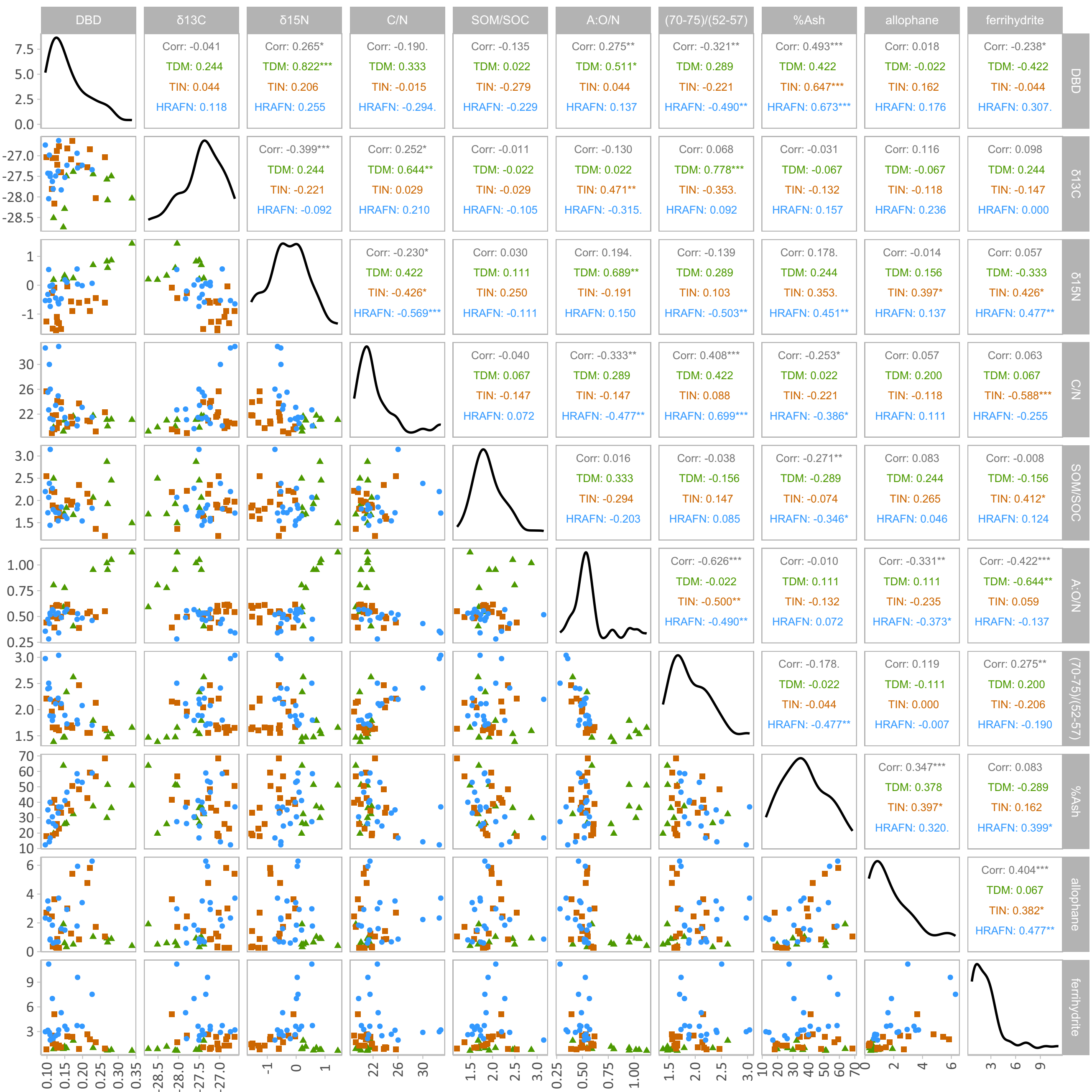

Fig. 3 Relationships between $\delta^{13}C$ (‰) and $\delta^{15}N$ (‰) values, SOM/SOC and C/N ratios, %Ash and DBD (g cm^{-3}), A:O/N and (70–75)/(52–57) ratios, and allophane (%) and ferrihydrite (%) by Kendall´s correlations. Overall correlation coefficient Kendall´s tau (Corr) and Kendall ‘s tau for each peatland is shown (Torfdalsmýri = TDM, Tindar = TIN, Hrafnabjörg = HRAFN). Four thresholds of p-values are indicated as following: "***" = p-value < 0.001, "**" = p-value < 0.01, "*" = p-value < 0.05, "." = p-value < 0.1. Colours in the scatter plots denote observations at the three sample sites. Observations at Torfdalsmýri are marked with green triangles, observations at Tindar are marked with orange quadrats, and observations at Hrafnabjörg are marked with blue circles. The black line graphs show density plots which visualize the distribution of the variables

Drollinger et al. 2019; Esmeijer-Liu et al. 2012; Krüger et al. 2017). The relationships show enrichment of ^{15}N as decomposition proceeds. The positive correlation between $\delta^{15}N$ values and DBD is strong and significant only at the most sheltered site, Torfdalsmýri. This should not lead to the simple conclusion that decomposition exerts no influence on $\delta^{15}N$ values at Tindar and Hrafnabjörg. It rather determines DBD as a poor proxy for decomposition at peatlands under increased influence of aeolian deposits (Möckel et al.2021a; Möckel et al. 2023). Windborne material results in higher DBD whatever the state of decomposition. The negative correlation between δ^{15}N values and C/N ratios at Tindar and Hrafnabjörg possibly indicates that decomposition also leads to an enrichment of ^{15}N at these sites (Esmeijer-Liu et al. 2012). While it is widely accepted that C/N ratios decrease as decomposition increases in peatlands with a homogenous vegetation history (Kuhry and Vitt 1996; Malmer and Holm 1984), depth profiles of both stable isotopes and C/N ratios can be wrongly interpreted as a result of decomposition. This is particularly true in peatlands with a heterogeneous vegetation history, where changes in species composition can be imprinted in C/N ratios, and the isotopic fingerprint of the peat (Broder et al. 2012; Hornibrook et al. 2000). An effect of vegetation shifts on C/N ratios and stable isotopes is conceivable in our peatlands, because palaeoenvironmental research in the area demonstrates vegetation changes imposed by interactions of volcanic eruptions, climate deterioration and land-use after ca. 870 CE (Eddudóttir et al. 2016; Möckel et al. 2017), particularly in marginal areas close to the highlands.

Correlations between δ^{13}C and δ^{15}N values, and A:O/N ratios

The interpretation of variables like DBD and C/N ratios can be complicated in dynamic environments like Iceland (Möckel et al. 2017, 2023). Therefore, we determined additional proxies for decomposition (Fig. 2) to facilitate better interpretation of the patterns of δ^{13}C and δ^{15}N values at our sites. The strong positive correlation (Fig. 3) between δ^{15}N values and A:O/N ratios at Torfdalsmýri, and between δ^{13}C values and A:O/N ratios at Tindar provide support for the influence of decomposition on isotopic fractionation at these sites. An increase in A:O/N ratios with depth is common both in natural and disturbed peatlands (Leifeld et al. 2012; Preston et al. 1987). It indicates advancing decomposition, leading to a relative increase in recalcitrant alkyl carbon compounds in expense of more labile O/N alkyl carbon compounds (Baldock et al. 1997). Therefore, a depth development of δ^{13}C and δ^{15}N values in line with A:O/N ratios could result from an accumulation of microbially derived recalcitrant material as decomposition proceeds (Kögel-Knabner 1997), leading to an enrichment of ^{15}N and ^{13}C (Groß-Schmölders et al. 2020; Mancini et al. 2003). Importantly, high contents of mineral material coincide with peaks in δ^{15}N and δ^{13}C values (Fig. 2). Therefore, nutrients leaching from the windborne minerals may enhance microbial activities. Alternative electron acceptors from the mineral material, which can propel anaerobic decomposition, probably also play a role (Broder et al. 2012; Hughes et al. 2013; Strawn et al. 2015b).

Interaction between mineral soil constituents and organic matter

An interaction between mineral material and organic matter (the peat) is indicated by correlations between several proxies at the inland sites Tindar and Hrafnabjörg (Fig. 3). At these sites, δ^{15}N values correlate positively with %Ash, ferrihydrite, and allophane (at Tindar only). The interpretation of these correlations is not straightforward. Feyissa et al. (2020) found higher δ^{15}N values in the labile soil organic matter fraction than in recalcitrant soil organic matter. Therefore, our results might support preferential stabilization of labile organic compounds, such as carbohydrates, by pedogenic minerals ferrihydrite and allophane, as suggested by several previous studies (Miltner and Zech 1998; Möckel et al. 2023; Schöning et al. 2005). Particularly the correlation between ferrihydrite and δ^{15}N values could also be an artefact, though. Water table fluctuations and associated shifts between oxic and anoxic conditions may facilitate increased formation of the secondary mineral ferrihydrite in the volcanic-ash influenced peat (Strawn et al. 2015a) parallel to an enrichment in ^{15}N (Groß-Schmölders et al. 2020). Similarly, allophane formation requires good aeration (Parfitt and Kimble 1989), but oxygenation also goes hand in hand with elevated δ^{15}N values. Therefore, the enrichment of ^{15}N in layers with high levels of mineral constituents might indicate changes in microbial composition and increased levels of microbially derived organic matter (Dijkstra et al. 2008; Groß-Schmölders et al. 2020), rather than stabilization of labile organic compounds in organo-mineral complexes. Aerobic decomposition is probably enhanced by nutrients from the mineral deposits, while anaerobic decomposition during times of waterlogging may be driven by alternative electron acceptors from the minerals (Broder et al. 2012; Hughes et al. 2013; Strawn et al. 2015b). In fact, the inverse relationship between ferrihydrite and C/N ratios at Hrafnabjörg and Tindar, and between %Ash and C/N ratios, and %Ash and (70–75)/(52–57) at Hrafnabjörg (Fig. 2) suggests that decomposition is enhanced by windborne mineral material (Bonanomi et al. 2013; Broder et al. 2012).

Correlations between δ^{13}C values and δ^{15}N values

Anaerobic and aerobic decomposition usually lead to depth development of δ^{13}C values roughly in line with δ^{15}N values (e.g. Drollinger et al. 2019; Groß-Schmölders et al. 2020). Aerobic decomposition induces downward increases in δ^{13}C and δ^{15}N values due to depletion in the lighter isotopes ^{12}C and ^{14}N (Alewell et al. 2011; Krüger et al. 2014; Zeh et al. 2020). Inhibited decomposition under anoxic conditions leads to more stable δ^{13}C and δ^{15}N values with depth, while slow decreases with depth are normally a sign of minor decomposition under anaerobic conditions. We propose that enhanced anaerobic decomposition in peat layers with elevated levels of nutrients and alternative electron acceptors derived e.g. by tephra layers (Broder et al. 2012) and other windborne material could likewise explain increases and turning points in δ^{13}C and δ^{15}N values (Bernstein et al. 2008; Mancini et al. 2003). In other cases, supply of nutrients to subsoils might be hindered by compacted tephra layers (De Vleeschouwer et al. 2008; Möckel et al. 2021a). This would lead to reduced decomposition below a tephra deposit, mirrored by rather stable or slowly decreasing δ^{13}C and δ^{15}N values with depth.

While we observe depth development of δ^{13}C values roughly in line with δ^{15}N values below Hekla 3 at Torfdalsmýri and Tindar (Fig. 2), and above Hekla 3 at Hrafnabjörg, the overall correlation between δ^{13}C and δ^{15}N values is negative (Fig. 3). Other processes than decomposition must also play a role for depth patterns of δ^{13}C and δ^{15}N values at our sites. For example, discrimination of peatland plants against ^{15}N during nitrogen uptake (Nadelhoffer et al. 1996; Serk et al. 2022) can contribute to elevated δ^{15}N values in the rooting zone (ca. upper 30 cm) without a parallel increase of δ^{13}C values. Past changes in vegetation have probably also contributed to shifts in δ^{13}C and δ^{15}N values, as the isotopic fingerprint varies between species and plant functional types (Asada et al. 2005; Zeh et al. 2020). The significance of shifts in species composition is supported by palaeoenvironmental reconstructions in the study area (Eddudóttir et al. 2017, 2020, 2016; Möckel et al. 2017), which demonstrate at least temporary vegetation changes induced by tephra deposits (notably the Hekla 4 tephra). This is particularly demonstrated in ecosystems in marginal areas close to the highlands. The effect of tephra deposits on vegetation composition and the isotopic composition of species can be aggravated by coinciding climate cooling such as during and following the eruption of Hekla 4 (Eddudóttir et al. 2016; Geirsdóttir et al. 2013; Larsen et al. 2012). Importantly, the isotopic signatures of the same species can vary due to temperature changes (Jędrysek and Skrzypek 2005; Skrzypek et al. 2008). Temperature changes in the past may have influenced the isotopic signature of the peatland vegetation, even without changes in the species composition.

Depth patterns of δ^{13}C and δ^{15}N values above Hekla 1104

Coastal peatland Torfdalsmýri

The downward increase of δ^{15}N values at Torfdalsmýri above Hekla 1104 (i.e. in post-settlement peat; Fig. 2) is similar to patterns observed in aerobic layers of peat columns of degraded (e.g. drained) peatlands in non-volcanic regions (e.g. Drollinger et al. 2019; Groß-Schmölders et al. 2020). Therefore, aerobic decomposition, which is associated with a relative enrichment of the heavier isotope ^{15}N (Zeh et al. 2020), could explain the increase in δ^{15}N values. However, this pattern is contrasted by stable δ^{13}C values above Hekla 1104, which is usually a sign of low decomposition and reduced isotopic fractionation under anoxic condition (Alewell et al. 2011; Krüger 2016; Krüger et al. 2014). Possibly, other processes than aerobic decomposition steer the downward increase in δ^{15}N values at the site. Perhaps discrimination of peatland plants against ^{15}N during nitrogen uptake contributes to the enrichment of ^{15}N with depth (Nadelhoffer et al. 1996; Serk et al. 2022). Alternatively, anaerobic decomposition propelled by alternative electron acceptors (Strawn et al. 2015b) from the mineral material within the peat substrate and the adjacent tephra layer (Fig. 1b, Fig. 2; Broder et al. 2012), could lead to an enrichment of ^{15}N (Bernstein et al. 2008). Assuming a scenario of enhanced anaerobic decomposition causing raised δ^{15}N values, the absence of a concomitant increase of δ^{13}C values remains conspicuous. As will be described in the following sections, we also see conspicuous increases or turning points of δ^{15}N values without similarly pronounced patterns of δ^{13}C values in deeper peat sections, and at other peatlands of this study. We hypothesize, that isotopic fractionation of nitrogen is more strongly affected by aeolian deposits than isotopic fractionation of carbon, causing contradictory depth developments of δ^{13}C and δ^{15}N values.

Lowland peatland Tindar and highland fringe peatland Hrafnabjörg

The downward increase of δ^{13}C values in the section above Hekla 1104 at Tindar (Fig. 2) could indicate aerobic decomposition (Alewell et al. 2011; Krüger 2016; Krüger et al. 2014; Zeh et al. 2020), which is conceivable in surface layers of undrained peatlands. It is a bit surprising that the downward increase of δ^{13}C values is not reflected by a parallel increase of δ^{15}N values at the site. However, an absence of ^{15}N enrichment parallel to ^{13}C enrichment with depth in oxic peat layers is not unprecedented (Krüger et al. 2017). Therefore, we still conclude that aerobic decomposition influences the depth pattern of δ^{13}C values here.

At Hrafnabjörg, there is a roughly parallel development of δ^{13}C values and δ^{15}N values, and aeolian indicators %Ash and DBD in the section above Hekla 1104, characterized by a peak at 10–20 cm depth (Fig. 2). Considering the shallow depth of the peak, the most probable explanation lies in high rates of aerobic decomposition, enhanced by nutrients from the windborne volcanic material (Broder et al. 2012; Hughes et al. 2013) and water table fluctuations (Groß-Schmölders et al. 2020). High levels of alternative electron acceptors (Strawn et al. 2015b) are probably also supplied by mineral material within the peat substrate. Therefore, anaerobic decomposition may also contribute to the turning point in

$\delta^{13}C$ values and $\delta^{15}N$ values (Bernstein et al. 2008; Broder et al. 2012; Mancini et al. 2003).

Depth patterns of $\delta^{13}C$ and $\delta^{15}N$ values between Hekla 1104 and Hekla 4

Coastal peatland Torfdalsmýri

While contents of the pedogenic minerals allophane and ferrihydrite are low at Torfdalsmýri (Fig. 2), mineral content is rather high between the Hekla 3 and Hekla 4 tephra layers (> 50%Ash). This is accompanied by a salient turning point in $\delta^{15}N$ values between the two tephra layers, and a turning point of A:O/N ratios. A straightforward interpretation of these turning points would be aerobic decomposition, associated with a relative enrichment of the heavier isotope ^{15}N (Zeh et al. 2020) and resulting from an accumulation of microbially derived recalcitrant compounds (Serk et al. 2022). A possible scenario could be enhanced microbial activity in the mesotelm of peatlands (Andersen et al. 2013; Groß-Schmölders et al. 2020). This layer, at the interface between aerobic and anaerobic conditions, often facilitates increased decomposition of intrinsically labile carbon compounds and the accumulation of microbially derived recalcitrant carbon compounds such as of the alkyl carbon range (Serk et al. 2022). The consistent downward increase in A:O/N ratios, culminating in a turning point between Hekla 3 and Hekla 4, and low (70–75)/(52–57) ratios strongly indicates an increase in intrinsically recalcitrant SOM in the Torfdalsmýri peat section (Baldock et al. 1997; Bonanomi et al. 2013; Preston et al. 1987). The undrained state of the peatland Torfdalsmýri renders the turning point in $\delta^{15}N$ values at a depth between 40–45 cm rather deep (Drollinger et al. 2019; Groß-Schmölders et al. 2020). We did not measure exact water table heights in the peatland, but estimate based on field observations, that the water table ranges between 0–10 cm. Decreasing or stable $\delta^{13}C$ values with depth signal low or anaerobic decomposition respectively (Alewell et al. 2011; Krüger 2016; Krüger et al. 2014). A probable explanation for the turning point in $\delta^{15}N$ values is thus anaerobic decomposition driven by alternative electron acceptors (Broder et al. 2012; Strawn et al. 2015b) from the mineral material and the adjacent tephra layers (Fig. 1b, Fig. 2) (Bernstein et al. 2008).

Lowland peatland Tindar

At the lowland peatland Tindar, there are interesting peaks or turning points around prominent tephra layers, similar to a study in Patagonian peatlands (Broder et al. 2012). A turning point of $\delta^{15}N$ values above Hekla 3 is accompanied by increasing A:O/N ratios with depth, indicating high microbial activity (Andersen et al. 2013; Groß-Schmölders et al. 2020), increased decomposition of intrinsically labile carbon compounds and an accumulation of recalcitrant carbon compounds (Serk et al. 2022). In conjunction with a near consistent increase in $\delta^{13}C$ values downwards to Hekla 3, the peak in $\delta^{15}N$ above Hekla 3 could be a result of aerobic decomposition (Alewell et al. 2011; Krüger 2016; Krüger et al. 2014; Zeh et al. 2020). Again, considering the depth of the peak, between 60 and 70 cm, we see enhanced anaerobic decomposition, due to a supply of mineral material and alternative electron acceptors (Strawn et al. 2015b), as a plausible explanation for the ^{15}N and ^{13}C enrichment (Bernstein et al. 2008; Broder et al. 2012; Mancini et al. 2003).

Between Hekla 3 and Hekla 4, $\delta^{13}C$ values become more stable, even though there is a small peak right above the Hekla 4 tephra layer (Fig. 2). This, in conjunction with fairly stable C/N, A:O/N and (70–75)(/52–57) ratios is typical for slow decomposition in water saturated parts of the peat profile (e.g. Groß-Schmölders et al. 2020). The turning point in $\delta^{15}N$ values above Hekla 4 and the small peak in $\delta^{13}C$ values could be induced by restricted downward movement of water and dissolved organic material because of the Hekla 4 deposit (De Vleeschouwer et al. 2008; Möckel et al. 2021a). Impeded fluid movement can impact microbial activity and decomposition (Broder et al. 2012), e.g. by reducing nutrient inputs into peat layers below the tephra layer, and by increasing element accumulations in upper layers. Therefore, increased nutrient levels above the Hekla 4 tephra layer in interaction with increased levels of alternative electron acceptors may enhance decomposition even under anaerobic conditions.

Highland fringe peatland Hrafnabjörg

No turning points are found between Hekla 1104 and Hekla 4 at Hrafnabjörg (Fig. 2). Stable $\delta^{13}C$ values and slowly declining $\delta^{15}N$ values are indicative of an anaerobic environment with limited decomposition and little isotopic fractionation, similar to peatlands in non-volcanic environments (Alewell et al. 2011; Krüger et al. 2015). A:O/N ratios are stable in this section of the peat column, while C/N ratios and (70–75)(/52–57) ratios increase slightly, further supporting the scenario of inhibited decomposition (Möckel et al. 2021a). At ca. 330 m a.s.l., the Hrafnabjörg site provides climatically harsher environment than the other two sites (Fig. 1). Factors like longer persistence of seasonal ground frost in spring and early summer and concomitant cooling effects on soil temperatures might slow down decomposition at the site (Bu et al. 2011). The result would be reduced effect of mineral aeolian material on isotopic fractionation.

Depth patterns of $\delta^{13}C$ and $\delta^{15}N$ values below Hekla 4

Below Hekla 4 tephra, the slow downwards decline in $\delta^{13}C$ and $\delta^{15}N$ values at Torfdalsmýri and Tindar, and stable $\delta^{15}N$ values at Hrafnabjörg indicate slow peat degradation under anoxic conditions (e.g. Alewell et al. 2011; Krüger et al. 2015). Reduced peat degradation below the tephra layer is supported by lowered A:O/N ratios at all sites, and by increased (70–75)(/52–57) ratios at Tindar and Hrafnabjörg; these are indicative of less decomposed organic material (Baldock et al. 1997). As explained by Möckel et al. (2021a), this shift in the chemical composition of the carbon around the tephra layer could be caused by the tephra deposit serving as a nearly impermeable layer. This would hinder the free vertical movement of water and the input of nutrients and fresh dissolved organic material into the older peat, thereby hampering microbial activities.

Strongly pronounced shifts of the decomposition proxies A:O/N ratios, (70–75)(/52–57) ratios, and C/N ratios point towards reduced decomposition, particularly at Hrafnabjörg. Meanwhile, $\delta^{13}C$ values increase below the Hekla 4 tephra deposit at Hrafnabjörg. It is possible that labile organic compounds with elevated $\delta^{13}C$ values (Feyissa et al. 2020), are being protected from decomposition. While the explanation may involve altered hydrology and nutrient state (Broder et al. 2012), vegetation change induced by the Hekla 4 deposit and sustained by deteriorating climate can also be involved (Eddudóttir et al. 2017, 2016). Vegetation shifts often lead to changes in the chemical composition of the organic matter (Leifeld et al. 2012; Möckel et al. 2021a; Zeh et al. 2020). On that basis we propose that the contradictory development of $\delta^{13}C$ and $\delta^{15}N$ values below the tephra layer at Hrafnabjörg stems from an interaction of shifts in vegetation, decomposition processes shaped by the tephra deposit, and deteriorating climate.

Conclusions

This study provides a first insight into depth profiles of $\delta^{13}C$ and $\delta^{15}N$ values in peatlands of active aeolian environments. Based on comparisons of three peatlands along a depositional and climatic transect in Iceland, we conclude that aeolian material derived from volcanic eruptions and erosion in the surroundings of peatlands influences depth profiles of $\delta^{13}C$ and $\delta^{15}N$ values. Inferences about processes shaping depth profiles of $\delta^{13}C$ and $\delta^{15}N$ values in such environments need to be made in relation to multiple other proxies, which provide information about the decomposition state and the structure of the organic material, and which provide information about mineral soil constituents. Based on multi-proxy comparison, we propose that a combination of the following mechanisms shapes depth patterns of $\delta^{13}C$ and $\delta^{15}N$ values at our sites:

- Enhanced aerobic decomposition facilitated by increased nutrient levels in peat layers with elevated levels of mineral material contributes to increases in $\delta^{15}N$ and $\delta^{13}C$ values. This is particularly relevant for surface peat layers formed under increased influence of aeolian deposition in the post-settlement environment.
- Our data suggest enrichment of ^{15}N and ^{13}N to be driven by preferential stabilization of certain organic compounds through complexation with pedogenic minerals like ferrihydrite and allophane.
- In deeper peat layers with mineral material embedded in the peat substrate and adjacent to tephra layers, anaerobic decomposition could be propelled by alternative electron acceptors and increased nutrient levels. In this way, increased decomposition under waterlogged conditions might cause increases and turning points in $\delta^{15}N$ and $\delta^{13}C$ values, resembling aerobic decomposition. $\delta^{15}N$ seems to react more strongly to influences of mineral constituents.
- Below fine grained and compacted tephra layers of limited permeability, the supply of nutrients to subsoils can be hindered. Under such circumstances, decomposition is reduced, as indicated by decreased A:O/N ratios and increased (70–75)(/52–57) and C/N ratios. At two of the three sites, the anticipated reduced decomposition is mirrored by stable or slightly decreasing $\delta^{15}N$ and $\delta^{13}C$ values.
- At the site at the highland fringe, $\delta^{13}C$ values increase below the Hekla 4 tephra, despite decreased A:O/N ratios and increased (70–75)(/52–57) and C/N ratios, indicating reduced decomposition. Two explanations are proposed. First, labile organic compounds, which exhibit elevated $\delta^{13}C$ values in comparison to recalcitrant compounds, could be preferentially stabilized. Second, vegetation changes in the past, induced by pressures imposed by the tephra deposition and cooling climate probably contribute to shifts in the isotopic fingerprint of the organic material.

Mineral constituents clearly play an important role in element cycling in peatlands of aeolian environments like Iceland. In these environments, $\delta^{13}C$ and $\delta^{15}N$ values alone are not suitable to reconstruct the environmental history and state of decomposition in peatlands. However, as part of multi-proxy studies, $\delta^{13}C$ and $\delta^{15}N$ values can contribute useful information. Inclusion of $\delta^{13}C$ and $\delta^{15}N$ values should therefore be considered in future studies as a step towards better understanding of the functioning of peatlands in aeolian environments. Further studies are needed to better understand the environmental history and decomposition processes in peatlands of these environments. We recommend to study variations in chemical and physical peat properties using a higher sampling resolution, particularly within critical parts of the peat profiles such as around tephra layers. Future research must involve peatlands which reflect an array of environmental conditions with regard to degree of aeolian deposition and climate, mineral wetlands in the highlands in particular. Lastly, we recommend the investigation of the influence of aeolian mineral material on element cycling and patterns of $\delta^{13}C$ and $\delta^{15}N$ in non-volcanic aeolian areas.

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Data Availability The datasets generated and analysed during the current study are included in this manuscript and available in the Supplementary Information (SI 1). Also, the data are available in the following dataset for Möckel et al. (2021a), available by Dryad: https://doi.org/10.5061/dryad.tmpg4f502.

Declarations

Competing Interests The authors have no financial or non-financial interests to disclose.

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