



Anthropogenic and climate signals in late-Holocene peat layers of an ombrotrophic bog in the Styrian Enns valley (Austrian Alps)

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Abstract: Using peat bogs as palaeoenvironmental archives is a well-established practice for reconstructing changing climate and anthropogenic activity in the past. In this paper, we present multi-proxy analyses (element geochemistry, pollen, non-pollen palynomorphs, stable Pb isotopes, humification, ash content) of a 500 cm long, ¹⁴C-dated peat core covering the past ~ 5000 years from the ombrotrophic Pürschachen Moor in the Styrian Enns valley (Austrian Alps). Early indications of low settlement and agricultural activity date to ~ 2900 cal BCE. An early enrichment of Cu was found in peat layers corresponding to the late Copper Age (~ 2500 cal BCE). These enrichments are attributed to Cu mining activities in the Eisenerz Alps. More pronounced increases in cultural indicators (cultivated plants, shrubs, herbs, charcoal) in the pollen record and enrichments of trace metals suggest significant human impact in the vicinity of Pürschachen Moor in the middle Bronze Age (~ 1450–1250 cal BCE), in the late Bronze Age (~ 1050–800 cal BCE) and in the period of the late La Tène culture (~ 300 cal BCE–1 cal CE). The greater part of the Iron Age and the Roman imperial period are each characterized by a general decline in anthropogenic indicators compared to previous periods. Distinct enrichments of Pb and Sb in the sample that corresponds to ~ 900 cal CE are attributed to medieval siderite mining activity in the immediate vicinity of Pürschachen Moor. The results of this interdisciplinary study provide evidence that strong, climate-controlled interrelations exist between the pollen record, the humification degree and the ash content in an ombrotrophic environment. Human activity, in contrast, is

mainly reflected in the pollen record and by enrichments of heavy metals. The study indicates a dry period in the region of the bog around ~ 1950 cal BCE.

Kurzfassung:

Hochmoore eignen sich zur Rekonstruktion des Paläoklimas und anthropogener Aktivität in der Vergangenheit. In der vorliegenden Arbeit werden Multiproxy-Analysen (Elementchemie, Pollen, Mikrofossilien, stabile Pb-Isotope, Humifizierung, Aschegehalt) eines 500 cm langen und mittels der C-14-Methode datierten Torfkerns aus dem ombrotrophen Pürgschachener Moor im steirischen Ennstal (Österreichische Alpen) vorgelegt und diskutiert. Der Bohrkern umfasst einen Zeitraum von ~ 5000 Jahren. Frühe Hinweise auf Besiedelung und landwirtschaftliche Nutzung datieren auf ~ 2900 cal BCE. Erste markante Cu-Anreicherungen, die auf Cu-Bergbau in den angrenzenden Eisenerzer Alpen zurückgeführt werden, zeigen sich in Torfschichten aus der späten Kupfersteinzeit (~ 2500 cal BCE). Deutlichere Zunahmen von Kulturindikatoren (Kulturpflanzen, Sträucher, Kräuter, Holzkohle) im Pollendiagramm und Anreicherungen von Spurenmetallen lassen auf signifikanten menschlichen Einfluss in der Umgebung des Pürgschachener Moores in der Mittelbronzezeit (~ 1450 – 1250 cal BCE), in der Spätbronzezeit und (~ 1050 – 800 cal BCE) sowie in der Periode der späten Latènezeit (~ 300 cal BCE– 1 cal CE) schließen. Der größte Teil der Eisenzeit sowie die römische Kaiserzeit sind durch einen allgemeinen Rückgang von anthropogenen Indikatoren im Vergleich zu früheren Perioden gekennzeichnet. Anreicherungen von Pb und Sb in einer Torfprobe aus dem Mittelalter (~ 900 cal CE) können mit Sideritabbau in unmittelbarer Nähe des Pürgschachener Moores in Verbindung gebracht werden. Die Ergebnisse dieser interdisziplinären Studie belegen starke klimagesteuerte Wechselbeziehungen zwischen Pollen, dem Humifizierungsgrad und dem Aschegehalt. Menschliche Aktivität in der Umgebung des Moores zeigt eine geringe Korrelation mit Humifizierung und Aschegehalt, findet allerdings stärkeren Niederschlag in den Pollen- und Schwermetalldaten. Die vorliegende Studie weist auf eine ausgedehnte Trockenperiode in der Umgebung des Pürgschachener Moors um ~ 1950 cal BCE hin.

1 Introduction

1.1 Peat bogs as geochemical and palaeoenvironmental archives

In recent years, several multi-proxy studies of bogs, involving elemental, isotopic, and palynological and/or plant macrofossil analyses, have gained in significance, enabling relatively accurate interpretations and quantifications of human impact in the past (e.g. Bindler, 2003; De Vleeschouwer et al., 2007; van der Knaap et al., 2011; Segnana et al., 2019; von Scheffer et al., 2019). Ombrotrophic (rain-fed) peat bogs are solely dependent on precipitation and isolated from the direct influence of rivers, springs or groundwater. Consequently, such bogs provide excellent archives for reconstructing past atmospheric fluxes and environmental conditions (Martínez-Cortizas et al., 1999; De Vleeschouwer, 2010; Drexler et al., 2016). As the world faces future global climate change, a profound understanding of the interrelations of palaeoenvironmental and past human signals is of crucial importance for obtaining a more comprehensive picture of changes in the biosphere throughout the past. With respect to the Alpine region during the Holocene, palaeoenvironmental studies have mainly concentrated on the reconstruction of environmental conditions and past human impact in the Western Alps and western parts of the Eastern Alps

(e.g. Büntgen et al., 2005; Nicolussi et al., 2005; Festi et al., 2014; Segnana et al., 2019). Only few data exist regarding areas in the eastern foothills of the Alpine main ridge in eastern Austria (e.g. Drescher-Schneider, 2003; Schmidt et al., 2006; Boch et al., 2009; Huber et al., 2010).

This present study seeks to close this research gap by combining (bio)geochemical, isotopic and palynological analyses of peat deposits of Pürgschachen Moor in the Austrian Alps. In particular, we provide further insights into palaeoenvironmental changes and the advent and chronology of prehistoric societies (from the Copper Age up to Roman times) and prehistoric copper mining in the Liezen area and the more eastern Eisenerz Alps. In addition, by also consulting the ash content and the humification degree, we aim to enhance the general knowledge regarding the interrelations between humification, mineralization, climate change and human impact in wetlands.

Pollen analysis is considered a reliable tool for inferring palaeoenvironmental changes and associated vegetational shifts (e.g. Finsinger et al., 2006; Herzschuh, 2007). Anthropogenic indicators in pollen records, such as crop plants and cereals, were first formalized by Behre (1981, 1988) and are nowadays commonly used to reconstruct agricultural and other human activities in the past (e.g. Bunting et al., 2001; Zhang et al., 2010; Rösch and Lechterbeck, 2016). The accuracy of assessments of past human activity by using

geochemical methods depends, among other factors, on the mobility of relevant trace elements (e.g. Pb, Sb, Cu) in the peat environment.

Even though emissions of copper smelting processes are detectable in regular soils across tens of kilometres (Ettler, 2016) and the potential of Cu as an anthropogenic tracer in peat deposits has been highlighted by different authors (e.g. Ukonmaanaho et al., 2002; Rausch et al., 2005; Mighall et al., 2009; Novak et al., 2011; Mariet et al., 2016), other studies have questioned the reliability of Cu as a marker of past human impact in peat environments, due to its dependence on pH value, mineralogy (Rausch et al., 2005), vegetation (Shotyk et al., 2002; Ukonmaanaho et al., 2004) and hydrology (Tipping et al., 2003; Bobrov et al., 2011).

Therefore, we also measured Pb and Sb, which have successfully been used to reconstruct anthropogenic activity in various studies as they show low mobility in peat environments (e.g. Cloy et al., 2009; De Vleeschouwer et al., 2009; Shotyk et al., 2017). However, post-depositional redistribution processes of Pb and Sb have also been demonstrated occasionally (Olid et al., 2010; Rothwell et al., 2010). Mobilization of heavy metals in peat, in general, has been attributed to long-term water table fluctuations (Tipping et al., 2003; Rothwell et al., 2010).

Stable Pb isotope measurements were conducted to improve the contextualization of the elemental results, attempting to differentiate between local, regional and non-regional anthropogenic and geogenic sources (e.g. Allan et al., 2018). Organic compounds, especially humic acids that are considered the main adsorption agents in peat, provide adsorption sites that enhance trace element accumulation (Yang et al., 2019). To improve the quality of the interpretation of past anthropogenic activity, heavy metal concentrations were contrasted with the humification degree, provided by Fourier-transformed infrared (FTIR) spectroscopy (see also Biester et al., 2012). FTIR spectroscopy can be used to identify changes in major peat chemical properties, such as changes in relative contributions of carbohydrates or aromatics (Niemeyer et al., 1992; Kalbitz et al., 1999). Due to preferential degradation of carbohydrates over aromatics, relative absorption indicative of these moieties can be used as an indicator of the degree of peat decomposition and/or humification (Artz et al., 2008; Broder et al., 2012; Biester et al., 2014).

Since the extent of decomposition of peat is mainly dependent on plant species (Drollinger et al., 2020), nutrient fluxes and hydrological conditions, a connection between climate and decomposition can be established (van der Linden and van Geel, 2006). An assessment of the humification degree can therefore also help to reconstruct climate changes in the past.

The Sr concentration in bogs, to a large extent controlled by groundwater inflow, is regularly used as an additional proxy for the trophic status of the bog (Shotyk et al., 2017). As humification is closely interlinked with mineralization

(Tolonen, 1984), an interpretation of ash content variations contributes to the reconstruction of past climate.

1.2 Regional setting and historical context

Pürgschachen Moor is the largest intact valley peat bog in Austria with an areal extent of ~ 62 ha (Drollinger et al., 2019). Because of the peatland's proximity to prehistoric mining sites and a large vertical extension of the peat body, it was chosen as the study site. The peat bog is located in the Styrian Enns valley, a large fault line that separates the Lower Tauern to the south from the Palaeozoic Greywacke zone and the Northern Calcareous Alps in the north (Keil and Neubauer, 2009). The mean annual temperature in the adjacent town of Admont is $\sim 7.3^\circ\text{C}$. Annual precipitation, referring to the time between 1990 and 2019, is ~ 1250 mm (Drollinger et al., 2019). The Greywacke zone, comprising the most significant copper ore resources of the Eastern Alps, lies between the Northern Calcareous Alps and the Central Eastern Alps (Kucha and Raith, 2009). The Greywacke zone in the study area contains Ordovician- to Devonian-age metamorphosed sedimentary rocks (turbidites, greywackes and limestones) and Ordovician-age mafic volcanic rocks (Gasser et al., 2009; Lutz and Pernicka, 2013; see Fig. 1).

Copper ores of the eastern Greywacke zone are typically characterized by mineral phases of the tennantite–tetrahedrite solid-solution series ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$ – $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) and chalcopyrite (CuFeS_2)–pyrite (FeS_2) mineralizations (Hanning, 2012; Haubner et al., 2015; Pernicka et al., 2016).

Palaeoenvironmental studies indicate a marked increase in metal pollution throughout Europe during the Bronze Age (e.g. Brännvall et al., 2001; Monna et al., 2004; Mighall et al., 2009; Longman et al., 2018; Wagreich and Draganits, 2018). This also applies to the Austrian Alps, where a gradual intensification of human activity is assumed for the middle Bronze Age and the early part of the late Bronze Age in different areas in Tyrol, Salzburg, Styria and Lower Austria (e.g. Röpke and Krause, 2013; Breitenlechner et al., 2014; Haubner et al., 2015; O'Brien, 2015; Pichler et al., 2018). Several studies have aimed to reconstruct the prehistoric human impact in the Mitterberg region in Salzburg, which was possibly the largest copper producer in Europe in the middle of the second millennium BCE (e.g. Stöllner, 2011; Breitenlechner et al., 2014; Pernicka et al., 2016). In contrast, relatively few detailed palaeoenvironmental studies exist regarding prehistoric settlement development and early mining in the Eisenerz Alps and the Gesäuse area. The earliest indications of large-scale settlement activity in the Palten valley, which forms the southernmost border of the Eisenerz region, date back to the late Neolithic period in the fourth millennium BCE (Drescher-Schneider, 2003; Preßlinger et al., 2009). Taking into account archaeological findings in the region, it is probable that a large number of non-specified prehistoric copper mining and smelting sites in the region can be attributed to the middle and/or late Bronze

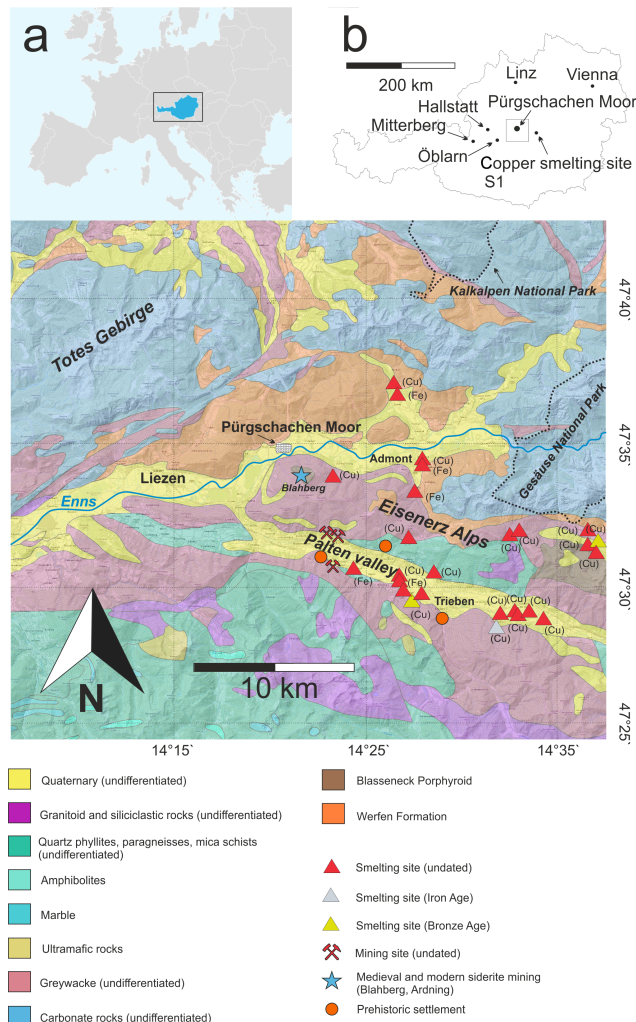


Figure 1. Overview map with the geographical location of Pürgschachen Moor in the Enns valley and known prehistoric smelting sites and settlements (Klemm, 2003), embedded in the regional geology (Geologische Bundesanstalt, 2019). Europe (a), the prehistoric mining areas Mitterberg and Hallstatt, Öblarn, the copper smelting site S1, Linz and Vienna (b) are given as geographic references.

Age (Klemm, 2003; Preßlinger et al., 2009). The largest excavated bronze smelting site in the Eisenerz Alps, S1 in the Supplement (Fig. 1), has also been radiocarbon dated to the middle Bronze Age (1600–1350 cal BCE; Kraus, 2014).

Given the lack of archaeological evidence assignable to the Iron Age, a decrease in anthropogenic activity during the following centuries is suggested (Klemm, 2003). More intense human impact during the Roman period is indicated by different archaeological finds and evidence for Roman trade routes in the region (Herbert, 2015). A decline in archaeological findings corresponding to the Migration Period points towards a decrease in human activity during this interval (Klemm, 2003). Siderite mining (FeCO_3) at Blahberg

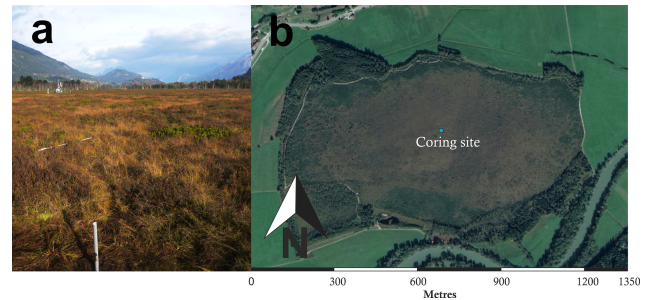


Figure 2. Location of the coring site in the centre of the ombrotrophic Pürgschachen Moor (a; eastern view from the coring site; photo: W. Knierzinger), Ardnig (Austria). Aerial view of Pürgschachen Moor (b) with the location of the coring site (modified from ©Google Maps, last access: 15 December 2019) and scale.

(Fig. 1) and in other parts of the area is documented, with interruptions, from the 11th century up to the year 1895 (Preßlinger and Köstler, 2002).

Even though no detailed palaeoclimate studies regarding the region of Eisenerz Alps have been conducted so far, we expect that the regional palaeoclimate variations show consistencies with palaeoclimate models of other parts of the Alps (e.g. Heiri, 2003; Nicolussi et al., 2005) and other climate records in the Northern Hemisphere (Vinther et al., 2006). Accordingly, we assume a general decrease in the average temperatures around 3000 cal BCE and an impact of recurring cold cyclical oscillations (Rotmoos 2, Lössen, Göschenen 1, Göschenen 2) in the late Holocene for this region (Ivy-Ochs et al., 2009; Kutschera et al., 2017).

2 Materials and methods

2.1 Sample location

The sample location is in the centre of Pürgschachen Moor ($47^{\circ}34'53.34''$ N, $14^{\circ}20'45.39''$ E), approximately 1.5 km southwest of Ardnig (district of Liezen) at an altitude of 632 m (see Fig. 2).

The peat body at the central treeless peatland area of Pürgschachen Moor reaches depths of 7–8 m; the transition from sedge to *Sphagnum* peat has been identified at a depth of 5 to 6 m (Birker, 1979). The bog is one of the last remains of a former string of peatlands along the Enns river valley (Drollinger et al., 2019). The vascular vegetation of the peat bog is comprised of mosaic patterns across the peat bog area, consisting of the most abundant shrub species *Pinus mugo*, *Calluna vulgaris*, and the graminoids *Eriophorum vaginatum* and *Rhynchospora alba*. The most abundant *Sphagnum* mosses are *Sphagnum capillifolium*, *Sphagnum magellanicum* and *Sphagnum tenellum* (Drollinger et al., 2019).

2.2 Coring and preparation

A ~ 500 cm long peat core (diameter of 80 and 50 mm) was extracted by means of a Russian peat corer of 8 cm diameter in late 2017. At a depth of ~ 500 cm, coring had to be aborted due to impenetrable layers associated with the more frequent presence of roots and other wooden material. The core was stored below 6 °C. Prior to analysis, the sample material was dried overnight and then pulverized. In total, 45 samples (~ 200 mg) were used for elemental analysis, 34 samples (~ 200 mg) for Pb isotopic analysis and 41 (~ 40 mg) for FTIR analyses. For the analyses of ash contents 100 samples (~ 1 g), taken at intervals of 5 cm, were used. The labelling of the samples denotes information on the sampling depth (i.e. P308 corresponds to 308 cm below surface). Due to a variety of analytical techniques, analyses were not stringently performed at regular measuring intervals.

2.3 Radiocarbon dating

Six samples, comprised of various *Sphagnum* plant fragments and one bark fragment of *Pinus sylvestris*, were radiocarbon dated at the Poznan Radiocarbon Laboratory in Poland. To remove unwanted components and to isolate the dateable fraction, the acid–alkali–acid procedure was applied (for further details see Czernik and Goslar, 2001). The top of the extracted peat core was assigned to the year 2012. A Bayesian radiocarbon model was established using Bacon (version 2.2; see Blaauw and Christen, 2011), which is based on the IntCal13 calibration curve (Reimer et al., 2013).

2.4 Pollen analysis

A total of 65 pollen samples at sub-sampling intervals varying between 2.5 and 10 cm were analysed. In order to obtain pollen concentration data, *Lycopodium* tablets were added to each sample (1 cm³ of material; see Stockmarr, 1971). Peat samples were chemically treated using acetolysis. Pollen counting was performed using a Leitz Biomed optical microscope with 400× and 1000× magnification with phase contrast. At least 900–1000 pollen grains per sample were counted and identified based on Beug (2004). The non-pollen palynomorphs (NPPs) were determined on the basis of numerous reference studies provided by Miola (2012). The results are presented as reduced-percentage diagrams, calculated and drawn using the software package Tilia 2.1.1 and TGView (Grimm, 2004). Pollen grains of trees, shrubs and upland herbs (arboreal pollen (AP) + non-arboreal pollen (NAP) = 100 %) are presented. Pteridophyta, mosses and water plants are not included in the pollen sum.

The pollen diagram is divided into local pollen zones (LPZ P1–P13) that reflect the vegetation development (Berglund and Ralska-Jasiewiczowa, 1986). Periods of human impact (K1–K7) are displayed separately.

2.5 Elemental analysis and ash contents

Quantitative analyses of Cu, Sr, Zr, Sb, and Pb were carried out by using an iCAP Qc ICP-MS system (Thermo Fisher Scientific, Bremen, Germany) at the Institute of Chemical Technologies and Analytics (TU Wien, Vienna). Different research groups demonstrated accurate elemental analysis of peat using quadrupole-based ICP-MS instruments (e.g. Shotyk et al., 2001; Krachler et al., 2002; Mihaljevič et al., 2006; Mighall et al., 2014). Peat aliquots of 200 mg were digested using an acid mixture of 4 ml HNO₃ (65 %), 2 ml HCl (37 %) and 2 ml H₂O₂ (30 %) in a microwave-assisted closed-vessel system (Multiwave 3000, HF 100 vessels, Anton Paar, Graz, Austria).

Calibration standards from 1 to 100 µg mL⁻¹ were prepared using the ICP multi-elemental standard solution VIII Certipur® (Merck Darmstadt, Germany), the ICP multi-elemental standard solution IV Certipur® (Merck Darmstadt, Germany) and a zirconium ICP standard Certipur® (Merck Darmstadt, Germany). All measurements were blank-corrected. Differences in sample introduction efficiency, due to variations in physical properties such as surface tension or viscosity, and also differences in sample atomization and excitation efficiency, due to variations in the plasma load, were minimal; concentrations after dilution of the sample digests were only in the range of micrograms per litre to milligrams per litre. ¹¹⁵In was used as an internal standard for correction of remaining effects and/or instrument drifts. The choice of the conservative element for normalization of metal concentrations generally depends on the given environmental, geographic and geological conditions (Boës et al., 2011; Kylander et al., 2016). In this study, Zr, indicative of geogenic siliciclastic input of adjacent relatively zircon-rich Austroalpine nappes (Stattegger, 1982) and Gosau Group sediments (Wagreich, 1988), was chosen as a conservative element for normalization purposes.

Due to the focus on the reconstruction of prehistoric anthropogenic activity, no elemental measurements were performed for the first 75 cm. Operation settings are given in the Supplement, Table S1. Due to the assumed absence of unambiguous non-anthropogenic reference sections in the core, no enrichment factors (see e.g. Weiss et al., 1999) were calculated. Ash contents were determined as the percentage of the dry weight (see Tolonen, 1984), with a precision balance after burning the samples at 550 °C for 10 h in a muffle furnace.

2.6 Pb isotope analysis

Stable Pb isotope measurements were carried out by using the iCAP Qc ICP-MS system described in Sect. 2.5. The isobaric interference between ²⁰⁴Hg and ²⁰⁴Pb was corrected by monitoring the signal of ²⁰⁰Hg. The Pb ICP standard Certipur® (Merck, Darmstadt, Germany), traceable to NIST standard reference material SRM® 928 Pb, was used as a bracketing standard for performance verification and correc-

tion of instrumental drift. The Pb ICP standard Certipur[®] was characterized with the aid of the certified reference material ERM-EB 400 (Federal Institute for Materials Research and Testing, BAM). The previously prepared 50 mL liquid samples were diluted (up to 1 : 50) to guarantee a high degree of comparability. The raw Pb isotope ratios obtained from the measured samples were corrected for contributions of Hg, spikes and blanks. In a subsequent step, the isotope ratios were corrected for isotopic fractionation based on bracketing standard measurements. Due to complete acid digestion and high-dilution factors, matrix effects were considered to be negligible, and hence no additional reference material with a biological matrix was analysed. Notwithstanding the fact that thermal ionization (TIMS) and multi-collector plasma mass spectrometry (MC-ICP-MS) provide higher analytical precision (e.g. Gulson et al., 2018), the Q-ICP-MS technique was deemed sufficient for establishing a temporal trend and for a general contextualization of the peat samples with regard to other European signals (Mihaljević et al., 2006; Kylander et al., 2005; Judd and Swami, 2010; Mighall et al., 2014).

2.7 Fourier-transform infrared spectroscopy

FTIR spectra of peat samples were recorded by means of a Cary 660 FTIR spectrometer (Agilent, Santa Clara, CA, USA) at the Institute of Landscape Ecology in Münster, Germany. On the one hand, the selection of samples for FTIR analyses was based on prominent trends in the ash content curve; on the other hand it was oriented at the sample selection for ICP-MS analysis. For FTIR analyses, 2 mg of powdered peat sample was mixed with 200 mg KBr (FTIR grade, Sigma Aldrich, St. Louis, MO, USA) and pressed to a 13 mm pellet. To reduce analytical noise and to obtain comparable spectra for all samples, 32 scans per sample and subsequent baseline correction of data were conducted. The humification index was approximated by calculating the ratio between the peak intensity at 1630 cm^{-1} (indicative of lignin and other aromatics) and at 1030 cm^{-1} (indicative of polysaccharides such as cellulose; see also Holmgren and Norden, 1988; Biester et al., 2014). Exact localization of wavenumbers of specific peaks in FTIR data was accomplished by using an automated R (version 3.5.1; R Core Team, 2018) custom script that enables a baseline correction of peaks and a conversion into relative abundances (Hodgkins et al., 2018).

3 Results

3.1 Peat chronology and pollen analysis

Generally, the retrieved core is dark brown to black; contains a lot of amorphous material; and appears to be moderately to highly decomposed, according to the von Post humification scale (von Post, 1924). The section $\sim 375\text{--}\sim 385\text{ cm}$ comprises very highly decomposed homogeneous peat. Macroscopic visual inspection revealed increased woody plant ma-

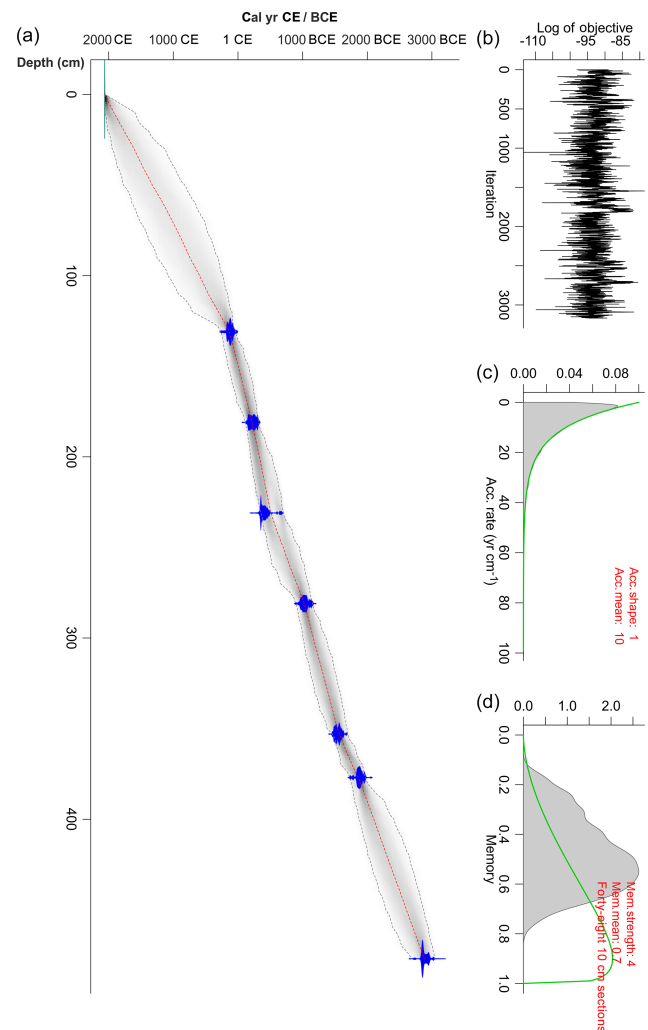


Figure 3. (a) Chronological model of the Pürgschachen core based on Bayesian statistics combining the radiocarbon dates and the surface date of the core (R package Bacon; see Blaauw and Christen, 2011). The top of the extracted peat core was assigned to the year 2017. Calculated dates are represented in blue; the grey area displays the 95 % confidence interval. The number of Markov chain Monte Carlo iterations (b) used to generate the age–depth model; the prior (green) and posterior (grey) distributions of accumulation rates (c) and memory (d).

terial at the base of the core ($\sim 480\text{--}\sim 500\text{ cm}$). Calibrated ages are given in Table 1. The Bayesian chronological model is displayed in Fig. 3 (see also the Supplement).

The pollen zone (PZ) P1 (484–450 cm; $\sim 3000\text{ BCE--}2380\text{ cal BCE}$), displays a relatively heterogeneous development. In PZ P1a (484–467.5 cm), the lowest sample (484 cm) is attributed to a wood layer (most likely pine), which formed the drilling-resistant base of the core. Compared to adjacent peat sections, a rarity of *Amphitrema* and *Neorhabdocoela* is apparent. At about 470 cm, a slight increase in Cannabaceae

Table 1. Radiocarbon dates from Pürgschachen Moor.

Site	Lab. no.	Depth (cm)	Material	^{14}C	Cal age (BCE/CE)
Pürgs. Moor	Poz-104287	130	<i>Sphagnum</i> moss	1930 \pm 30 BP	4–130 CE (95.4 %) 50–89 CE (43.5 %) 100–122 CE (17.8 %)
Pürgs. Moor	Poz-104286	180	<i>Sphagnum</i> moss	2210 \pm 30 BP	370–198 BCE (95.4 %) 260–206 BCE (33.0 %) 320–274 BCE (27.9 %)
Pürgs. Moor	Poz-104284	230	<i>Sphagnum</i> moss	2365 \pm 30 BP	536–386 BCE (95.4 %) 432–394 BCE (44.3 %) 478–442 BCE (23.9 %)
Pürgs. Moor	Poz-104285	280	<i>Sphagnum</i> moss	2900 \pm 30 BP	1134–1004 BCE (78.8 %) 1122–1024 BCE (68.2 %) 1207–1141 BCE (16.6 %)
Pürgs. Moor	Poz-99567	350	<i>Sphagnum</i> moss	3320 \pm 30 BP	1683–1521 BCE (95.4 %) 1586–1534 BCE (38.3 %) 1637–1600 BCE (29.9 %)
Pürgs. Moor	Poz-99566	375	<i>Sphagnum</i> moss	3580 \pm 30 BP	2028–1878 BCE (94.2 %) 1964–1889 BCE (68.2 %) 1838–1828 BCE (1.2 %)
Pürgs. Moor	Poz-99565	477	Periderm of <i>Pinus sylvestris</i>	4305 \pm 35 BP	3015–2882 BCE (95.4 %) 2930–2886 BCE (60.9 %) 3004–2990 BCE (7.3 %)

was found. PZ P1b is characterized by dense spruce forest, mixed with beeches and firs (see Figs. 4 and 5).

In PZ P2 (450–425 cm), a fir- and beech-rich spruce forest still predominates in the vicinity of the bog. In the pollen record, a slight decrease in *Fagus* and increases in charcoal and *Corylus avellana* are apparent. Besides, high values of *Amphitrema flavum* were determined.

Apart from an expansion of *Fagus*, PZ P3 (425–387 cm) is characterized by a relatively invariable vegetation development, showing more or less consistent values of *Alnus*, *Picea* and *Abies*.

In PZ P4 (387–378 cm; ± 2025 –1913 cal BCE) a massive increase in *Pinus* and slightly higher values of *Calluna*, *Eriaceae* and *Caltha* were noted. In contrast, the values of other forest trees, *Amphitrema* and *Callidina* decrease during this period.

A continuous increase in *Fagus* characterizes the vegetation of PZ P5 (378–362.5 cm). PZ P6/K1 (362.5–305 cm) covers a more prolonged period (~ 1720 – ~ 1255 cal BCE), ranging from the end of the early Bronze Age to the middle Bronze Age. In the lower section (PZ P6a/K1a, 362.5–337.5 cm; ~ 1720 – ~ 1500 cal BCE) a decrease in beech and fir as well as an increase in birch, hazel and cultural indicators like *Cerealia*, *Cannabaceae*, *Plantago lanceolata*, *Rumex* type, *Artemisia*, *Chenopodiaceae* and *Pteridium aquilinum* was determined.

PZ P6b/K1b (1500–1255 cal BCE) is characterized by frequent finds of *Cerealia* and *Cannabaceae* and an increase in *Urtica*, *Plantago lanceolata*, *Juniperus* and grasses, accompanied by a strong decline in elms, lime trees, maples and oaks and an expansion in birch. Especially in the younger part of PZ P6b, a decline in fir and spruce is apparent. A significantly higher input of charcoal was noted.

PZ P7 (305–275 cm) covers the early and a part of the late Urnfield period (1250–1010 cal BCE). The pollen record of PZ P7 show lower levels of *Cannabaceae* and *Rumex* as well as a decrease in charcoal. Around 290 cm, there is an apparent decrease in beech and an increase in alder and hazel. Higher charcoal input was detected at a depth of 285 cm. PZ P8/K2 (275–252 cm) is associated with the late Urnfield period (1020–780 cal BCE). In this section, a decline in firs, spruces and – to a lesser extent – beeches was found; hazel was becoming more common. A more frequent occurrence of *Cerealia* was found. Elevated charcoal levels were detected in younger sections of this zone.

PZ P9/K3 (252–225 cm) is characterized by a decrease in *Cannabaceae* and *Poaceae*. Decreases in charcoal, spruce and beech and a marked increase in hazel are associated with PZ P10/K4 (225–172 cm). *Amphitrema flavum* shows a marked decrease at ~ 235 cm.

The pollen record of PZ P11/K5 (172–135 cm) still implies a dense forest stand and displays pronounced increases

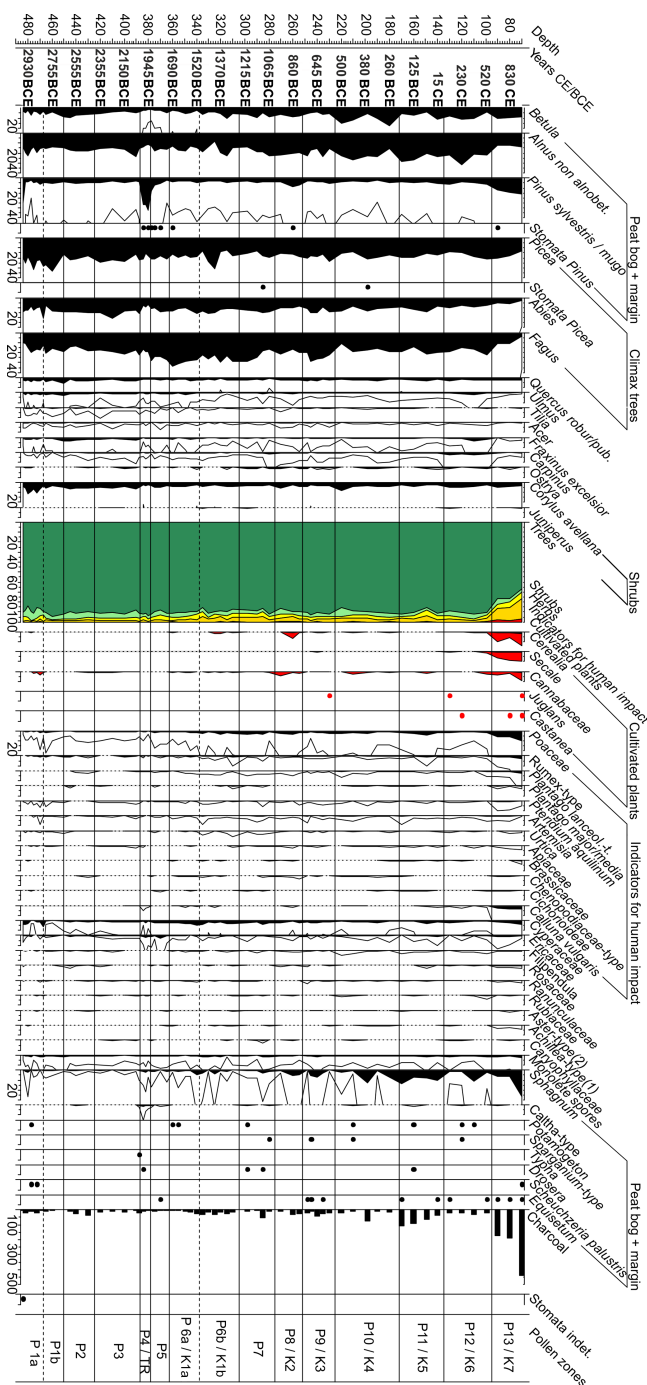


Figure 4. Reduced pollen diagram of the peat core, comprising trees, shrubs, cultivated plants, other indicators of human impact and typical wetland flora. For reasons of clarity, 10× exaggeration curves (thin black lines) were integrated to highlight the abundance of infrequent components.

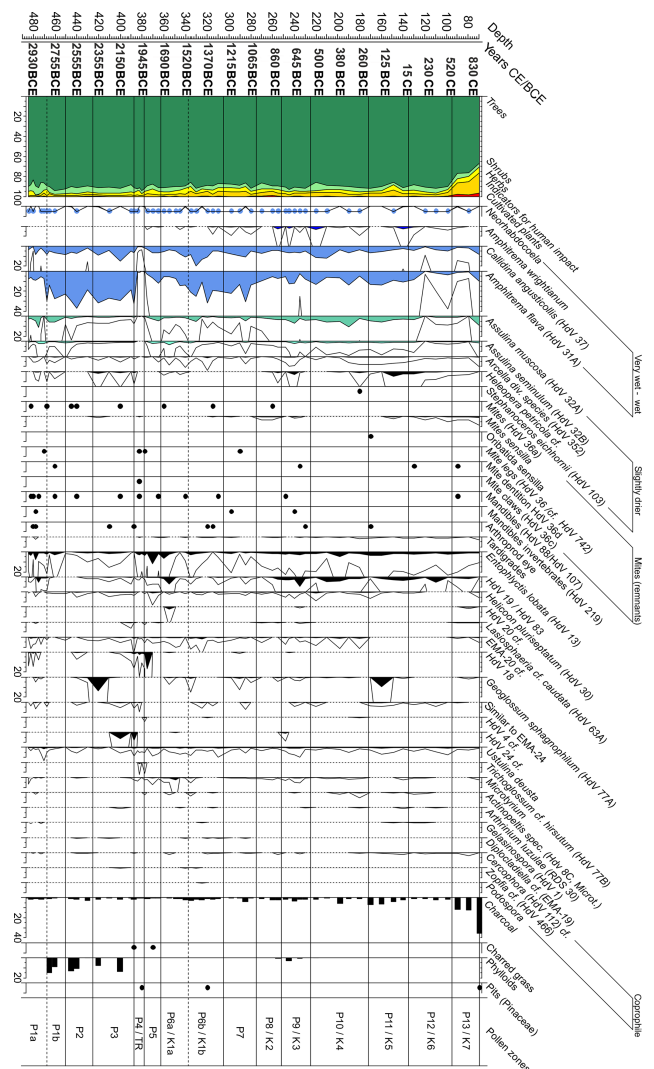


Figure 5. Diagram of non-pollen palynomorphs (NPPs), showing changes in wetness and animal content. NPP types with a constant presence of less than 0.5 % are shown as dotted lines. For reasons of clarity, 10× exaggeration curves (thin black lines) were integrated to highlight the abundance of infrequent components.

in Poaceae, *Rumex* and *Artemisia*. The charcoal input between 172 and ~ 150 cm is higher than ever before.

The first occurrences of rye, walnut and sweet chestnut stretch back to PZ P12/K6 (135–95 cm), accompanied by a slight decrease in beech, fir and spruce. Charcoal is barely detectable.

In PZ P13/K7 (95–70 cm) the number of most forest trees, with the exception of pines and birches, is strongly reduced. In addition to a more frequent occurrence of rye and other cereals, an increase in charcoal and walnut was found. Furthermore, the presence of heather and an increase in pine as well as a decrease in wetness indicators were determined.

3.2 Elemental and biochemical analyses

Sr concentrations are rather invariable throughout the core, ranging from 3 to 10 mg kg⁻¹. A slight increase in Sr was noted in the basal section (450–482 cm) of the core (see Fig. 6). A relatively high degree of invariability also applies to Zr (~0.1 to 2 mg kg⁻¹). Only the middle section of the core (233–283 cm) is characterized by comparatively higher Zr concentrations, peaking at 236 cm with ~19 mg kg⁻¹. Cu/Zr ratios show enrichments at 153 cm, at 155 cm, in the section 305–310 cm, at 335, at 415 and at 430 cm. Pb/Zr and Sb/Zr ratios largely run parallel to each other, showing peaks at 75, 118, 145, 175, 277, 303, 305 and 310 cm. Apart from that, Pb/Zr ratios are elevated at 415, 450, 475 and 482 cm. A rather strong positive Pearson's correlation coefficient (r) of 0.49 between Sb and Pb was found. Sb and Cu are also weakly positively correlated ($r = 0.27$). In comparison to the average ash content (1.07 %) of the homogeneous lower sections of the core (50–350 cm), the average ash content of the uppermost section (1–50 cm) is clearly elevated (2.19 %). Marked increases were determined for 380 cm (5.1 %) and the lowermost section ranging from 490 to 500 cm (up to 9.8 %). The FTIR humification proxy (ratio 1630 cm⁻¹ / 1030 cm⁻¹) displays increased values at 75, 150, 165, 175, 230, 235, 250 and 380 cm. Particularly low humification degrees were determined at 160, 272, 400, 450 and 460 cm and in the section 330–350 cm. The humification proxy shows a positive correlation with Pb ($r = 0.55$) and Sb ($r = 0.76$). While Cu ($r = -0.11$) and Zr ($r = 0.29$) display no or no strong particular relationships with humification, Sr ($r = -0.45$) is negatively correlated with the FTIR humification proxy (see the Supplement). The colour of the peat ash varies from brownish white (e.g. middle section of the core) to greyish white (core section 375–385 cm).

3.3 Pb isotopes

²⁰⁶Pb/²⁰⁷Pb ratios of peat from Pürgschachen Moor (75–482 cm) range between 1.1602 and 1.1829, showing a decreasing trend towards the uppermost section. The two lowermost samples (P482, P475) deviate significantly from this trend. A similar development is evident regarding ²⁰⁶Pb/²⁰⁸Pb ratios. No particular temporal evolution was found for the ²⁰⁷Pb/²⁰⁸Pb ratios (see the Supplement).

4 Discussion

4.1 Climate-driven interrelations of peat proxies

The results of our study demonstrate climate-driven interrelations between the pollen record, the ash content and peat decomposition. Cultural activity, in contrast, is mainly reflected in the pollen record and by enrichments of trace elements (see Sect. 4.2). Varying ash contents in peat bogs have been linked to climate changes in two ways: on the one hand, the ash content is affected by a varying dust flux due to cli-

mate variations and human land-use change, which directly influence the amount of mineral matter in the bog (Pratte et al., 2017). On the other hand, the amount of mineral matter in peat is strongly interrelated with humification processes (Tolonen, 1984). Due to mass loss of organic matter in peat bogs in the course of proceeding decomposition during drier periods (see also Huang et al., 2013; Xiao et al., 2017), an enrichment of mineral matter per volume unit takes place, resulting in an increase in the ash content (Boelter, 1969). This, in turn, might improve nutrient availability and could lead to a positive feedback on microbial decomposition of peat (Kempster, 1996).

On Pürgschachen Moor, the strongest positive correlation between humification and ash content was generally found in sections with higher ash contents. Positive correlations between decomposition rates and the ash content in peat are emphasized by different authors (e.g. Tolonen, 1984; Kempster, 1996; Martínez Cortizas et al., 2007; Engel et al., 2010; Leifeld et al., 2011; Drzymulska, 2016). However, a direct linkage between higher ash contents and warmer climate conditions causing slower growth rates and higher mineralization rates (see also Sire et al., 2008; Huang et al., 2013; Xiao et al., 2017) does not always hold up to scrutiny, as Stivrius et al. (2017) imply by underlining the capacity of peat bogs to buffer climate variations. This is further aggravated by the fact that, from a climatological perspective, no stable relationship between temperature and precipitation exists (Bell et al., 2018).

Despite that, with regard to the present study, the erratic increase in the ash content (up to ~5 %) and the humification index (see Fig. 6) at a core depth of ~380 cm can be linked to increased decomposition and mineralization rates of organic material during a late-Atlantic climate optimum in the time between ~2300 and ~1700 cal BCE (Kutschera et al., 2017), which most likely initiated a temporal drying phase of the bog around ~1950 cal BCE. This interpretation is further corroborated by a decrease in *Amphitrema* and *Callidina*, a massive increase in *Pinus*, and slightly higher values of *Calluna*, *Ericaceae* and *Caltha* in this section.

A pronounced Zr peak and a decrease in *Amphitrema flavum* at 236 cm, corresponding to ~600 cal BCE, might be related to dry climate conditions during the Göschener 1 oscillation. Distinct colour differences in ash samples between sample material with relatively higher ash contents (brighter in section 385–375 cm) and sample material with lower ash contents (e.g. darker in section 180–240 cm) also indicate a linkage between ash colour on the one hand and the humification degree and ash content on the other. In the literature, brighter colours of ash are attributed to varying plant species (Babayemi et al., 2010), higher fire severity (Hogue and Inglett, 2012) or higher ash content (enhanced mineral matter; Bodí et al., 2014). As the vegetation of the peat is relatively stable throughout the core and given the fact that the same burning conditions have been applied to all peat samples, the

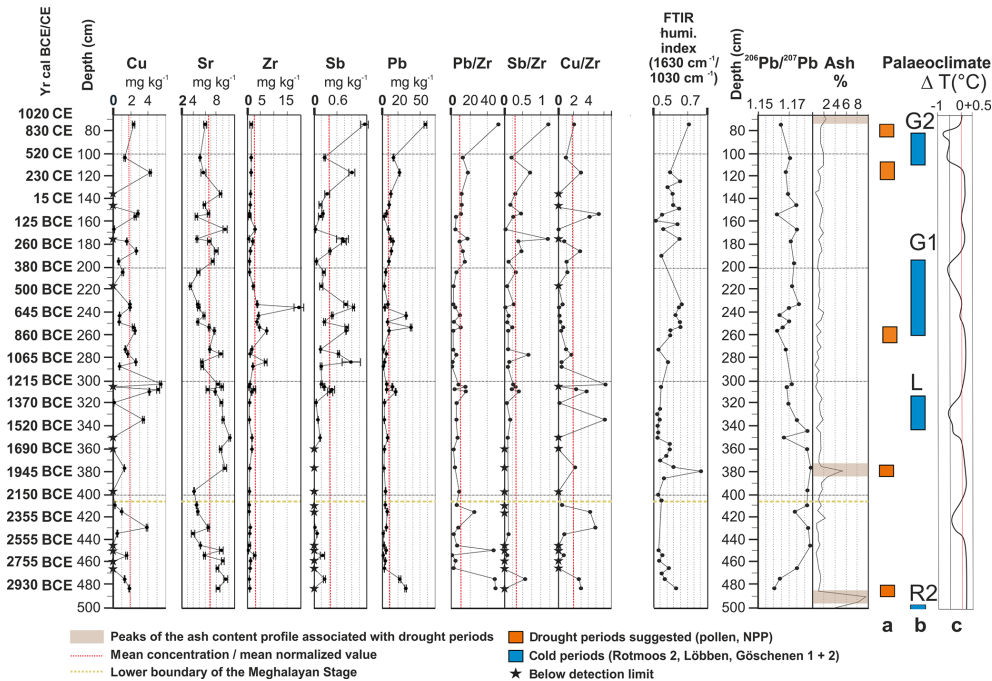


Figure 6. Element concentrations, as obtained from ICP-MS analyses, of Cu, Sr, Zr, Sb and Pb (mg kg⁻¹); Zr-normalized Pb, Sb and Cu values; FTIR humification index (1630 cm⁻¹/1030 cm⁻¹); Pb²⁰⁶/Pb²⁰⁷; and ash content vs. depth. Marked changes in wetness proxies (based on values of *Pinus*, *Callidina* and *Amphitrema*) in the pollen and NPP records (a; see also Figs. 4 and 5), indicating drought periods, are largely consistent with peaks in the ash content profile. Climate oscillations (b) Rotmoos 2 (R2), Lössen (L), Göschenen 1 (G1) and Göschenen 2 (G2) (Ivy-Ochs et al., 2009) and the relative summer palaeotemperature variation in the European Alps (c; see Kutschera et al., 2017) are given as references. Error bars (3-sigma) were calculated on three replicates. Concentrations below the detection limit (black stars) are predominantly concentrated below 350 cm. The dashed yellow line corresponds to the formally defined base of the late Holocene, the Meghalayan Stage (Walker et al., 2019). The red line (see c; 0 °C) represents the mean temperature between 1990 and 2000 CE in the Alps.

brighter ash colours in section 385–375 cm are likely to be attributed to the higher mineral content in this section.

Similar interrelations (high ash content, marked changes in the wetness indicators, increasing humification) are apparent in the section 80–70 cm that corresponds to the initial phase of the Medieval Warm Period (Kutschera et al., 2017) and in the section 500–490 cm, corresponding to the warm period around 3000 cal BCE, following the Rotmoos II oscillation (Ivy-Ochs et al., 2009). Strongly increased ash contents in this lowermost section are, however, at least partly linked to the more frequent presence of roots and tree trunks that precluded deeper drilling.

In general, low average Sr concentrations below 10.5 ppm and low ash contents ($\sim 0.15\%$) point towards an ombrotrophic nature of the upper 500 cm of Pürgschachen Moor. The marked increase in ash contents in subsurface layers of Pürgschachen Moor is in good accordance with conditions in comparable European peat bogs (Smieja-Król and Fiałkiewicz-Kozieł, 2014).

4.2 Late-Holocene human activities in the Liezen area

Strong positive correlations between Pb and Sb in peat soils affected by anthropogenic activity such as mining, smelting

and industrialization have been highlighted by different authors (e.g. Steinnes, 1997; Shotyk et al., 2004; Cloy et al., 2005; Galuszka et al., 2014). Yet, anthropogenic activities are not necessarily the only reason for higher concentrations of Pb and Sb in ombrotrophic peat, as a positive relationship between Pb and Sb on the one hand and the humification degree on the other is demonstrated in various studies (e.g. Pilarski et al., 1995; Ho et al., 2000; Gao and Huang, 2009; Biester et al., 2012). However, with regard to this study, humification-normalized Pb and Sb values do not change the interpretation of past anthropogenic activity in the area of Pürgschachen Moor.

Though positive correlations between Cu and humification are known from the literature (e.g. Yang and Hodson, 2018), no such correlation was determined for peat of Pürgschachen Moor. This correlation might have been overwritten by occasional input of anthropogenic copper smelting dust. The weak positive correlation between Sb and Cu might be linked to the smelting of antimony-rich copper ores.

A comparative analysis of anthropogenic proxies in the pollen record (i.e. cultivated plants, herbs shrubs, charcoal) and in the geochemical record (Pb, Sb, Cu) reveals interrelations. However, since no continuous concordance between

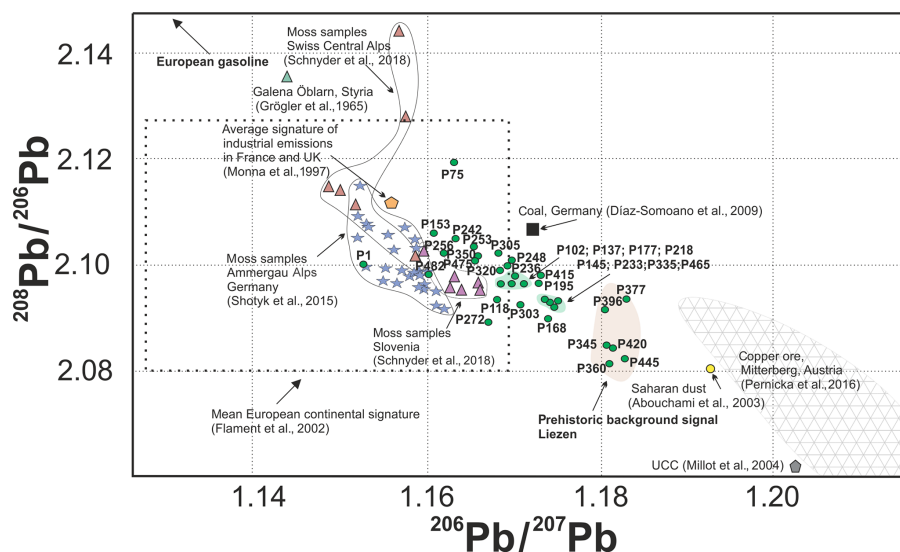


Figure 7. Pb isotopic signatures ($^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$) from peat samples of Pürschachen Moor (P sample numbers, green dots) in comparison with copper ores at Mitterberg (Salzburg, Austria; Pernicka et al., 2016), galena at Öblarn (Styria, Austria; Grögler et al., 1965), moss samples from the Ammergau Alps (Bavaria, Germany; Shotyk et al., 2015), and moss samples taken in Slovenia and in the Swiss Central Alps (Schnyder et al., 2018). Average Pb isotopic signatures of industrial emissions from France (Monna et al., 1997) and of the upper continental crust (UCC; Millot et al., 2004) as well as the Pb isotopic composition of German coal (Díaz-Somoano et al., 2009) and Saharan dust (Abouchami et al., 2003) are given as further references. The average European gasoline Pb isotopic composition is characterized by low $^{206}\text{Pb}/^{207}\text{Pb}$ and high $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (e.g. Monna et al., 1997), indicated by an arrow (top left). The low $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of P1 is attributed to increased industrialization processes and the peak of leaded gasoline consumption in recent decades (see also Cloy et al., 2008; Forel et al., 2010; Shotyk et al., 2015; Drexler et al., 2016; Schnyder et al., 2018). Radiocarbon dates from Pürschachen Moor (see Table 1).

the palynological and geochemical anthropogenic proxies were found over time or depth, it is reasonable to assume that prehistoric regional settlement activity in the Liezen area was only partly connected to mining.

Taking into account the low average Pb concentrations ($\sim 7 \text{ mg kg}^{-1}$) of the prehistoric samples of the peat core, high Pb concentrations of up to $\sim 30 \text{ mg kg}^{-1}$ in the lowermost Copper Age section (~ 3000 to 2800 cal BCE) of the core are very untypical and are not considered to be anthropogenic in origin. These peaks in the Pb profile are not correlated with Cu and are most probably caused by higher influx of galena (PbS). Galena is a relatively frequent accessory mineral in different lithologies in the Liezen area (Schumann, 2002). A higher geogenic influx of galena – possibly connected to a slightly increased groundwater influence as indicated by slightly higher Sr concentrations in the lowermost section – might also be the reason for untypically low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios at 475 and 482 cm (see the isotopic signature of galena from Öblarn in Fig. 7; see also Wagreich and Draganits, 2018). Moreover, galena tends to incorporate, among other elements, higher amounts of Sb (e.g. Laflamme and Cabri, 1986; Sharp and Buseck, 1993), and this might explain a high Sb/Zr ratio at 475 cm. Another explanation for these lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratios may be diffuse contamination of the peat samples during core retrieval or sample preparation.

A weak forest opening combined with higher levels of cultivated plants at 470 cm, corresponding to $\sim 2800 \text{ cal BCE}$, might reflect early agricultural activity in the surroundings of the peat bog.

A slight decrease in *Fagus* with a concomitant increase in charcoal and *Corylus avellana* may indicate a weak anthropogenic disturbance in the following PZ P2. A Cu enrichment at 430 cm, corresponding to PZ P2, around 2500 cal BCE , is interpreted as the incipient indication of larger copper mining activity in the region. Despite the fact that the pollen analyses do not imply human activity in the immediate proximity of Pürschachen Moor at that time, Neolithic settlement activity is known from the Liezen area and the Eisenerz Alps (Drescher-Schneider, 2003). The absence of cultural indicators and low trace element enrichments in the section PZ P3–PZ P5 (425–362.5 cm) suggest a decrease in settlement and mining activity in the following centuries. This time (~ 2400 – $\sim 1700 \text{ cal BCE}$) roughly corresponds to a late-Atlantic warm period characterized by Alpine glacial recession (Kutschera et al., 2017).

Increasing human impact in the region in the middle Bronze Age (~ 1450 – $\sim 1250 \text{ cal BCE}$) is implied by cultural indicators in the pollen record and elevated trace metal concentrations. Intense human activity in the immediate vicinity of Pürschachen Moor seems to diminish again during the period of the early Urnfield culture (~ 1250 – \sim

1050 cal BCE). Nevertheless, enrichments of Cu and Sb indicate ongoing mining activity in the region during this time. While intense local agricultural and human activity is reflected in peat sections (more frequent occurrence of cereals and Cannabaceae) associated with the period of the late Urnfield culture ($\sim 1050\text{--}\sim 800$ cal BCE), the geochemical data do not imply significant metallurgical activity in the region. The following centuries of the early and middle Iron Age ($\sim 750\text{--}\sim 300$ cal BCE) are characterized by decreasing trace metal enrichments and slightly decreasing cultural indicators in the pollen record. This finding is consistent with archaeological evidence from the region (Klemm, 2003) and might be connected to a cooling period in the second half of the first millennium BCE (Nicolussi et al., 2005). Significantly higher charcoal influx and enrichments of Sb and Cu in the period of the late La Tène culture ($\sim 230\text{--}\sim 50$ cal BCE) point towards a phase of reinvigorated settlement and mining activity. Unlike areas in the Eisenerz Alps (Klemm, 2003; Drescher-Schneider, 2003), no indications of intense human activity during Roman times were found with regard to the local environment of Pürgschachen Moor.

Distinct enrichments of Pb and Sb in one sample, corresponding to ~ 900 cal CE, are attributed to medieval siderite mining activity in the immediate vicinity of Pürgschachen Moor (Preßlinger and Köstler, 2002).

5 Conclusions

By combining palynological and geochemical analyses, we were able to provide a substantial reconstruction of prehistoric human and metallurgical activity as well as the palaeoclimate in the region of Pürgschachen Moor that is largely coherent with previous palaeoenvironmental and archaeological studies. After first indications of low settlement (~ 2900 cal BCE) and mining activity (~ 2500 cal BCE) in the region in the late Copper Age, a reduction in human presence in the early Bronze Age is suggested by a lack of evidence in the geochemical and palynological records. The period from ~ 1450 to ~ 1250 cal BCE and another period from ~ 1050 to ~ 800 cal BCE, both related to a phase of climate warming ($\sim 1400\text{--}\sim 800$ cal BCE) after the Löss oscillation in the middle and late Bronze Age, are characterized by slightly increased geochemical and palynological signals of human presence. We propose that these signals reflect elevated mining activity in the Eisenerz Alps and in the more southern Palten valley. Following a clear decrease in anthropogenic signals in the early and middle Iron Age ($\sim 750\text{--}\sim 300$ cal BCE), a phase of more intense human activity occurs in the period from ~ 300 to ~ 1 cal CE. Relatively insignificant evidence of human presence and metallurgical activity during the Roman period was found.

The palaeoenvironmental assessment of the pollen data was further substantiated and refined by interrelating it with the humification degree and ash content. Owing to this fact,

we were able to correlate climate optima in the late Holocene with changes in the geochemical and pollen and NPP records. Even though considered negligible for the interpretation of this present study, the close interrelationship between humification and tracer elements such as Pb and Sb demonstrates the necessity for a stronger analytical consideration of the humification index in the context of interpreting anthropogenic pollutants from peat bog archives. In order to improve the explanatory power of palaeoenvironmental assessments, future studies may try to further disentangle humification-related trace element sorption from mineralization processes in peat soils.

Data availability. All underlying chemical data have been submitted to PANGAEA <https://doi.org/10.1594/PANGAEA.919320> (Knierzinger, 2020).

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/egqsj-69-121-2020-supplement>.

Author contributions. WK (corresponding author) designed the study, prepared sample material for subsequent analysis, conducted geochemical and laboratory analyses, and wrote the manuscript. The peat core was retrieved by WK and RDS. Pollen analysis was performed by RDS. KHK conducted the FTIR analyses; SD provided FTIR data normalization. AL, LB and FH were involved in planning and supervision of the geochemical analyses. MW contributed to the design and the structure of the manuscript. DF established the Bayesian age–depth model.

Competing interests. The authors declare that they have no conflict of interest.

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