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Mineral dust and lead deposition from land use and metallurgy in a 4800-year-old peat record from the Central Alps (Tyrol, Austria)

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A R T I C L E I N F O

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A B S T R A C T

Humans have occupied the Alps over most of the Holocene. Yet, continuous records on the impact of using montane resources and landscapes are scarce or confined to segregated areas or periods. We present a high-resolution geochemical record of the last 4800 years from the ombrotrophic peatland Piller Moor in the Central Alps (Tyrolean Oberland, western Austria), using inductively coupled mass plasma spectrometry (ICP-MS) and highly efficient inter-calibrated portable X-ray fluorescence analysis (pXRF). Fluctuations of metal enrichment factors (EF) for lead (Pb), copper (Cu), zinc (Zn) and antimony (Sb), accumulation rates of anthropogenic lead (Pb_{anth} AR) and mineral matter (MAR), based on titanium (Ti), are in line with archaeological and pollen evidence for human presence and environmental change. Periods of intensified, erosive land use are indicated by MAR around 4400 cal BP, 3400 cal BP and, very prominently, at 2400 cal BP. After low MAR in the early Middle Ages, soil disturbances reappear around 1200 cal BP (750 AD), after 200 cal BP (1750 AD) and during the 20th century AD. We found evidence that metallurgy was practised in the area as early as 4450 cal BP, again from 3500 to 2900 cal BP and episodically between 2400 and 1400 cal BP. The Central Alps were presumably a source of increased Pb-emissions in the post-Roman period from 1500 to 1400 cal BP (450–550 AD). Generally, our findings suggest that mining predates archaeological and historical evidence. Following a continuous increase since the Middle Ages, atmospheric Pb EF and Pb_{anth} AR peak around 1980 AD. The record of mineral atmospheric input illustrates the notable impact of human activities on soil erosion and dust entrainment in the Central Alps. Furthermore, links between Little Ice Age cold phases and reduced human impact and mining are established. Our high-resolution peat-geochemistry data quantifies atmospheric deposition of mineral matter and Pb, which act as proxies for landscape evolution and metallurgy on a local and regional scale. It provides new insights and a deeper understanding of the interaction of climate, environment and humans in mountainous landscapes like the Central Alps.

1. Introduction

Ombrotrophic peatlands are precious palaeoenvironmental archives. Specific characteristics render them reliable geochemical records of certain contaminants like lead (Pb), copper (Cu) or Antimony (Sb) as industrial or metallurgical emissions (Damman, 1978; De Vleeschouwer et al., 2007; Forel et al., 2010; Jones and Hao, 1993; Nieminen et al., 2002; Shotyk, 1996; Shotyk et al., 2004). They also act as archives of fluctuating mineral atmospheric dust deposition, indicating droughts, storminess or changes in land cover and land use (e.g. Chambers et al., 2012; Hölzer and Hölzer, 1998; Lomas-Clarke and Barber, 2007; Schofield et al., 2010).

Yet, such geochemical studies are rare in the Central Alps, because mires in mountainous landscapes are rather small, heterogeneous, and often disturbed by livestock and drainage (Spitale, 2021; Yang et al., 2017). Furthermore, they are affected by natural geomorphological processes or events and peat accumulation can be low due to short vegetation periods.

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When reconstructing human impact and interaction with mountain landscapes, considering proximate archaeological sites is imperative and a key to proper interpretation. The mire Piller Moor (Tyrol, Austria, Fig. 1) is one of the rare, well-preserved ombrotrophic peatlands in direct vicinity to well-known archaeological sites, which are a bronze-hoard and a ritual fire site (Heiss, 2008; Tomedi, 2012, 2002a; Tschurtschenthaler and Wein, 2002). Palynological data is available for the site (Hubmann, 1994), while nearby palaeovegetation studies give a good perspective on regional developments (e.g. Festi et al., 2014; Grabherr, 2006; Wahlmüller, 2002; Walde, 2006). Reconstructions of glacier activity and tree line changes from the nearby Kauner Valley (Fig. 1) further provide insight on past regional climate variability during the late Holocene (Nicolussi et al., 2005; Nicolussi and Patzelt, 2000). Although the Eastern Alps became an important mining district during the Bronze Age (O'Brien, 2015; Stöllner and Oeggl, 2015), little is known on prehistoric mining activity for this area of the Central Alps (Grutsch et al., 2019b; Krause, 1987; Stöllner, 2015).

In our study, we use geochemical ICP-MS and portable XRF (pXRF) data to identify periods of metallurgy and to assess the degree and scale of human impact at the junction between the Eastern and Western Alps. Portable XRF can be a time and cost-efficient tool to analyse the chemistry of a wide variety of materials (e.g. Kalnicky and Singhvi, 2001; Liritzis and Zacharias, 2011; Palmer et al., 2009). However, palaeoenvironmental studies using pXRF remain scarce (Gałka et al., 2017; Kapustová et al., 2018; von Scheffer et al., 2019). One of the challenges is that preinstalled calibrations rarely cover the highly organic sample matrix of peat. Hence, we developed an (inter) calibration between semi-quantitative pXRF and ICP-MS measurements, following full acid digestion in a clean room. Certified reference materials (CRM) for both methods act as an independent verification of the quality and reliability of our approach. Our geochemical proxy data is supported by pollen data from the same site (Hubmann, 1994) and other local palynological and archaeological studies, providing a comprehensive picture of regional human land use, metallurgy and environmental conditions in the past.

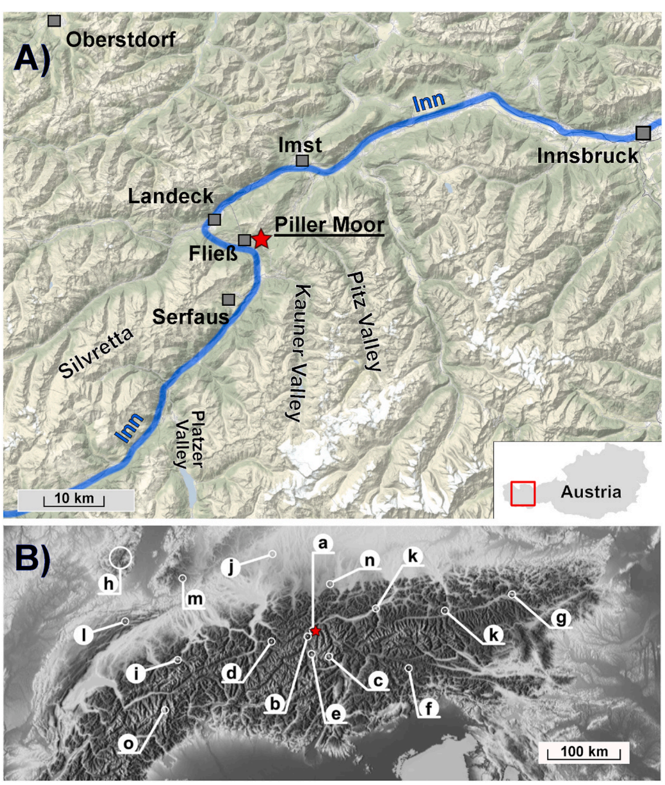

Fig. 1. A) Northern Central Alps with study site (star). Edited from source: Stamen Design under CC-BY-3.0 and OSM contributors under ODbl. B) Selection of references in discussion. Star: Study site and Hubmann (1994). Palaeoenvironmental studies a) to d), metallurgy and Pb-accumulation e) to o). a: (Walde, 2006), b: (Wahlmüller, 2002), c: (Festi et al., 2014), d: (Röpke et al., 2011), e: (Vavtar, 1988), f: (Segnana et al., 2020), g: (Knierzinger et al., 2020), h: (Forel et al., 2010), i: (Carvalho and Schulte, 2021), j: (Kern et al., 2021), k: (Stöllner, 2015b), l: (Shotyk et al., 1998), m: (Le Roux et al., 2005), n: (Kempter et al., 2010), o: (More et al., 2017); background map openstreetmap.org, OSM contributors under ODbl.

2. Methods

2.1. Study area and site

As part of the Tyrolean Oberland, the climate at Piller Moor is alpine-continental with a mean annual precipitation of ca. 800 mm and main wind directions are between west and south (46%) and north to north-east (18.5%) for the period between 1971 and 2000 AD as measured in the weather station in the nearby city of Landeck (Central Institution for Meteorology and Geodynamics of Austria, (ZAMG, 2022)). The Piller Saddle is in the altitudinal lower subalpine zone (c. 1550 m a.s.l.). The Inn River (c. 800 m a.s.l.) approaches the Piller Saddle from the South before joining with the Sanna River at Landeck and turning east (Fig. 1). The Kauner, Pitz and Oetz Valleys are south-east of the Saddle. A brook (Pillerbach) drains the area in north-easterly direction over the Pitze River into the Inn Valley, which separates the Penninic metamorphic zone to the south from the northern Limestone Alps.

The peatland lies within a depression at 1540 m a.s.l., stretching approx. 380 m W to E and 30–100 m N to S, with the water-level at approx. 10 cm below surface. *Sphagnum* spp. dominates the vegetation, together with *Andromeda polifolia, Drosera* spp., *Cyperaceae* and *Pinus mugo rotundata* stands towards the periphery, which is typical for ombrotrophic mires. The surrounding forest consists of *Picea* spp., *Pinus* spp. and *Larix* spp.

2.2. Coring and sub-sampling

Coring of Piller Moor took place in 2017. For the profile Pi17 (47°07′24.85″ N, 10°39′45.45″ E), a Wardenaar system (10 × 10 cm; Wardenaar, 1987) was used to core the top meter of the mire and a piston corer (Usinger 8 cm barrel; Mingram et al., 2007) was used for the deeper layers. Slightly offset parallel profiles (A and B) were taken to get a composite core. A maximum depth of 380 cm was reached before hitting an impenetrable layer, supposedly consisting of woody material. The segments were wrapped in cling film, transferred into a PVC-casing and sealed in a plastic hose. Cores A and B were sliced continuously to subsamples of c. 1.1 cm thickness for geochemistry and dating. Dry bulk density was calculated using the dimensions and dry weight of the geochemistry samples. Clean coring and subsampling followed the protocol of De Vleeschouwer et al. (2010) and Givelet et al. (2004). Three macrofossil samples were picked in ultrapure water for radiocarbon dating at Poznan AMS Radiocarbon Laboratory (Poz), Poland. The other samples were selected with the same method, pre-treated at the Gliwice Radiocarbon Laboratory (GdA), Poland and measured at the Rafter Radiocarbon Laboratory, New Zealand.

2.3. Geochemistry

143 dry samples for pXRF and 63 samples for ICP-MS analyses were selected and processed following Le Roux and De Vleeschouwer (2010). The samples were crushed to a homogenous powder in 15 or 50 ml tubes with eight glass beads of 4 mm using a FastPrep®-24 ball mill (3 × 20 s at 6 m^*s^{-1}). For pXRF-analysis, sample and CRM measurements were done on dried and homogenised peat, following the protocol from von Scheffer et al. (2019). The samples were transferred into polystyrene containers, covered with 4-μm thick polypropylene film and measured using a handheld Thermo Fisher Scientific Niton Xl3t in soil mode for

180s each inside a test stand chamber. The pXRF-device was regularly rebooted to account for daily temperature and atmospheric pressure fluctuations.

Samples for ICP-MS analyses were digested in a class 100 clean room at „Laboratoire Ecologie Fonctionnelle et Environnement“ Toulouse, France. Following the protocol for acid-digestion of peat samples detailed in Vanneste et al. (2015), 100 mg peat powder was treated consecutively with ultrapure chemicals, first with 2 ml of 65% nitric acid for 24 h at room temperature before adding 0.5 ml of hydrofluoric acid to the nitric acid and heating the mixture at 110 °C for 48 h. Steps three and four are treatment with 31% ultrapure peroxide at room temperature for 24 h and lastly heating in 2 ml 65% nitric acid at 110 °C for 48 h. Before every step, the mix of dried sample and liquid was treated with ultrasound. The samples were evaporated at 50 °C in between each step. An In/Re spike was added to each sample. Five multi-element standards were run every 10 samples to correct for instrument drift during ICP-MS measurements. A blank and two different organic CRMs (NIST-1547a, NIST-1515, GBW-07603, NJV-942, NJV-941) were treated per batch of 21 samples and measured in regular intervals. In addition to the CRMs used in ICP-MS, the materials BCR-060, IAEA-336, IPE-176 and NIST-1575a were used for pXRF.

2.4. Computing and calculations

The calculations and regression analyses are performed in R version 4.0.3. (R Core Team, 2021). The Bayesian age-depth model (ADM) is created using the package *rbacon* version 2.5.3 (Blaauw and Christen, 2011) with a 95% confidence interval and the IntCal20 radiocarbon calibration curve (Reimer et al., 2020). Boundaries are added based on obvious changes in density and humification. Median ages are given as ‘cal BP’ (calibrated years before 1950). Historical or certain cited ages are given as AD. The peat accumulation rate represents the bulk thickness of one peat sample and the period of time covered (Δthickness/Δtime) in mm*year^{-1}.

Metal enrichment factors (Me EF) for Pb, Sb, Cu and Zn and atmospheric mineral accumulation rates (MAR) are calculated using the conservative behaviour of Ti in peat (Nesbitt and Markovics, 1997), as done in Shotyk et al. (2002), to detect past metal enrichment and land use change (e.g. Kempter et al., 1997). The choice of Ti was also pre-determined by the range of elements of the pXRF (i.e. Ti is the only available lithogenic element for the calculation of EF and MAR). Pb, Sb, Cu, and, sometimes, Zn are commonly used to trace metallurgical or industrial emissions (e.g. Damman, 1978; Jones and Hao, 1993; Nieminen et al., 2002; Shotyk, 1996; Shotyk et al., 2004).

$$Me\ EF = \frac{\left(Me/_{Ti}\right)_{Sample}}{\left(Me/_{Ti}\right)_{UCC}}$$

$$MAR = {}^{100}/_{0.41} \ * \ Ti_{Sample} * \delta * \mathrm{PA}$$

δ is the dry bulk density of the peat sample and PA is the peat accumulation rate.

An anthropogenic Pb accumulation rate (Pb_{anth} AR) is calculated following Weiss et al. (1999). First, the concentrations of Pb in local and natural soil dust (Pb_{nat}) are determined for every sample:

$$Pb_{nat} = Pb_{Sample} * \left(Pb/_{Ti}\right)_{UCC}$$

Then, Pb_{nat} is subtracted from every sample to obtain the anthropogenic contribution Pb_{anth}, which is then used to calculate Pb_{anth} AR as follows:

$$Pb_{anth}AR = Pb_{anth.} \ * \delta * \mathrm{PA}$$

The upper continental crust (UCC) concentrations (McLennan, 2001) are used as reference or background values to calculate MAR, metal EFs and Pb_{anth} AR with Ti (4100 mg*kg^{-1}), Pb (17 mg*kg^{-1}), Cu (25 mg*kg^{-1}), Zn (71 mg*kg^{-1}) and Sb (0.2 mg*kg^{-1}). Using the UCC-values is partly because of the heterogenous geology of the Alps and their surroundings as potential dust sources, but it also makes the results more comparable to similar studies. Furthermore, the mineral base was not reached, so that a local sediment reference could not be retrieved, and defining a natural reference level within our samples would be difficult within the age range of the peat record.

Model estimates are made for all unmeasured peat samples from the continuous profile by linear interpolation between measurements. These modelled data-points are of course not data and hence are not included in the main data table and figures. They, however, allow a simple approximation of the cumulative anthropogenic Pb-deposition and of both the average MAR and Pb_{anth} AR over time.

The chronological interpretations are separated into five different periods from Neolithic until present, which largely correspond to cultural periods in the Central Alps, which are also used by Röpke et al. (2011).

3. Results

3.1. Chronology

The deepest section of profile B was fitted and merged to the deepest section of profile A, using density, geochemistry and radiocarbon dates (Table 1).

The age-depth-model (Fig. 2) provides a median age of 4750 cal BP for the core bottom. Up to 182 cm depth (2000 cal BP), the peat accumulation rate (AR) remained mostly below 0.7 mm*a^{-1} before increasing to 0.8–1.2 mm*a^{-1} until 91 cm (1200 cal BP). A significant decrease to less than 0.4 mm*a^{-1} prevails from 91 to 61 cm (1200–100 cal BP). In the uppermost part, the AR increases to over 10 mm*a^{-1}. The most recent part of the model relies upon a single bomb-pulse date (GdA-5492), which reduces the uncertainty in the upper 50 cm.

3.2. Geochemistry

The full data for dry bulk density, raw pXRF and ICP-MS results (data vs depth and calibrated ages) are given in Table SI_1. The raw data output of the analyses is presented as ICP-MS vs pXRF (Fig. 3) for the purpose of visual comparison and performing regression analyses.

3.2.1. Quality control

The results relevant for quality control (blanks, CRM) are provided in the supplementary information (Table SI_1). Concentrations in the blanks attest clean sample processing. Measurements of Ti, Pb, Zn, Rb, K, Sb, Fe, Sr and Cu deviate less than 20% from certified values in ICP-MS. In contrast, raw pXRF results of the CRMs are generally much higher than their certified concentrations. Yet, only the pXRF-measurements of Cu, Zn, and K show standard deviations (sd) over 20% in certain organic CRMs (e.g NJV-941).

Elements that are not detectable with pXRF in most samples, for example due to detection limits, or elements that produced arbitrary results, are not considered in the regression analysis. This is the case for Cu and Sb, leaving only Fe, K, Pb, Rb, Ti, Zn and Sr for further use in this study.

3.2.2. Regression analysis

von Scheffer et al. (2019) demonstrated the general reliability and cost and time efficiency of pXRF analyses for Ti and Pb in peat. In the same way, we here performed an individual regression analysis of pXRF versus ICP-MS and CRMs on a broader set of elements. The regression functions of CRMs, ICP-MS and pXRF-results (Fig. 3) show a good linear fit for Ti ($R^2 = 0.98$), Pb ($R^2 = 0.99$), Sr ($R^2 = 0.99$), K ($R^2 = 0.98$), Rb ($R^2 = 0.97$), Zn ($R^2 = 0.92$) and Fe ($R^2 = 0.86$). Although pXRF-results are above certified values, these elements can be cross-calibrated with quantitative methods or by using appropriate organic CRMs. Depending

Table 1
Radiocarbon sample information on origin, depth, dated material and uncalibrated 14C-ages. Lab codes: GdA = Gliwice, Poz = Poznan. Depths of Poz-101726 and GdA-5493 are corrected to master core A.

Lab. No.	Core	Depth [cm]	Material	^{14}C-age [BP]/F^{14}C	Comment
GdA-5492	Pi17A	43.2	*Sphagnum* spp. stems and leaves	1.4250 ± 0.0022	F14C Bomb pulse
Poz-99320	Pi17A	80.3	*Sphagnum* spp. stems and leaves	725 ± 30	0.5 mgC
GdA-5494	Pi17A	105.9	*Sphagnum* spp. stems and leaves	1505 ± 35	
Poz-101724	Pi17A	184.6	*Sphagnum* spp. stems and leaves	2150 ± 30	
GdA-5495	Pi17A	209.5	*Sphagnum* spp. stems and leaves	2455 ± 40	
GdA-5496	Pi17A	267.3	*Sphagnum* spp. stems and leaves	3255 ± 25	
Poz-101726	Pi17B	268.7	*Sphagnum* spp. stems and leaves, *Ericaceae* leaf	3260 ± 30	
GdA-5493	Pi17B	339.9	*Sphagnum* spp. stems and leaves	4150 ± 30	

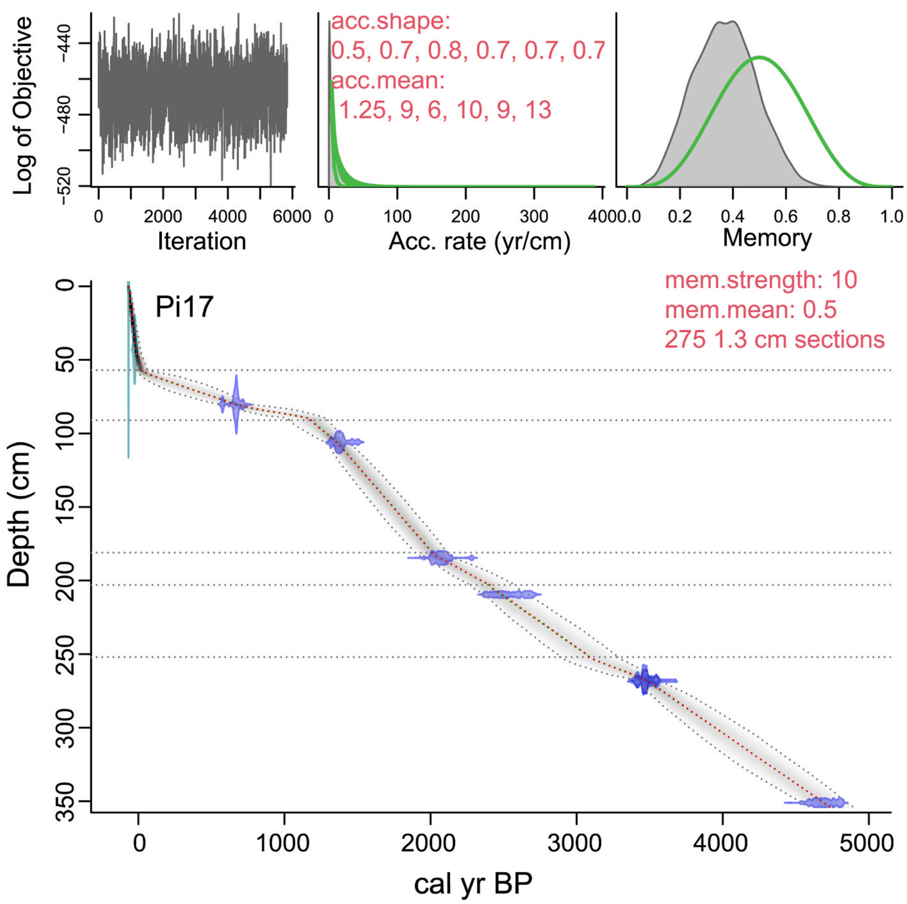

Fig. 2. ADM of Pi17 composite core. Grey shaded area = 95% within dotted line is the confidence interval. Dotted line in confidence interval is the median age. Dotted horizontal lines are boundaries between changes in core characteristics. Model input variables in red for the different sections between boundaries from top to bottom.

on the elements in question, a regression analysis could be based on a larger set of CRMs alone (red/full circles in Fig. 3).

3.2.3. Elemental profiles

The relevant concentration vs depth profiles of lithogenic conservative (Ti), potentially mobile elements (Rb, K, Sr, Fe) and metals (Pb, Cu, Sb, Zn), and further interpretations are mostly based on the pXRF data calibrated for quantification via ICP-MS using the regressions (Fig. 3). Only Cu and Sb were measured by ICP-MS (Fig. 4).

Peaks in Ti exceeding 400 mg*kg^{-1} and 600 mg*kg^{-1} appear at 312.5 and 200 cm (4140 and 2330 cal BP), respectively, with some minor peaks of 400 mg*kg^{-1} and 260 mg*kg^{-1} at 88 cm and 62 cm (1050 and 110 cal BP).

Rb resembles the course of Ti, staying mostly below 5 mg*kg^{-1} except for the five peaks parallel to Ti. A slight increase in Rb is also recorded in the surface layers. K ranges between 300 and 700 mg*kg^{-1}, with peaks at 312.5 cm (3000 mg*kg^{-1}) and again at 200 cm, followed by 2300 and 1500 mg*kg^{-1} at 88 cm and 62 cm. A rising trend shows in the uppermost 25 cm. Sr gradually rises from 10 mg*kg^{-1} to a maximum of 30 mg*kg^{-1} at 200 cm (2330 cal BP). After a local minimum of 2 mg*kg^{-1}, a declining trend sets in at 155 cm (1770 cal BP). Fe doubles from 1500 mg*kg^{-1} at the bottom to approx. 3000 mg*kg^{-1} at 125 cm depth before decreasing again.

Pb concentrations remain low around 3–10 mg*kg^{-1} between 350 and 100 cm (4710–1260 cal BP). An increase to 20 mg*kg^{-1} appears around 328 cm. In three subsequent peaks in the uppermost metre, the maximum concentration increases from 35 mg*kg^{-1} at 90 cm (1120 cal BP) to 70 mg*kg^{-1} at 39 cm (−29 cal BP). Cu peaks at 326 cm (39 mg*kg^{-1}) and 282 cm (23 mg*kg^{-1}). Smaller increases appear at 310, 262 and 200 cm. However, a decreasing trend is obvious towards the

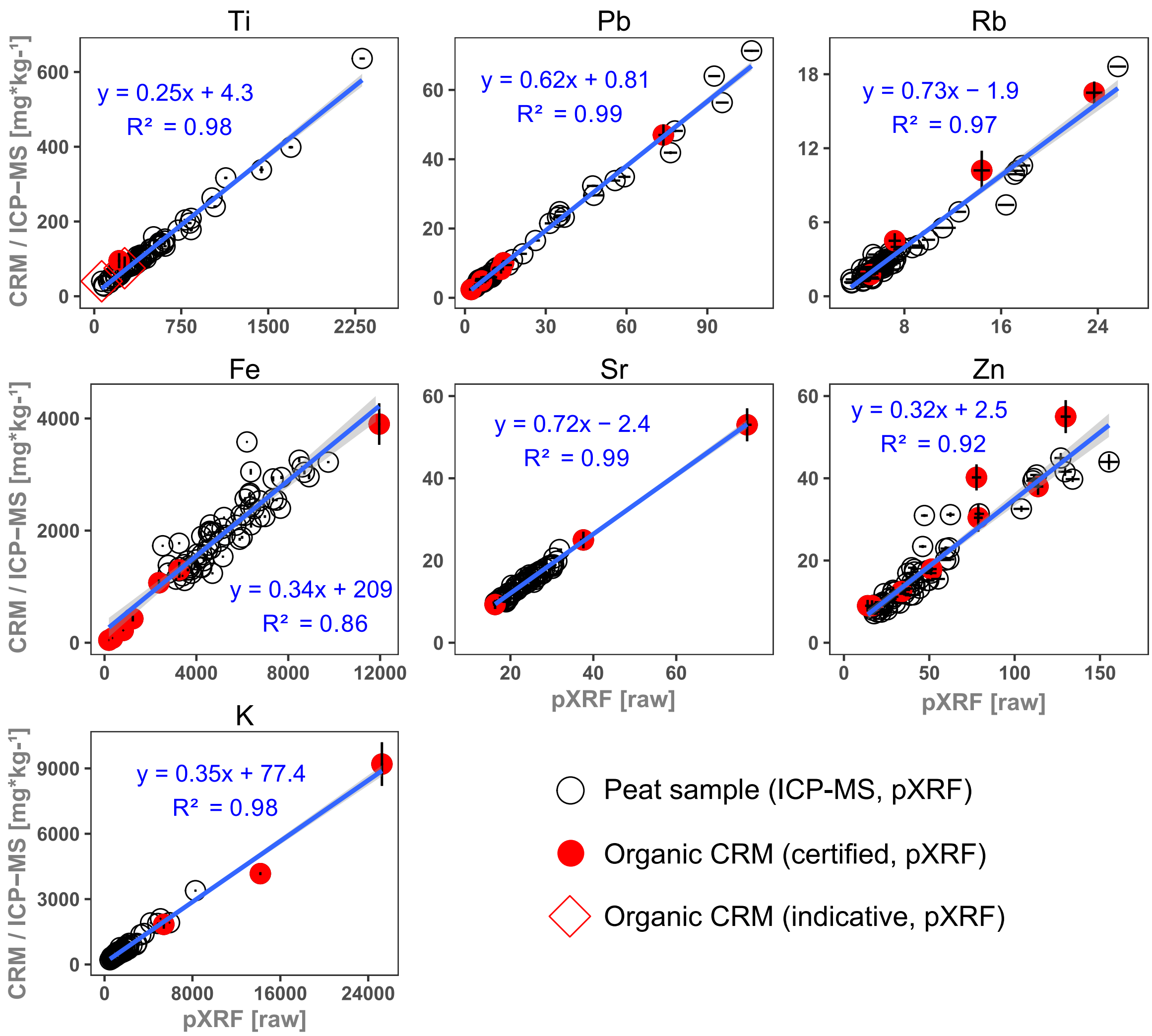

Fig. 3. Cross-plots with regression analysis of ICP-MS and pXRF measurements. Open circles: peat, filled red circles: CRMs in concentration range, blue lines: linear regressions. Error bars depict the standard deviation of the measurements or the CRMs' errors.

surface. Sb increases to 3 mg*kg^{-1} at 326 cm but is mostly below 1 mg*kg^{-1} until 90 cm. A maximum of 7 mg*kg^{-1} at 67 cm is followed by concentrations over 1 mg*kg^{-1}. Zn is on a level between 10 and 20 mg*kg^{-1}, rises to c. 30 mg*kg^{-1} at 312.5, 270, 200 and 62 cm (4140, 3500, 2330 and 110 cal BP) and exceeds 40 mg*kg^{-1} near-surface.

The dry bulk density gradually increases from 0.05 to 0.1 g*cm^{-3} in the lowest 100 cm and sharply returns to 0.05 g*cm^{-3} at 250 cm. A density peak to over 0.1 g*cm^{-3} covers 90 to 62 cm.

3.2.4. Accumulation rates and enrichment factors

MAR stays mostly below or around 1.5 g*a^{-1}*m^{-2}, but remarkable peaks of c. 9 g*a^{-1}*m^{-2} appear at 2350 cal BP and again in in the last century (Fig. 5). Moderate increases in MAR appear prior to 4000, and around 3400, 1600, 1100 and 200 cal BP.

A peak of Pb_{anth} AR around 4400 cal BP (approx. 0.8 mg*a^{-1}*m^{-2}) is followed by a slowly rising trend from 4000 until 3250 cal BP to 0.5 mg*a^{-1}*m^{-2}. After another single peak around 1450 cal BP (approx. 0.7 mg*a^{-1}*m^{-2}), Pb_{anth} AR values are constantly elevated after 1200 cal BP. An extreme peak occurs for both Pb_{anth} and Pb EF between 50 and -50 cal BP (1900–2000 CE), corresponding to 30 mg*a^{-1}*m^{-2} and an enrichment over 300. EFs of Zn, Cu and Sb show smaller increases along the profile, but rise strongly in the top layers corresponding to the 20th century CE. Cu EF shows a continuously declining trend until approx. 1000 cal BP.

Table 2 summarises the estimated average accumulation rates as well as the estimated cumulative loads of Pb_{anth} during the five periods (discussed in chapters 4.2 to 4.6).

4. Peatland and landscape evolution and human impact

4.1. Trophic status and atmospheric input

The low dry bulk density and low concentrations of Sr paired with the observed *Sphagnum* spp. dominance suggest ombrotrophic conditions over the full profile. Although the Sr-concentration profile fluctuates from top to bottom, it does return to low concentrations in the deepest section of our peat record, which is unlike a typical fen (minerotrophic peat) profile. Furthermore, the deepest section is not the mineral bottom, as we hit an impenetrable woody layer. Rather gentle slopes around the peatland, and the fact that the core was taken in the peatland's centre, makes surface runoff input unlikely. Even with a spatially restricted higher availability of nutrients from the more mineral rich layers (e.g. 60–90 cm and 200 cm), which would favour other *Sphagnum* species or more vascular plants, the main elements used for interpretation (Ti, Pb) show a generally conservative behaviour in peat. While the immobility of Ti is well accepted and it is often used as a

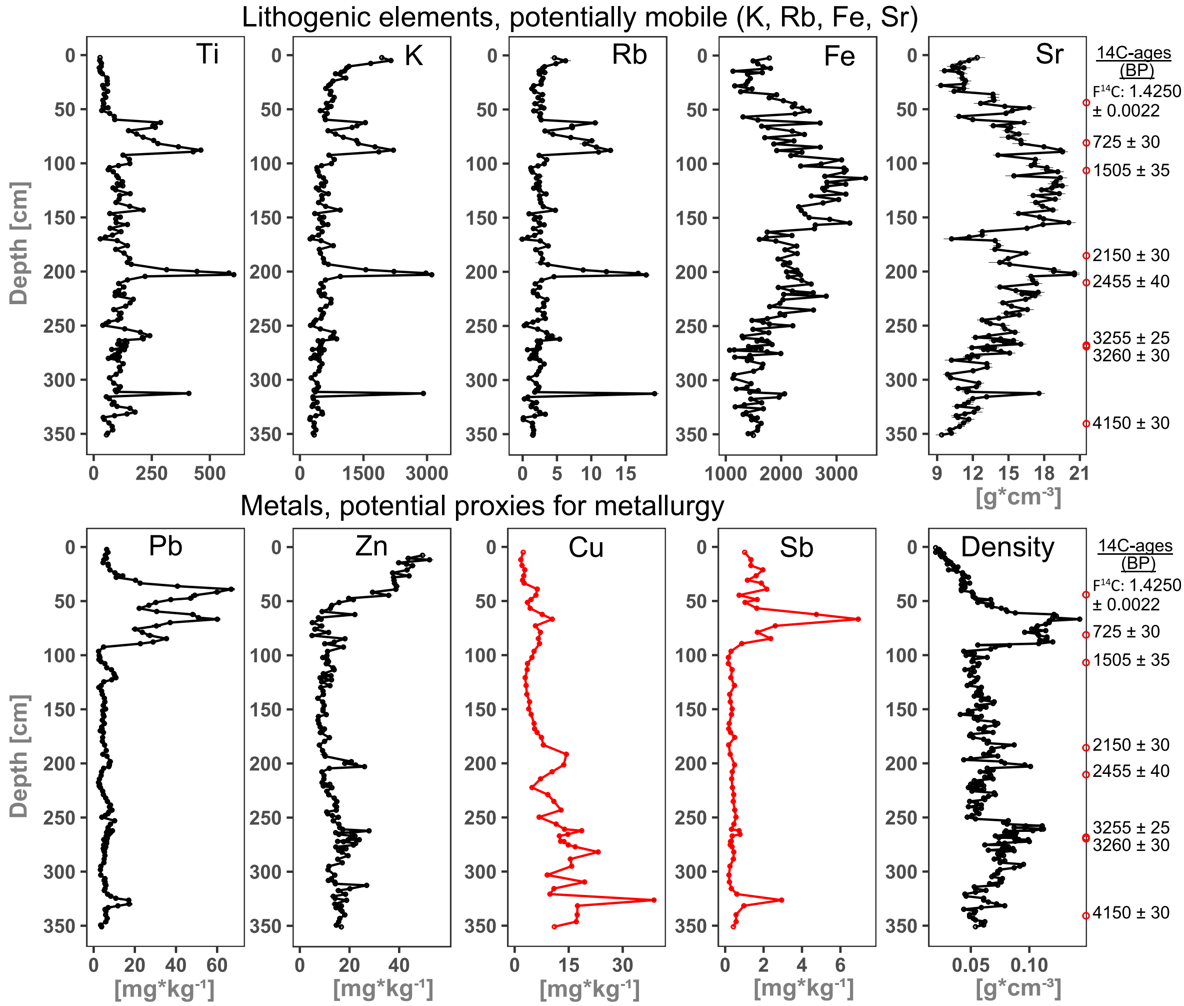

Fig. 4. Piller Moor profiles of elements measured by pXRF (in black) and ICP-MS (in red) and dry bulk density. $F^{14}C$ and ^{14}C-ages (uncalibrated years BP) given on the right.

conservative reference element (e.g. Bao et al., 2012; Sapkota et al., 2007; Shotyk et al., 2002), Pb also remains largely immobile even when affected by strongly fluctuating water tables (Rothwell et al., 2010) and it shows the strongest adsorption to organic matter in peat (Koivula et al., 2009; Krumins and Robalds, 2015).

Pb_{anth} AR and Pb EF (Fig. 5) can appear inconsistent when, for example, the anthropogenic Pb input is diluted by local soil dust input with a low natural background signature. During times of low energy dust entrainment and deposition (MAR), the consequently finer particles could bear higher concentrations of Pb or trace metals (Shotyk et al., 2002; Ujević et al., 2000). The former can be assumed when Pb_{anth} AR is high and Pb EF low. The latter is to consider with Pb_{anth} AR being low and Pb EF high. Pb-enriched atmospheric dust could also be more distal or very small, and therefore not significantly increasing the total accumulation. With simultaneously rising Pb_{anth} AR and Pb EF, and especially in prehistoric times, local or regional metallurgy is very likely. In any event, most of the interpretation is based on the more robust Pb_{anth} AR.

4.2. *Neolithic-Bronze Age transition (period 1 from 4800 to 4000 cal BP)*

Land use: Increases of mineral matter input at 4450 and 4150 cal BP from less than 0.5 to ca. 2 and 5 $g*a^{-1}*m^{-2}$, respectively, are in line with indicators for forest clearances, increased pastoralism indicators and burning in the area (Hubmann, 1994; Walde, 2006). Wahlmüller (2002) suggests first human impact around 4250 cal BP near Serfaus (Fig. 1), southwest of Piller Moor.

Around the same time, agricultural terraces (Zoller et al., 1996) and alpine pasture systems (Reitmaier, 2012) emerged in other areas of the Central Alps. Dietre et al. (2014) report increasing charcoal values and agricultural evidence from 4400 to 4200 cal BP in the Fimba Valley. Bortenschlager (2010) documents tree cover loss and cultural pollen at 4400 cal and Dietre et al. (2017) suggest fire management in the lower Engadine, Switzerland.

From a climatic perspective, the peaks in MAR around 4450 and 4150 cal BP coincide with minimum glacier stands in the region (Nicolussi and Patzelt, 2000). Afterwards, a continuously declining tree line in the Kauner Valley (Nicolussi et al., 2005) could have resulted from both climate and human forcing and contributed to an increasing trend of MAR, starting around 4000 cal BP. Yet, it is still the period with the lowest estimated average MAR (1.01 $g*a^{-1}*m^{-2}$, Table 2).

Metallurgy: Only few hints for prehistoric mining exist in northwestern Tyrol (Grutsch et al., 2019b). Even the ancient mining districts of the Eastern Alps bear only limited evidence before 3750 cal BP (O'Brien, 2015), although copper mining could have started around 4450 cal BP (Knierzinger et al., 2020, 2021). However, metallurgy in general was already present in the Alps at that time (Höppner et al., 2005). Ore extraction is suggested for the Southern Alps (Artioli et al., 2016) and Cu-mining is suggested for the Eastern Alps (Knierzinger et al., 2020). In the Piller Moor record, an increase of Pb_{anth} AR from 0.2 to 0.8 $mg*a^{-1}*m^{-2}$ between 4500 and 4200 cal BP is the highest until the late Middle Ages. This pronounced signal also coincides with

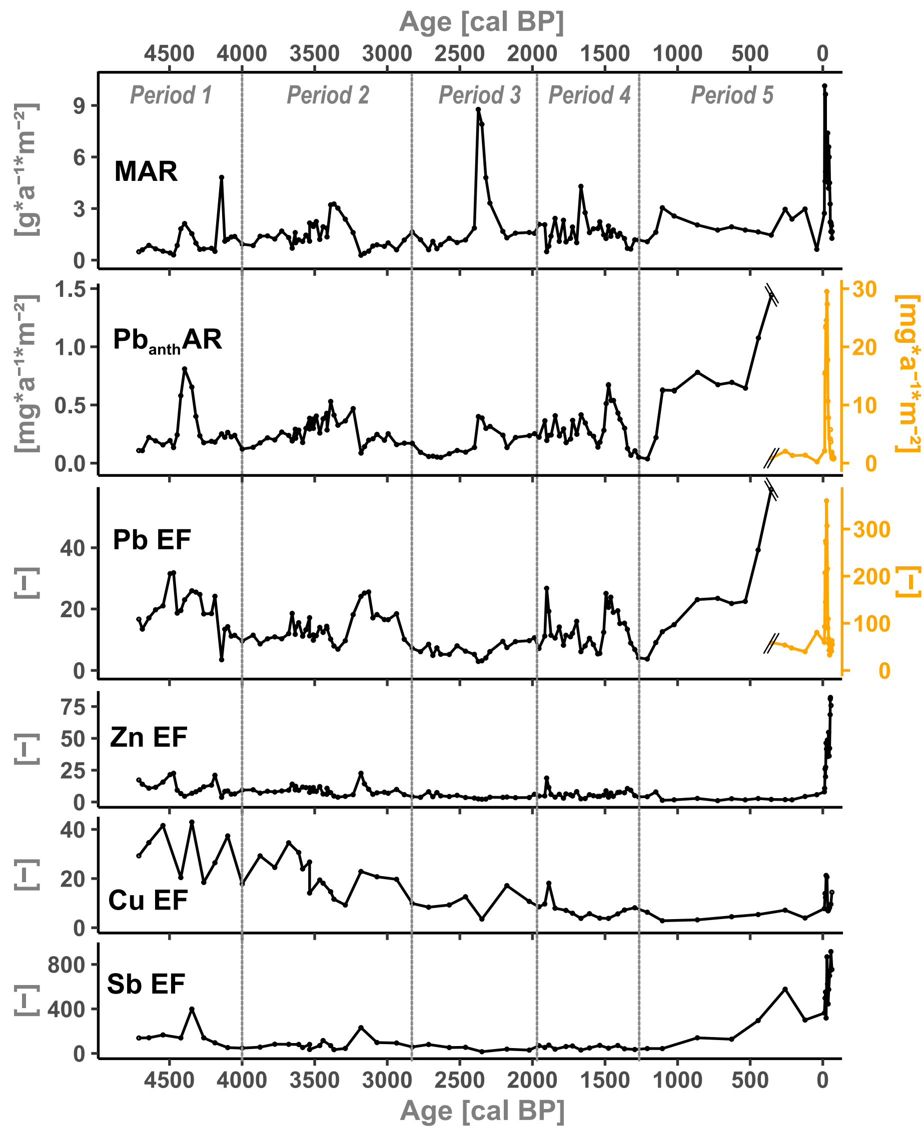

Fig. 5. Mineral accumulation rate (MAR), anthropogenic Pb accumulation rate (Pb_{anth} AR) and metal enrichment factors (Pb EF, Zn EF, Cu EF, Sb EF). Orange lines (Pb AR and Pb E) zoomed in (secondary x-axis). Periods loosely correspond to cultural periods (e.g. Period 1 = Neolithic-Bronze Age transition; Period 2 = Bronze Age; Period 3 = Iron Age; Period 4 = Roman occupation in the Alps; Period 5 = Middle Ages to Postmodernity).

Table 2
Synthesis of model estimates for approximates of average mineral and Pb_{anth}-accumulation rates and for the approximate cumulative deposition of Pb_{anth} within the periods 1 to 5 and in the most recent sample.

Period	Age [cal BP]	Estimated average MAR [$g*m^{-2}*a^{-1}$]	Estimated average Pb_{anth} AR [$mg*m^{-2}*a^{-1}$]	Estimated cumulative Pb_{anth} [$g*m^{-2}$]
1	4800–4000	1.01	0.26	0.19
2	4000–2800	1.94	0.33	0.4
3	2800–2000	1.84	0.16	0.12
4	2000–1300	1.41	0.25	0.17
5	After 1300	3.94	2.51	1.79
Surface	c. −65	1.6	1.21	**Total:** 2.68

synchronously enriched Pb and Sb and with the MAR and pollen indicators mentioned above, which suggests a link between these proxies of human impact. A lake record to the south-west (Thevenon et al., 2011) shows Pb-isotope supported evidence for metallurgy, which shows that the technology was around. However, the coincidence of proxies with the marked rise of Pb_{anth} AR indicates that the inputs found in the Piller Moor peat record had a regional or even local source at that time. Various polymetallic ore deposits in the area contain Cu, Ag, Pb, As and Sb, and some had been exploited over the last millennium (Grutsch et al., 2019b; Hammer, 1915; Hanneberg et al., 2009; Neuhauser, 2015; Vavtar, 1988; Weber et al., 1997). Local small-scale metallurgy is therefore likely, even if it was not mining, and it would predate any direct archaeological evidence in the area, but the possibility of remote transport cannot be completely ruled out. Despite the depth, influence of minerotrophic conditions on the estimated Pb_{anth} AR average of 0.26 $mg*a^{-1}*m^{-2}$ (Table 2) is unlikely, as the described Pb-peak is very distinct from the background level and the Sr-concentration profile is very low.

4.3. Bronze Age (period 2 from 4000 to 2800 cal BP)

Land use: Towards 3400 cal BP, increasing land use activity is suggested by rising MAR, which is in good agreement with *Cerealia* pollen recorded in the Piller Moor peat (Hubmann, 1994) as well as open landscape and pastoral indicators in nearby study sites (Wahlmüller, 2002; Walde, 2006). Coinciding elevated charcoal values in these studies are in line with increased fire clearances in the Alps (Valese et al., 2014).

Local archaeological evidence of Bronze Age buildings in Fließ (Tomedi et al., 2009) and Kaunerberg (Staudt and Tomedi, 2015), and the ritual site on the Piller Saddle dating between 3450 and 3230 cal BP (Tschurtschenthaler and Wein, 2002; 1998, 1996), indicate extensive human activity in the study area, which was probably responsible for the doubling of the estimated average MAR in this period (1.94 $mg*a^{-1}*m^{-2}$).

A pulse of stronger human activity is also evident in other regional records from the Central Alps (Dietre et al., 2014; Festi et al., 2014; Röpke et al., 2011; von Scheffer et al., 2019). In the Eastern Alps, intensified human impact is documented (Knierzinger et al., 2020; Viehweider et al., 2013), possibly to sustain copper mining operations (Stöllner, 2015).

Following on glacier progression around 3600 cal BP, a recession until 3350 cal BP (Nicolussi et al., 2005) could have promoted land use at higher elevations mentioned earlier. Inferred from low MAR and pollen (Hubmann, 1994; Walde, 2006), local and regional land use declined after 3200 cal BP, possibly induced by a large-scale cooling trend (e.g. Ivy-Ochs et al., 2009).

Metallurgy: Slightly elevated but fluctuating EFs for Pb, Cu and Zn are recorded between 3750 and 3450 cal BP, while Pb_{anth} AR slowly rises to 0.5 $mg*a^{-1}*m^{-2}$ until 3400 cal BP, before dropping again (Fig. 5). Compared to sites in the Vosges, Alpine Foreland and Swiss Jura, with max. Pb_{anth} ARs of c. 0.2, 0.016 and 0.075 $mg*a^{-1}*m^{-2}$ respectively (Forel et al., 2010; Kern et al., 2021; Shotyk et al., 1998), the estimated average of 0.33 $mg*a^{-1}*m^{-2}$ in our record is considerably higher during this period. Not far from the Piller Saddle, Bronze Age ceramic mixed with copper slag found near a malachite ore deposit suggests local metallurgy and mining (Tomedi, 2002b). A large middle Bronze Age bronze hoard and unworked copper was found nearby (Tomedi, 2002a, 2012) and the covering layer was dated to ca. 3400 cal BP (Tschurtschenthaler and Wein, 1998). The chemical signature of this hoard's artefacts largely corresponds to the well-studied Mitterberg mining district in the Eastern Alps (Pernicka et al., 2016), although the main wind directions make trajectories from there to Piller Moor less likely. In any case, the lack of characterisations (e.g. lead isotopes) of local polymetallic ores around Piller Moor makes tying any artefacts to nearby sources impossible. It is, however, striking that larger proportions of copper artefacts that were found in the Alps and dated to the early and late Bronze Age were manufactured from fahlores, which are significantly richer in Sb (Grutsch et al., 2019a). This observation fits very well to increased Sb EF and Zn EF in period 1 between 4500 and 4200 cal BP (see section 4.2 or Fig. 5) and again at c. 3200 cal BP. In contrast, the locally found bronze hoard artefacts were probably from the mid Bronze Age and produced from chalcopyrite, which has lower Sb-contents (Grutsch et al., 2019a; Pernicka et al., 2016). Mostly low Sb EFs in our record could reflect that chalcopyrite mining was dominating in this period. With mainly copper ores having been exploited during this time, the generally increased Cu EF over the older part of the record is logical.

A Pb-isotope record from a peatland in southern Germany suggests Iberian ores as the main source of atmospheric Pb fluxes during this time (Kern et al., 2021). However, more proximate and thus more likely source regions like the Alps or Black Forest, have not been considered so far. The behaviour of Pb EF and AR is challenging to interpret in this period, but the combined evidence suggests that metallurgy was practised locally to regionally.

4.4. Iron Age (period 3 from 2800 to 2000 cal BP)

Land use: Around 2400 cal BP, Hubmann (1994) reports increased abundances of charcoal, *Plantago* spp., *Poaceae, Cyperaceae* and *Cerealia* at Piller Moor as evidence of land use change, fitting to similar palaeoecological signals of increased human impact at Fließ (Walde, 2006) and Serfaus (Wahlmüller, 2002). The drastic rise of MAR to more than 9 $g*m^{-2}*a^{-1}$ illustrates the intense human impact, with strong deforestation and agro-pastoralism, followed by heavy soil destabilisation. Archaeological sites on and around the Piller Saddle show widespread human occupation (Lutz and Schwab, 2015; Staudt, 2011; Sydow, 1995; Tschurtschenthaler and Wein, 2002; Zemmer-Plank, 1992), explaining the strong impact on Piller Moor.

Metallurgy: Pb EF does not suggest local metallurgical activity during the early Iron Age. However, strong mineral input masked increased Pb input around 2400 cal BP. This is shown by simultaneously elevated Pb_{anth} AR, which remains on a higher level afterwards. Although direct evidence is lacking for the Central Alps, silver production as early as 2250 cal BP is suggested for the Swiss Wallis (Guénette-Beck et al., 2009), making also local mid or late Iron Age metallurgy in the study area a possibility. Still, this period has the lowest estimated average Pb_{anth} AR with 0.16 $mg*a^{-1}*m^{-2}$, but the trend largely agrees with records from Black Forest, and the Vosges (Forel et al., 2010; Le Roux et al., 2005).

4.5. Roman period to early Middle Ages (period 4 from 2000 to 1400 cal BP)

Land use: In agreement with an initial MAR minimum at Piller Moor, larger forests and reduced pastoralism are reported once the region fell under Roman influence around 1950 cal BP (Bortenschlager, 2010; Hubmann, 1994; Wahlmüller, 2002; Walde, 2006). This is reflected in the estimated average MAR of 1.41 $g*a^{-1}*m^{-2}$ being lower than the pre-Bronze Age and the Iron Age estimated averages (periods 3 and 5). Yet, MAR fluctuations around 1750 cal BP match indicators for burning and landscape openings in Fließ (Walde, 2006). Just prior to a MAR peak around 1660 cal BP, increased charcoal values in Piller Moor (Hubmann, 1994) indicate reoccupation of the higher slopes, coinciding with crisis in the Roman Empire (Wierschowski, 1994).

Walde (2006) and Hubmann (1994) document a significant forest recovery and absence of cultural indicators around 1400 cal BP, when the MAR declines below 1 $g*m^{-2}*a^{-1}$. This gap of human impact agrees with other observations in the Central Alps (e.g. von Scheffer et al., 2019) and is connected to a cold climate extreme referred to as Late Antique Little Ice Age (Büntgen et al., 2016; Helama et al., 2017; Ivy-Ochs et al., 2009).

Metallurgy: Compared to the Iron Age, the mean estimated Pb_{anth} AR of 0.25 $mg*a^{-1}*m^{-2}$ during this period is significantly higher. Elevated Pb_{anth} AR and Pb EF during the earlier part of this period are likely associated with distal origin and diffuse Roman influence (e.g. Longman et al., 2020), in contrast to peaks of Pb EF and Pb_{anth} AR (c. 0.7 $mg*a^{-1}*m^{-2}$) around 1450 cal BP. Similar signals are registered across Western and Central Europe, for example in the Bernese Alps (Carvalho and Schulte, 2021), and in the northern Central Alps (von Scheffer et al., 2019), but also in Eastern Europe (Bohdálková et al., 2018). A rise is also visible in the Colle Gnifetti ice (More et al., 2017), but a 90-year hiatus starts just at this particular age. Kern et al. (2021) attribute this Pb signal to a transition to small scale and local mining operations across Europe, although atmospheric Pb-emissions and deposition were generally reduced during this period (e.g. Forel et al., 2010). Yet, it is striking that neither records from the Southern Alps (Segnana et al., 2020), nor south-west from our site (Thevenon et al., 2011), nor from the Eastern Alps (Knierzinger et al., 2020), nor from locations west and north-west of them (Vosges, Black Forest, Massif de Morvan, Swiss Jura), show increased Pb EF or Pb_{anth} AR at that time (Forel et al., 2010; Le Roux et al., 2005; Monna et al., 2004; Shotyk et al., 1998). Considering that the supra-regional Roman Pb-signal is not very defined in our record, the distinct and synchronous Pb EF and AR signals from 1500 to 1400 cal BP suggest an origin rather close to Piller Moor. This period was a time of warfare and territorial reorganisation, but the Central Alps were not in the centre of these conflicts (Kulikowski, 2012). Late Antiquity silver mining in the Swiss Alps is, however, suggested by Guénette-Beck et al. (2009) and regional Pb and Ag deposits around Imst (Gstrein, 2013), in the Austrian Vorarlberg region (Hofmann and Wolkersdorfer, 2013), and in Tirol (Vavtar, 1988), and their sheltered locations could have made parts of the Central Alps potential hotspots of Pb-emissions during the advent of the Middle Ages.

4.6. Middle Ages to Postmodernity (period 5 from 1400 cal BP to present)

Land use and climate: In line with a rising MAR in our record, Walde (2006) and Hubmann (1994) report a general rise of pastoral, cultural and grassland pollen after 1250 cal BP nearby (see Fig. 1). A landscape opening is also observed at Serfaus by Wahlmüller (2002). Still elevated mineral input at 900 cal BP coincides with increased charcoal, crops, *Plantago* spp. and decreased tree pollen in the Piller Moor peat, while lesser land use is indicated at c. 650 and 350 cal BP by both MAR in our record and pollen (Hubmann, 1994).

The gradually declining MAR after 1000 cal BP coincides with glacier advances in the nearby Kauner Valley (Nicolussi and Patzelt, 2000). Consequently, a lower MAR towards the early Modern Period could have resulted from declining mountain farming in the Alps (Lichtenberger, 1965), which Bender (2010) attributes to a cooler climate. In contrast, the MAR peak after 200 cal BP is associated with a temporary surge of expanding local and regional agriculture and forestry. The forest at Kaunerberg (c. 5.5 km south of the mire) lost about 140 ha between 1774 and 1880 AD and losses up to 85% are documented in the nearby Radurschl, Pitz, Oetz and Paznaun valleys (Fromme, 1957). Thereafter, documentation from 1850 to 1951 AD can explain the shrinking MAR: Agricultural yields and livestock declined by 50% and 40% respectively (Fromme, 1957). The construction of tourist infrastructure, large voltage line poles and roads, and the subsequent nature conservation measures possibly caused the recent MAR-peak and its decline over the last few decades. Apart from this, the estimated average MAR in this period ($3.94\ g{*}a^{-1}{*}m^{-2}$) is higher than in any of the previous periods.

Lower peat accumulation and higher density observed within the top metre (90–62 cm) of our record could relate to indirect anthropogenic disturbances, similar to observations of Sjögren et al. (2007). The area was listed as a natural resource (von Klebelsberg, 1939), leading to industrial peat mining in an adjacent bog between 1949 and 1971 AD. A potential hydrological link to the exploited site could have promoted disturbance in the Piller Moor's surface layers. Recently introduced conservation measures in the area were likely beneficial for a return to previous peat accumulation rates and current growth rates of over 1 $cm{*}a^{-1}$.

Metallurgy and pollution: All EFs as well as a sharp rise of the Pb_{anth} AR indicate constant metallurgy in the area after 1200 cal BP (750 cal AD), preceding first historical sources on Ag, Pb and Zn extraction in the 12th century AD (Hanneberg et al., 2009; Wolkersdorfer, 1991) and the awarding of mining rights in 1352 AD (von Srbik, 1929). Increasing trends of Pb-input are also reported from other sites (e.g. More et al., 2017; Segnana et al., 2020; Thevenon et al., 2011), which illustrates that the development was supra-regional and more distal sources likely contributed as well.

By 500 cal BP (1450 cal CE), strongly rising EFs (Pb and Sb) are in line with the introduction of a new and more pollutive ore processing technology (Breitenlechner et al., 2013; Longman et al., 2020). A link to intensifying silver mining around Imst (Hanneberg et al., 2009) and the Arlberg region (Haditsch and Krainer, 1992), north and west of our record, is also likely. South of Piller in Platzertal (Platzer Valley), Pb was mined and smelted from 1538 CE to 1900 CE (Vavtar, 1988). A climate induced temporary abandonment of this mining site (1610–1888 CE) is synchronous with a decreasing Pb EF in our record. In addition, regional mining was outcompeted by overseas' ores (Wolkersdorfer, 1991). The recent maximum of Pb_{anth} AR (c. 30 $mg{*}m^{-2}{*}a^{-1}$) and Pb EF (>300) are the result of leaded gasoline emissions (Pacyna and Pacyna, 2001). The sharp drop in the late 1980s is the response to its stepwise reduction and final ban across Europe. Compared to the maximum values in the Alpine Foreland (c. <6 $mg{*}m^{-2}{*}a^{-1}$; Kern et al., 2021) and to the records summarised in Forel et al. (2010), which are the Black Forest (c. 14 $mg{*}m^{-2}{*}a^{-1}$), Jura (c. 14 $mg{*}m^{-2}{*}a^{-1}$) and Vosges (c. 12 and 39 $mg{*}m^{-2}{*}a^{-1}$), the maximum Pb_{anth} AR in our record is mostly higher. Whilst the Pb_{anth} AR does not return to natural background levels, it is within the upper range of Pb AR around 1 $mg{*}m^{-2}{*}a^{-1}$ recently observed in Central Europe (e.g. Kempter et al., 2010), yet, lower than values in the black triangle of Eastern Germany, Poland and the Czech Republic (e.g. Zuna et al., 2011). Our Pb record is in good agreement with the history of pollution in Central Europe. Its steep decline acts just as another time marker, which is confirming our age depth model. Since our peat profile covers a longer time period, the estimated cumulative anthropogenic Pb-deposition of c. 2.7 $g{*}m^{-2}$ (Table 2) is slightly higher than in most of the Swiss peat records summarised in Shotyk et al. (2000).

5. Conclusions

Mineral and metal accumulation rates (MAR) and enrichment factors (EF), calculated based on geochemical analyses and combined with other palaeoecological proxies, provide continuous evidence of human occupation when archaeological evidence is lacking or isolated. Past episodes of metallurgy and anthropogenic soil disturbances in the Central Alps are revealed in our Piller Moor record. Methodological evidence shows that pXRF facilitates high-resolution, quantitative data acquisition of certain elements in ombrotrophic peat (Ti, Pb, Zn, Sr, K, Rb, Fe), whereas others (e.g. Cu) cannot be quantified.

Our results suggest mining or metallurgy in the Central Alps between 4500 and 4200 cal BP, predating any archaeological evidence in the area. Around 3400 cal BP, both mineral input and Pb_{anth} AR are elevated synchronously with palynological and archaeological evidence for human activity. A strong mineral input pulse at 2400 cal BP is simultaneous with proximate palynological and archaeological indicators for heavy human landscape disturbance. Despite Roman presence in the Inn valley, their direct impact at higher elevation seems to have remained rather small. Temporary but distinct increases of Pb_{anth} AR and Pb EF from 1500 to 1400 cal BP strongly indicate post-Roman mining and metallurgy in this part of the Central Alps, encouraging further research to locate potential sources in the area. However, the anthropogenic impact was very weak in the early Middle Ages, before soil disturbance and metallurgy resumed around 1200 cal BP and continued increasing. Our data indicate early medieval mining operations, which predate historical documentation by several centuries. While the LIA likely impaired regional agriculture, forestry, and mining operations episodically, the comparison of our record to historical documentation highlights the severe influence of expanding forestry and agriculture on regional soil erosion and dust entrainment over the last centuries. Over the last century, nearby peat extraction and construction, but also nature conservation, seem to have influenced mineral and peat accumulation. The abrupt decline of Pb EF and Pb_{anth} AR after the year 1980 AD acts as a time marker. In the form of quantitatively reconstructed atmospheric input, geochemical signals found in our Piller Moor peat record mainly reflect the development of local and regional human activities and their impact on the Alpine landscape over the past 4800 years.

Author contributions

Clemens von Scheffer: Fieldwork, Investigation, Validation, Formal analysis, Data curation, Writing- Original draft preparation, Project administration, Visualisation, Conceptualisation, Methodology, Funding acquisition.: **Ingmar Unkel:** Fieldwork, Conceptualisation, Supervision, Writing- Reviewing and Editing, Funding acquisition.: **François De Vleeschouwer:** Conceptualisation, Methodology, Supervision, Writing- Reviewing and Editing, Funding acquisition.: **Gaël Le Roux:** Supervision, Methodology, Writing- Reviewing and Editing, Funding acquisition.

Data availability

Data is provided in the supplementary material and will be made available in the PANGEAE online database.

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Declaration of competing interest

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Appendix A. Supplementary data

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