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

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15

16 **Abstract**

17 Humans have occupied the Alps over most of the Holocene. Yet, continuous records on the impact of
18 using montane resources and landscapes are scarce or confined to segregated areas or periods. We
19 present a high-resolution geochemical record of the last 4800 years from the ombrotrophic peatland
20 Piller Moor in the Central Alps (Tyrolean Oberland, western Austria), using inductively coupled mass
21 plasma spectrometry (ICP-MS) and highly efficient inter-calibrated portable X-ray fluorescence analysis
22 (pXRF). Fluctuations of metal enrichment factors (EF) for lead (Pb), copper (Cu), zinc (Zn) and antimony
23 (Sb), accumulation rates of anthropogenic lead (Pb_{anth} AR) and mineral matter (MAR), based on
24 titanium (Ti), are in line with archaeological and pollen evidence for human presence and
25 environmental change. Periods of intensified, erosive land use are indicated by MAR around 4400 cal
26 BP, 3400 cal BP and, very prominently, at 2400 cal BP. After low MAR in the early Middle Ages, soil
27 disturbances reappear around 1200 cal BP (750 CE), after 200 cal BP (1750 CE) and during the 20th
28 century CE. We found evidence that metallurgy was practised in the area as early as 4450 cal BP, again
29 from 3500 to 2900 cal BP and episodically between 2400 and 1400 cal BP. The Central Alps were
30 presumably a source of increased Pb-emissions in the post-Roman period from 1500 to 1400 cal BP
31 (450–550 CE). Generally, our findings suggest that mining predates archaeological and historical
32 evidence. Following a continuous increase since the Middle Ages, atmospheric Pb EF and Pb_{anth} AR peak
33 around 1980 CE. The record of mineral atmospheric input illustrates the notable impact of human
34 activities on soil erosion and dust entrainment in the Central Alps. Furthermore, links between Little
35 Ice Age cold phases and reduced human impact and mining are established. Our high-resolution peat-
36 geochemistry data quantifies atmospheric deposition of mineral matter and Pb, which act as proxies
37 for landscape evolution and metallurgy on a local and regional scale. It provides new insights and a
38 deeper understanding of the interaction of climate, environment and humans in mountainous
39 landscapes like the Central Alps.

40 Keywords: Alps; Prehistoric metallurgy; Land use; Peat geochemistry; Atmospheric dust; Portable XRF

41

42 1. Introduction

43 Ombrotrophic peatlands are precious palaeoenvironmental archives. Specific characteristics render
44 them reliable geochemical records of certain contaminants like lead (Pb), copper (Cu) or Antimony (Sb)
45 as industrial or metallurgical emissions (Damman, 1978; De Vleeschouwer et al., 2007; Forel et al.,
46 2010; Jones and Hao, 1993; Nieminen et al., 2002; Shotyk, 1996; Shotyk et al., 2004). They also act as
47 archives of fluctuating mineral atmospheric dust deposition, indicating droughts, storminess or
48 changes in land cover and land use (e.g. Chambers et al., 2012; Hölzer and Hölzer, 1998; Lomas-Clarke
49 and Barber, 2007; Schofield et al., 2010).

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

54 When reconstructing human impact and interaction with mountain landscapes, considering proximate
55 archaeological sites is imperative and a key to proper interpretation. The Piller Moor (Tyrol, Austria,
56 Figure 1) is one of the rare, well-preserved ombrotrophic peatlands in direct vicinity to well-known
57 archaeological sites, which are a bronze-hoard and a ritual fire site (Heiss, 2008; Tomedi, 2012, 2002a;
58 Tschurtschenthaler and Wein, 2002). Palynological data is available for the site (Hubmann, 1994), while
59 nearby palaeovegetation studies give a good perspective on regional developments (e.g. Festi et al.,
60 2014; Grabherr, 2006; Wahlmüller, 2002; Walde, 2006). Reconstructions of glacier activity and tree
61 line changes from the nearby Kauner Valley (Figure 1) further provide insight on past regional climate
62 variability during the late Holocene (Nicolussi et al., 2005; Nicolussi and Patzelt, 2000). Although the
63 Eastern Alps became an important mining district during the Bronze Age (O'Brien, 2015; Stöllner and
64 Oeggel, 2015), there is little known on prehistoric mining activity for this area of the Central Alps
65 (Krause, 1987; Stöllner, 2015).

66 In our study, we use geochemical ICP-MS and portable XRF (pXRF) data to identify periods of metallurgy
67 and to assess the degree and scale of human impact at the junction between the Eastern and Western
68 Alps. Portable XRF can be a time and cost-efficient tool to analyse the chemistry of a wide variety of
69 materials (e.g. Kalnicky and Singhvi, 2001; Liritzis and Zacharias, 2011; Palmer et al., 2009). However,
70 palaeoenvironmental studies using pXRF remain scarce (Gałka et al., 2017; Kapustová et al., 2018; von
71 Scheffer et al., 2019). One of the challenges is that preinstalled calibrations rarely cover the highly
72 organic sample matrix of peat. Hence, we developed an (inter)calibration between semi-quantitative

73 pXRF and ICP-MS measurements, following full acid digestion in a clean room. Certified reference
74 materials (CRM) for both methods act as an independent verification of the quality and reliability of
75 our approach. Our geochemical proxy data is supported by pollen data from the same site (Hubmann,
76 1994) and other local palynological and archaeological studies, providing a comprehensive picture of
77 regional human land use, metallurgy and environmental conditions in the past.

78

79 2. Methods

80 2.1 Study area and site

81 As part of the Tyrolean Oberland, the climate at the Piller Moor is alpine-continental with a mean
82 annual precipitation of ca. 800 mm and main wind directions are between west and south (46%) and
83 north to north-east (18.5%) for the period between 1971 and 2000 CE in Landeck (Central Institution
84 for Meteorology and Geodynamics of Austria, (ZAMG, 2018)). The Piller Saddle is in the altitudinal
85 lower subalpine zone (c. 1550 m a.s.l.). The Inn River (c. 800 m a.s.l.) approaches the Piller Saddle from
86 the South before joining with the Sanna River at Landeck and turning east (Figure 1). The Kauner, Pitz
87 and Oetz Valleys are south-east of the Saddle. A brook (Pillerbach) drains the mire in north-easterly
88 direction over the Pitze River into the Inn Valley, which divides the Penninic metamorphic zone to the
89 south and the northern Limestone Alps.

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

95

96 2.2 Coring and sub-sampling

97 Coring in the Piller Moor took place in 2017. For the profile Pi17 (47°07'24.85" N, 10°39'45.45" E), a
98 Wardenaar system (10x10 cm; Wardenaar, 1987) was used to core the top meter of the mire and a
99 piston corer (Usinger 8 cm barrel; Mingram et al., 2007) was used for the deeper layers. Parallel profiles
100 (A and B) were taken to get a composite core. A maximum depth of 380 cm was reached before hitting
101 an impenetrable layer, supposedly consisting of woody material. The segments were wrapped in cling
102 film, transferred into a PVC-casing and sealed in a plastic hose. Cores A and B were sliced continuously
103 to subsamples of c. 1.1 cm thickness for geochemistry and dating. Dry bulk density was calculated using
104 the dimensions and dry weight of the geochemistry samples. Clean coring and subsampling followed
105 the protocol of De Vleeschouwer et al. (2010) and Givelet et al. (2004). Three macrofossil samples were

106 picked in ultrapure water for radiocarbon dating at Poznan AMS Radiocarbon Laboratory (Poz), Poland.
107 Other samples were selected with the same method, pre-treated at the Gliwice Radiocarbon
108 Laboratory (GdA), Poland and measured at the Rafter Radiocarbon Laboratory, New Zealand.

109

110 2.3 Geochemistry

111 143 dry samples for pXRF and 63 samples for ICP-MS analyses, were selected and processed following
112 Le Roux and De Vleeschouwer (2010). The samples were crushed to a homogenous powder in 15–50
113 ml tubes with eight glass beads of 4 mm using a FastPrep®-24 ball-mill (3x20 s at 6 m*s⁻¹). For pXRF-
114 analysis, sample and CRM preparations and measurements were done on dried and homogenised
115 peat, following the protocol in von Scheffer et al. (2019). The samples were transferred into
116 polystyrene containers, covered with 4-µm thick polypropylene film and measured using a handheld
117 Thermo Fisher Scientific Niton Xl3t, inside a test stand. The pXRF-device was rebooted regularly to
118 account for fluctuations of temperature and atmospheric pressure during the day. The Xl3t was used
119 in soil-mode, running the main and low-filter for 180 s each.

120 Samples for ICP-MS analyses were digested in a class 100 clean room at „Laboratoire Ecologie
121 Fonctionnelle et Environnement“ Toulouse, France. Following the protocol for acid-digestion of peat
122 samples detailed in Vanneste et al. (2015), 100 mg peat powder was treated consecutively with
123 ultrapure chemicals, first with 2 ml of 65 % nitric for 24 h at room temperature and, after adding 0.5
124 ml hydrofluoric acid, at 110 °C for 48 h, then with 31 % ultrapure peroxide at room temperature for 24
125 h and lastly in 2 ml 65 % nitric acid at 110 °C for 48 h. Before every step, the mix of dried sample and
126 liquid was treated with ultrasound and the samples were evaporated at 50 °C in between steps. An
127 In/Re spike was added to each sample. Five multi-element standards were run every 10 samples to
128 correct for instrument drift. A blank and two different organic CRMs (NIST-1547a, NIST-1515, GBW-
129 07603, NJV-942, NJV-941) were treated per batch of 21 samples and measured in regular intervals. In
130 addition to the CRMs used in ICP-MS, BCR-060, IAEA-336, IPE-176 and NIST-1575a were used for pXRF.

131

132 2.4 Computing and calculations

133 The calculations and regression analyses are performed in R version 4.0.3. (R Core Team, 2021). The
134 Bayesian age-depth model (ADM) is created using the package *rbacon* version 2.5.3 (Blaauw and
135 Christen, 2011) with a 95 % confidence interval and the IntCal20 radiocarbon calibration curve (Reimer
136 et al., 2020). Boundaries are added based on obvious changes in density and humification. Median
137 ages are given as ‘cal BP’ (calibrated years before 1950). Historical or certain cited ages are given as

138 CE. The peat accumulation rate represents the bulk thickness of one peat sample and the period of
139 time covered ($\Delta\text{thickness}/\Delta\text{time}$) in $\text{mm}\cdot\text{year}^{-1}$.

140

141 Metal enrichment factors (Me EF) for Pb, Sb, Cu and Zn and atmospheric mineral accumulation rates
142 (MAR) are calculated using the conservative behaviour of Ti in peat (Nesbitt and Markovics, 1997), as
143 done in Shotyk et al. (2002), to detect past metal enrichment and land use change (e.g. Kempter et al.,
144 1997). The choice of Ti was also pre-determined by the range of elements of the pXRF. Pb, Sb, Cu, and,
145 sometimes, Zn are commonly used to trace metallurgical or industrial emissions (e.g. Damman, 1978;
146 Jones and Hao, 1993; Nieminen et al., 2002; Shotyk, 1996; Shotyk et al., 2004).

147
$$\text{Me EF} = \frac{(Me/Ti)_{\text{sample}}}{(Me/Ti)_{\text{UCC}}}$$

148

149
$$\text{MAR} = 100/0.41 * Ti_{\text{sample}} * \delta * \text{PA}$$

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

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

153
$$\text{Pb}_{\text{nat}} = \text{Pb}_{\text{sample}} * (Pb/Ti)_{\text{UCC}}$$

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

156
$$\text{Pb}_{\text{anth.}}\text{AR} = \text{Pb}_{\text{anth.}} * \delta * \text{PA}$$

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

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

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

170

171 3. Results

172 3.1 Chronology

173 *Sphagnum* spp. mosses dominate throughout the core sections. The deepest section of profile B was
174 fitted and merged to the deepest section of profile A, using density, geochemistry and radiocarbon
175 dates (Table 1).

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

182

183 3.2 Geochemistry

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

187

188 3.2.1 Quality control

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

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

197

198 3.2.2 Regression Analysis

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

207

208 3.2.3 Elemental profiles

209 The relevant concentration vs depth profiles (Figure 4) and further interpretation are based on the
210 pXRF data calibrated for quantification via ICP-MS using the regressions (Figure 3). The pXRF profiles
211 have a higher depth resolution, except for Cu and Sb which were only measured by ICP-MS (Figure 4).

212 Peaks in Ti exceeding $400 \text{ mg} \cdot \text{kg}^{-1}$ and $600 \text{ mg} \cdot \text{kg}^{-1}$ appear at 312.5 and 200 cm (4140 and 2330 cal
213 BP), respectively, with some minor peaks of $400 \text{ mg} \cdot \text{kg}^{-1}$ and $260 \text{ mg} \cdot \text{kg}^{-1}$ at 88 cm and 62 cm (1050
214 and 110 cal BP). Rb resembles the course of Ti, staying mostly below $5 \text{ mg} \cdot \text{kg}^{-1}$ except for the five peaks
215 parallel to Ti, indicating stronger terrigenous influx into the mire during these periods. A slight increase
216 in Rb is also recorded in the surface layers. K ranges between 300 and $700 \text{ mg} \cdot \text{kg}^{-1}$, with peaks at 312.5
217 cm ($3000 \text{ mg} \cdot \text{kg}^{-1}$) and again at 200 cm, followed by 2300 and $1500 \text{ mg} \cdot \text{kg}^{-1}$ at 88 cm and 62 cm. A
218 rising trend shows in the uppermost 25 cm. Sr gradually rises from $10 \text{ mg} \cdot \text{kg}^{-1}$ to a maximum of 30
219 $\text{mg} \cdot \text{kg}^{-1}$ at 200 cm (2330 cal BP). After a local minimum of $2 \text{ mg} \cdot \text{kg}^{-1}$, a declining trend sets in at 155
220 cm (1770 cal BP). Fe doubles from $1500 \text{ mg} \cdot \text{kg}^{-1}$ at the bottom to approx. $3000 \text{ mg} \cdot \text{kg}^{-1}$ at 125 cm
221 depth before decreasing again.

222 Pb concentrations remain low around 3 to $10 \text{ mg} \cdot \text{kg}^{-1}$ between 350 and 100 cm (4710–1260 cal BP).
223 An increase to $20 \text{ mg} \cdot \text{kg}^{-1}$ appears around 328 cm. In three subsequent peaks in the uppermost metre,
224 the maximum concentration increases from $35 \text{ mg} \cdot \text{kg}^{-1}$ at 90 cm (1120 cal BP) to $70 \text{ mg} \cdot \text{kg}^{-1}$ at 39 cm
225 (-29 cal BP). Cu peaks at 326 cm ($39 \text{ mg} \cdot \text{kg}^{-1}$) and 282 cm ($23 \text{ mg} \cdot \text{kg}^{-1}$). Smaller increases appear at
226 310, 262 and 200 cm. However, a decreasing trend is obvious towards the surface. Sb increases to 3
227 $\text{mg} \cdot \text{kg}^{-1}$ at 326 cm but is mostly below $1 \text{ mg} \cdot \text{kg}^{-1}$ until 90 cm. A maximum of $7 \text{ mg} \cdot \text{kg}^{-1}$ at 67 cm is
228 followed by concentrations over $1 \text{ mg} \cdot \text{kg}^{-1}$. Zn is on a level between 10 and $20 \text{ mg} \cdot \text{kg}^{-1}$, rises to c. 30
229 $\text{mg} \cdot \text{kg}^{-1}$ at 312.5, 270, 200 and 62 cm (4140, 3500, 2330 and 110 cal BP) and exceeds $40 \text{ mg} \cdot \text{kg}^{-1}$ near-
230 surface.

231 The dry bulk density gradually increases from 0.05 to 0.1 g*cm⁻³ in the lowest 100 cm and sharply
232 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.

233

234 3.2.3 Accumulation rates and enrichment factors

235 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
236 2350 cal BP and again in in the last century (Figure 5). Moderate increases in MAR appear prior to 4000,
237 and around 3400, 1600, 1100 and 200 cal BP.

238 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
239 from 4000 until 3250 cal BP to 0.5 mg*a⁻¹*m⁻². After another single peak around 1450 cal BP (approx.
240 0.7 mg*a⁻¹*m⁻²), Pb_{anth} AR values are constantly elevated after 1200 cal BP. An extreme peak occurs for
241 both Pb_{anth} and Pb EF between 50 and -50 cal BP (1900–2000 CE), corresponding to 30 mg*a⁻¹*m⁻² and
242 an enrichment over 300. EFs of Zn, Cu and Sb show smaller increases along the profile, but rise strongly
243 in the top layers corresponding to the 20th century CE. Cu EF shows a continuously declining trend until
244 approx. 1000 cal BP.

245 In Table 2, the estimated averages of accumulation rates as well as the estimated cumulative loads of
246 Pb_{anth} during the five periods (discussed in section 3.3) are summarised.

247

248 4. Peatland and landscape evolution and human impact

249 4.1 Trophic status and atmospheric input

250 The low dry bulk density and low concentrations of Sr paired with the observed *Sphagnum* spp.
251 Dominance suggest ombrotrophic conditions over the full profile Although the Sr-concentration profile
252 fluctuates from top to bottom, it does return to low concentrations in the deepest section of our
253 record, which is unlike a typical profile of a fen. Furthermore, the deepest section of the peat record
254 is not the mineral bottom, as we hit an impenetrable layer of wood. Rather gentle slopes around the
255 peatland and the fact that the core was taken in the peatland's centre, makes surface input unlikely.
256 Even with a spatially restricted higher availability of nutrients from the more mineral rich layers (e.g.
257 60-90 cm and 200 cm), which would favour other *Sphagnum* species or more vascular plants, the main
258 elements used for interpretation (Ti, Pb) show a generally conservative behaviour in peat. While the
259 immobility of Ti is well accepted and often used as a conservative reference element (Bao et al., 2012;
260 Sapkota et al., 2007; Shotyk et al., 2002), Pb also remains largely immobile even when affected by
261 strongly fluctuating water tables (Rothwell et al., 2010) and it shows the strongest adsorption to
262 organic matter in peat (Koivula et al., 2009; Krumins and Robalds, 2015). In contrast, the increasing
263 trend of Cu with depth could indicate some mobility, which is why it is interpreted with caution.

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

273 4.2 Neolithic-Bronze Age transition (Period 1 from 4800 to 4000 cal BP)

274 **Land use:** Increases of mineral matter input at 4450 and 4150 cal BP from less than 0.5 to c. 2 and 5
275 $g \cdot a^{-1} \cdot m^{-2}$, respectively, are in line with indicators for forest clearances, increased pastoralism
276 indicators and burning in the area (Hubmann, 1994; Walde, 2006). Wahlmüller (2002) suggests first
277 human impact in the region near Serfaus southwest of the Piller Moor around 4250 cal BP.

278 Around the same time, agricultural terraces (Zoller et al., 1996) and alpine pasture systems (Reitmaier,
279 2012) emerged in other areas of the Central Alps. Dietre et al. (2014) report increasing charcoal values
280 and agricultural evidence from 4400 to 4200 cal BP in the Fimba Valley. Bortenschlager (2010)
281 documents tree cover loss and cultural pollen at 4400 cal BP, and Dietre et al. (2017) suggest fire
282 management in the lower Engadine, Switzerland.

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

288 **Metallurgy:** Only few hints for prehistoric mining exist in western Tyrol (e.g. Grutsch and Martinek
289 2012). Even the ancient mining districts of the Eastern Alps bear only limited evidence before 3750 cal
290 BP (O'Brien, 2015), although copper mining could have started around 4450 cal BP (Knierzinger et al.,
291 2021, 2020). Metallurgy in general was already present in the Alps at that time (Höppner et al., 2005).
292 Ore extraction is suggested for the Southern Alps (Artioli et al., 2016) and Cu-mining is suggested for
293 the Eastern Alps (Knierzinger et al., 2020). In the Piller Moor record, an increase of $Pb_{anth}AR$ to 0.8
294 $mg \cdot a^{-1} \cdot m^{-2}$ between 4500 and 4200 cal BP is the highest until the end of the Middle Ages. This
295 pronounced signal also coincides with synchronously enriched Pb and Sb and with the MAR and pollen
296 indicators mentioned above, which suggests a link between these proxies of human impact. A lake
297 record to the south-west (Meidsee) (Thevenon et al., 2011) shows Pb -isotope supported evidence for

298 metallurgy, which shows that the technology was around. However, the coincidence of proxies with
299 the marked rise of Pb_{anth} AR indicates that the inputs of the Piller Moor peat record had a proximate
300 source at that time. Various polymetallic ore deposits in the area contain Cu, Ag, Pb, As and Sb, and
301 some had been exploited over the last millennium (Grutsch and Martinek, 2012; Hammer, 1915;
302 Hanneberg et al., 2009; Neuhauser, 2015; Vavtar, 1988; Weber et al., 1997). Local small-scale
303 metallurgy is therefore likely, but it would predate any direct archaeological evidence and the
304 possibility of remote transport cannot be ruled out completely. Despite the depth, influence of
305 minerotrophic conditions on the estimated Pb_{anth} AR average of $0.26 \text{ mg} \cdot \text{a}^{-1} \cdot \text{m}^{-2}$ (Table 2) is unlikely,
306 as the described Pb-peak is very distinct from the background level and the Sr-concentration profile is
307 very low.

308

309 4.3 Bronze Age (Period 2 from 4000 to 2800 cal BP)

310 **Land use:** Towards 3400 cal BP, increasing land use activity is suggested by rising MAR, which is in good
311 agreement with *Cerealia* pollen in the Piller mire (Hubmann 1994) as well as open landscape and
312 pastoral indicators in nearby study sites (Wahlmüller, 2002; Walde, 2006). Coinciding elevated
313 charcoal values in these studies are in line with an increased fire clearance in the Alps (Valese et al.,
314 2014).

315 Local archaeological evidence of Bronze Age buildings in Fließ (Tomedi et al., 2009) and Kaunerberg
316 (Staudt and Tomedi, 2015), and the ritual site on the Piller Saddle dating between 3450 and 3230 cal
317 BP (Tschurtschenthaler and Wein, 2002, 1998, 1996), indicate extensive human activity in the study
318 area, which was probably responsible for the doubling of the estimated average MAR ($1.94 \text{ mg} \cdot \text{a}^{-1} \cdot \text{m}^{-2}$).
319

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

324 Following on glacier progression around 3600 cal BP, a recession until 3350 cal BP (Nicolussi et al.,
325 2005) could have promoted land use at higher elevations mentioned earlier. Inferred from low MAR
326 and pollen (Hubmann, 1994; Walde, 2006), local and regional land use declined after 3200 cal BP,
327 possibly induced by a cooling trend (e.g. Ivy-Ochs et al., 2009).

328 **Metallurgy:** Slightly elevated but fluctuating EFs for Pb, Cu and Zn are recorded between 3750 and
329 3450 cal BP, while Pb_{anth} AR slowly rises to $0.5 \text{ mg} \cdot \text{a}^{-1} \cdot \text{m}^{-2}$ until 3400 cal BP, before dropping again
330 (Figure 5). Compared to sites in the Vosges, Alpine Foreland and Swiss Jura, with max. Pb_{anth} ARs of c.

331 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),
332 the estimated average of 0.33 mg*a⁻¹*m⁻² in our record is considerably higher during this period. Not
333 far from the Piller Saddle, Bronze Age ceramic mixed with copper slag found near a malachite ore
334 deposit suggests local metallurgy and mining (Tomedi, 2002b). A large Middle or Late Bronze Age
335 bronze hoard and unworked copper were found nearby (Tomedi, 2012, 2002a, Nicolussi Castellan et
336 al., 2008). The chemical signature of this hoard's artifacts largely corresponds to the well-studied
337 Mitterberg mining district in the Eastern Alps (Pernicka et al., 2016), although the main wind directions
338 make trajectories from there to the Piller Moor less likely. In any case, the lack of characterisations
339 (e.g. isotopy, composition) of local polymetallic ores around the Piller Moor makes tying any artifacts
340 to nearby sources impossible. A Pb-isotope record from a peatland in southern Germany suggests
341 Iberian ores as the main source of atmospheric Pb fluxes during this time (Kern et al., 2021). However,
342 more proximate and thus more likely source regions like the Alps or Black Forest, have not been
343 considered so far. The behaviour of Pb EF and AR is challenging to interpret in this period and pointing
344 out a source even more, but the combined evidence suggests that metallurgy was practised regionally.

345

346 4.4 Iron Age (Period 3 from 2800 to 2000 cal BP)

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

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

362

363 4.5 Roman Period to Early Middle Ages (Period 4 from 2000 to 1400 cal BP)

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

372 Walde (2006) and Hubmann (1994) document a significant forest recovery and absence of cultural
373 indicators around 1400 cal BP, when the MAR declines below $1 \text{ g} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$. This gap of human impact
374 agrees with other observations in the Central Alps (e.g. von Scheffer et al., 2019) and is connected to
375 a cold climate extreme referred to as Late Antique Little Ice Age (Büntgen et al., 2016; Helama et al.,
376 2017; Ivy-Ochs et al., 2009).

377 **Metallurgy:** Compared to the Iron Age, the mean estimated Pb_{anth} AR of $0.25 \text{ mg} \cdot \text{a}^{-1} \cdot \text{m}^{-2}$ during this
378 period is significantly higher. Elevated Pb_{anth} AR and Pb EF during the earlier part of this period are
379 likely associated with distal origin and diffuse Roman influence (e.g. Longman et al 2020), in contrast
380 to peaks of Pb EF and Pb_{anth} AR (c. $0.7 \text{ mg} \cdot \text{a}^{-1} \cdot \text{m}^{-2}$) around 1450 cal BP. Similar signals are registered
381 across Western and Central Europe, for example in the Bernese Alps (Carvalho and Schulte, 2021), and
382 in the northern Central Alps (von Scheffer et al., 2019), but also in Eastern Europe (Bohdálková et al.,
383 2018). A rise is also visible in the Colle Gnifetti ice (More et al., 2017), but a 90-year gap starts just at
384 this particular age. Kern et al. (2021) attribute this Pb signal to a transition to small scale and local
385 mining operations across Europe, although atmospheric Pb-emissions and deposition were generally
386 reduced during this period (e.g. Forel et al., 2010). Yet, it is striking that neither records from the
387 Southern Alps (Segnana et al., 2020), nor south-west from our site (Thevenon et al., 2011), nor from
388 locations west and north-west of them (Vosges, Black Forest, Massif de Morvan, Swiss Jura), nor from
389 the Eastern Alps (Knierzinger et al 2020), show increased Pb EF or Pb_{anth} AR at that time (Forel et al.,
390 2010; Le Roux et al., 2005; Monna et al., 2004; Shotyk et al., 1998). Considering that the supra-regional
391 Roman Pb-signal is not very defined in our record, the distinct and synchronous Pb EF and AR signals
392 from 1500 to 1400 cal BP suggest an origin rather close to the Piller Moor. This period was a time of
393 warfare and territorial reorganisation, but the Central Alps were not in the centre of these conflicts
394 (Kulikowski, 2012). Late Antiquity silver mining in the Swiss Alps is, however, suggested by Guénette-
395 Beck et al. (2009) and regional Pb and Ag deposits around Imst (Gstrein, 2013), in the Austrian
396 Vorarlberg region (Hofmann and Wolkersdorfer, 2013), and in Tirol (Vavtar, 1988) could have made
397 parts of the Central Alps potential hotspot of Pb-emissions during this particular period.

399 4.6 Middle Ages to Postmodernity (Period 5 from 1400 cal BP to present)

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

406 The gradually declining MAR after 1000 cal BP coincides with glacier advances in the nearby Kauner
407 Valley (Nicolussi and Patzelt, 2000). Consequently, a lower MAR towards the early Modern Period
408 could have resulted from declining mountain farming in the Alps (Lichtenberger, 1965), which Bender
409 (2010) attributes to a cooler climate. In contrast, the MAR peak after 200 cal BP is associated with a
410 temporary surge of expanding local and regional agriculture and forestry. The forest at Kaunerberg (c.
411 5.5 km south of the mire) lost about 140 ha between 1774 and 1880 CE and losses up to 85 % are
412 documented in the nearby Radurschl, Pitz, Oetz and Paznaun valleys (Fromme, 1957). Thereafter,
413 documentation from 1850 to 1951 CE can explain the shrinking MAR: Agricultural yields and livestock
414 declined by 50 % and 40 % respectively (Fromme, 1957). The construction of a tourist infrastructure,
415 high voltage line poles and roads and the subsequent nature conservation measures possibly caused
416 the recent MAR-peak and its decline over the last few decades. Apart from this, the estimated average
417 MAR in this period ($3.94 \text{ g} \cdot \text{a}^{-1} \cdot \text{m}^{-2}$) is higher than in any of the previous periods.

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

425 **Metallurgy and pollution:** All EFs as well as a sharp rise of the Pb_{anth} AR indicate constant metallurgy
426 in the area after 1200 cal BP (750 cal CE), preceding first historical sources on Ag, Pb and Zn extraction
427 in the 12th century CE (Hanneberg et al., 2009; Wolkersdorfer, 1991) and the awarding of mining rights
428 in 1352 CE (von Srbik, 1929). An increasing Pb EF is also reported from other sites (e.g. More et al.,

429 2017; Segnana et al., 2020; Thevenon et al., 2011), which illustrates that the development was
430 supraregional and more distal sources likely contributed as well.

431 By 500 cal BP (1450 cal CE), strongly rising EFs (Pb and Sb) are in line with the introduction of a new
432 and more pollutive ore processing technology (Breitenlechner et al., 2013; Longman et al., 2020). A
433 link to intensifying silver mining around Imst (Hanneberg et al., 2009) and the Arlberg region (Haditsch
434 and Krainer, 1992), north and west of our record, is also likely. South of Piller in Platzertal (Platzer
435 Valley), Pb was mined and smelted from 1538 CE to 1900 CE (Vavtar, 1988). A climate induced
436 temporary abandonment of this mining site (1610–1888 CE) is synchronous with a decreasing Pb EF in
437 our record. In addition, regional mining was outcompeted by overseas' ores (Wolkersdorfer, 1991).
438 The recent maximum of Pb_{anth} AR (c. $30 \text{ mg} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$) and Pb EF (>300) are the result of leaded gasoline
439 emissions (Pacyna and Pacyna, 2001). The sharp drop in the late 1980s is the response to its stepwise
440 reduction and final ban across Europe. Compared to the maximum values in the Alpine Foreland (c. <6
441 $\text{mg} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$; Kern et al., 2021) and to the records summarised in Forel et al. (2010), which are the Black
442 Forest (c. $14 \text{ mg} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$), Jura (c. $14 \text{ mg} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$) and Vosges (c. 12 and $39 \text{ mg} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$), the maximum
443 Pb_{anth} AR in our record is mostly higher. Whilst the Pb_{anth} AR does not return to natural background
444 levels, it is within the upper range of Pb AR around $1 \text{ mg} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$ recently observed in Central Europe
445 (e.g. Kempter et al., 2010), yet, lower than values in the black triangle of Eastern Germany, Poland and
446 the Czech Republic (e.g. Zuna et al., 2011). Our Pb record is in good agreement with the history of
447 pollution in Central Europe. Its steep decline acts just as another time marker, which is confirming our
448 age depth model. Since our peat profile covers a longer time period, the estimated cumulative
449 anthropogenic Pb-deposition of c. $2.7 \text{ g} \cdot \text{m}^{-2}$ (Table 2) is slightly higher than in most of the Swiss peat
450 records summarised in Shotyk et al. (2000).

451

452 5. Conclusions

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

460 Our results suggest mining or metallurgy in the Central Alps between 4500 and 4200 cal BP, predating
461 any archaeological evidence in the area. Around 3400 cal BP, both mineral input and Pb_{anth} AR are
462 elevated synchronously with palynological and archaeological evidence for human activity. A strong

463 mineral input pulse at 2400 cal BP is simultaneous with proximate palynological and archaeological
464 indicators for heavy human landscape disturbance. Despite Roman presence in the Inn valley, their
465 direct impact at higher elevation seems to have remained small. Temporary but distinct increases of
466 Pb_{anth} AR and Pb EF from 1500 to 1400 cal BP strongly indicate post-Roman mining and metallurgy in
467 this part of the Central Alps, encouraging further research to locate potential sources in the area.
468 However, the anthropogenic impact was very weak in the Early Middle Ages before soil disturbance
469 and metallurgy resumed around 1200 cal BP and did not return to previous levels again. Our data
470 indicate early medieval mining operations, which predate historical documentation by several
471 centuries. While the LIA likely impaired regional agriculture, forestry and mining operations
472 episodically, the comparison of our record to historical documentation highlights the severe influence
473 of expanding forestry and agriculture on regional soil erosion and dust entrainment over the last
474 centuries. Over the last century, nearby peat extraction and construction, but also nature
475 conservation, seem to have influenced mineral and peat accumulation. The abrupt decline of Pb EF
476 and Pb_{anth} AR after the year 1980 CE acts as a time marker. In the form of quantitatively reconstructed
477 atmospheric input, geochemical signals found in our peat record from the Piller Moor mainly reflect
478 the development of local and regional human activities and their impact on the Alpine landscape over
479 the past 4800 years.

480 Author contributions

481 **Clemens von Scheffer:** Fieldwork, Investigation, Data curation, Writing- Original draft preparation,
482 Project administration, Visualisation, Conceptualisation, Methodology, Funding acquisition.: **Ingmar**
483 **Unkel:** Fieldwork, Conceptualisation, Supervision, Writing- Reviewing and Editing, Funding
484 acquisition.: **François De Vleeschouwer:** Conceptualisation, Methodology, Supervision, Writing-
485 Reviewing and Editing, Funding acquisition.: **Gaël Le Roux:** Supervision, Methodology, Writing-
486 Reviewing and Editing, Funding acquisition.

487

488 Data availability

489 Data is provided in the supplementary material and will be made available in the PANGAE online
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491

492 Declaration of competing interest

493 We declare that there are no conflicts of interest.

494

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511

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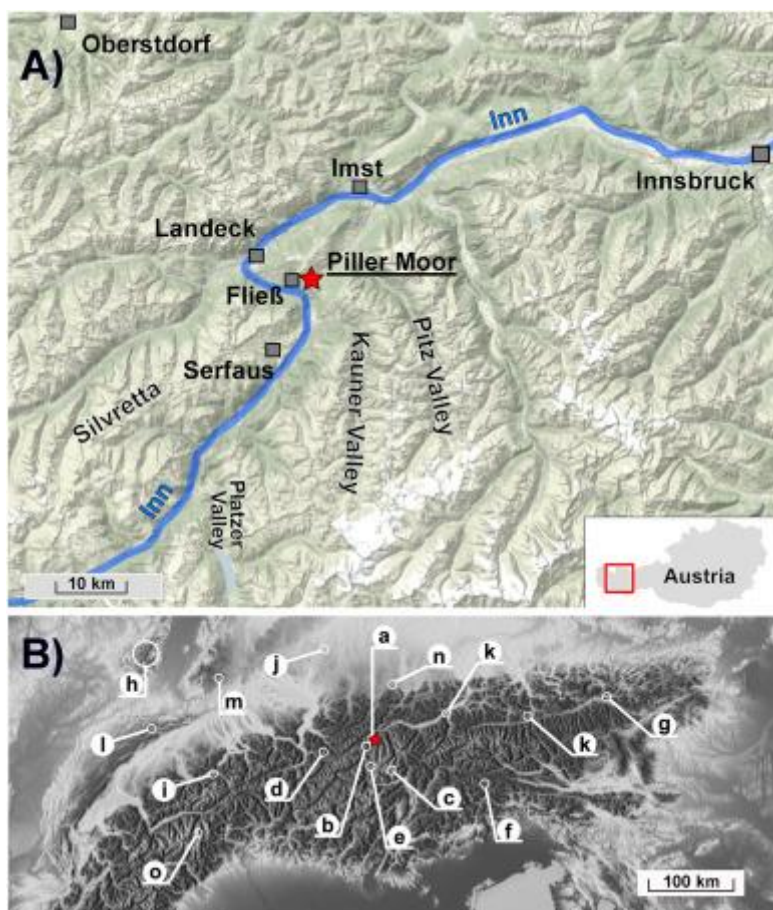
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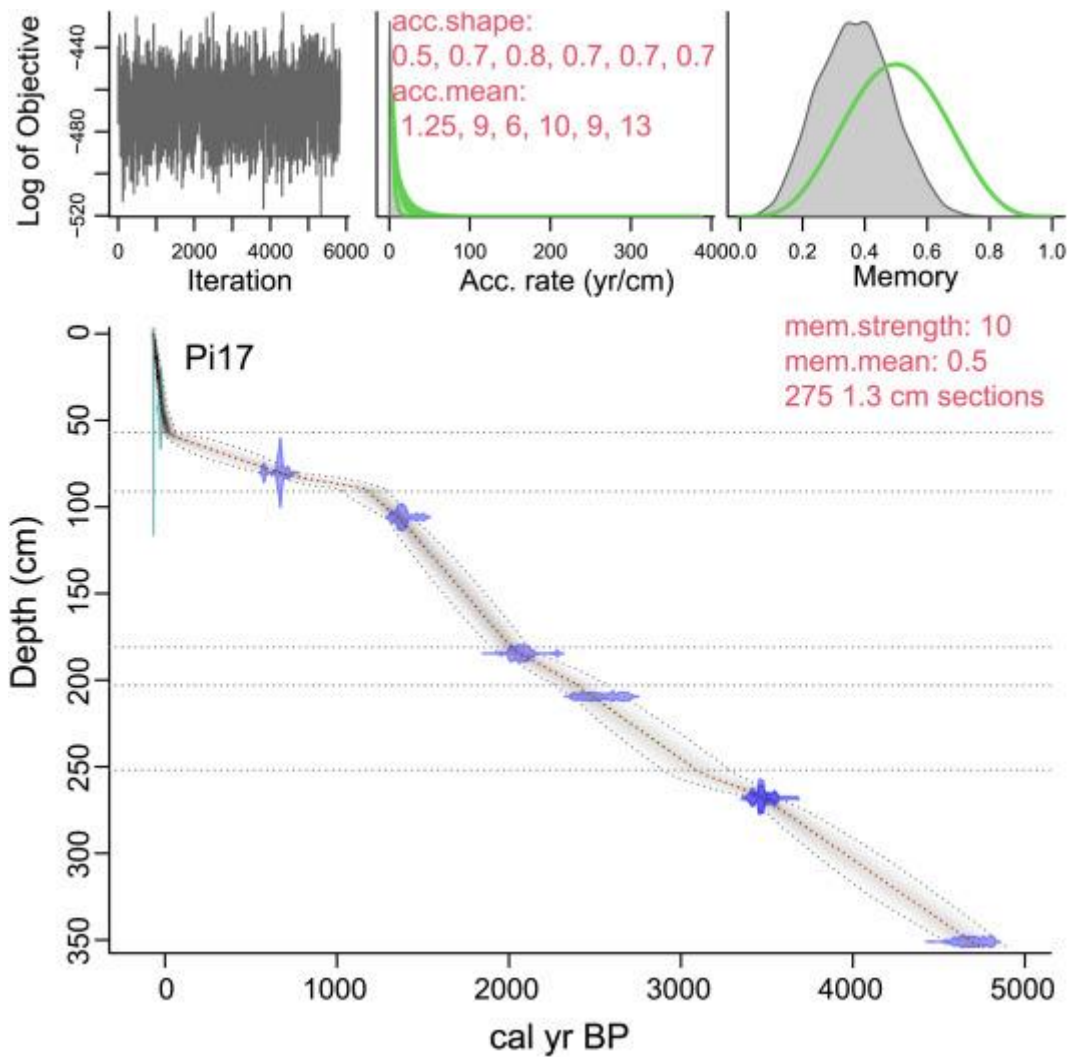
851 Figure 1: A) Northern Central Alps with study site (star). Edited from source: Stamen Design under CC-

852 BY-3.0 and OSM contributors under ODbL. B) Selection of references in discussion.

853 Palaeoenvironmental studies a) to d), metallurgy and Pb-accumulation e) to o). a: (Walde, 2006), b:

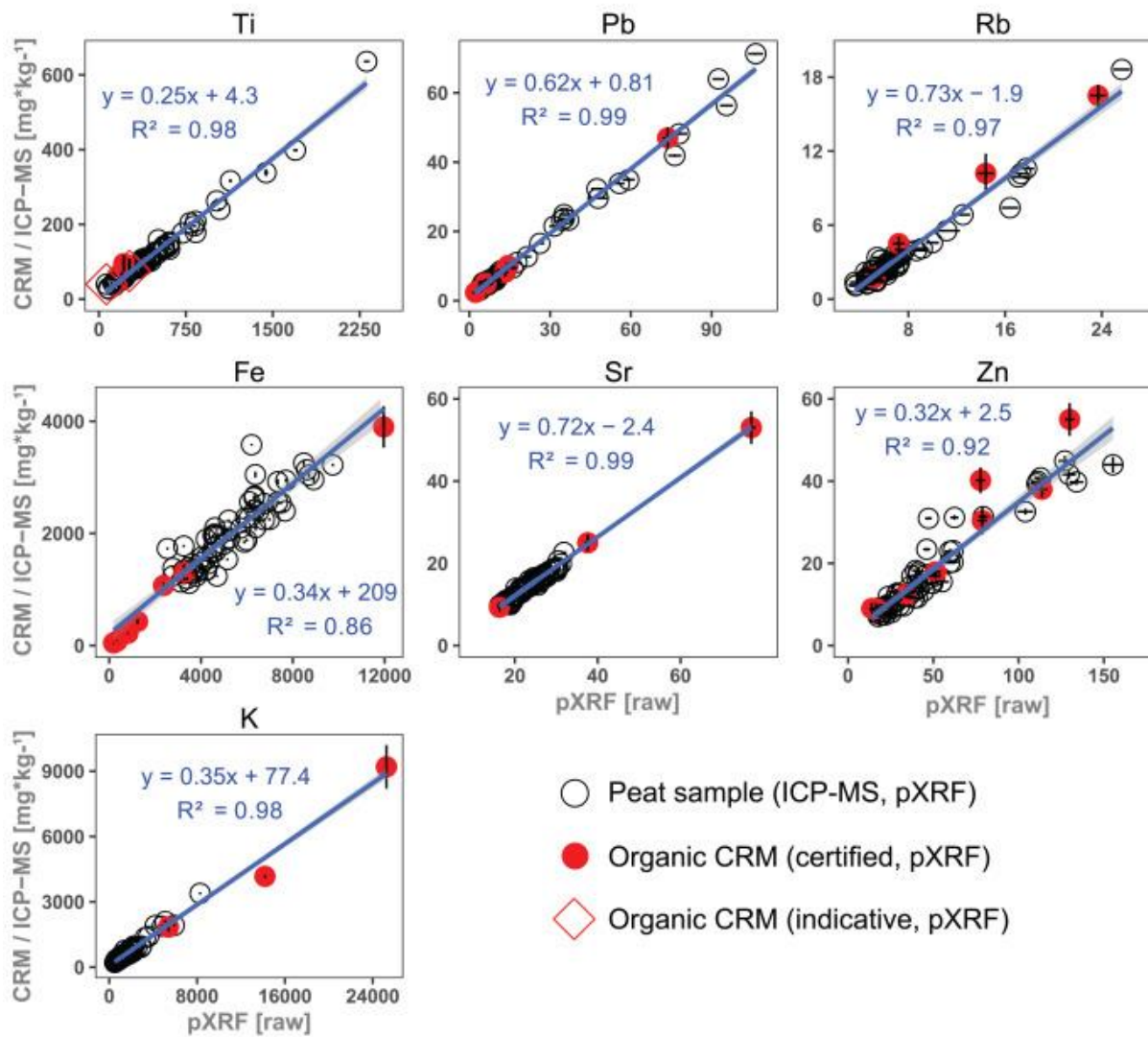
854 (Wahlmüller, 2002) , c: (Festi et al., 2014), d: (Röpke et al., 2011), e: (Vavtar, 1988), f: (Segnana et al.,

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 856 2021), k: (Stöllner, 2015b), l: (Shotyk et al., 1998), m: (Le Roux et al., 2005), n: (Kempster et al., 2010),
 857 o: (More et al., 2017); background map openstreetmap.org, OSM contributors under ODbL.



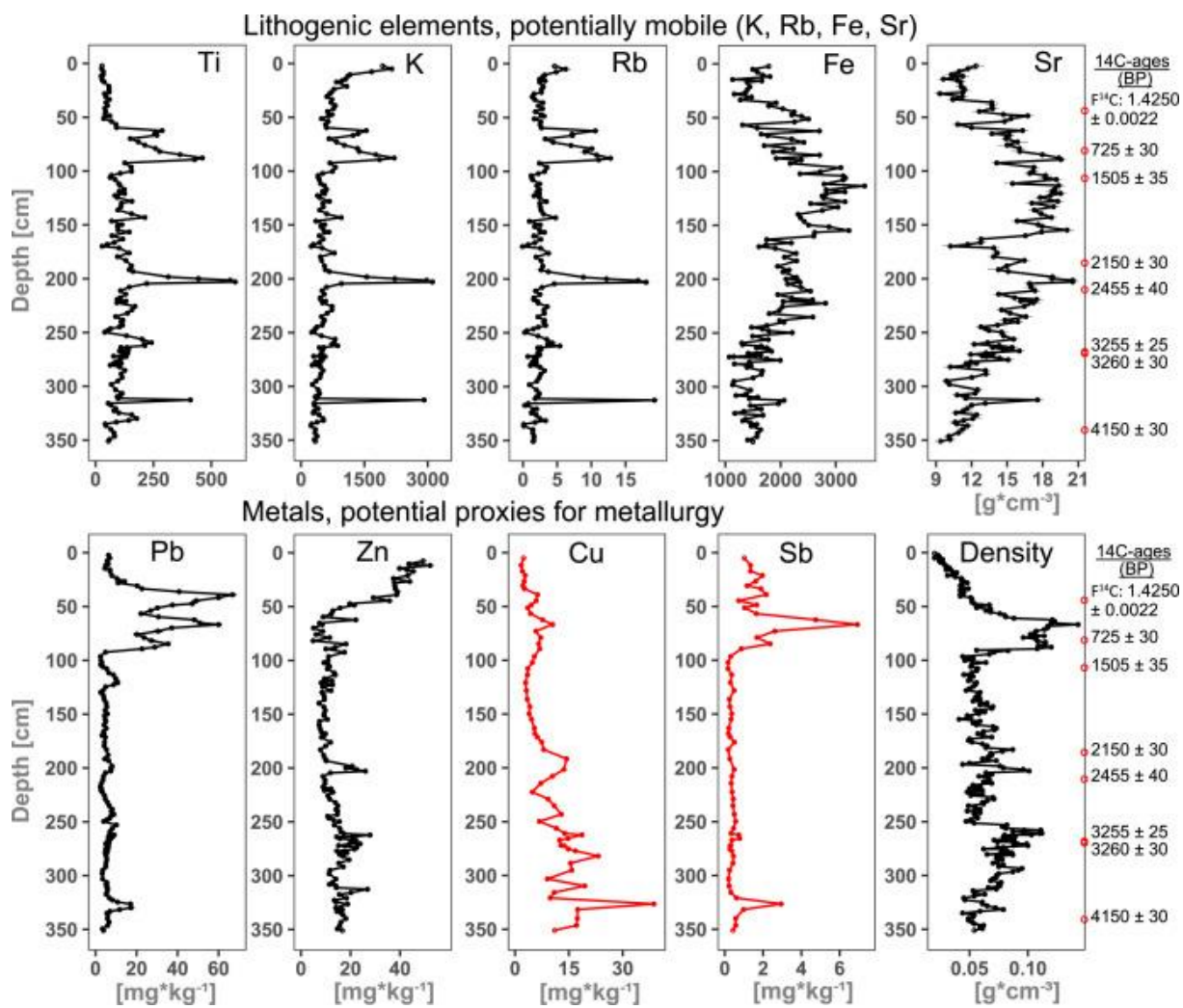
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859 Figure 2: ADM of Pi17 composite core. Grey shaded area=95% within dotted line is the confidence
 860 interval. Dotted line in confidence interval is the median age. Dotted horizontal lines are boundaries
 861 between changes in core characteristics.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



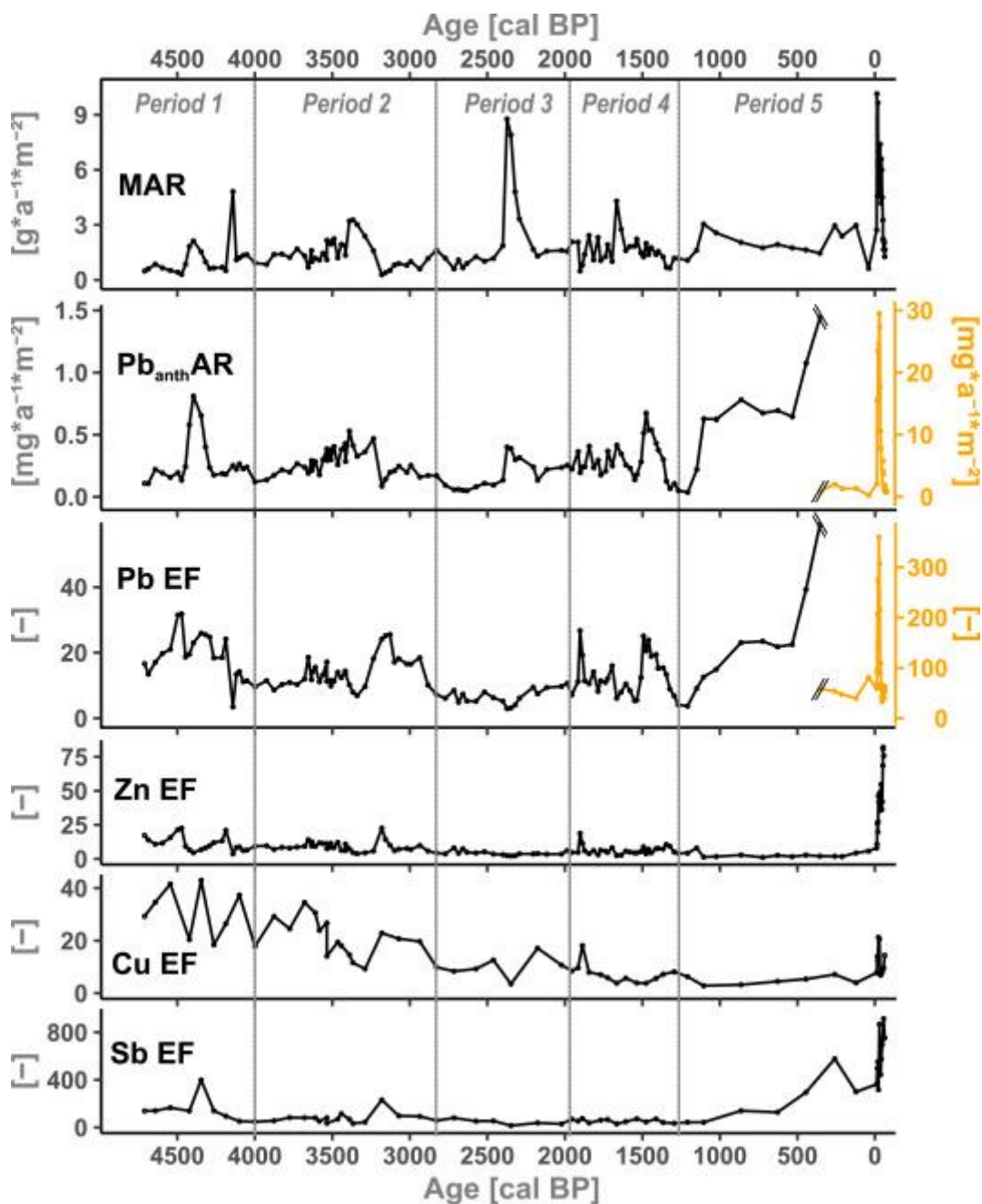
863

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



867

868 Figure 4: Piller Moor profiles of elements measured by pXRF (in black) and ICP-MS (in red) and dry bulk
 869 density. $F^{14}\text{C}$ and ^{14}C -ages (cal BP) given on the right.



870

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

876

877

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

880 core A.

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

881

882 Table 2: Synthesis of model estimates for approximates of average mineral and Pb_{anth}-accumulation
 883 rates and for the approximate cumulative deposition of Pb_{anth} within the periods 1 to 5 and in the most
 884 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

885