Multi-proxy analyses of a minerotrophic fen to reconstruct prehistoric periods of human activity associated with salt mining in the Hallstatt region (Austria)

Wolfgang Knierzinger a, *, Daniela Festi b, Andreas Limbeck c, Felix Horak c, Lukas Brunnbauer c, Simon Drollinger d, Michael Wagreich a, Jyh-Jaan Steven Huang e, Michael Strasser e, Klaus-Holger Knorr f, Hans Reschreiter g, Susanne Gier a, Werner Kofler h, Christopher Herzig c, Kerstin Kowarik g

a Department of Geology, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria
b Institute for Interdisciplinary Mountain Research, Austrian Academy of Science, Technikerstrasse 21a, 6020 Innsbruck, Austria
c Institute of Chemical Technology and Analytics, Technical University Vienna, Getreidemarkt 9, 1060 Vienna, Austria
d Department of Physical Geography, University of Göttingen, Goldschmidtstrasse 5, 37077 Göttingen, Germany
e Institute of Geology, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria
f Institute of Landscape Ecology, Ecphydology and Biogeochemistry Group, University of Muenster, Heisenbergstrasse 2, 48149 Muenster, Germany
g Natural History Museum, Vienna, Burgring 7, 1010 Vienna, Austria
h Institute of Botany, University of Innsbruck, Sternwartestraße 15, 6020 Innsbruck, Austria

ARTICLE INFO

Keywords:
Peat
Geochemistry
Trace elements
Bronze age
Iron age
Alps

ABSTRACT

In this study, periods of prehistoric anthropogenic activity in the Hallstatt salt mining area (Upper Austria) are reconstructed from elemental (XRF-scanning, Q-ICP-MS) and Pb isotopic analyses ($^{206}$Pb/$^{207}$Pb, $^{208}$Pb) of a radiocarbon-dated, 137-cm-long peat core covering the past ~7,000 years. The peat core was retrieved from a minerotrophic fen in the Hallstatt High Valley. Distinct metal enrichments attributed to low anthropogenic impact in Hallstatt can be traced back to a time around 2350 cal BCE and to another period around 1800 cal BCE. The period from the Late Bronze Age to the Early Iron Age (~1300 cal BCE to ~500 cal BCE) is characterised by increased anthropogenic activity. Relatively high Sn concentrations between ~1210 cal BCE and ~540 cal BCE) point towards intensive bronze casting processes, probably associated with the production of bronze picks that were used for local salt mining during this time. Intense human impact was also determined for the early Roman imperial period (1st century BCE – 2nd century CE). Increasing Pb and Sb concentrations and a marked decrease of $^{206}$Pb/$^{207}$Pb ratios in the uppermost fen layers are attributed to rising industrialization processes in the modern period. Even though peaks of the trace elements Pb, Sb, Cu and Sn do not always correspond directly to anthropogenic activity, a combination with erosional, archaeological and palaeovegetational records enables a relatively accurate and reliable interpretation of prehistoric human impact at Hallstatt.

1. Introduction

To assess the role of raw material extraction in the evolution of mountainous landscapes and human land use a thorough understanding of the human-environment interaction in its scale and chronology is required. The UNESCO World Heritage area Hallstatt-Dachstein/ Salzkammergut, situated in the Upper Austrian Northern Calcareous Alps, is considered one of the oldest and most continuously used mining areas and salt production centers in Europe (Harding, 2013; Reschreiter and Kowarik, 2019). Underground salt mining at depths of up to 170 m has been ascertained, dating back as far as the 14th century BCE (Stadler, 1999; Reschreiter, 2013). Prehistoric mining phases are attested for the Bronze Age, the early Iron Age and the late Iron Age (Barth and Lobisser, 2002; Reschreiter, 2013). The archaeological record evidences extensive Roman settlement activity, but no traces of mining are known at this time (Igl, 2009). Written sources date the beginning of medieval
salt mining at latest to 1311 CE and attest a continuous salt mining activity throughout the medieval and modern period (Urštger, 2000).

The earliest hints of human presence in the Hallstatt region can be traced back to the early Neolithic (Reschreiter and Kowarik, 2019). Permanent mining in the Mitterberg region, probably the most important copper production region in Europe in the 2nd millennium BCE (Pichler et al., 2018), located approximately 35 km southwest of Hallstatt, started around 2000 BCE (Stollner, 2011; Breitenlechner et al., 2014). Multifaceted relations between the Mitterberg region and Hallstatt during the Bronze and Iron Ages are probable (Stollner et al., 2016). Due to the excellent preservation conditions inside the salt mountain and substantial archaeological sites on the surface close to the mining areas working and living conditions, mining technology and the scale of the mine workings in Hallstatt are well known (Reschreiter and Kowarik, 2009, 2019). However, palaeoenvironmental investigations have not been carried out until very recently in the region and the environmental impact of the mining activity was poorly understood (Festi et al., 2021). With regard to the Chalcolithic Europe, intense mining activity is known to have taken place in Tyrol (Barthelheim et al., 2002; Tröpper et al., 2017), northern Iberia (Martínez-Cortizas et al., 2016), Eastern Serbia (Jovanović, 2009) and Bulgaria (Jovanović, 2009). Palaeoenvironmental studies indicate that metal pollution in Europe increased markedly in the Bronze Age (e.g. Brannvall et al., 2001; Monna et al., 2004a; Mighall et al., 2009; Longman et al., 2018). Reconstructions of past atmospheric pollution have been conducted using different environmental archives, such as lakes (e.g. Brävnall et al., 2001), ice (e.g. McConnell et al., 2018) and peatlands (e.g. Shotyk, 2002). On a general level, this study aims to gain a better understanding of the chronology of prehistoric societies and their palaeoenvironments in the Hallstatt region by investigating trace metalloid/s (Cu, Sn, Sb, Pb), commonly associated with anthropogenic activity (see also Shotyk et al., 2004; Delgado et al., 2012; Martínez-Cortizas et al., 2016), in combination with erosional and palaeo-vegetational proxies in a peat core sequence of a minerotrophic fen (Siegmoos).

Compared to ombrotrophic bogs (e.g. De Vleeschouwer et al., 2007) the behavior of trace elements in minerotrophic fens is more variable, due to the connection to groundwater and concomitant alterations of redox conditions and a higher biological diversity (Krumins et al., 2011; Griffiths and Sebestyen, 2016). Despite this fact, Pb and Sn enrichments in fens can provide highly relevant information on anthropogenic emissions, as has been shown by different studies (e.g. Shotyk, 2002; Monna et al., 2004b; Mighall et al., 2009; Breitenlechner et al., 2014; Hanson et al., 2017). In the context of palaeoenvironmental research, enrichments of Pb might also indicate increased combustion of wood (Kabata-Pendias and Pendias, 2001; Eby, 2004).

While Rothwell et al. (2010) and Novak et al. (2011) speak of a high immobility of Cu in ombrotrophic peat environments, the potential of Cu as a tracer element for human impact in minerotrophic peatlands is considered controversial (e.g. Rausch et al., 2005; Takahashi et al., 2012), as Cu has been found to be mainly associated with organic matter in fens (Krumins et al., 2011). Nevertheless, several studies have shown that Cu has strong potential as an anthropogenic tracer in minerotrophic wetlands (e.g. Breitenlechner et al., 2014; Mariet et al., 2016). Even though the geochemical behavior of Sn in wetlands has not received much study, Sn enrichments in ombrotrophic peat bogs have been successfully used to infer local past mining activities (Meshag et al., 2012). Because of a lack of Sn deposits and Sn-bearing minerals in the Northern Calcareous Alps (Penchullrich, 1986; Pirkl et al., 2015), peaks of Sn might indicate local bronze production or metal casting processes (see also Kazenas et al., 1996, Beigemann et al., 1999). The cation-exchange capacity of soil and peat is strongly interrelated with humic substances (Blume et al., 2016). Diverse peat decomposition proxies have been suggested and discussed by different authors (e.g. Chambers et al., 2010; Biester et al., 2013; Hanson et al., 2013; Drolinger et al., 2019, 2020).

In this study, Fourier transform infrared (FTIR) spectroscopy analyses of peat material are performed to assess the the humification degree and to contextualize elemental results obtained by XRF and ICP-MS (see Section 4.3).

European Pb isotope ratios have been influenced by anthropogenic activity for thousands of years (e.g. Shotyk, 1998; Brannvall et al., 2001; Wagreich and Dragantis, 2018). Considering the relative proximity to the Mitterberg region and the predominant westerly winds in the region, a clear separation between local and regional geochemical signals at Hallstatt is essential. Pb isotope measurements are conducted to establish a time-depth trend throughout the core, enabling an illustration of chronological changes of the isotope signature, and thus a separation between to between local Pb isotope signals and non-local signals.

Here, we hypothesize that (bio)geochemical signals in combination with palynological and archaeological results reflect the onset, chronology and type of anthropogenic activity in the Hallstatt High Valley. This study tries to establish a better understanding of the geochemical impact of prehistoric large scale underground salt mining in an alpine setting and to provide valuable empirical data, upon which further discussions on the evolution of human settlement in the Alpine region can be based (see also e.g. Driete et al., 2017; Festi et al., 2011, 2014, 2021; Knierzinger et al., 2020; Putzer et al., 2016; Segnana et al., 2020; von Scheffer et al., 2019). In this context, our analyses aim to clarify whether extended prehistoric bronze casting processes (Kazenas et al., 1996; Beigemann et al., 1999) in the Hallstatt High Valley have taken place and whether geochemical signals capture regional copper metallurgy.

Generally, the main focus lies on the chronological reconstruction of anthropogenic activity in the Hallstatt region during the Bronze and Iron Ages. Thus, a rigorous examination of anthropogenic pollution during medieval times and the modern period in Hallstatt is not object of the present study.

2. Material and methods

2.1. Sample location

The study site Siegmoos (a sub-neutral meso-eutrophic lowland mere) is situated in the Hallstatt High Valley (Austria) at an altitude of ~ 1100 m a.s.l. and comprises a laterally continuous peat body with a thickness of approximately two meters. The nearby prehistoric salt mines of Hallstatt are located within the upper Permian to lower Triassic Haselgebirge Formation of the Northern Calcareous Alps (Schorn and Neubauer, 2014). This formation mainly occurs in Juvacic tectonic units of the central and eastern Northern Calcareous Alps, characterised by a mixture of evaporites and shales (Schorn et al., 2013). A ~ 150-cm-long peat core was extracted at Siegmoos (N 47°33′38.35″; E 13°37′57.30″) by means of a hard plastic tube of 10 cm in diameter in May 2011. Subsequently, the core was stored in a cooling chamber at ~4 °C. The sample location is close to prehistoric mining shafts associated with the Bronze Age and the Iron Age (Fig. 1).

Considering archaeological findings and the available palynological and geochemical data regarding Hallstatt and adjacent regions (see Sections 1 and 4.1), the large majority of the samples were retrieved from the depth section of 50–85 cm, corresponding to a time from the Late Iron Age to the Early Bronze Age.

Sample names denote information on the specific depth from which they were retrieved (e.g. S74 was taken at a depth of 74 cm below the surface).

2.2. Radiocarbon dating

Radiocarbon dating of 12 wood and bulk peat samples was performed at Beta Analytic INC, Florida and calibrated using BetaCal 3.21. Bayesian radiocarbon models were obtained by rbacon (version 2.2; see Blauuw and Christen, 2011), which is based on IntCal13 (Reimer et al., 2013). Radiocarbon calibration was independently checked with the aid of OxCal (Version 4.3.2/Bronk Ramsey, 2017).
2.3. Elemental analyses

Elemental analyses of the first 137 cm of the peat core were performed by using a COX Analytics ITRAX XRF core scanner (CS-45, Austrian Core Facility, University of Innsbruck; see also Chawchai et al., 2015; Longman et al., 2019). Due to a strong increase of mineral matter in the lower part, no elemental analyses of the lowermost 13 cm of the core were carried out. XRF results correspond to counts and are considered semi-quantitative (Croudace et al., 2006; Huang et al., 2016a; operating settings are detailed in the Appendix Table J).

A reduction of the original data was performed by discarding elements that showed low determination coefficients ($r^2 < 0.7$) between two duplicate measurement runs and low average scanning intensities. The following elements were considered reliable for scientific
digestion experiments in the laboratory, an acid mixture of 4 ml HNO₃, 2 ml HCl (37%; Emsure®), 0.1 ml HF (48%; Emsure®) was found to be most appropriate for complete digestion of the minerotrophic peat samples. After digestion, the samples were transferred into sample vessels, filled up to 50 ml with high purity deionized water and subsequently further diluted for elemental analysis. Calibration standards from 1 μg ml⁻¹ to 100 μg ml⁻¹ were prepared using the ICP multi-elemental standard solution VIII certipur® (Merck Darmstadt, Germany), the ICP multi-elemental standard solution IV certipur® (Merck Darmstadt, Germany) and a zirconium ICP standard certipur® (Merck Darmstadt, Germany). Indium (¹¹⁵In) was used as an internal standard for correction of remaining effects and/or instrument drifts. All measurements were blank-corrected. Differences in sample introduction efficiency, due to variations of surface tension or viscosity, and differences in sample atomization and excitation efficiency, due to variations in the plasma load, were minimal. Concentrations after dilution of the sample digests were only in the range of micrograms per litre to milligrams per litre.

Ti (XRF) and Zr were used as conservative elements for normalization purposes. For further information on the potentials of conservative elements in peat archives see Kylander et al. (2016). The interpretation of anthropogenic activity is based on relative enrichments in the core sections. Due to complete acid digestion and strongly increasing mineral matter in the lower part of the core, no additional analysis of a certified reference material with a biological matrix was conducted (see also Krachler et al., 2002; Breitenlechner et al., 2014).

In total, ICP-MS elemental analysis of 40 samples, mainly corresponding to the Bronze and Iron Ages, were performed. Sample S68 was contaminated and could not be included in the analysis. Due to logistical inhomogeneity within the core, no enrichment factors (e.g. Kylander et al., 2006) were calculated. Instrumental settings are detailed in Appendix K.

2.4. Ash contents

The ash contents (precision balance PLS 510-3/Kern & Sohn, Balingen-Frommern, Germany) of the sample material were determined by burning peat samples at 550 °C for 10 h in a muffle furnace. By comparing the sample dry weight (>0.6 g) with the weight of the residual ash, the percentage of the ash content concerning the dry weight of the sample was calculated (e.g. Tolonen, 1984).

2.5. Fourier transform infrared spectroscopy

FTIR spectra were recorded with a Cary 660 FTIR spectrometer (Agilent, Santa Clara, CA, USA) at the Institute of Landscape Ecology in Münster, Germany. 2 mg of powdered sample were mixed with 200 mg KBr (FTIR grade, Sigma Aldrich, St. Louis, MO, USA) and pressed to a 13 mm pellet. Overall, 32 scans per sample were performed and combined with a subtraction of the KBr background. As sorption effects of humified substance regarding trace metals in Siegmoos were found to be negligible, FTIR results will not be discussed in detail here but are provided in the supplementary material (see also Fig. 5).

2.6. Pb isotope measurements

Stable Pb isotope measurements were performed on 30 samples (again, mainly corresponding to Bronze and Iron Ages) by using the iCAP Qc ICP-MS system described in Section 3.2. Despite the fact that thermal ionization (TIMS) or multi-collector plasma mass spectrometry (MC-ICP-MS) provide higher analytical precision (e.g. Guillon et al., 2018), the Q-ICP-MS technique was deemed sufficient for the purpose of this study (e.g. Mihaljevic et al., 2002; Judd and Swami, 2010; see also interpretation in Section 5.1). The correction of isobaric interference between ²⁰⁸Hg and ²⁰⁶Pb was applied by monitoring the signal of ²⁰⁸Hg. For performance verification and correction of instrumental drifts, the Pb ICP Standard certipur® (Merck, Darmstadt, Germany), traceable to standard reference material (SRM)@NIST 928 Pb, served as bracketing standard. We characterised this standard using the certified reference material ERM-EB 400 (Federal Institute for Materials and Research Testing, BAM).

Standard solutions of 3 μg l⁻¹ and 10 μg l⁻¹ were prepared from dilutions of the standard stock solution (1000 mg l⁻¹). The previously prepared 50 ml liquid samples were adequately diluted (up to 1:50) to guarantee a high degree of comparability. The raw Pb isotope ratios obtained from the measured samples were corrected for contributions of Hg, spikes and blanks. In a subsequent step, the isotope ratios were corrected for isotopic fractionation based on the bracketing standard measurements. Due to complete acid digestion and high dilution factors significant matrix effects were considered negligible. The sample selection, including samples with relatively high organic content (uppermost section) and mineral-rich samples with relatively low organic content (lowermost section), provided an additional quality check on data consistency. The great concurrence between those sections regarding Pb isotopes (see also Sections 4.3 and 5.1) further illustrates the reliability of the analyses. The accuracy was tested using the certified reference material ERM-EB 400. It varied between 1.71% and 1.78% for ²⁰⁶Pb/²⁰⁴Pb, 0.80% and 0.90% for ²⁰⁶Pb/²⁰⁷Pb, 0.84% and 0.88% for ²⁰⁷Pb/²⁰⁸Pb.

2.7. Statistics and additional software

Principal component analyses (PCA) were conducted by means of Past (version 3.21) to illustrate differences between specific time periods characterised by varying anthropogenic activity. Prior to PCA, Box-Cox transformations were applied for normalisation of data and stable variance throughout the data set (Box and Cox, 1964). A further standardisation of the data set was achieved by using a correlation matrix of the transformed data. Peat samples with concentrations below the detection limit were discarded for PCA. The analysis was carried out using ICP-MS data (Cu, Sr, Zr, Sn, Sb and Pb), the Mo Inc/Coh ratio, the FTIR humification proxy and the ash contents of 28 samples.

Geographical and geological maps were created with the aid of QGIS (version 3.0 Girona) and CorelDRAW X8.

3. Results

3.1. Age modeling, elemental analysis (XRF) and ash contents

Radiocarbon dates of samples taken at specific locations between 23.5 cm and 120 cm below the surface are shown in Table 1. The Bayesian chronological model is shown in Fig. 2 (see also Appendix C).

In the uppermost 15 cm of the Siegmoos core, enhanced concentrations of Fe, Mn and Zn prevail (Fig. 3). While Si and Sr do not show distinct trends throughout the greater part of the uppermost section and the middle section of the core, the lowermost section of the peat core...
starting at about 96 cm (~2530 cal BC) is characterised by sharp increases of all elements except Mn and a decrease of Mo Inc/Coh. The intensity curves of Ti and Rb exhibit peaks at the depth section 67 – 69 cm (~1020 cal BC to ~1140 cal BC). The ash content of the peat core undergoes considerably large fluctuations, reaching its highest values at the very bottom at 136 cm with ~ 88% and its lowest values at 30 cm with ~ 13%. The Mo Inc/Coh and Ti profiles obtained from the XRF data set show a strong negative correlation ($r = 0.84$).

A similar relationship between Mo Inc/Coh and the ash content ($r = 0.85$) was noted (see Appendix B). A general increase of the ash content in the lower section is associated with increases of Si, Ca, K, Ti, Fe, Rb, Sr and Zn. Increasing Ti and Rb intensities in the middle section of the core are concurrent with higher ash contents and a lower Mo Inc/Coh ratio in the 63 – 68 cm interval, corresponding to the Late Bronze Age.

Decreases of various element concentrations (Si, Ca, K, Ti, Fe, Sr and Rb) at specific points in the Chalcolithic at 102 cm and 124 cm coincide with slightly elevated Mo Inc/Coh ratios.

### 3.2. Trace elemental analysis (ICP-MS)

The uppermost sample taken at a depth of 1 cm shows high concentrations of Pb (164.52 mg kg$^{-1}$) and Sb (4.68 mg kg$^{-1}$). Higher Pb concentrations were only found in S10 (170.46 mg kg$^{-1}$; Sb = 3.33 mg kg$^{-1}$). Other samples of the uppermost section of the core (S15; S17) corresponding to the modern period, are also characterised by relatively high concentrations of Pb (16.20 mg kg$^{-1}$ – 98.47 mg kg$^{-1}$) and Sb (0.64 mg kg$^{-1}$ – 1.97 mg kg$^{-1}$). In comparison with adjacent samples corresponding to pre-modern times (below S17; $\bar{\text{Pb}} = 11.04$ mg kg$^{-1}$; $\bar{\text{Sb}} = 0.46$ mg kg$^{-1}$), the normalised Pb value (n. Pb) reaches distinct peaks at the depths of 45 cm, 52 cm, 58 cm, 62 cm and 79 cm. At these depths and additionally also at 92 cm, similar enrichments were found for the

### Table 1

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Lab code</th>
<th>Material (Picea abies)</th>
<th>Conventional Age (yr BP)</th>
<th>Calibrated Age 2s range yrs cal AD/BC</th>
<th>Age in diagram Yr Cal BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.5</td>
<td>Beta-488389</td>
<td>wood</td>
<td>900 ± 30</td>
<td>1039–1210 CE</td>
<td>825</td>
</tr>
<tr>
<td>28</td>
<td>Beta-507266</td>
<td>sediment</td>
<td>1290 ± 30</td>
<td>664–770 CE</td>
<td>1233</td>
</tr>
<tr>
<td>35</td>
<td>Beta-488390</td>
<td>sediment</td>
<td>1600 ± 30</td>
<td>398–339 CE</td>
<td>1482</td>
</tr>
<tr>
<td>45</td>
<td>Beta-481518</td>
<td>sediment</td>
<td>1730 ± 30</td>
<td>242–386 CE</td>
<td>1636</td>
</tr>
<tr>
<td>50</td>
<td>Beta-507267</td>
<td>sediment</td>
<td>2230 ± 30</td>
<td>328–204 BCE</td>
<td>2215</td>
</tr>
<tr>
<td>55</td>
<td>Beta-496547</td>
<td>sediment</td>
<td>2300 ± 30</td>
<td>407–356 BCE</td>
<td>2331</td>
</tr>
<tr>
<td>65</td>
<td>Beta-496548</td>
<td>sediment</td>
<td>2760 ± 30</td>
<td>980–830 BCE</td>
<td>2854</td>
</tr>
<tr>
<td>70</td>
<td>Beta-507268</td>
<td>sediment</td>
<td>3060 ± 30</td>
<td>1411–1257 BCE</td>
<td>3283</td>
</tr>
<tr>
<td>75</td>
<td>Beta-481517</td>
<td>sediment</td>
<td>3300 ± 30</td>
<td>1643–1504 BCE</td>
<td>3523</td>
</tr>
<tr>
<td>94</td>
<td>Beta-487261</td>
<td>wood (Picea abies)</td>
<td>3940 ± 30</td>
<td>2496–2338 BCE</td>
<td>4366</td>
</tr>
<tr>
<td>103.5</td>
<td>Beta-487262</td>
<td>wood (Picea abies)</td>
<td>4390 ± 30</td>
<td>3092–2918 BCE</td>
<td>4954</td>
</tr>
<tr>
<td>120</td>
<td>Beta-481516</td>
<td>wood (Picea abies)</td>
<td>5020 ± 30</td>
<td>3822–3710 BCE</td>
<td>5715</td>
</tr>
</tbody>
</table>

### Fig. 2

Age-depth model of the Siegmoos peat core based on Bayesian statistics combining the radiocarbon dates and the surface date of the core (i.e. 2011) produced with R package Bacon (Blaauw and Christen, 2011). Dates are represented in blue; the grey area displays the 95% confidence interval. The graphs at the top display the number of Markov chain Monte Carlo iterations (left) used to generate the age-depth model, the prior (green) and posterior (gray) distributions of accumulation rates (center) and memory (right). See also Blaauw and Christen (2012).
Fig. 3. XRF intensity (ITRAX counts) diagram comprising the elements Si, Ca, Ti, Fe, Mn, Sr, Rb, Zn, the Mo Inc/Coh ratio and the ash content. Intensity curves are based on every tenth data point (0 cm–137 cm; n = 138). The chronology of the core and of the stratigraphy (a–e) relies on a Bayesian model based on IntCal13 (Reimer et al., 2013; see also Appendix C). K, strongly correlated with Ti, was considered reliable for scientific interpretation but was not integrated into the diagram.
normalised Sb (n. Sb) curves (Fig. 4). Both the n. Pb curve and the n. Sb curve show a significant average increase above a depth of 70 cm. This increase corresponds to the palynological index (Festi et al., 2021). The prominent bulge in the ash content curve (see Fig. 3). The depth interval ranging from 84 to 90 cm displays the lowest n. Pb and n. Sb values of the core.

The highest Zr concentration (82.38 mg kg$^{-1}$) was measured in the uppermost sample, S1, exceeding concentrations of lower samples by a factor of up to ~7 (12.03 mg kg$^{-1}$ at a depth of 50 cm). Pearson’s correlation coefficient (r) highlight a strong positive correlation between the Zr concentration and the ash content (see Fig. 3). The depth interval ranging from 84 to 90 cm displays the lowest n. Pb and n. Sb values of the core.

In addition to the uppermost part, the n. Sn curve shows peaks at 40 cm, 47 cm, 52 cm, 59 cm, 63 cm, 64 cm, 65 cm, 75 cm and 82 cm. Apart from these peaks, an increasing trend above a depth of about 70 cm is obvious. S33 and S55 exhibit relatively low concentrations of Pb (7.3 mg kg$^{-1}$). Sb (0.35 mg kg$^{-1}$), Cu (13.2 mg kg$^{-1}$), and Zr (12.03 mg kg$^{-1}$). The highest Sn concentration in a sample that does not correspond to the modern period was measured at 59 cm (3.54 mg kg$^{-1}$). Cu peaks at 63 cm (158.91 mg kg$^{-1}$). A general increase of the absolute concentrations of all measured trace elements below S100 does not coincide with the calculated enrichments for the lowermost section: n. Sb only shows a peak at 105 cm, n. Cu, n. Sn and n. Pb do not display any enrichments in this section.

### 3.3. Principal component analysis

The first three principal components (PC 1–PC 3) account for 83.6% of the total variance (see Appendix H).

PC 1 is characterised by positive factor loadings of variables that account for the geogenic input (ash content = 0.86; Zr = 0.81; Sr = 0.79). In the case of the minerotrophic Siegmoos, this geogenic input is related to atmospheric influence, runoff water and other post-depositional processes (Fig. 5). High scores of PC 1 are concurrent with a higher ash content and increasing conservative elements (Ti, Rb and Zr) in the middle (~780 cal BCE to ~1210 cal BCE) and lower sections (~2720 cal BCE to ~5000 BCE) of the core.

In contrast, factor loadings of PC 2 are predominantly related to Pb (0.93), Pb (0.89) and Sn (0.63), which can be attributed to anthropogenic activity in the High Valley or in the local surroundings.

PC 3 is mainly characterised by variables associated with lithogenic input, runoff water and vegetation (Sn = 0.56; Sr = 0.50; Mo Inc/Coh = 0.42). The scores of PC 3 suggests that a relevant proportion of Sn, unlike Pb and Sb, is also related to geogenic and biological sources.

PCA of the XRF data set is provided in Appendix M.

### 3.4. Pb isotopes

Clear temporal trends can be identified for the ratio$^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{206}$Pb and $^{207}$Pb/$^{206}$Pb, displaying continuously decreasing and increasing values, respectively, up to the uppermost sample S1 (Table 2; see also Appendix G). This allows for a proper differentiation of samples at the base from younger samples in the middle section and more recent samples in the uppermost part of the mire. Correlations between the total Pb concentrations and the Pb isotope ratios of the analysed peat samples vary considerably, ranging from −0.73 (Pb vs. $^{206}$Pb/$^{208}$Pb) to 0.73 (Pb vs. $^{207}$Pb/$^{206}$Pb).

---

1 This depth interval was chosen because ash contents are similar to the uppermost section and because it was presumably not exposed to significant anthropogenic influence.

2 r of Zr was calculated without considering S1.
4. Discussion

4.1. Local and non-local effects on the Pb isotope signature

Starting with the transition from the late Roman period to the Middle Ages (from S40 upwards), Pb isotopic ratios change more progressively towards the surface. The isotopic composition of the uppermost peat sample (S1) is in good accordance (Fig. 5) with Pb isotope ratios of recent industrial activities and leaded gasoline (Monna et al., 1997; Chiaradia and Cupelin, 2000; Wu et al., 2010; Gallon et al., 2011; Pinedo-González et al., 2018).

Fig. 5. Principal component analysis (PCA) of the ICP-MS data set (Cu, Sr, Zr, Sn, Sb, Pb), Mo Inc./Coh, humification and the ash content. PC 1 and PC 2 denote the first and second principal component, respectively. Numbers of colored circles between 1 and 136 refer to the depth section (in cm). While PC 1 is predominantly related to the ash content, Zr and Sr, PC 2 is mainly influenced by Pb, Sb and Sn. PC 1 accounts for 43.0% and PC 2 accounts for 27.2% of the total variance. The humification index was approximated by calculating the ratio between the peak intensity at 1630 cm\(^{-1}\) (indicative of lignin and other aromatics) and at 1030 cm\(^{-1}\) (indicative of polysaccharides such as cellulose; see also Holmgren and Norden, 1988; Biester et al., 2013).

Mass-dependent fractionations of Pb isotopes during smelting processes are rather limited, as was demonstrated by Baron et al. (2009) and Shiel et al. (2010). Since Pb isotopes of ores of the Mitterberg main lode differ noticeably from Pb isotopes from Siegmoos (see Fig. 7), it seems reasonable to assume that during periods of intense mining activity in the 2nd millennium BCE, the average Pb isotope ratios of peat from Siegmoos may have been shifted towards the average Pb isotopic signature of the Mitterberg. However, such an isotopic shift at Hallstatt induced by regional copper mining is not discernible from the results.

Despite the fact that the Pb isotope composition of the eastern part of the Mitterberg region (Buchberg lode) is relatively similar to the Pb isotope composition of the Siegmoos, a significant influence from Mitterberg in general on samples from Siegmoos can be largely ruled out since copper production at the Buchberg lode was very limited in comparison with the Mitterberg main lode (Pernicka et al., 2016). The general temporal trend in \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios is consistent with the results of various other studies (e.g. Kylander et al., 2005; Allan et al., 2010).

### Table 2

Pb isotopic ratios of peat from siegmoos.

<table>
<thead>
<tr>
<th>Sample (depth cm)</th>
<th>(^{206}\text{Pb}/^{208}\text{Pb}) ± 2SD</th>
<th>(^{207}\text{Pb}/^{208}\text{Pb}) ± 2SD</th>
<th>(^{206}\text{Pb}/^{207}\text{Pb}) ± 2SD</th>
<th>Cal. Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>2.0986 ± 0.0013</td>
<td>0.4093 ± 0.0012</td>
<td>1.1641 ± 0.0018</td>
<td>~1990 CE</td>
</tr>
<tr>
<td>S10</td>
<td>2.0960 ± 0.0005</td>
<td>0.4088 ± 0.0004</td>
<td>1.1648 ± 0.0023</td>
<td>~1750 CE</td>
</tr>
<tr>
<td>S15</td>
<td>2.0809 ± 0.0014</td>
<td>0.4087 ± 0.0002</td>
<td>1.1766 ± 0.0006</td>
<td>~1620 CE</td>
</tr>
<tr>
<td>S30</td>
<td>2.0811 ± 0.0002</td>
<td>0.4080 ± 0.0012</td>
<td>1.1776 ± 0.0032</td>
<td>~590 CE</td>
</tr>
<tr>
<td>S40</td>
<td>2.0854 ± 0.0021</td>
<td>0.4076 ± 0.0008</td>
<td>1.1761 ± 0.0031</td>
<td>~430 CE</td>
</tr>
<tr>
<td>S45</td>
<td>2.0821 ± 0.0005</td>
<td>0.4050 ± 0.0011</td>
<td>1.1994 ± 0.0033</td>
<td>~120 CE</td>
</tr>
<tr>
<td>S50</td>
<td>2.0725 ± 0.0013</td>
<td>0.4057 ± 0.0004</td>
<td>1.1891 ± 0.0011</td>
<td>~110 BCE</td>
</tr>
<tr>
<td>S52</td>
<td>2.0781 ± 0.0026</td>
<td>0.4023 ± 0.0004</td>
<td>1.1896 ± 0.0006</td>
<td>~200 BCE</td>
</tr>
<tr>
<td>S53</td>
<td>2.0652 ± 0.0019</td>
<td>0.4048 ± 0.0020</td>
<td>1.1967 ± 0.0037</td>
<td>~250 BCE</td>
</tr>
<tr>
<td>S55</td>
<td>2.0594 ± 0.0002</td>
<td>0.4048 ± 0.0009</td>
<td>1.1992 ± 0.0034</td>
<td>~490 BCE</td>
</tr>
<tr>
<td>S59</td>
<td>2.0693 ± 0.0006</td>
<td>0.4043 ± 0.0009</td>
<td>1.1893 ± 0.0033</td>
<td>~540 BCE</td>
</tr>
<tr>
<td>S60</td>
<td>2.0604 ± 0.0010</td>
<td>0.4054 ± 0.0003</td>
<td>1.1969 ± 0.0019</td>
<td>~590 BCE</td>
</tr>
<tr>
<td>S61</td>
<td>2.0643 ± 0.0003</td>
<td>0.4042 ± 0.0022</td>
<td>1.1982 ± 0.0062</td>
<td>~650 BCE</td>
</tr>
<tr>
<td>S62</td>
<td>2.0616 ± 0.0013</td>
<td>0.4043 ± 0.0014</td>
<td>1.1995 ± 0.0021</td>
<td>~710 BCE</td>
</tr>
<tr>
<td>S64</td>
<td>2.0573 ± 0.0007</td>
<td>0.4042 ± 0.0002</td>
<td>1.2023 ± 0.0014</td>
<td>~840 BCE</td>
</tr>
<tr>
<td>S66</td>
<td>2.0596 ± 0.0005</td>
<td>0.4037 ± 0.0004</td>
<td>1.2025 ± 0.0001</td>
<td>~960 BCE</td>
</tr>
<tr>
<td>S70</td>
<td>2.0585 ± 0.0008</td>
<td>0.4027 ± 0.0008</td>
<td>1.2026 ± 0.0015</td>
<td>~1210 BCE</td>
</tr>
<tr>
<td>S74</td>
<td>2.0631 ± 0.0009</td>
<td>0.4055 ± 0.0014</td>
<td>1.2015 ± 0.0018</td>
<td>~1470 BCE</td>
</tr>
<tr>
<td>S75</td>
<td>2.0504 ± 0.0008</td>
<td>0.4049 ± 0.0013</td>
<td>1.2043 ± 0.0021</td>
<td>~1540 BCE</td>
</tr>
<tr>
<td>S79</td>
<td>2.0634 ± 0.0008</td>
<td>0.4059 ± 0.0009</td>
<td>1.1936 ± 0.0048</td>
<td>~1790 BCE</td>
</tr>
<tr>
<td>S81</td>
<td>2.0550 ± 0.0006</td>
<td>0.4046 ± 0.0019</td>
<td>1.2024 ± 0.0031</td>
<td>~1910 BCE</td>
</tr>
<tr>
<td>S82</td>
<td>2.0554 ± 0.0007</td>
<td>0.4049 ± 0.0005</td>
<td>1.2019 ± 0.0023</td>
<td>~1940 BCE</td>
</tr>
<tr>
<td>S84</td>
<td>2.0546 ± 0.0005</td>
<td>0.4047 ± 0.0012</td>
<td>1.2023 ± 0.0031</td>
<td>~2020 BCE</td>
</tr>
<tr>
<td>S92</td>
<td>2.0595 ± 0.0021</td>
<td>0.4047 ± 0.0016</td>
<td>1.1997 ± 0.0023</td>
<td>~2350 BCE</td>
</tr>
<tr>
<td>S93</td>
<td>2.0515 ± 0.0016</td>
<td>0.4054 ± 0.0014</td>
<td>1.2021 ± 0.0027</td>
<td>~2390 BCE</td>
</tr>
<tr>
<td>S100</td>
<td>2.0562 ± 0.0004</td>
<td>0.4039 ± 0.0008</td>
<td>1.2038 ± 0.0017</td>
<td>~2720 BCE</td>
</tr>
<tr>
<td>S107</td>
<td>2.0525 ± 0.0017</td>
<td>0.4039 ± 0.0008</td>
<td>1.2060 ± 0.0058</td>
<td>~3170 BCE</td>
</tr>
<tr>
<td>S136</td>
<td>2.0511 ± 0.0010</td>
<td>0.4052 ± 0.0003</td>
<td>1.2009 ± 0.0015</td>
<td>~3270 BCE</td>
</tr>
</tbody>
</table>
Stronger deviations of Pb isotope ratios and high Pb concentrations found in more recent samples from the mire (S1; S10; S17) are mainly due to altered resource consumptions, industrial activity and the introduction of leaded petrol in the modern period.

4.2. Geogenic input and human activity in the Hallstatt high Valley

The strong negative correlation between the XRF measured Mo Inc/Coh and the Ti concentrations is attributed to a closed-sum effect caused by the dilution of organic materials (Huang et al., 2016a). Sharp decreases in the XRF profile at ~102 cm and ~125 cm are probably connected to surface irregularities of the core. Comprehensive changes of the core composition (higher silt content; lower organic content; higher ash contents) and chemistry (rising of main and trace elements) in the lowermost section of the core are attributed to a substantially stronger input of mineral soil (see also X-ray diffraction results in Appendix I). For this reason, peaks of trace elements provided by ICP-MS below 100 cm are difficult to compare to element concentrations in the upper sections. Despite that, first enrichments of Pb and Sb at 105 cm, corresponding to a time of ~3000 cal BCE, are likely connected to local human activity. This interpretation is corroborated by palynological analyses indicating human presence near the site (Festi et al., 2021).

Another early period of human activity can be attributed to depth 92 cm in the peat core, corresponding to a time of ~2350 cal BCE. At this depth, enrichments in Sb in the ICP-MS data set might indicate human activity, possibly connected to smelting of Sb-bearing fahlores in the region.3 Human presence in the Eastern Alps at this time period is well attested by different authors (e.g. Drescher-Schneider, 2003; Tropper et al., 2017). Peaks in trace element profiles (Pb, Sb, Cu) and first signs of human impact on the vegetation (see Fig. 4) around 1800 BCE suggest a short period of increased human activity compared to the late Chalcolithic signal. From this point onwards continuous increases of Pb and Sb point towards gradually intensifying human activity culminating in section 70–58 cm (~1210 cal BCE to ~500 cal BCE).

The period between the 13th and the 6th century BCE is characterised by geochemical and palaeovegetational proxies that imply intense anthropogenic activity. Marked peaks of Pb and Sb point towards gradually intensifying human activity culminating in section 70–58 cm (~1210 cal BCE to ~500 cal BCE).

The Pb isotopic signature of ancient Greenland ice (Rosman et al., 1997) and the average Pb isotopic composition of the upper continental crust (UCC/Millot et al., 2004) are given as further references. The average European gasoline Pb isotopic composition is characterised by low 206Pb/207Pb and high 208Pb/206Pb ratios (e.g. Monna et al., 1997; Wittler et al., 2004), indicated by an arrow (top left). The dotted line denotes the time trend of the peat samples from the Siegmoos.

3 A more comprehensive analysis of palynological proxies regarding palaeoenvironmental changes in the Hallstatt High Valley is provided by Festi et al. 2021.
Relatively high Sn concentrations were detected between 70 cm and 59 cm (~1210 cal BCE to ~540 cal BCE) and in section 47–30 cm (~30 cal CE to ~590 cal CE). These concentrations might evidence intensive bronze casting processes during this time. With regard to the period during the Bronze and Iron Age, this interpretation is based on two strands of evidence. Archaeological finds from the prehistoric mine workings demonstrate that the bronze picks used by Bronze Age and early Iron Age miners broke regularly and experimental studies show that the picks were subject to high abrasion rates (Reschreiter, 2017; Reschreiter et al., 2018). Kazenas et al. (1996) and Begemann et al. (1999) documented considerable losses by evaporation of Sn up to 10 wt% during heating experiments. Distinctive Cu peaks (up to 7 times higher than the average values throughout the core) at 64 cm and 63 cm (~840 cal BCE to ~780 cal BCE) further corroborate this interpretation. Thus, continuous smelting processes of worn bronze tools in the Hallstatt High Valley during the Bronze and Iron Ages are very likely.

Sn enrichments and the prominent Cu peaks in peat sections corresponding to the Late Bronze Age coincide with intensive mining activities at Mitterberg (Breitenlechner et al., 2014). Due to the proximity of the two locations, it seems probable that, at this time, copper mining at Mitterberg created an increased demand for salt, stimulating mining and associated bronze casting in Hallstatt. Nevertheless, for reasons given in 5.1 we do not assume a significant atmospheric influence from copper production at Mitterberg on elemental enrichments at Siegmoos. Several authors have documented higher erosion levels in the Alps during the Middle and Late Bronze Age induced by increased human activity (e.g., Festi et al., 2014; Arnaud et al., 2016; von Schefler et al., 2019). With regard to Siegmoos, elevated concentrations of conservative elements and ash contents in the section 70–63 cm (~1210 cal BCE to ~780 cal BCE) are attributable to land clearing, periods of intensive human activity and/or climatic changes (e.g., Kempter, 1996; Weiss et al., 2002; Chersich et al., 2015). Apart from that, these enrichments were presumably also influenced by a large-scale landslide in the Hallstatt High Valley, which destroyed the Bronze Age mine workings (see Rohn et al., 2005). It should be assumed that the occurrence of the landslide, which has been radiocarbon dated to the end of the 2nd millennium BCE (see Ehret, 2009), and ongoing anthropogenic activity have altered geomorphological conditions (i.e., exposed slopes; reduced tree population) in the High Valley, causing additional dust input and hence higher ash contents of the peat.

Relatively high concentrations of Pb and Sb at a depth of 45 cm, corresponding to ~120 cal CE, might be partly attributed to diffuse distant sources in Europe and in the Near East, associated with mining activities of the Roman Empire (Bränvall et al., 2001; Grattan et al., 2007; Allan et al., 2018; Wagreich and Draganits, 2018). However, archaeological evidence and changes in the palaeovegetation proxies (see Fig. 4) clearly indicate local anthropogenic activity in Hallstatt at this time. Whether these signals are also connected to mining activity is unclear, since there is no archaeological evidence of salt mining during this period (Igl, 2009). Relatively high Sn concentrations might imply bronze processing in this period.

A combination of the palynological data and XRF and ICP-MS results obtained point towards a decrease in mining activity in Hallstatt during the Middle Ages (~6th century – 13th century CE). A significant increase of Pb in the uppermost section results from intensified industrialization processes in recent centuries (see also e.g., Shoytik et al., 2000; Cloy et al., 2008; Silamikele et al., 2011). High Zr concentrations in the uppermost section are also attributed to industrial activity and higher soil erosion rates in more recent centuries (Fialkiewicz-Koziel et al., 2011).

5. Conclusions

Elemental (ICP-MS; XRF), stable Pb and FTIR analyses of radiocarbon-dated peat material enabled a chronological reconstruction of prehistoric periods of anthropogenic activity in the Hallstatt region. The validity of the obtained geochemical signals is underlined by a local Pb isotopic fingerprint that seems to be largely unaffected by prehistoric Cu mining activity in the relatively nearby Mitterberg region.
archaeological findings and palaeovegetational proxies.

The first distinct metal enrichments attributed to initial anthropogenic impact in Hallstatt can be traced back to the Late Chalcolithic period, around 2350 cal BCE. After a period of moderate anthropogenic activity, presumably associated with salt mining, around 1800 cal BCE, continuous increases of trace elements associated with anthropogenic activity during the following centuries culminate in a section corresponding to the Late Bronze Age to Early Iron Age (~1300 cal BCE to ~500 cal BCE). Elevated Sn concentrations between the 12th and the 6th century can be attributed to bronze casting processes in Hallstatt. The 11th century BCE was probably marked by a landslide that altered geomorphological conditions in the High Valley, leading to an additional increase of dust flux. Intense human activity in Hallstatt from ~1st century BCE to ~2nd century CE is proven by archaeological findings and also suggested by elevated Pb, Sb and palaeovegetational proxies. Even though Cu was found to be largely unreliable as an anthropogenic tracer in the present study, in general, concurrent variations of geochemical and palaeoenvironmental proxies and archaeological evidence confirmed the suitability of the minerotrophic fen for archiving past human activity.

The results of this multi-proxy study elucidate the chronology of prehistoric human activity in the Hallstatt area and are consistent with previous archaeological studies. A broader regional contextualization by future palaeoenvironmental studies, involving detailed palynological and geochemical studies of other environmental archives in the region and (further) multi-proxy studies of adjacent prehistoric Cu mining areas in the Eastern Alps, is desirable for gaining a better and more complete understanding of early human activity in the Alpine region.

Acknowledgments

This present work was funded by the uni:docs fellowship programme for doctoral candidates (University of Vienna; grant no. 6395) and the Austrian Academy of Sciences/Earth System Science programme. The authors would like to thank Sabine Hruby-Nichtenberger, Hugh Rice, Christian Baal, Lars Scharfenberg, Christoph Kettler, Ruth Drescher-Schneider, Erik Wolfgang, Anita Eschner and Zita Takacs for technical and logistical support. Special thanks to Benjamin Schmid for language polishing and valuable comments on the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jasrep.2021.102813.

References


