Geochemical and Pb isotopic signatures of an Alpine minerotrophic peat core: A geochemical study to reconstruct periods of salt mining in the high valley of Hallstatt (Austria) in prehistoric times

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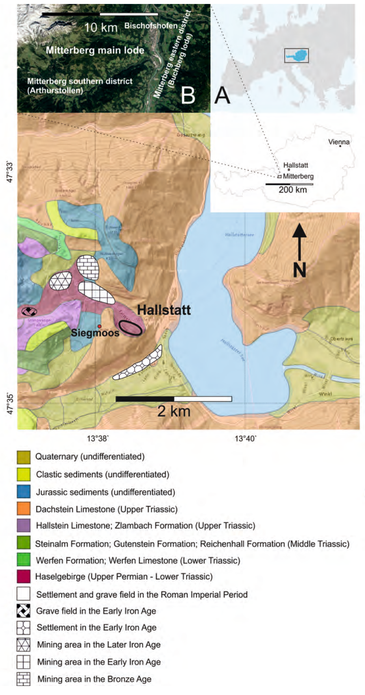
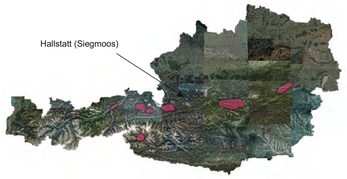
Introduction + sampling

The Hallstatt-Dachstein region is considered one of the most significant prehistoric production centers in Europe (Kern et al. 2009). Underground salt mining at depths up to 170 m is ascertained as far back as at least 1500 years BC (Reschreiter 2013; Hammer et al. 2018). This work combines an extensive set of methods to reconstruct and correlate anthropogenic activity in the Hallstatt region. The main focus of this study lies on the reconstruction of human activity in the region during the Bronze and Iron Age. The 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). Various Lower to Upper Triassic rocks of the NCA (Dachstein Formation; Steinalm Formation; Gutenstein Formation; Reichenhall Formation; Hallstatt Formation) crop out close to the study area (Mandl et al. 2012). A ~150 cm long peat core was retrieved from the minerotrophic fen *Siegmoos* (47°33'38.53''N; 13°37'43.45''E) is located in the Hallstatt High Valley at an altitude of ~ 1100 m. Overall, 49 peat samples with a thickness of 1cm were drawn and subsequently prepared for multi-proxy analyses.

Sample location



Prehistoric salt (blue) and copper (red) activities in Austria



Overview map with the geographical location of *Siegmoos* in the Hallstatt High Valley, old mining and settlement districts and grave fields, embedded in the regional geology of the Hallstatt lake region (see also Kern et al. 2009).Europe (A), the prehistoric copper mining area Mitterberg (B) and Vienna are given as geographic references.

Methods

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Elemental analyses
- COX Analytics ITRAX XRF core scanner
- ICP-MS Thermo iCAP Q

Pb isotope analyses
- ICP-MS Thermo iCAP Q

Biogeochemical analyses
- Cary 660 FTIR spectrometer

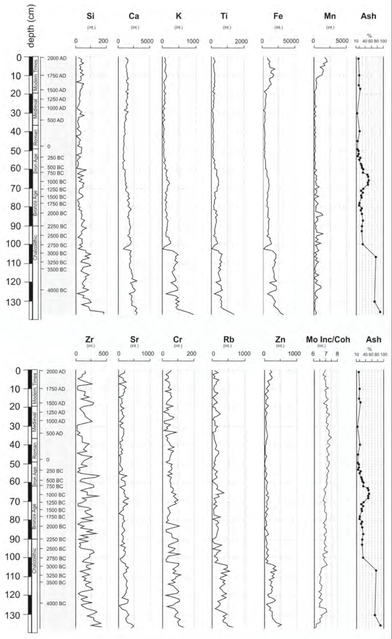
Mineralogical analyses
- PANalytical X'Pert PRO diffractometer system
- FEI Inspect S QUANTA SEM

Chronology
- Bayesian radiocarbon modelling

Digestion of peat samples for ICP-MS analyses was performed by using a microwave digestion system (Anton Paar Multiwave 3000)
sample weight: 100 mg (dry peat powder)
acid digestion: 4ml HNO_3 + 2ml HCL + 2ml H_2O_2 + (0.1ml HF)

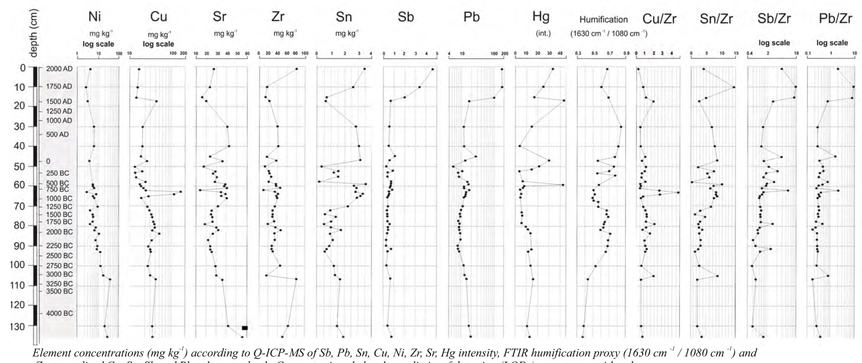
Results

XRF core scanning



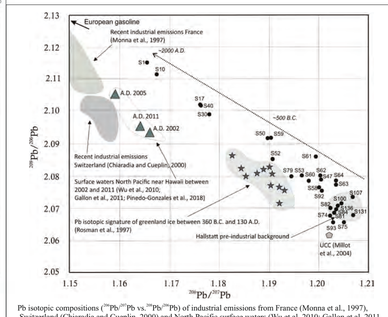
XRF intensity diagram comprising the elements Si, Ca, K, Ti, Fe, Mn, Zr, Sr, Cr, Rb, Zn, the Mo Inc/Coh ratio and the ash content. Intensity curves are based on every tenth data point (0 cm-137 cm; n = 138). The chronology of the core relies on a Bayesian model based on IntCal13 (Reimer et al. 2013)

Q-ICP-MS analyses

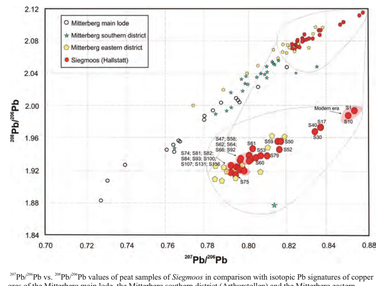


Element concentrations (mg kg^{-1}) according to Q-ICP-MS of Sb, Pb, Sn, Cu, Ni, Zr, Sr, Hg intensity, FTIR humification proxy (1630 cm^{-1} / 1080 cm^{-1}) and Zr-normalized Cu, Sn, Sb and Pb values vs. depth. Concentrations below lower limits of detection (LODs) were not considered.

Pb isotope analyses



Pb isotopic compositions ($^{206}Pb/^{207}Pb$ vs.$^{208}Pb/^{207}Pb$) of industrial emissions from France (Monna et al., 1997), Switzerland (Chiaradia and Cueplin, 2000) and North Pacific surface waters (Wu et al. 2010; Gallon et al. 2011, Pinedo-Gonzales et al. 2018) in comparison with peat samples of *Siegmoos*. 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 characterized by low $^{206}Pb/^{207}Pb$ and high $^{208}Pb/^{207}Pb$ ratios (e.g. Monna et al. 1997; Ettler et al. 2004), indicated by an arrow (top left).The dotted line with an arrow denotes the time trend of the peat samples of *Siegmoos*. S15 is not displayed in the diagram



$^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ values of peat samples of *Siegmoos* in comparison with isotopic Pb signatures of copper ores of the Mitterberg main lode, the Mitterberg southern district (Arthurstollen) and the Mitterberg eastern district (Buchberg lode) (Pernicka et al. 2016). S15 strongly diverges from the rest of the samples and is therefore not displayed in the diagram.

Conclusions:

-- first signals (Cu, Pb, Sb) for anthropogenic activity around 1830 cal BC

-- prehistoric anthropogenic signals peak between ~ 850 cal BC – 500 cal BC

-- Sn enrichments between 70 cm and 59 cm (~1210 cal BC - ~ 540 cal BC) imply extended bronze casting processes attributed to the production of bronze picks used for mining

-- Pb isotopic signature of the Mitterberg main lode differs from average Pb isotopic signals of *Siegmoos*, implying no significant influence on the enrichment of Pb and other trace elements in Hallstatt

-- due to the high ash content of the minerotrophic fen, influence of humification on trace elemental enrichment is considered to be negligible

-- the occurrence of a landslide which affected the salt production in Hallstatt (around 1140 cal BC) is signalized by significant higher ash contents

-- a distinct Hg peak in sample S59, corresponding to the 6th[t] century BC, might be linked to regional smelting of Hg bearing fahlores

-- high concentrations of Pb and Sb at a depth of 45 cm, corresponding to ~130 cal AD, are attributed to anthropogenic activity in Hallstatt or non-local sources during the Roman Imperial Period

-- increases of trace elements and a decrease of the $^{206}Pb/^{207}Pb$ value in the uppermost layers are attributed to non-local and local increased industrialization processes

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