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Reconstruction of mining activities in the Western Alps during the past 2500 years from natural archives

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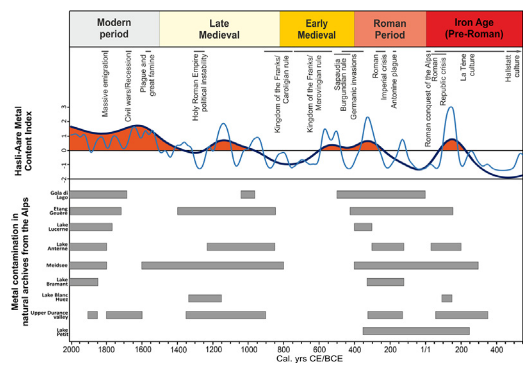
HIGHLIGHTS

- Anthropogenic metal contamination in the Bernese Alps dates back to the Iron Age.
- Sediments exhibited the most significant metal peak anomalies in the last 500 yrs.
- Shifts in metal trends correspond with socioeconomic changes in central Europe.
- Similar anthropogenic pollution trends are observed across the Alpine region.
- Other archives and knowledge of ancient mining validated sediment metal trends.

GRAPHICAL ABSTRACT



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ABSTRACT

The geochemical analysis of natural archives can improve our knowledge of past mining activities and their environmental imprint. The sedimentary records from the Hasli-Aare floodplain (Bernese Alps) over the last 2500 years were analysed for metals. Evidence of past mining contamination was obtained from the XRF analyses of iron, copper, zinc and lead. These results were analytically and statistically processed to produce a metal content index. Positive metal anomalies indicate four major pulses of contamination coinciding with the end of the Iron Age, from the end of the Roman Period to the Early Medieval Period, the Late Medieval Period, and the Modern Period. These pulses show good agreement with local historical sources of mining in the Hasli-Aare catchment, dating back to the beginning of the 15th century. Furthermore, they are in phase with anthropogenic pollution trends inferred from glacier ice cores, lake sediments and peat bogs across the Western Alps, most notably during the Roman, Late Medieval and Modern Periods. However, close comparison between these records can show some differences, suggesting local variations in mining activities and/or a lag in metal transfer. The reconstructed periods of anthropogenic metal pollution are located in their political, economic and social contexts and compared with the climate periods of central Europe.

1. Introduction

Modern industrialization is a major contributor to present-day levels of metal contamination worldwide (Salomons, 1995), nevertheless, evidence of anthropogenic metal pollution, related with mining and smelting activities, date back to at least 5000 years BP (Killick and Fenn, 2012; Martínez Cortizas et al., 2016). This pollution increased during the ancient Greek and Phoenician civilizations and especially throughout the Carthaginian and Roman Empires (McConnell et al., 2018), as a consequence of the rise of mining, smelting and trading activities (Edmondson, 1989; Durali-Mueller et al., 2007). Metal production techniques during this period were simple and highly polluting,

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releasing high concentrations of metals into the atmosphere, hydrosphere, sediments, and soils (Shotyk and Krachler, 2004; Martínez Cortizas et al., 2013; Preunkert et al., 2019).

When metals are released into the environment as a consequence of human activity, they are dispersed primarily into the atmosphere and hydrosphere and, subsequently, deposited on the Earth's surface (Callender, 2003), where they become accumulated in terrestrial, fluvial, lacustrine or marine environments. The reconstruction of past mining activity based on the analysis of natural archives is based on the premise that, during periods of mining and smelting, significant amounts of sediment and metals are released into the atmosphere and ecosystems. For this reason, the noncrustal metal fractions detected in natural archives can be interpreted as a footprint and, in some cases, as a precise marker of past human interference in natural systems (Renberg et al., 2001). Additionally, the study of metal concentrations or changes in metal isotope ratios in natural archives can be a valuable proxy for historical human activities, because, in optimal conditions, these records constitute a continuous time series over centuries and, even, millennia. The study of past metal concentrations can also offer an insight into past human development, because throughout human history, local and global mining activities have been closely related with the prevailing climate, economic and social conditions (McConnell et al., 2019).

In recent decades, many key studies have examined past European mining activity based on the analysis of different types of natural archives. Some focused their attention on atmospheric metal pollution by analysing ice cores (Hong et al., 1996; Rosman et al., 1997; McConnell et al., 2018) and peatlands (Shotyk et al., 1998; Mighall et al., 2002; Monna et al., 2004; Baron et al., 2005; Forel et al., 2010; Martínez Cortizas et al., 2013), the latter receiving inorganic solids entirely from atmospheric deposition (Bindler, 2006). Most of these studies identified ancient anthropogenic pollution and detected a European pollution signal derived from the dispersion of metals in the atmosphere as a result of human activities. Other studies analysed anthropogenic pollution in lake (Coulthard and Macklin, 2003; Arnaud et al., 2004), fluvial (Macklin, 1985; Leblanc et al., 2000; Schulte et al., 2008) and estuarine-coastal sediments (Alfonso et al., 2001; Nizou et al., 2019). These archives may include anthropogenic signals from both atmospheric and terrigenous sources. They also prove effective in recording past human pollution from either regional or local sources, provided no sizeable gaps are present in the sedimentary sequence (Schulte et al., 2008, 2015) and a sufficient amount of materials originating from human activities were released into the ecosystems (Knox, 1987; Preunkert and Legrand, 2013). To be able to use heavy metal content as a proxy for historical mining, the natural crustal source should be minimal and the vertical mobility of metals in the profile must be limited.

Among the many mineral resources exploited in mining, the most frequently studied are lead, copper, and mercury. In the case of lead, this can be attributed to the fact that it has low mobility in sedimentary layers (Renberg et al., 1994; Gobeil et al., 1995) and it is associated with different types of ore deposits, thus facilitating the study of many different types of mining exploitation (Forel et al., 2010). In regard to copper, it can be attributed to the fact that it enjoys a long history of exploitation, dating back to the late 8th millennium BCE (Thornton et al., 2002). As for the mercury, it is also related with the mining of several types of ore in preindustrial and industrial periods and it provides a valuable perception of natural and anthropogenic variability in numerous spatial and temporal scales (Farmer et al., 2009; Engstrom et al., 2014; Cooke et al., 2020 and references therein).

The study of the historical evolution of metal pollution in Europe, as illustrated by the aforementioned natural archives and by archaeological findings (Morin et al., 2007; Bourgarit et al., 2008; Py et al., 2014) and historical archives (Pelet, 1974; Brännvall et al., 1999; Callender, 2003), allows us to identify a marked degree of overlap in the major trends of mining activity. Some studies indicate that anthropogenic pollution recorded in natural records can be traced back to the Chalcolithic (Martínez Cortizas et al., 2016) and that the pollution signal continued to increase during the Greek, Phoenician and Carthaginian civilizations (Renberg et al., 1994; Martınez-Cortizas et al., 1999; Shotyk et al., 2001). Later, during the Roman Period, mining activities were intensified and the analysis of natural archives highlights widespread contamination throughout Europe (Vesely, 2000; Alfonso et al., 2001; Giguet-Covex et al., 2011; Delgado et al., 2012; Martínez Cortizas et al., 2013), extending as far as Greenland (Hong et al., 1994; Rosman et al., 1997; McConnell et al., 2018). During this period, the most important mining regions were located in the Iberian Peninsula and England (Martínez Cortizas et al., 2013; McConnell et al., 2018). With the fall of the Roman Empire and the onset of the Medieval Period, a significant decline of these activities was recorded, mainly due to economic and social instability (Nriagu, 1996; McConnell et al., 2019). This was to last until approximately the beginning of the Late Medieval Period (around 900 CE), when mining activities began to expand and metal pollution, as recorded in the natural archives, rose again (Renberg et al., 2001). The increase in mining activities during this period was particularly significant in the regions of central Europe, especially in the centre and south of present-day Germany (Nriagu, 1998). Throughout the Modern Period, anthropogenic metal pollution continued to rise, especially after the industrial revolution. Various studies have examined the impact of modern atmospheric pollution, industrialization and mining on sedimentary environments and water systems (Kober et al., 1999; Mil-Homens et al., 2006; Cantwell et al., 2007; Irabien et al., 2008; Bindler et al., 2012; Martínez-Cortizas et al., 2012; Thevenon et al., 2013a; Amos et al., 2015) revealing an intensification of episodes of contamination from the middle of the 19th century onwards. Peaks of zinc and lead contamination are typically identified in many European 20th-century deposits, associated with pre-World War I zinc and tin production, urban and industrial expansion and the maximum consumption of unleaded gasoline around 1970 CE (Weiss et al., 1999).

Although the main trends in historical anthropogenic pollution are similar across most of Europe, regional and local signals seem to point to different practices at these levels (Martínez Cortizas et al., 2013 and references therein). Indeed, these differences can offer a better understanding of the more specific traits of human activities on the continent, particularly as regards local mining and smelting.

Among the regions of Europe where mining was practiced, the Alpine region is of particular interest because it offers almost perfect conditions for recording the impact of human activities on high-altitude natural environments. Other mountain regions of interest are the Cantabrian Mountains (Martínez Cortizas et al., 2016) and the Pyrenees (Camarero et al., 1998). Although the extent of historical mining activities in the Alps are not comparable to those of other major mining regions, such as the Iberian Peninsula, England or Germany (at least based on production), a large number of local mines, practically all over the Alpine range, were operative and the quantity of profitable ore deposits was considerable (Cortecci et al., 1992; Senn-Luder et al., 1993; Arnaud et al., 2005; Bourgarit et al., 2010; Forel et al., 2010; Breitenlechner et al., 2010; Simonneau et al., 2014; Artioli et al., 2016).

Despite the long mining history of the Alps (Shotyk et al., 2001; Shotyk, 2002; Guyard et al., 2007; Py et al., 2014; Preunkert et al., 2019), in some regions the advent and development of these activities are still poorly understood. One such region is the Bernese Alps, forming part of the western Alpine range and located roughly in the centre of modern day Switzerland. The most recent periods of mining activity in this region are fairly well known thanks to historical documents, the remnants of mining infrastructure and archaeological finds (Kutzer, 1996; Ebersbach and Gutscher, 2008); yet, the ancient periods are clouded in uncertainty, despite traces of ancient mining having been found in sedimentary archives (Schulte et al., 2008). Indeed, there are cases in which the archaeological evidence of mining activity cannot be accurately dated and others in which periods of known activity from historical sources are not confirmed by regional archaeological evidence (Ebersbach and Gutscher, 2008).

The aim of this study is to improve our knowledge of past mining activity and of metal transfer to the floodplains in the Bernese Alps during the last 2500 years, as inferred from fluvial archives of the Hasli-Aare catchment. From the analysis of alluvial sediments, we examine the geochemical responses of four chemical elements: iron, copper, zinc and lead. Mining activity in the alpine catchments of the Bernese Alps is dated by historical and archaeological sites since the 15th century. However, our analysis centres on the detection of metal content anomalies in floodplain sediments during earlier periods of mining activity beyond the range of local accurately dated archaeological and historical sources. We also seek to shed light on local and regional patterns of past anthropogenic metal pollution based on the contamination signals reported in previous studies of the Western Alps. These studies include archives from lake sediments, peatlands, ice cores, archaeological and mining remnants. By comparing geochemical, archaeological and historical mining records from the Hasli-Aare catchment with the results published in similar studies conducted in the Western Alps, we aim to identify the major trends in mining activities in this region and to distinguish local characteristics of human occupation and mining exploitation in high altitude areas. The regional comparison addresses the question if these pulses of metal anomalies provide evidence for similar periods of regional mining in the Western Alps or indicate more local development of ore exploitation.

2. Study area and early mining activities

2.1. The larger setting: the Western Alps

This study analysed the historical anthropogenic metal pollution of different natural archives within the limits of the new division of the Western Alps (Marazzi, 2012), an area that includes the Alpine mountain range located west from an imaginary line drawn between Lakes Constance and Como (Fig. 1). This crescent-shaped mountain region is approximately 500 km long and 150 km wide, and encompasses the French Alps, most of the Swiss Alps, as well as most of the Italian Alps (the western and a large part of the northern range). The geology of this vast region is characterized by Precambrian and Palaeozoic basement units, together with Mesozoic and Tertiary cover units. The main structural domains are the Helvetic, Ultrahelvetic, and Penninic nappes, together with the external domains of the Prealps and the Jura Mountains (for an extended geological and structural characterization see Stampfli et al., 2002 and references therein).

2.2. The Hasli-Aare catchment

Our case study of historical mining, inferred from geochemical floodplain proxies, focuses on the Hasli-Aare catchment (also referred to as the upper Aare catchment) that covers an area of 596 km^2. The main geological units of this region are the crystalline Aare massif, corresponding to the highest mountain areas, and alpine tectonic units consisting of sedimentary rocks of Mesozoic and Early Cainozoic age (i.e., rocks of marine origin: limestone, shale and sandstone), corresponding to the north-western catchment areas (Fig. 2). This geology is marked by a clear NE-SW division, resulting in the differentiation of the mineralogical composition of the sediments transported by the Aare river (Sturm and Matter, 1978; Schulte et al., 2009a; Carvalho and Schulte, 2013). The iron ore deposits are associated with oolitic iron minerals intertwined in massive limestone. These deposits are from the Cenozoic weathering of limestone and are found along a NE-SW axis, at altitudes between 2170 and 2250 m a.s.l. (Doswald, 2012). The lead, copper and zinc ore deposits are associated with galena minerals found in metamorphic rocks (micaschists) of the Aare massif, and are the result of magmatic and hydrothermal activity.

The lower altitude records analysed herein are from the Hasli-Aare delta plain, located before the inflow of the Aare River into Lake Brienz at 564 m a.s.l. (see core location in Fig. 2). This lake is crucial for the formation of the very low-angled Hasli-Aare delta plain that acts as an efficient sediment sink, storing large volumes of sediment transported by the Aare River. Interdistributary basins on this delta plain provide ideal depositional environments in which sedimentation is mostly continuous and unconformities do not disturb the palaeoenvironmental record (Schulte et al., 2008).

2.3. Early land use and mining in the Hasli-Aare catchment

Archaeological finds indicate a human presence in this basin stretching back to the Late Neolithic, but a significant human impact on the natural system is not recorded until much later with the establishment of permanent settlements in the valley floors and upper alpine areas (Ebersbach and Gutscher, 2008). Most of the human impact documented in this region dates from the last millennium, especially from the last 700 years, with archaeological evidence, written sources, and pollen records (Schulte et al., 2009a) testifying to widespread human occupation, intensive land use changes (especially in forested areas) and modifications to the fluvial environment (Vischer, 2003; Schulte et al., 2015).

There is no archaeological evidence of mining activity in the Hasli-Aare catchment during the Bronze Age (Ebersbach and Gutscher, 2008), but artefacts found near Innertkirchen and Grimselpass confirm the presence of metal objects in this period (Türler et al., 1934). Likewise, in the Roman Period, there is no clear evidence of mining from archaeological remains, but it is widely assumed that this activity was practiced (Senn-Luder et al., 1993), and Roman artefacts indicative of exploration activities were found at altitudes above 2000 m a.s.l. (Ebersbach and Gutscher, 2008). During the last millennium, various documentary sources and archaeological remains indicate the importance of iron mining in the catchment, especially in Late Medieval times and during the Modern Period (Kutzer, 1996; Zahn, 2001; Doswald, 2012; Dariz and Schmid, 2015). Most of the mining activity was not sufficiently profitable for exportation during these periods, but there was a regional demand for the ores from the Hasli-Aare catchment, at least since the 15th century (Willi, 1884). Indeed, there are written sources that demonstrate the interest shown in the catchment mining activity by the State of Bern (Müller-Landsmann, 1900; Rennefahrt, 1962; Zahn, 2001). What is clear is that the political autonomy and geographic proximity of the ore deposits compensated for the poor concentration and difficulties of access, as most of the mines were located on steep slopes while ore processing was concentrated in the valley floors (Boschetti and Gutscher, 2004).

There have been significant human interventions in the fluvial system of the region over the last five centuries. In 1434, the monks from the monastery of Interlaken constructed a dam at the point where the Aare flows out of Lake Brienz that caused flooding of the distal areas of the Hasli-Aare and Lütschine deltas. Several hydraulic corrections have been undertaken in the main valley floors to prevent flood damage and promote land-use practices. In addition, several hydroelectric dams were built during the 20th century (the first in 1932), which totally modified the Upper Aare natural river regime.

Historical sources indicate extensive wood cutting since the 16th century to meet the needs of the mining and smelting activities. This forestry exploitation contributed to changes in the Aare flood regime and flood magnitudes (Schulte et al., 2019a), the alteration of its sediment yield dynamics (Carvalho and Schulte, 2013) and an increase in debris-flow activity on the corresponding hill slopes (Willi, 1884).

3. Methods

3.1. Geochemical analysis

Sediments from three cores (see Fig. 2 for core location), obtained from depths of up to 8 m, were described macromorphologically

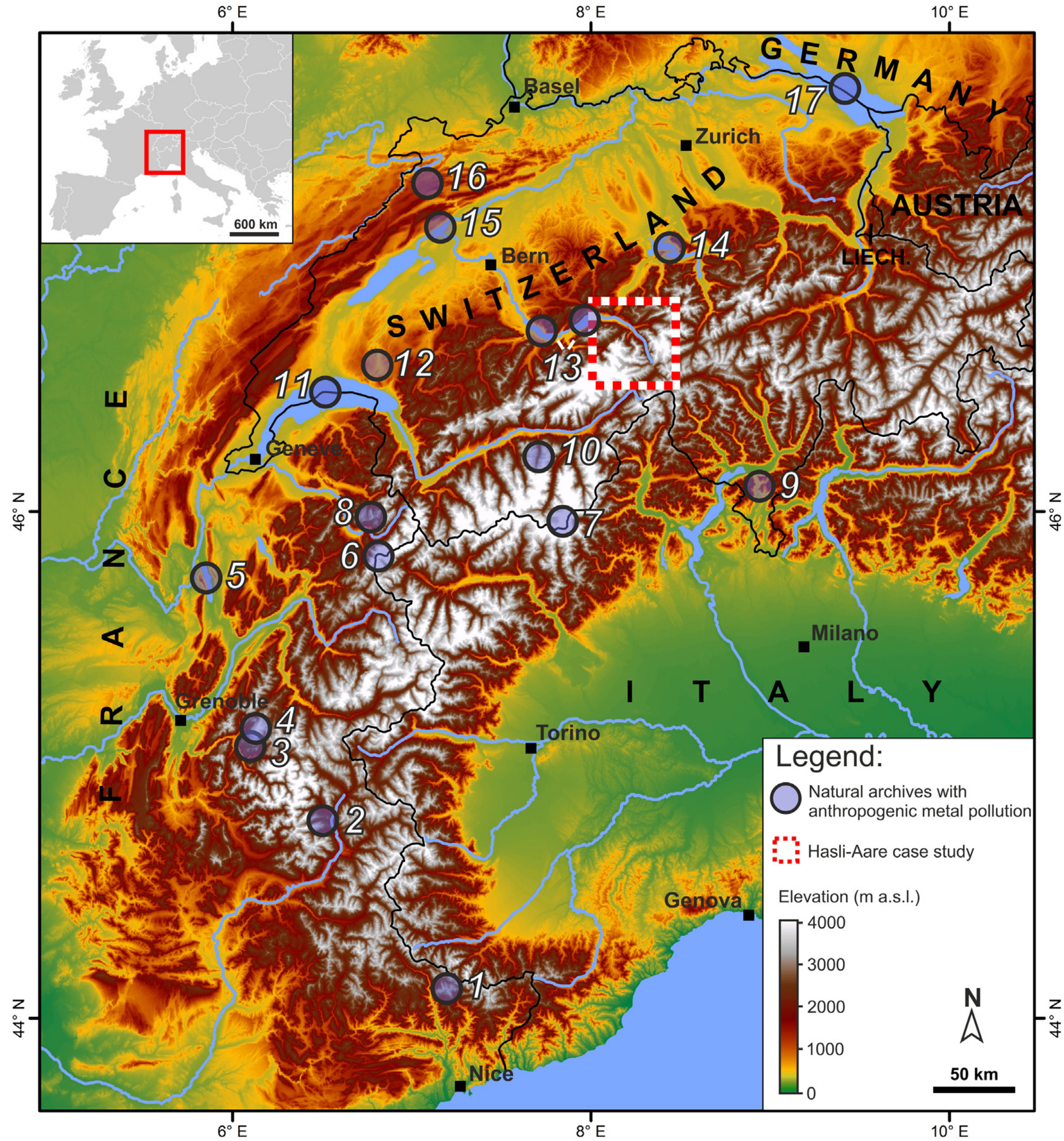

Fig. 1. Digital Terrain Model of the Western Alps with the location of the Hasli-Aare case study and other natural archives were ancient anthropogenic metal pollution was detected. 1-Lake Petit; 2-Upper Durance valley; 3-Lake Blanc Huez; 4-Lake Bramant; 5-Lake Le Bourget; 6-Col du Dôme (Mont Blanc Massif); 7-Colle Gnifetti (Mont Rosa Massif); 8-Lake Anterne; 9-Gola di Lago; 10-Meidsee; 11-Lake Geneva; 12-Lake Brêt; 13-Lakes Brienz and Thun; 14-Lake Lucerne; 15-Lake Biel; 16-Etang de la Gruère and Tourbière des Genevez; 17-Lake Constance. For a complete description of each archive, see Supplementary information Table ST2.
DEM from NASA SRTM.

according to grain size, porosity, colour (Munsell colour chart), carbonate content, organic content and existence of roots or organic remains. The chemical element analysis of fluvial sediments was performed primarily by X-ray fluorescence (XRF), at the MARUM Centre of the University of Bremen, using an Avaatech XRF core scanner with a molybdenum (Mo) X-ray source (10 and 30 kV), and a PSI Peltier Kevex detector cooled with a beryllium (Be) window and a multi-channel analyser with a resolution of 20 kV (Röhl and Abrams, 2000; Richter et al., 2006). Analyses allowed the detection of the chemical elements present in soil samples from aluminium (Al) to bismuth (Bi). Measurement of iron (Fe) content in the sediment was performed using a voltage of 10 kV and that of cooper (Cu), zinc (Zn) and lead (Pb) were measured at 30 kV. Down-core resolution was 1 cm, providing semi-quantitative and relative estimates of the absolute concentration of the chemical elements at different depths (results of each reading were obtained in total counts).

XRF total counts were also compared with 82 conventional XRF pearl samples from cores AA-2 and AA-5 (selected from different depths). This analysis was performed at the Scientific and Technological Centre of the University of Barcelona using a Philips PW2400 (WDXRF) X-ray spectrophotometer with a rhodium X-ray source (60 kV, 125 mA, 3000 W). The comparison of major elements (Fe, Ti, Ca, K, Si and Al) showed a low to moderate-high correlation between the two methods, with correlation coefficients ranging from 0.6 to 0.81 depending on the chemical element (see Supplementary information, Table ST1 and Fig. S1). This demonstrates that for the cores analysed in this paper, the XRF scanner provides reliable results (Schulte et al., 2015) in a fast, non-destructive and efficient fashion (Jansen et al., 1998).

Here, we focus on the specific response of four chemical elements – Fe, Cu, Zn and Pb – as these metals are associated with the main mining and smelting contaminants in the rivers of this region. One of the distinctive features of metal content anomalies in fluvial sedimentation environments is the affinity of metals for organic-rich horizons (Tack and Verloo, 1995; Vile et al., 1999; Forel et al., 2010), specially elements such as Cu, Zn, and Pb. These horizons are also prone to pyrite oxidation and the formation of acid waters (Panzer and Elving, 1975), which can affect

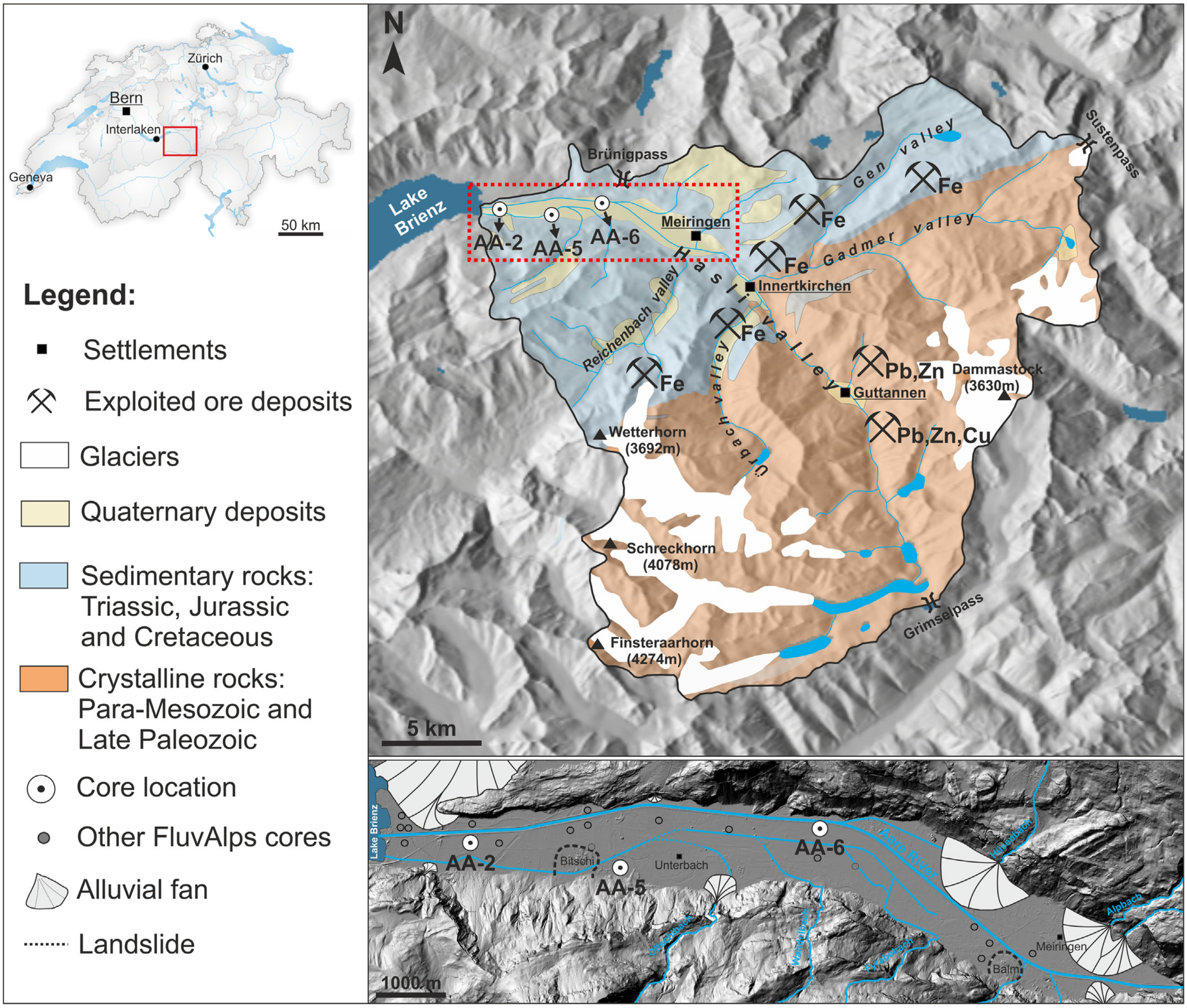

Fig. 2. Geological setting of the Hasli-Aare catchment and detailed relief of the lower Hasli valley. The location of the ore deposits and sedimentary records used herein are also included. DEM from Swisstopo©.

Fe concentration. Therefore, organic-rich horizons can produce changes to Fe, Cu, Zn and Pb, which may be associated with natural soil processes and not necessarily with anthropic sources.

To reduce the effect of the uncertainties introduced by the XRF scanning, the metal series were normalized, by performing a ratio of metal total counts against a conservative element such as rubidium (Figs. 3, 4 and 5; see also Supplementary information, Figs. S2, S3 and S4). Rubidium (Rb) is an element that maintains fairly stable throughout the analysed cores, therefore it is considered as an effective ratio to account for distinct organic content (Rothwell et al., 2006; Guyard et al., 2007; Davies et al., 2015).

In order to highlight the positive metal anomalies in organic rich horizons we show the results according to their organic content. Thus, here, all XRF results were classified according to the percentage of total organic carbon (TOC) obtained by loss on ignition (Santisteban et al., 2004), with a sampling spacing of 1-cm. Metal peaks in sediments with a TOC higher than 5% were marked (see grey bars in the Fe, Pb, Zn and Cu peaks in Figs. 3, 4 and 5). In this way, we can assess accurately the palaeoenvironmental signal of metal pollution in the context of diagenetic processes.

The chronology of the 2500-year long sedimentary records was established by AMS-radiocarbon dating, based on 16 samples of peat, organic-rich horizons, organic macro-remains and wood. The chronological model of the Hasli-Aare floodplain records is detailed on Carvalho and Schulte (2013). Metal content is presented as 10-year intervals, obtained from the mean of the XRF total counts for all the samples included in the 10-year period. The mean sedimentation rates were related to the core location on the delta plain and vary from 2.3 mm y^{-1} in core AA-2 to 4.2 mm y^{-1} in core AA-6 (Carvalho and Schulte, 2013).

3.2. Processing of the metal content index

To detect the pollution signal from the metal content of each core, peak anomalies were selected from Z-scores of metal/Rb ratios higher or equal to one standard deviation above the mean (samples above the red line in Figs. 3, 4, 5). When this threshold was reached, samples were identified as samples with high metal content (right column of Figs. 3, 4 and 5). This threshold could be established, because the metal anomalies during the historical reference period were generally

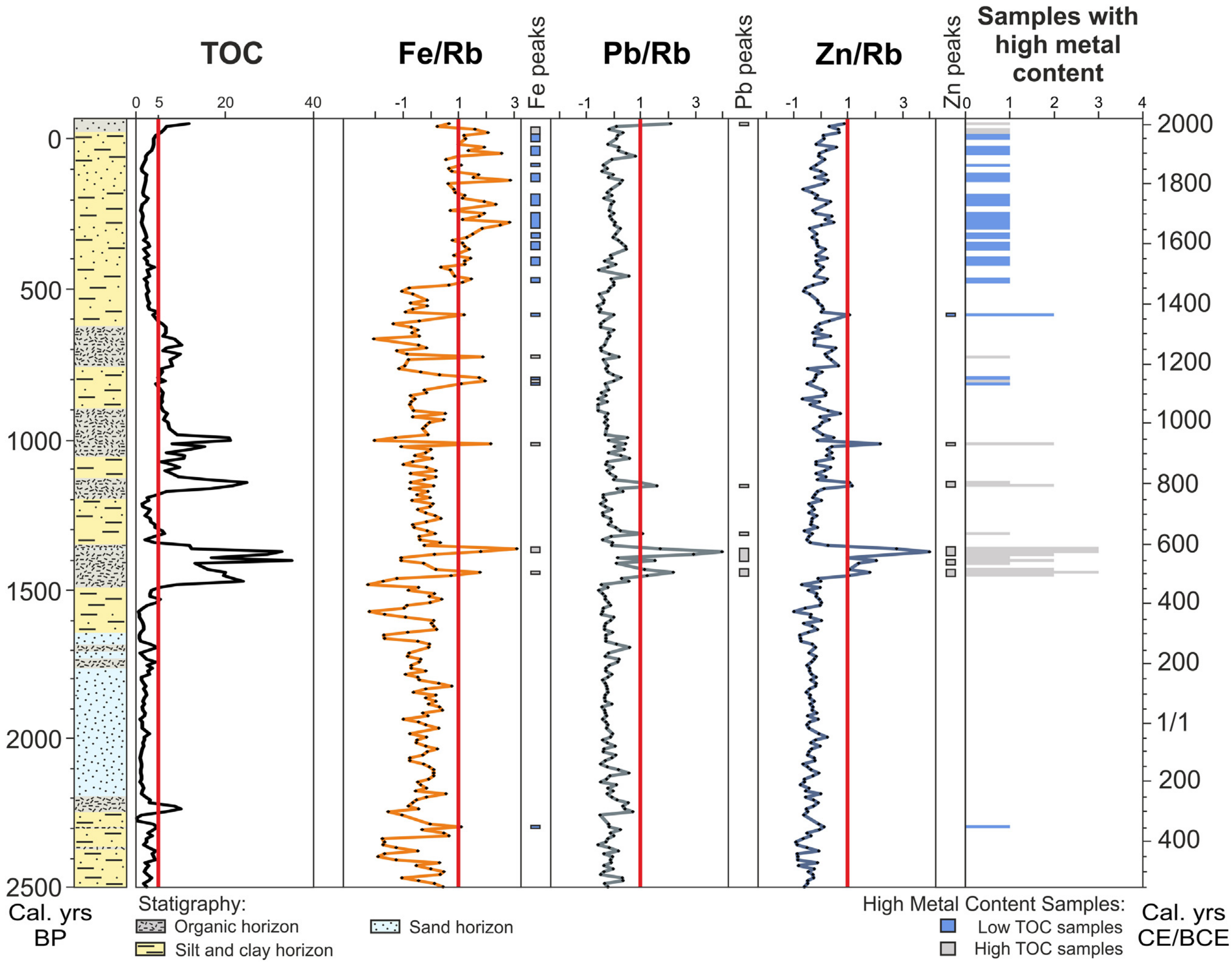

Fig. 3. Metal content in core AA-2, presented with a 10-year interval. Total organic carbon (TOC) is shown as a percentage (wt%) and metal content as Z-scores of XRF total counts normalized by rubidium. Metal anomalies shown on the right were identified in samples with Z-scores higher than one standard deviation above the mean.

higher or equal to one standard deviation above the mean (Figs. 3, 4 and 5). The reference period begins in 1416 CE, when mining activity was first reported in written historical sources.

The definition of the final metal content index for the Hasli-Aare catchment was obtained from the aggregation of the samples with high metal content from all the cores (Fig. 6). To improve the identification of major trends, a Gaussian filter was applied to the metal content index. This filter was performed with a 100- and 500-year smoothing window and a breadth (alpha) equal to 3.

4. Results

4.1. Metals in different sedimentary floodplain facies

The geochemical data analysis presented in Figs. 3, 4, and 5 identifies several elevated metal/Rb ratios over the past 2500 years. Most of the high metal/Rb ratios were generally recorded in fine sand, silt and organic-rich layers. This was the case, for example, of organic-rich samples between 500 and 600 CE in Core AA-2 (Fig. 3); silt layers between 1130 and 1200 CE in core AA-5 (Fig. 4); and layers of fine sands between 1750 and 1950 CE in core AA-6 (Fig. 5). Values of metal counts in layers of medium to coarse sands were usually lower, that is, in samples between 150 BCE and 170 CE in core AA-2 or samples over 1120 and 1280 CE in core AA-6. However, several samples did not follow this pattern. For example, in core AA-6 layers of medium sand were found with high metal counts (the case of samples between 360 and 400 CE) and finer layers dominated by silts with low counts (the case of samples between 400 and 480 CE). This indicates that the historical variability of metal content can be identified in various types of sediments, with different lithological characteristics.

4.2. Clusters of metal anomalies

An examination of the overall response of the three cores shows that the last 600 years presented the greatest number of metal anomalies, which appear to reflect the importance of mining during this period. In core AA-2 (Fig. 3), most of the positive metal anomalies are identified over the last 500 years and are related particularly with high Fe counts, found in layers dominated by silts and clays. Core AA-5 (Fig. 4) shows high counts (Fe, Pb and Zn) from 1730 to 1830 CE and during the last three decades of the 20th century. In Core AA-6 (Fig. 5), we identify several elevated metal/Rb ratios during the period between 1400 and 1970 CE.

Considering the results of the positive anomalies and the 500-year Gaussian filter of the metal XRF counts, four major clusters of higher metal content can be identified (see Fig. 6). The first major cluster (cluster A in Fig. 6) occurs at the end of the Iron Age, between 160 and 100 BCE. In this cluster, all positive values come from core AA-5, mostly from layers with high organic content. The second major cluster (composed by clusters C and D) occurs between the end of the Roman Period

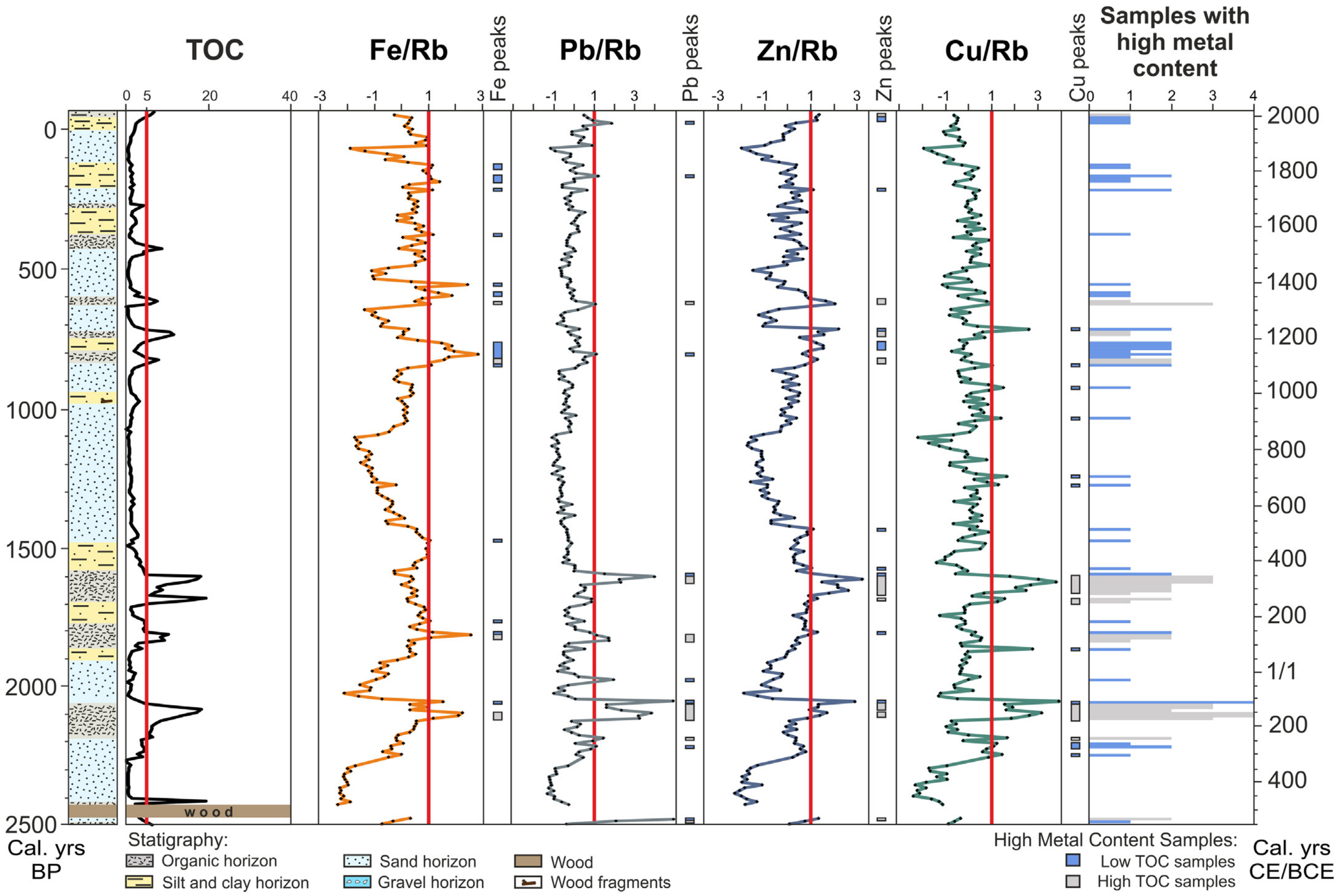

Fig. 4. Metal content in core AA-5, presented with a 10-year interval. Total organic carbon (TOC) is shown as a percentage (wt%) and metal content as Z-scores of XRF total counts normalized by rubidium. Metal anomalies shown on the right were identified in samples with Z-scores higher than one standard deviation above the mean. Data discontinuity occurs in a wood fragment at the base of the core.

and the beginning of the Early Medieval Period, between 250 and 590 CE. In this cluster, most of the positive values come from layers of fine sediments with organic content in cores AA-2 and AA-5. The third major cluster (formed by clusters E and F) occurs in the Late Medieval Period between 905 and 1250 CE and positive values come from layers dominated by clays and silts in cores AA-2 and AA-5. Finally, the fourth major cluster (comprising the merger between clusters H, I and J) occurs at the end of the Late Medieval Period and continues throughout the Modern Period. It starts around 1450 CE and the most significant metal concentrations occur in cluster H, and originate from layers of fine and organic rich sediments primarily in cores AA-2 and AA-6. Clusters I and J occur during the second half of the Modern Period in silty and sandy horizons, mainly from cores AA-2 and AA-6.

Other smaller clusters (B and G) are apparent, occurring typically before a major contamination cluster (positive trends in the 500-year Gaussian filter in Fig. 6). One of these clusters occurs between 100 and 190 CE (B) and is identified mainly in organic-rich layers of core AA-5. The other cluster of heavy metal content occurs at the end of the Late Medieval Period (G), between 1390 and 1450 CE and, in this case, it represents high counts in the three cores.

5. Discussion

5.1. Analysis of local trends, archaeological evidences and historical sources

The metal content index of the Hasli-Aare catchment was achieved by comparing the response of metal/Rb ratios in the floodplain sediments with local historical sources of mining activities. This comparison allowed us to establish a threshold (one standard deviation above the mean) that defined the metal content anomalies for the last 2500 years. The reference period used in this comparison centres in the last 600 years, when we have more written sources and also when there is an increase of mining and smelting activities in the catchment (see further discussion in Section 5.1.2). Consequently, the reason for establishing this specific threshold is explained because it was the boundary that adjusted better to the historical sources and reflected the expected increase of metal content from the last 600 years.

The overall analysis of metal anomalies in the Hasli-Aare catchment (Fig. 6 and Table 1) reveals various trends that could be indicative of periods of metal contamination and possible phases of mining activity (as shown in Section 4.2). We start this trend analysis by examining those anomalies that cannot be corroborated with comprehensive historical information nor with significant archaeological finds, before discussing the later periods that are archeologically and historically better constrained.

5.1.1. Prehistoric metal content

During the prehistoric period, the most important cluster of metal content occurs at the end of the Iron Age (cluster A in Fig. 6), and is associated with the middle/end of the La Tène culture. It is widely accepted that this prehistoric culture made extensive use of metal tools, armour and adornments (mainly iron, but also bronze for jewellery and decoration) and were considerably advanced in their metalworking (Fitzpatrick, 1984). However, there is no evidence in the region

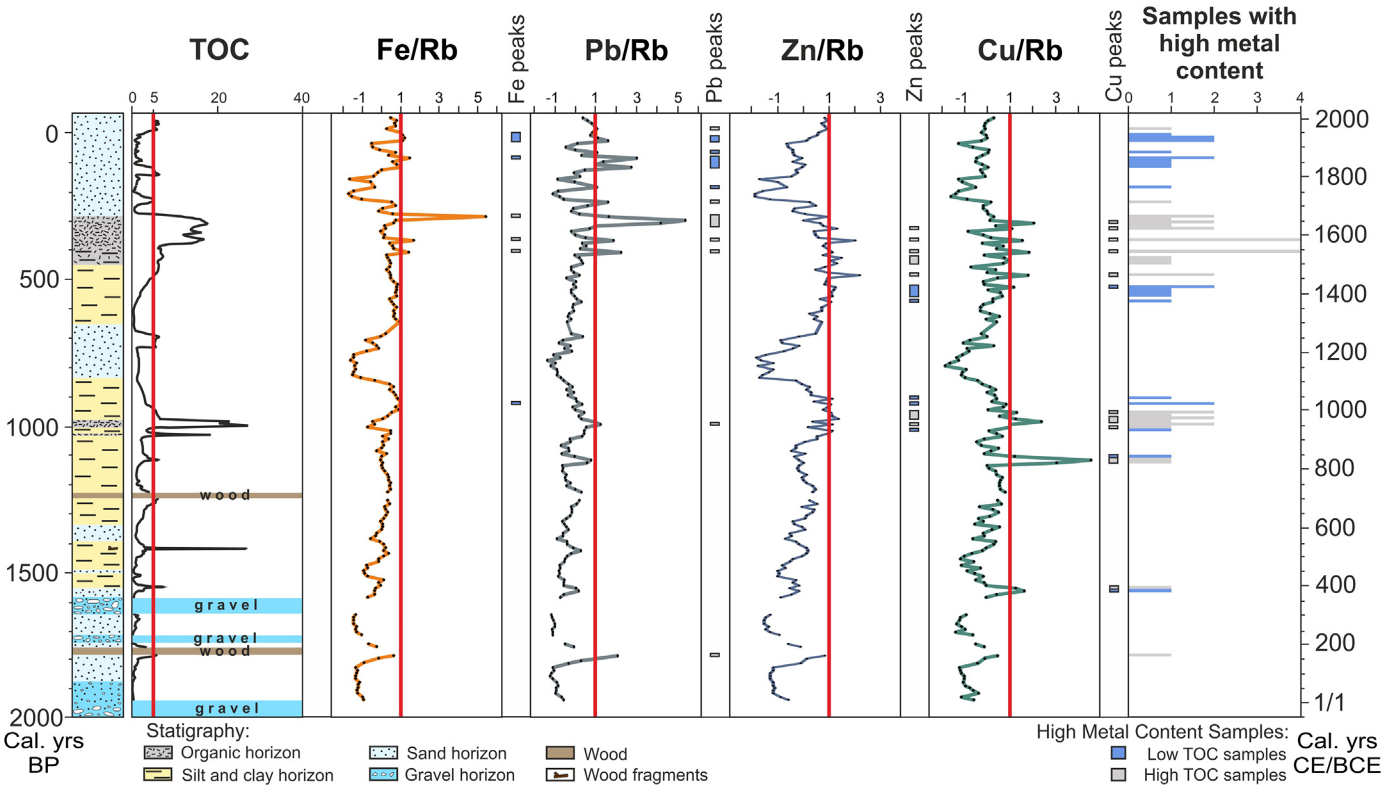

Fig. 5. Metal content in core AA-6, presented with a 10-year interval. Total organic carbon (TOC) is shown as a percentage (wt%) and metal content as Z-scores of XRF total counts normalized by rubidium. Metal anomalies shown on the right were identified in samples with Z-scores higher than one standard deviation above the mean. Data discontinuities occur in gravel layers and wood fragments.

of iron smelting during this period (Ebersbach et al., 2010). Moreover, the fact that the high cluster A values occur mainly in the organic layers and in just one core (AA-5) increases uncertainty as to whether we are dealing with a major contamination scenario related to mining. For this reason, the cluster should only be considered indicative of a hypothetical mining period for the Bernese Alps (see further discussion in Section 5.2). Other metal concentration peaks occur during the Iron Age, but overall trends are low (see 500-year Gauss filter in Fig. 6) and, therefore, they cannot be considered as important periods of mining in the catchment.

5.1.2. Periods of metal contamination supported by historical evidence

During the Roman Period, between 80 and 400 CE, two clusters of high metal content can be identified (B and C in Fig. 6). These signals of metal contamination are observed in all the analysed cores, but the highest values occur primarily in organic layers, which could be responsible for uncertainties in the metal/Rb ratios. However, other peaks in sediments with low organic content can also be found, suggesting that metal contamination during this period probably did occur. The Roman Period is usually associated with a population increase in Central Europe and the flowering of trade (Hopkins, 1980), which may have increased mining activities. It is also widely accepted that metal, especially lead and copper, played an important role in the Roman economy (De Callatay, 2005). Despite the fact that there is no archaeological evidence of mining activity in the region, metal contamination during this period is largely corroborated by other natural archives: for example, Swiss and French peatlands (Shotyk et al., 1998, 2001; Forel et al., 2010), Spanish peatlands (Martínez Cortizas et al., 2013) Alpine lake sediments (Arnaud et al., 2005; Guyard et al., 2007), Swedish lake sediments (Renberg et al., 2001) and Greenland ice cores (Hong et al., 1996; Rosman et al., 1997; McConnell et al., 2018). Archaeological data from other alpine regions (Alpes-Maritimes) also indicate the presence of iron mining in high valleys during this period (Morin et al., 2007). The analysis of arboreal pollen during this period from the fan delta sediments of the neighbouring Lütschine catchment (Schulte et al., 2009a), show lower percentages, which point to the clear-cutting of mesic trees on the valley floor. In addition, the geochemical analysis of sediments from the Lütschine catchment also presented positive anomalies of metals during the same period (Schulte et al., 2008).

The transition from the Roman Period to the Early Medieval Period was marked by the Germanic invasions of the Roman Empire, which led to military and socioeconomic instability, political turmoil, and population migration (McCormick, 2001; Bielmann, 2014). Mentions of the Swiss Alps in historical sources are few, but it is known that several Roman colonies were looted and partially destroyed during this period (Drack and Fellmann, 1988) and it is highly likely that the Alpine region was also affected (either during or after this period). In our record, we fail to detect any metal content peaks between 400 and 460 CE, which probably provides evidence of the instability that characterized this transition period and could be indicative of a possible decline in mining activities.

Between 460 and 590 CE, another cluster of high metal content can be identified (D). There is no known archaeological evidence supporting mining activity in the Bernese Alps at this time, but finds made in Bellaires, Ferreyres and Montcherand (municipalities of the Jura region) point to considerable mining activity with dozens of high-temperature furnaces and dross remains, all dated between the 5th and 7th centuries (Pelet, 1974).

Throughout almost the whole of the Late Medieval Period, metal peaks are observed in the floodplain sediments, which seems to indicate that some kind of mining exploitation occurred, especially towards the middle/end of this period. There are, however, some exceptions to this pattern during the second half of the 9th and the second half of the

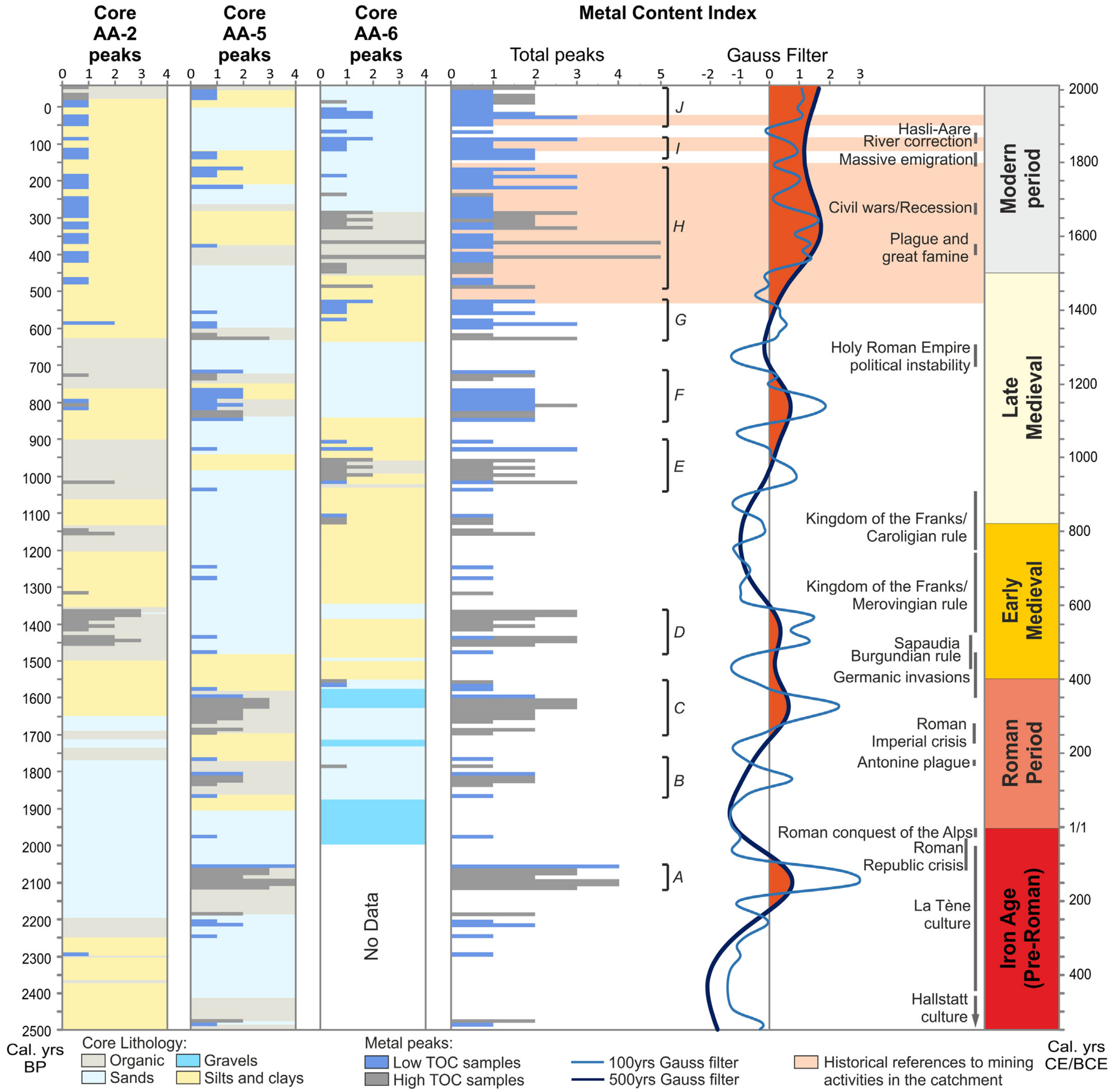

Fig. 6. Metal content with a 10-year interval, based on the identification of Fe, Pb, Zn and Cu anomalies from sedimentary records. Clusters of metal content are identified from A to J and major trends of metal content are highlighted in red, according to the positive trends of the 500-year Gaussian filter. Historical mining activity in the catchment is shown in light red and refers to documentary records according to Willi (1884), Türler et al. (1934), Saheurs (1965), Krähenbühl (1981) and Doswald (2012). Chronology of cultural periods in accordance with Huntley et al. (2002).

13th centuries. This could be attributed to political instability in the region, including the crisis of the Great Interregnum in the Holy Roman Empire that lasted from 1245 until 1312 CE (Buntinx, 1975). Despite these exceptions, the results indicate a clear positive trend (clusters E, F and G) supporting the hypothesis that mining activities underwent some growth.

The most important positive trend in the metal content in our record starts at the end of the Late Medieval Period, that is, in the 14th and 15th centuries (500-year Gauss filter in Fig. 6). Indeed, the geochemical response of all the sedimentary records shows a presence of metal peaks during this time span, indicative of widespread metal contamination in the valley that could be associated with an increase in Fe mining activities (see Supplementary information, Fig. S5).

This claim is supported by various historical records and a few archaeological remains. The first written historical references to mining activities in the catchment appear in documents dated from the 15th century, involving agreements between the Bernese central authorities and the inhabitants of the Hasli valley. A document from 1416 CE conceded the rights for the exploitation of mountain areas in the Hasli-Aare catchment and mentions the existence of an iron-melting furnace at Bürglen (Willi, 1884). This was an old settlement, approximately 2 km northwest of Meiringen that was destroyed during severe flooding

Table 1
Clusters of metal content, identified in the floodplain deposits of the Hasli-Aare Catchment. See clusters in Fig. 6.

Historical periods	Clusters of metal content
Modern	1900 CE to present (Cluster J)
Modern	1805 to 1870 CE (Cluster I)
Modern	1450 to 1790 CE (Cluster H)
Late Medieval	1390 to 1450 CE(Cluster G)
Late Medieval	1100 to 1250 CE (Cluster F)
Late Medieval	905 to 1050 CE (Cluster E)
Early Medieval	450 to 590 CE (Cluster D)
Roman	250 to 400 CE (Cluster C)
Roman	100 to 190 CE (Cluster B)
Iron Age	160 to 100 BCE (Cluster A)

in the 16th century (Kurz et al., 1979). A second historical document, dated 1418 CE, speaks of the exploitation of the iron ores at Erzegg and Planplatten in the Gen Valley and of the existence of an iron-melting infrastructure near Innertkirchen (see Fig. 2). Later sources, from the 16th century, record that another, larger, smelting complex was built in 1562–65 CE at Milital, on a site at the confluence between the Gen and Gadmer valleys (see Fig. 2). This infrastructure was to be the main centre of iron smelting in the valley for the next 250 years, processing all the iron ores from the mines at Planplatten, Balmeregg and Erzegg (Kurz et al., 1979; Wenger, 2013). Due to the lack of written records, it is very difficult to give an accurate estimate of how much material was extracted from this catchment. However, Doswald (1996) assumed that during the 16th century the furnaces were in full operation, because in 1587 the State of Bern demanded 500 cannon balls per year to meet the mining rights.

Clear-cutting for smelting activities was probably one of the main triggers of the severe flood events that occurred during the second half of the 16th century (Schulte et al., 2015). These activities caused extensive damage to the downstream settlements of the Hasli Valley, destroying Balm and Bürglen in 1550. This, in conjunction with cooler climate pulses in the Alps (Büntgen et al., 2011; Schulte et al., 2019b) and several episodes of plague and famine, seems to correlate with the detection of fewer metal anomalies in our record, reflecting demographic decline and a probable decrease in mining activity.

Historical sources indicate that the amount of wood required for smelting during the 16th and 17th centuries was so high that most of the surrounding forests were cut down (Kurz et al., 1979). Because of these intensive mining and deforestation activities, and due to the increase in flood damage, some sources record that the local inhabitants became dissatisfied with the mining ventures and even tried to shut the activity down (Müller-Landsmann, 1900). In 1628, all the buildings making up the Milital smelting complex were destroyed and burned by disgruntled local inhabitants (Rennefahrt, 1962). However, this did not put an end to the mining activities and the infrastructure was quickly rebuilt. As the Bernese authorities did not wish to have to depend on foreign sources for the production of arms and armour (Doswald, 2012), mining activities were always quickly re-established to meet the demands of the central power. In 1630 CE, another agreement between Bern and the Hasli valley inhabitants conceded the rights to exploit extensive forested areas to guarantee the continuation of smelting activities (Doswald, 2012).

The second half of the Modern Period is marked by the presence of various metal peaks. There is an abundance of historical information from this period and several sources stress the importance of mining to the local economy, although metal trade reached only neighbouring regions (Willi, 1884; Saheurs, 1965; Thut, 2008). A short interruption of the metal content signal at the beginning of the 19th century can be attributed to a decline in the valley's mining activity (Zahn, 2001). This decline and the impact of catastrophic floods in 1831 and 1851 CE (Schulte et al., 2015) caused a local impoverishment and massive migration to other continents, especially America (Hoerder and Moch, 1996). Other sources also record that the mining of iron ore was abolished in 1798 CE and only taken up again in the 1810s, after the Bernese authorities had transferred ownership of the smelting infrastructure at Milital to the local authorities (Kurz et al., 1979). However, the Milital infrastructure remained active only until 1813 CE, when the site was closed and iron mining ceased in the catchment (Türler et al., 1934).

The fluctuating contamination signal in the 19th and 20th centuries could, in some part, be attributable to the decline in local metal production induced by the Industrial Revolution and shifts in regional economic activities. The improvements made to techniques of extraction, smelting and transportation contributed to lowering the price of imported metals and to creating new locations for the heavy metal industry. As such, prices were affected not only by the increase in production capabilities, but also by the flourishing of secondary smelters, steel factories and refineries (Berninger and Pelet, 2006).

While the iron mines were abandoned at the beginning of the 19th century (Zahn, 2001), another mining activity – namely, that of silver-bearing galena – was developed at a different site in the catchment (Guttannen, Fig. 2) and continued until the first half of the 20th century (Saheurs, 1965). Although this activity was not as intensive as the earlier iron mining had been, it seems that it was responsible for the last clusters of metal contamination in our record, that is, clusters I and J, corresponding to the period from 1810 until the present day. Historical sources corroborate that lead mining occurred during this period, but also stress that it was limited to the local scale and was poorly remunerated (Saheurs, 1965). During the First World War there was a slight rise in production, but this was short lived (Fehlmann, 1919). The continuous signal in our record in the following decades could be attributed to: i) other sources of contamination, such as the atmospheric deposition of lead in the top soil horizons and ii) erosion and sedimentation processes during floods, which require time for the erosion of contamination sources and the transport and deposition of sediments in the lower delta plain.

5.2. Anthropogenic metal contamination over the Western Alps

The main trends presented by metal content in the Hasli-Aare catchment (Fig. 6) correlate well with mining activity records in this region and with its economic and social changes. The question, however, arises as to whether these pulses of high metal content coincide with episodes of mining activity in the Greater Western Alpine Region. To address this, we analyse the prehistoric and historical anthropogenic metal pollution recorded in the natural archives of the Western Alps (see Fig. 1). Our analysis of the results presented in various papers (listed in Supplementary information Table ST2 and main trends synthetized in Fig. 7) shows the presence of metal contamination related to mining activities across the whole of this region and that the phenomenon dates back to at least the Bronze Age, around 1920 BCE (Guyard et al., 2007). Anthropogenic contamination can be identified in a wide range of geographical locations (from valley floors and endorheic basins to mountain slopes), of diverse altitudes (ranging from 232 to 4300 m a.s.l.) and in different types of natural archives (from fluvial and lake sediments, to peatlands and ice cores).

A comparison of these different records (see Supplementary information, Table ST2) makes it evident that human action and metal pollution have not been homogeneous over the last 2500 years. Distinct clusters of anthropogenic contamination may result from i) regional differences in the timing and intensity of ore exploitation and ii) different sensitivities of natural systems when recording metal pollution from mining activities. The existence of different signals can also be explained by the considerable size and environmental, climatic and socio-economic diversity of the Western Alps. It is highly unlikely that local mining activities would have developed in a synchronized fashion over such a large region. Even in cases where natural archives are located relatively close to each other, distinct signals are observed. This is the case of the Lake Bramant (Guyard et al., 2007) and Lake Blanc

Huez metal records (Simonneau et al., 2014). Although these two lake records are less than 12 km apart, they show non-coincident signals with different periods of anthropogenic metal pollution (Figs. 1 and 7). The main reason for these contrasting signals seems to be the predominant local response of Lake Blanc Huez, related to mining activity very close to its lake shore (Chapron et al., 2007; Garçon et al., 2012).

Furthermore, the comparison of results from the different Alpine records is also affected by the variety of depositional environments. Signals of high metal content from fluvial or lake records may be more prone to revealing mining pollution originating from local sources, whereas, in the case of peatlands and ice cores, the signal could be a mixture of both local and regional sources, including pollution from other European regions. In addition to these differences, the results from the natural archives in the Western Alps include a wide range of chemical elements (Sc, Cr, Fe, Cu, Zn, Pb, Ag and Hg), as well as different temporal scales (ranging from millennia to centuries).

Despite these differences, the general trends presented by anthropogenic metal pollution are mostly in phase with each other across the Western Alps and can, in general, be related to the political, economic and social contexts of central Europe. The most important metal pollution trends occur: i) at the end of the Iron Age, approximately between 300 and 50 BCE; ii) during the Roman Period, between 0 and 400 CE; iii) throughout the Late Medieval Period, between 800 and 1350 BCE and iv) during the Modern Period, from 1600 CE down to the present day (see Fig. 7).

During the Late Iron Age (160 to 100 BCE), a high metal content is found in the alluvial archives of the Hasli-Aare valley (A in Figs. 6 and 7). Likewise, other Alpine archives record anthropogenic metal pollution during this period (350 BCE to 1 CE), in particular, those of Lake Blanc Huez (Simonneau et al., 2014), Upper Durance Valley (Py et al., 2014), Lake Anterne (Giguet-Covex et al., 2011), Lake Petit (Morin and Rosenthal, 2002; Brisset et al., 2013), Col du Dôme (Preunkert et al., 2019), Etang de la Gruère (Shotyk et al., 2001) and Meidsee (Thevenon et al., 2011b). While some archives indicate a continuous signal towards the Roman Period (archives 1, 7 and 15 in Fig. 7), others indicate a discontinuous response (archives 2, 3 and 8), similar in this respect to the Hasli-Aare Valley. This discontinuity might be explained by a decline in mining activities in these sites, probably due to local variability in human occupation and socio-economic stability and/or a discontinuous transfer and deposition of metal contamination.

If we examine the pollution signal across the Roman Period (0 to 400 CE), the Hasli-Aare record shows a parallel response to that of the majority of archives in the Western Alps. In fact, the pollution signal during this period is undoubtedly one of the most significant, given that all the analysed records, with the exception of that of Lake Blanc Huez, show evidence of anthropogenic metal pollution (Fig. 7). This analogous trend across the Alpine region confirms the importance of mining in this period (Nriagu, 1998). The signal, moreover, is also evident in many other natural records from distant regions (Alfonso et al., 2001;

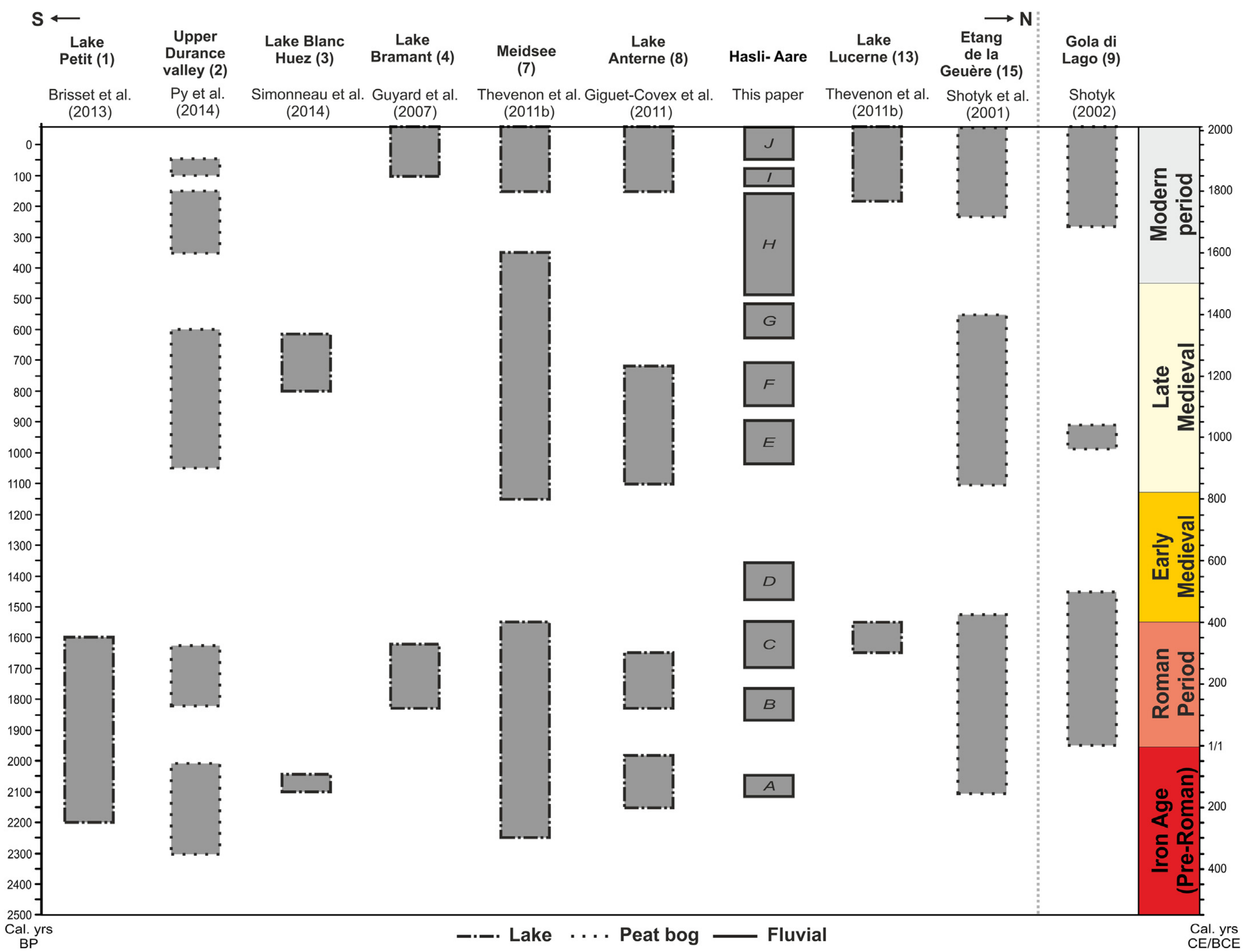

Fig. 7. Ancient anthropogenic metal pollution identified from different natural archives in the Western Alps. The different records are organized according to their geographic location, from south (left) to north (right), expect for that of Gola di Lago (9) which is set apart due to its particular location on the southern slopes of the Alpine mountain range. For a complete description of each archive, see Supplementary information Table ST2.

Mighall et al., 2009; Martínez Cortizas et al., 2013; McConnell et al., 2019) and in both historical and archaeological sources (Nriagu, 1983; Walsh and Giguet-Covex, 2019). The mining activity that occurred during this period would have benefited greatly from the socioeconomic stability of the Roman Empire, combined with the favourable warmer climatic conditions of the Roman Climatic Optimum, which were doubtless important for human activity in Alpine environments.

During the Early Medieval Period, most of the records (Fig. 7) indicate a decrease in pollution, coinciding with a transitional period, marked by sizable migrations and notable political and social instability, and economic decline (McCormick, 2001; Bielmann, 2014). Yet, at the beginning of this period a high metal content was observed in the Hasli-Aare valley (D in Figs. 6 and 7). The existence of this geochemical signal is not analogous with the majority of records in the Western Alps, but Alpine ice cores from the Mont Blanc and Mont Rosa Massifs show an increase of metal pollution from 600 CE onwards (Loveluck et al., 2018; Preunkert et al., 2019). Other mountain areas in Europe have also recorded similar trends during this period. Camarero et al. (1998) found a large increase in metal concentration in a lake sediment record from the Pyrenees, during c. 450 to 900 CE (peaking by c. 680 CE). Dissimilarities between alpine records can be explained either by local differences in mining activities during this period or by the sensitivity of natural archives to record lower pollution phases. Nevertheless, it should be noted that between 600 and 800 CE, most of the alpine sedimentary records, including the Hasli-Aare metal content, do not show any sign of anthropogenic metal pollution, which could indicate a pronounced decline in mining across the entire region.

The Late Medieval Period (900 to 1500 CE) marks the beginning of a new increase in anthropogenic metal pollution, evident across several archives in the Western Alps. In the Hasli-Aare alluvial archives, several clusters of high metal content can be identified during this period (E, F and G in Figs. 6 and 7). This is also evident in the Western Alpine records of Lake Blanc Huez (Simonneau et al., 2014), Upper Durance Valley (Py et al., 2014), Lake Anterne (Giguet-Covex et al., 2011), Colle Gnifetti glacier (Gabrieli and Barbante, 2014), Etang de la Gruère (Shotyk et al., 2001), Meidsee (Thevenon et al., 2011b) and Lake Gola (Shotyk et al., 2001). The increase in mining activity during this period could have been influenced by more stable socio-economic conditions and by more favourable climatic conditions, coinciding with the Medieval Climate Anomaly (MCA, Lüning et al., 2019). The warmer temperatures of the MCA could also have contributed to an increase in the mining of high-altitude ore deposits, which probably became more accessible and meant mining could be practiced over a longer period (due to the reduction in snow cover). In the main valleys, the settlements and trade routes may also have benefited from a period of low to moderate flood frequencies (Schulte et al., 2015; Wirth et al., 2013).

During the Modern Period, anthropogenic metal pollution has become more generalised across the Western Alps, especially over the last 300 years. Almost all the natural archives analysed herein record an input of pollution during this period (see Supplementary information, Table ST2). This rising trend in metal pollution corresponds closely to the increase in population throughout central Europe and to the use of new mining and smelting techniques. Metal pollution after the Industrial Revolution is also evident in most of the Alpine records, especially during the 20th century (Rosman et al., 2000; Thevenon et al., 2011a; Preunkert and Legrand, 2013; Thevenon et al., 2013b), corresponding also with the increase in the burning of fossil fuels.

5.3. Factors responsible for metal content in floodplain deposits

The variations in the geochemical proxies and the metal signals are influenced by grain size, porosity, organic content, and diagenetic and soil processes. This heterogeneity may result in inconsistencies in the response of the geochemical XRF signal, which affects the measurements of metal total counts (Weltje and Tjallingii, 2008; Davies et al., 2015). Furthermore, the XRF signals used in this analysis are neither absolute measures nor percentages of chemical elements, so the higher values cannot be directly interpreted as indicating higher rates of contamination.

Geochemical signal uncertainties observed in organic-rich sediments are related with samples were metal content is enhanced by metal bound to the organic matter (see Supplementary information, Fig. S6). Nevertheless, other peaks of metal content in organic layers may reflect accurately periods of mining activity, showing an anthropic influence on the fluvial system. For this reason, we did not discard metal content from organic horizons and applied a metal/Rb ratio to reduce the effect of these uncertainties (Davies et al., 2015). In addition, although the single metal peaks observed in the organic layers should be interpreted with caution, they occur in layers that indicate warmer climate conditions and less flooding (Schulte et al., 2015), conditions that are favourable to mining activities.

Other XRF signal uncertainties occur in coarser sediments, were lower values of XRF total counts are usually detected and, with them, fewer positive metal anomalies. There are various reasons why coarser textures are normally characterized by lower XRF counts: i) their surface properties, ii) the lower proportions of eroded soil material (solum) with higher metal concentrations and iii) the lower content of organic material. The influences of the core surface properties can be attributed to the higher surface roughness and porosity volume of coarse textures.

Changes of Fe content due to redox conditions can also bring some uncertainties to the metal pollution signal. The mobility of this element is particularly important in reducing and acid conditions (Colombo et al., 2014), and solubilisation or precipitation can occur along the different sedimentary layers due to fluctuations of the water table and differences in hydraulic conductivity. In the case of the Hasli-Aare floodplain, the water table is relatively high, so iron mobility should be more significant in the most superficial layers (first meter), were water level fluctuations occur. In effect, considering these conditions, we observe high Fe content in the first meter of the cores analysed in this work. Therefore, we cannot fully discard Fe mobility in these cores, especially in the case of core AA-2, were no other metals are detected in superficial layers (Fig. 3). In cores AA-5 and AA-6, other metal elements, not affected by this mobility, can be found in the most superficial layers (Figs. 4 and 5).

Considering the existence of Fe mobility in our cores does not imply that Fe pollution from mining activities is inexistent in the Hasli-Aare floodplain. High Fe content in the superficial layers must have a source and historical written sources confirm that the last 600 years was an important period of iron mining and smelting in the catchment. Therefore, the particularly high Fe content found in our cores, in sediments from the same period (last 600 years), corroborate the possible anthropogenic Fe pollution from mining activities.

The comparison of the metal content in the three cores shows distinct responses over the last 2500 years (Fig. 6). This is attributed to the heterogeneous dynamics of erosion and sedimentation along the floodplain. Significant differences of accretion can occur at the same time, depending for example on the floodplain location (i.e., close to a channel or in an interdistributary basin). This means that the metal-laden alluvium that reaches the floodplain is not deposited at the same time, neither in all the analysed cores. Unlike other natural archives, such as lake sediments or bogs (Shotyk et al., 2001; Thevenon et al., 2011b), that present a continuous and homogeneous signal of metal pollution for the entire study area, fluvial cores may present a fragmented signal, which must be completed by additional cores from other areas of the floodplain. In the case of the Hasli-Aare floodplain, we consider that the combination of the metal content from cores AA-2, AA-5 and AA-6 covers adequately the major metal inputs from mining activities over the last 2500 years.

Shotyk et al. (2001), Forel et al. (2010) and Süfke et al. (2019) suggest that most of the evidence of metal anthropogenic contamination during Roman and Medieval Periods is associated with atmospheric pollution, since metal peaks are identified primarily in peatlands and small catchment lakes. Roman and Medieval casting methods were rudimentary and responsible for high levels of atmospheric pollution. This pollution would have been disseminated across vast regions of the northern hemisphere (Hong et al., 1996). Therefore, the contamination of alluvial archives may originate both from atmospheric and fluvial deposition. A comparison of the Pb/Rb ratios in our results with Pb concentrations reported in the Greenland ice sheet (Hong et al., 1996; Rosman et al., 1997; McConnell et al., 2018) or in alpine glaciers (More et al., 2017; Preunkert et al., 2019) is difficult because we lack concentration values. Comparison is also limited by the differences in timescales and temporal resolution of the different records. Nevertheless, if we focus on the major trends of Pb contamination over the last 2500 years, similar periods can be identified between our results and Pb concentrations in ice cores, especially during the Roman Period and throughout the Modern Period (see Supplementary information, Fig. S7). Likewise, a comparison of our results with those from other studies conducted in the Alps shows that, despite methodological and sedimentological differences, there are certain parallels in the metal contamination throughout the historical period.

Fluvial processes, including erosion from increased slope surface run-off, river-bank erosion, transfer and deposition of metal-rich sediments or legacy metals on floodplains during major floods, are considered a fundamental driver of the metal contamination of floodplains, producing an immediate response in the sedimentary record (Miller, 1997; Schulte et al., 2008, 2015). However, a time-lag in the metal concentration period can occur. This could be due to: i) the various geomorphological stages that sediments went through (which all require time); ii) the lack of geomorphological connectivity between the mining sites (most of them located on slopes), iii) the natural variability of channel migrations (a 500-year reconstruction of the fluvial geomorphology of the Hasli valley is provided by Schulte et al., 2015); iv) channel management and hydraulic infrastructures and v) the dimension and characteristics of the fluvial system.

Taking into consideration the previous points, it should be noted that when performing a contamination trend analysis, the number of metals recorded in any given 10-year interval can be affected by a delayed and/or an enhanced signal of metal pollution in the fluvial system. For the delayed signal, a prolonged input of chemical elements from mining activities of the Hasli-Aare can occur when the pollution source lies far from the sedimentation area (the furthest sources of mining pollution in the catchment are 20 km from the delta plain). According to our findings, the metal contamination pulses from the Roman Period and Early Medieval Period (clusters C and D) could in fact present such a lag of 100 to 200 years. This could be supported by evidences that Roman mining activities started at an earlier date (De Callatay, 2005) and that there are not many historical or archaeological data that support mining activities in the region during the Early Medieval Period (Ebersbach and Gutscher, 2008). In the case of the enhancement of the metal pollution signal, legacy metals can be mobilised with soil/sediment during phases of increased erosion and sedimentation, thus incrementing the signal in the floodplain.

Climate variability may also have a significant indirect influence on positive metal anomalies, particularly when: i) the provenance of alluvial sediment of different textures is controlled by erosion and deposition during episodes of flooding and ii) organic soils are developed during periods of decreasing flood activity. This is a crucial point because Schulte et al. (2009a, 2009b, 2015) showed that floodplain deposition and their related floods in the Hasli-Aare, Lütschine and Lombach rivers are strongly influenced by climatic and solar activity (Steinhilber et al., 2009; Peña et al., 2015; Peña and Schulte, 2020). The development of organic-rich horizons during periods of lower flood activity also signifies a lower deposition of metal-laden alluvium, but in some cases our records show a high metal content (between 160–100 BCE, 105–140 CE, 250–350 CE, 490–590 CE and 940–1000 CE, Fig. 6). This could indicate that the metals from upstream mining activities can also be delivered to the floodplain during lower magnitude floods and that lower intensity flows may enhance the transport and sedimentation of fine sediments enriched in metals.

In order to rule out the possibility that climate variability is the main factor responsible for positive metal anomalies in our records, the standardised metal content indices (500- and 100-year Gauss filters in Fig. 6) were compared with the signals of the sedimentary flood proxy of the Hasli-Aare (Schulte et al., 2015) and other climatic series from the Alps (Büntgen et al., 2011; Luterbacher et al., 2016; Arnaud et al., 2016), but no significant correlation was found. However, the warmer climate experienced during the Roman Climate Optimum and the Medieval Warm Period may have improved conditions for ore exploitation, smelting and commerce in Alpine environments and coincided with periods of reduced flooding (Schulte et al., 2015).

6. Conclusions

The approach adopted in this study has allowed for significant progress to be made in terms of providing evidence of historical mining activities. Inferences based on geochemical proxies of floodplain sediments from the Bernese Alps, especially during periods when written sources and archaeological finds are scarce or non-existent, has proved particularly productive. The results obtained from the delta floodplain deposits of the Hasli-Aare catchment show that anthropogenic metal contamination in this area may well date back to the Roman Period and possibly even earlier, to the end of the Iron Age.

Metal content detected in the Hasli-Aare catchment indicate four major pulses of contamination: during the Late Iron Age, from the Roman Period to the beginning of the Early Medieval Period, in the Late Medieval Period and throughout the Modern Period. Over the last 500 years, the sediments of the Hasli-Aare valley record the most significant peak anomalies in the whole time sequence. These correspond to an increase in population and to improved extraction and smelting techniques. From the 17th century onwards, periods of lower metal content and shifts in these trends correspond quite accurately with the social and economic changes in central Europe, regional migratory events within Switzerland and significant demographic fluctuations.

These results also seem to indicate that the transfer of metals originating in the slopes of mining and smelting areas to floodplains occurred not only in recent periods but could also have occurred throughout historical times, during periods of higher mining activities. However, while the flood-induced contamination of the Modern Period has been recorded with an extremely short time lag, favoured by deforestation on slopes that has increased connectivity, we propose that during the Roman Period there may have been a time lag of 100 to 200 years, because the vegetation on slopes had not yet been exposed to an enduring process of perturbation.

The analysis of the natural archives located in the Western Alps has allowed us to identify similar anthropogenic pollution trends across the region. The most important of these occurring at the end of the Iron Age, during the Roman Period, across the Late Medieval Period and throughout the Modern Period; however, pollution signals may in some specific locations differ, indicating local variations in mining activities and/or a lag in metal transfer.

We conclude that the results reported here contribute to Alpine mining history, especially given the lack of archaeological evidence for the Western Alpine region. Indeed, as such, this study constitutes a step towards gaining a better understanding of human activities in the Western Alps over the last 2500 years.

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CRediT authorship contribution statement

Filipe Carvalho: Investigation, Data curation, Formal analysis, Methodology, Writing - original draft. **Lothar Schulte:** Conceptualization, Funding acquisition, Data curation, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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