Exceptionally high levels of lead pollution in the Balkans from the Early Bronze Age to the Industrial Revolution

Jack Longman[a,1,2], Daniel Veres[b,1], Walter Finsinger[c], and Vasile Ersek[a,b]

[a]Department of Geography and Environmental Sciences, Northumbria University, NE1 8ST Newcastle-upon-Tyne, United Kingdom; [b]Institute of Speleology, Romanian Academy, 400006 Cluj-Napoca, Romania; and [c]Palaeoecology - ISEM, Univ Montpellier, CNRS, EPHE, IRD, F34095 Montpellier, France

Edited by François M. M. Morel, Princeton University, Princeton, NJ, and approved April 30, 2018 (received for review December 11, 2017)

The Balkans are considered the birthplace of mineral resource exploitation and metalworking in Europe. However, since knowledge of the timing and extent of metallurgy in southeastern Europe is largely constrained by discontinuous archaeological findings, the long-term environmental impact of past mineral resource exploitation is not fully understood. Here, we present a high-resolution and continuous geochemical record from a peat bog in western Serbia, providing a clear indication of the extent and magnitude of environmental pollution in this region, and a context in which to place archaeological findings. We observe initial evidence of anthropogenic lead (Pb) pollution during the earliest part of the Bronze Age [~3,600 years before Common Era (BCE)], the earliest such evidence documented in European environmental records. A steady, almost linear increase in Pb concentration after 600 BCE, until ~1,600 CE is observed, documenting the development in both sophistication and extent of southeastern European metallurgical activity throughout Antiquity and the medieval period. This provides an alternative view on the history of mineral exploitation in Europe, with metal-related pollution not ceasing at the fall of the western Roman Empire, as was the case in western Europe. Further comparison with other Pb pollution records indicates the amount of Pb deposited in the Balkans during the medieval period was, if not greater, at least similar to records located close to western European mining regions, suggestive of the key role the Balkans have played in mineral resource exploitation in Europe over the last 5,600 years.

peat bog | metal resources | Balkans | lead pollution | medieval

The discovery of metals and refinement of alloys has been fundamental to the development of modern industrialized society (1). The earliest use of metals in the form of native copper in Anatolia roughly 9,000 y before common era (BCE) (2) preceded the invention of extractive metallurgy and alloying at around 5,000 BCE (3). Evidence of intentional thermal treatment of ores to produce metals, and complex metalworking around this time has been uncovered in several places throughout the Balkans (3–6) as well as in the Middle East (7). Building on the discoveries of these early metalworking pioneers, humans have continuously employed metals in a wide range of applications. However, the exploitation of mineral resources has a broad range of environmental impacts, including metal-contaminated wastewater and the release of chemical particulates to the atmosphere (8), from mining (9) and smelting (10), and the use of toxic metals in tools and artifacts [e.g., Pb in Roman water pipes (11)]. As a result, the effects of highly toxic Pb poisoning on the broader ecosystem (12) and on human health during the past two millennia are well documented, particularly for the Roman Empire, where Pb was a highly sought-after metal commodity (13).

Trends and amplitudes of mineral resource exploitation have been documented in central-western Europe primarily via the geochemical composition of peat, building on earlier work on polar ice cores (14, 15) and lake sediments (16–18). Released to the atmosphere through mining and smelting, once deposited within peat or lake sediments, Pb is effectively immobile (19), resulting in its reliability as a proxy for reconstructing past pollution directly related to such anthropogenic activities (20). Due in part to its biogeochemical immobility, and after the early detection (21) of a clear environmental Pb pollution peak from Roman times in British peat records, much of the focus has been on this metal (20). To date, traces of Roman period Pb pollution have been found in records spanning most of Europe (20), including Spain (22–24), Switzerland (25), and even areas outside Rome's reach such as Sweden (26) and Central Europe (27). Typically, such reconstructions focus on ombrotrophic peat fed only by direct atmospheric fallout (25), but the applicability of minerogenic bogs and even lake sediments in recording a reliable geochemical signal of past pollution has also been proven (28). As a result, the development, impact, and scale of mineral resource exploitation through time in central and western Europe has been well assessed, providing an improved understanding of both socioeconomic development, and of our impact on the environment through time.

Significance

A detailed record of historical lead (Pb) pollution from a peat bog in Serbia provides a unique view on the extent and timing of Balkan mining and metallurgy. Evidence of the earliest European environmental pollution is followed by large-scale and sustained increases in the amount of anthropogenically derived Pb after 600 BCE, through the Roman/Byzantine periods, and into the medieval period. Occasional evidence of drops in pollution output reflects the disruptive socioeconomic impact of periods of turmoil. Our data show a trend significantly different to records in western Europe, where Pb pollution decreases dramatically after the collapse of the Roman Empire. These results suggest metal-rich southeastern Europe should be considered a more major player in environmental metal pollution through time.

Author contributions: J.L., D.V., and V.E. designed research; J.L. performed research; W.F. contributed new reagents/analytic tools; J.L., D.V., W.F., and V.E. analyzed data; and J.L., D.V., W.F., and V.E. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

[1]To whom correspondence may be addressed. Email: j.longman@soton.ac.uk or daniel.veres@ubbcluj.ro.

[2]Present address: School of Ocean and Earth Sciences, University of Southampton, SO14 3ZH Southampton, United Kingdom.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1721546115/-/DCSupplemental.

Such work also indicates the reality of atmospheric long-distance transport of Pb, although differences between records hint at strong regional and temporal variability (8), necessitating further investigations of pollution loading in regions (both sources and sinks) with a rich ore endowment and a documented long history of metal use. Pertinently, long-term Pb pollution records for southeastern Europe have not yet been investigated (Fig. 1), thereby limiting the inference of past metal use, the associated environmental pollution, and the likely impact on human health in this region and beyond. However, the rich archaeological heritage of the Carpathian-Balkan region includes the earliest known sites of mining and extractive metallurgy in Europe (29), with exploitation centers at Rudna Glava in Serbia (30) and Ai Bunar in Bulgaria (31), and workshops in Pločnik and Belovode in Serbia (4, 32) all dating broadly to ∼5,500–4,500 BCE (Fig. 1). These early activities ushered in significant metalworking activities for several millennia related mainly to the Vinča and other contemporaneous or successive material cultures (3, 30), extending from the Carpathians in the north throughout most of the Balkans. Metal production in the area further bloomed during the Copper Age and especially during the Bronze Age, with metallic artifacts reaching exceptional quantities and sophistication in design (33, 34) after 3,000–2,800 BCE (35). Further significant metal exploitation was undertaken by the Romans and their Byzantine successors, with evidence of exploration and large-scale mining in the area at the time (36, 37). Despite this apparent understanding of Balkan metal use history, metallurgical activities during significant periods of time are still inferred from a scarce and at times ambiguous archeological record. Periods such as the Early Bronze Age are represented by only a handful of artifacts of uncertain age and provenance (34, 38). Additionally, little reference is made to medieval mining activity (39), although it has been suggested that silver (Ag)-rich ores in modern-day Serbia were likely exploited since the medieval period (40, 41). As such, the exact scale and impact of such activity in the broader region are unclear in many respects, especially after modern-scale exploitation of mineral resources, which has largely destroyed many old vestiges. It may be that such finds are indeed representative of a rich metallurgical history, but that has yet to be proven unequivocally.

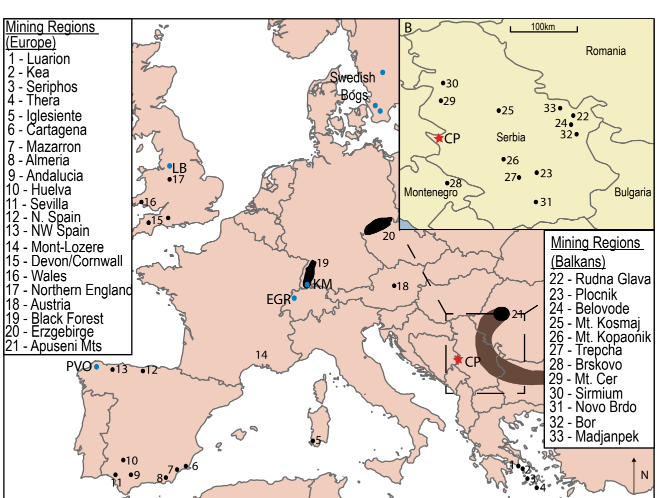

Fig. 1. (*A*) Map of Europe indicating location of Crveni Potok (red star) and of other studies referenced in text; Lindow Bog (LB) (21), Penido Vello (PVO) (85), Etang de la Gruyere (EGR) (25), Kohlhütte Moor (KM) (88), and three Swedish bog records (26). Also presented are locations of major metallogenic mining regions exploited before 1,800 CE (85) and the Banatitic Magmatic and Metallogenic Belt (highlighted in brown). (*B*) Serbia and surrounding countries, indicating the location of Crveni Potok with respect to the locations of mining and metal production sites as mentioned in text.

The ∼7,500-y-long history of mining and metallurgy in the Balkans was likely facilitated by the significant endowment in polymetallic ores, very rich in base and precious metals (Fig. 1). For instance, the Apuseni Mountains (western Romania) host the Metaliferi mining district, home to Europe's largest gold and silver (Au–Ag) deposits (42, 43). In addition, other mining fields have been or are still being exploited on the 1,500-km-long Banatitic Magmatic and Metallogenic Belt, which runs from Romania, through Serbia, and into Bulgaria, and is the most important ore-bearing (particularly Cu, Au, and Pb–Zn) belt of the Alpine–Balkan–Carpathian realm (44, 45), itself a section of the Thethyan Eurasian Metallogenic Belt (46).

Here, we present a high-resolution record of past anthropogenic pollution based on the geochemical data from Crveni Potok peat bog (Fig. 1), reconstructing past metal-related environmental pollution linked to mineral resource exploitation in the Balkans. The approach delivers a view on the chronology of past mineral resource exploitation and related pollution load in southeastern Europe. It allows for the gap between indirect geochemical inferences and direct archaeological evidence to be bridged in a region that has likely been crucial from the first steps of metal exploitation at the onset of human technological development, and through all of European metallurgical history (3–6, 29).

Crveni Potok (43°54′49.63″ N; 19°25′11.08″ E) is a small bog (<3 ha) located in the Tara Mountains National Park, on Serbia's western border with Montenegro, at 1,090 m above sea level (a.s.l.), within the Dinaric Alps (Fig. 1). Today, the mire is surrounded by forest, with the majority of the tree cover consisting of conifers (*Abies alba*, *Picea abies*) and *Fagus sylvatica* (47) and a small population of the endemic Serbian spruce (*Picea omorika*). The mean annual temperature is 7 °C, with the bog receiving ∼970 mm of precipitation per year (48). The bedrock consists of Triassic limestone, with Cretaceous marbles and ultrabasic (and extremely Pb-poor) igneous bedrock located to the southwest of the site (47).

Results and Discussion

Reconstructing the History of Metal Pollution in the Central Balkans. Although the Crveni Potok peat record covers the last 9,500 y, the shift from a minerogenic sediment to peat occurred at around 5,600 BCE (*SI Appendix*, *Supplementary Text*), and therefore discussion of the geochemical record of this early section in terms of human activity is avoided. After 5,600 BCE (Figs. 2*B* and 3*A*), the Pb_{Anthro} record, a measure of the Pb originating from anthropogenic activities (*Materials and Methods*), remains at low levels until ∼3,900 BCE. We found clear evidence of Pb_{Anthro} enrichment, and a modeled change point in the dataset (Fig. 2*G*), at 3,600 ± 122 BCE and peaking by 3,490 ± 128 BCE (Fig. 3*A*). This finding strengthens the limited archaeometallurgical evidence of the inception of the Bronze Age in the Carpathian–Balkan region, with evidence for arsenical bronze use at this time (6) especially close to the Cu-rich deposits south of Danube. This finding strengthens the limited archeological indications of the southeastern European Bronze Age onset a millennium earlier compared with similar developments in central and western Europe (49). Such activity may be linked with several regionally representative cultures (e.g., Baden, Tiszapolgar), although archaeological evidence is scarce (29, 30, 50). Copper may have been sourced from documented centers of metallurgy in central Serbia such as Rudnik in the Early Bronze Age (51), although evidence points to a wide trading network at this time in Europe (52). In terms of tin (Sn), the other main constituent of bronze, a more local origin may be possible. Uncertain archaeological evidence for Sn mining in

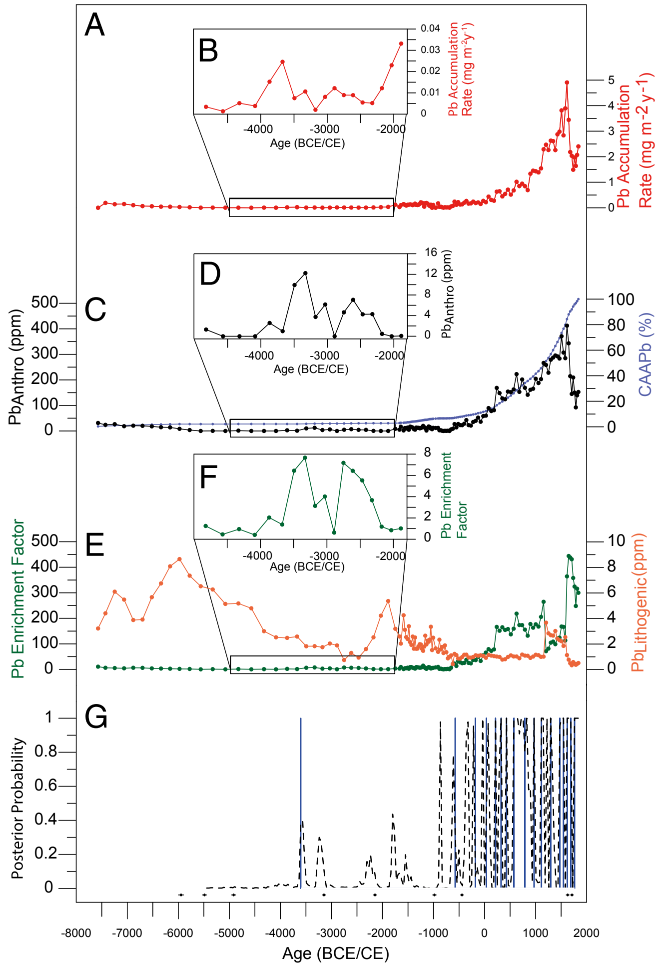

Fig. 2. Methods for elucidating the depositional history of Pb pollution at Crveni Potok. (*A*) The Pb AR, presented alongside the peak medieval Pb AR from Kohlhütte Moor (88). (*B*) *Inset* focusing on Pb AR between 5,000 BCE and 1,800 BCE. (*C*) CAAPb (blue line), alongside the anthropogenic Pb component (Pb_{Anthro}). (*D*) *Inset* focusing on Pb_{Anthro} between 5,000 BCE and 1,800 BCE. (*E*) The lithogenic Pb component ($Pb_{Lithogenic}$) and Pb enrichment factor. (*F*) *Inset* focusing on Pb enrichment factor between 5,000 BCE and 1,800 BCE. (*G*) Change-point modeling documenting (black dashed line) posterior probability of a change point occurring at each age, calculated from Pb_{Anthro}. Blue lines document points at which change points are statistically likely to have occurred. Also displayed at the base of *G* are radiocarbon dates and errors used to construct the age model.

western Serbia may indeed be linked to local metallurgy at this time (53, 54), although more research is needed to verify this. The timing of the initial Pb_{Anthro} enrichment as documented in the Crveni Potok data places it as the earliest record of environmental Pb pollution observed within a paleoenvironmental record in Europe (55), and is therefore the earliest indirect geochemical evidence of the well-constrained (via archaeological finds) early development of the Bronze Age in the Balkans at this time. The geochemical evidence is supported by a concurrent rise in charcoal concentration (Fig. 4*B*), suggestive of an increase in biomass burning, potentially related to a broad range of economic activities, including perhaps fuel production for metal smelting.

Interestingly, Pb_{Anthro} values remain low (Fig. 3*A*) during the transition into the Middle Bronze Age (2,500 BCE to 1,750 BCE), confirming a postulated nonlocal supply (although possible local smelting) of metal for the numerous bronze artifacts within Serbia (56), and the neighboring Carpathian Basin (57). The western Carpathians and eastern Alps have been proposed as the most likely metal sources during this period (57, 58).

Pb_{Anthro} displays high, but fluctuating values between 1,750 BCE and 950 BCE (Fig. 3*A*), a trend reflected also in the Cu, Zn, and Cr records (*SI Appendix*, Fig. S1). This corresponds to the rapid expansion of metal working in the Carpathian–Balkan region during the Middle and Late Bronze Age (33), and the first major forest clearances attributed to human activity both locally, in the Dinaric Alps (59) but also more regionally, over the Danube lowland basins (60). Across the Balkans, a large number of metal artifacts have been documented, many attributed to the Vatin (53) culture of the Late Bronze Age. This regional pollution may have been linked to mining and associated bronze manufacturing that presumably took place at locations around Mt. Cer (150 km north of Crveni Potok), proposed as a source for Sn found within archaeological artifacts of the Late Bronze Age (53, 56). Additional evidence for increasingly strong anthropogenic impact at this time is seen in Crveni Potok's enhanced fire activity reconstruction based on microcharcoal data, and centered around 1,550 BCE (47) (Fig. 4*B*). Furthermore, land-use changes, likely associated to enhanced regional human pressure and possible metal processing activities (53), may be inferred from the first appearance of coprophilous fungi (*Cercophora* and *Sporormiella*, Fig. 4*D*), and increasing values for the anthropic pollen indicators (*Plantago lanceolata* and *Cerealia*-type, Fig. 4*C*) in the Late Bronze Age at Crveni Potok.

The onset of the Iron Age is characterized by very low values for all metals investigated (Fig. 3 and *SI Appendix*, Fig. S2), clearly indicative of the disruptive socioeconomic impact the well-known Late Bronze Age Collapse has had in the wider Balkan region as inferred from archaeological and paleoenvironmental data (61, 62). This period represents the last interval of peat deposition without significant evidence of Pb_{Anthro} (Fig. 3*A*) as, remarkably, from roughly 600 BCE onward the Crveni Potok record shows a near-constant increase in the level of Pb_{Anthro} deposited through time, until ∼1,700 CE. The increased Pb_{Anthro} between 600 BCE and 200 BCE is likely reflective of the ability of the local La Tène material cultures, including the Celtic Scordisci who occupied much of the western Balkans at this time, and the Dacians, Thracians, Illyrians, and Greeks throughout the remainder of the region, to mine and smelt metals. Indeed, the Scordisci were known for their metallurgical proficiency and are considered the craftsmen behind a major Pb ingot discovery at Valle Ponti (northeastern Italy) (63), and several silver hoards (64). The source of the Pb ingot is thought to be Sirmium (located 200 km north of Crveni Potok) (Fig. 1), an important smelting center, before the Roman conquest of the area, and exploiting Ag–Pb sources in the Dinaric Alps (63). The Crveni Potok record likely reflects contribution from regional metal smelting activities, with rapid, stepwise increases in Pb_{Anthro} throughout Classical Antiquity and into the Roman period paralleling the historical socioeconomic development in the wider region (600–150 BCE, Fig. 3). This economic activity is also reflected in the extent of regional forest clearance, as observed in Bosnia, 100 km west of Sirmium (65), coincident with the increase in Pb_{Anthro} at Crveni Potok throughout Roman times, and into the subsequent medieval period. At Crveni Potok, no major decrease in forest cover is inferred from the pollen data in the Iron Age (47) (Fig. 4 *C* and *D*).

The Romans conquered much of the Balkans between 200 and 100 BCE. As in other regions with rich mineral deposits (e.g., Hispania and later Dacia), the Romans systematically cataloged and mined ores (66). In the Crveni Potok record, Pb_{Anthro} increases dramatically to a peak at ∼240 CE, with particularly sharp increases around 50 CE and 150 CE. The second pulse is clearly identified via change-point modeling at ∼181 CE (Fig. 2*F*), reflecting the extent of Roman mining and smelting throughout the Balkans (Fig. 1). Further evidence of intense

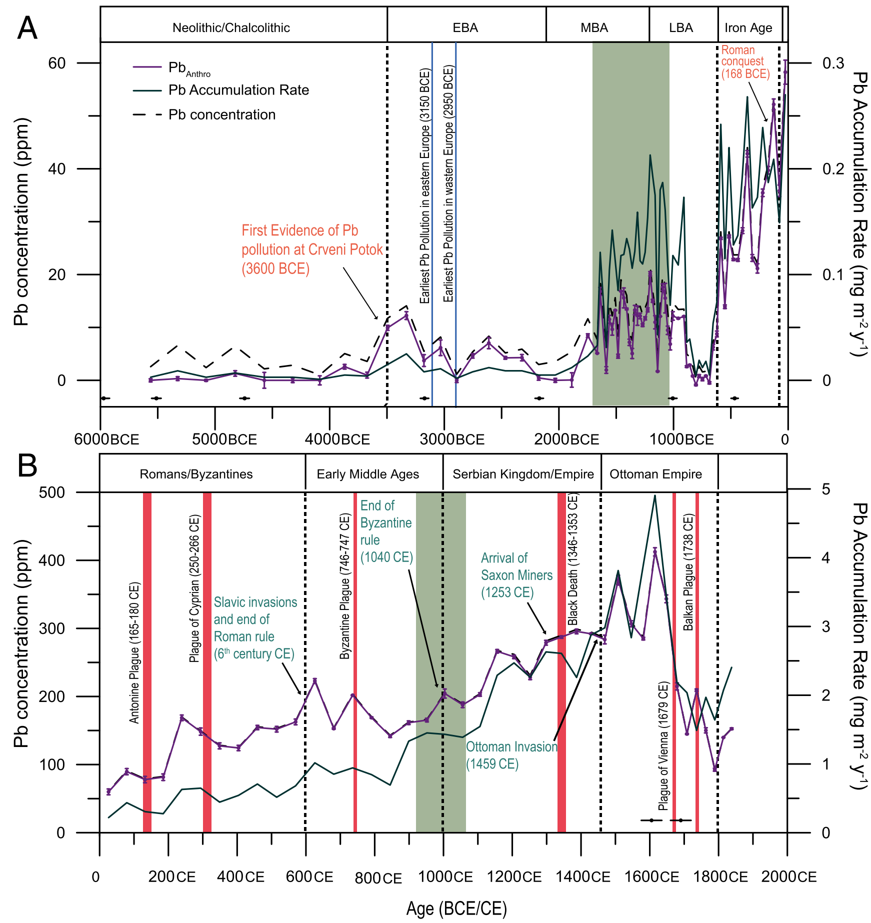

Fig. 3. Pb concentration (dashed black line), calculated anthropogenic contribution (Pb$_{Anthro}$, purple line), and PbAR (green line) for Crveni Potok core. *Upper* panel shows the earliest section of core, from 6,000 BCE to 0 CE, while the *Lower* panel indicates the period from 0 CE to 2,000 CE. Also indicated are major periods of change in the region (green labels), and the timing of major European plagues (red bars). Changes in cultural development are indicated by black dashed lines. Green rectangles display periods of increased fire activity (47). Blue vertical lines in *A* denote the earliest appearance of Pb pollution in previous European paleoenvironmental records, from western (55) and eastern (104) Europe. Also displayed at the base of each panel are radiocarbon dates and errors used to construct the age model. Note *A* displays a smaller scale to *B*, to allow for variations in the older section to be observed.

metallurgy may be seen in the cumulative atmospheric anthropogenic Pb (CAAPb) percentage (relative to the entire Pb deposited within the core) deposited over this period at Crveni Potok, nearly 20% (Fig. 2*B*), a significant fraction, especially once the large Pb enrichment of the Medieval period is considered. Under the Roman influence, south of the Danube, Illyricum and Moesia became typical mining provinces, with a particular focus on gold (Au) and Pb deposits (67). Moesia hosted two major mining regions, in the south (Dardania) and in the north (*ripa Danuvii*; along the Danube including the mineral-rich Timok valley) (66). In Dardania, examples of Roman mining have been excavated at *Municipium Dardanorum* (*Ulpiana*) (68), while numerous traces of Roman metallurgy exist throughout the Balkans (37). Closer to Crveni Potok, it appears mineral resources within the Dinaric Alps were also exploited, particularly at Mt. Cer (150 km north of Crveni Potok), and in particular the area around Rumska (66). Other major mining areas included Mt. Kosmaj near Belgrade (69, 70) and Mt. Kopaonik (68) (Fig. 1). From Kosmaj alone, the significant quantities of ancient slag (~1,000,000 tons) are testament to the scale of Roman metal exploitation and environmental pollution in the region, primarily from the processing of Ag–Pb ores (70).

After the peak at ~240 CE, the levels of Pb$_{Anthro}$ decline (Fig. 3*B*), possibly indicative of a regional slowdown in mining output, relating to repeated invasions and upheavals that affected the Balkan area, including the abandonment by the Romans of the mineral-rich provinces north of Danube (71). However, subsequent increases after 400 CE indicate mineral exploitation in the region recovered during the Byzantine Empire, which, contrary to developments in the rest of Europe, reached its peak in economic and cultural development at this time (72). Subsequently, the decrease in Pb$_{Anthro}$ evident after ~740 CE and lasting up to 1,000 CE echoes the gradual decrease in influence of the Byzantine Empire in the northern Balkans as documented in historical sources (72). After 1,100 CE, and with the arrival of Saxon miners from 1,253 CE onward (73), the Serbian statehood developed into one of Europe's leading Ag producers (41, 74), reflected also in significant Pb$_{Anthro}$ increases in the Crveni Potok record (Fig. 3*B*). The major Balkan medieval mining centers all opened between 1,250 and 1,300 CE, with Rudnik (1,293 CE), Trepcha (1,303 CE), and most pertinently to the Crveni Potok record, the Brskovo mines, which opened on the Tara Mountains in 1,254 CE, 150 km to the south (41, 75) (Fig. 1). This development in mineral resource exploitation is emphasized by the percentage of Pb deposited at Crveni Potok after 1,000 CE, nearly 60% of the total Pb accumulated in the core (Fig. 2*B*). The ongoing increase in Pb$_{Anthro}$ from 1,100 CE, with the clearest change highlighted by the change-point modeling at 1,141 CE (Fig. 2*F*), at Crveni Potok clearly reflects the continued regional opening of new mines and development of this industry

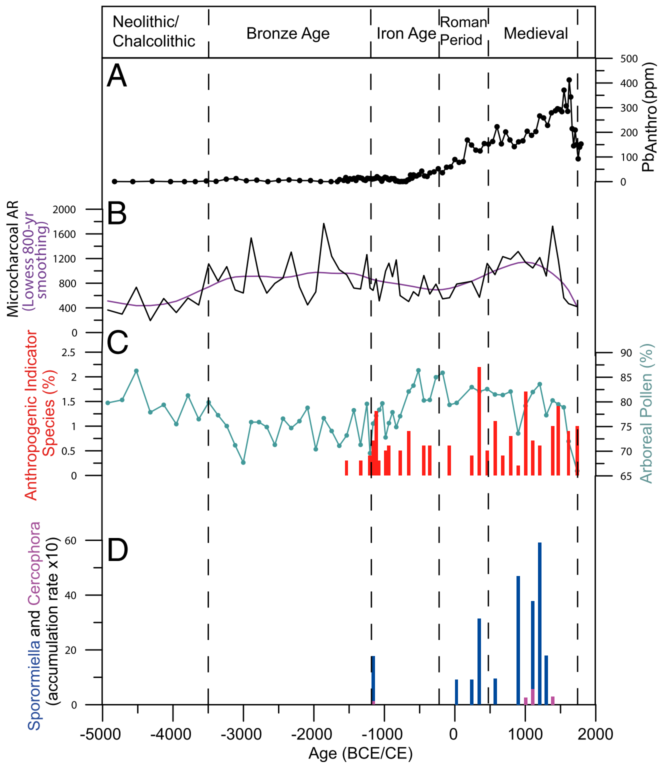

Fig. 4. Comparison of Pb$_{Anthro}$ with other proxies of human activity from Crveni Potok for the past 7,000 y. (*A*) Pb$_{Anthro}$ data as displayed in Fig. 2*B*. (*B*) Microcharcoal AR, with both raw values (black line) and a smoothed curve (purple line), produced using a Lowess 800-y smoothing window (41). (*C*) Percentage values of anthropogenic indicator pollen species (*Plantago lanceolata* and *Cerealia*-type), alongside arboreal pollen percentages. (*D*) Stacked bar chart of ARs for two coprophilous fungi species: *Cercophora* and *Sporomiella*.

throughout the early medieval period (41) to satisfy demand for silver in Europe and the Middle East (41). The Pb$_{Anthro}$ reaches a high level at ∼1,500 CE (Fig. 3*B*), and just after the Ottoman conquest of Serbia in 1,459 CE (76). This was a period of rapid growth in mining output throughout the Balkans, as most other European mining centers were in decline at the time (41, 77). Under Ottoman rule, metal resource exploitation continued to be productive, even after the introduction of the Kanun-name (Ottoman law) regulating and restricting mining in 1,536–1,537 CE (76), until Pb pollution peaked in ∼1,620 CE (Fig. 3*B*), by which time mines in the region were producing over 24.9 tons of Ag a year (77, 78).

The rapid decrease in Pb$_{Anthro}$ at Crveni Potok at 1,649 CE, clearly identified as change point (Fig. 2*F*), appears linked with the restrictive impact of Ottoman laws and taxation system, which became progressively more convoluted and inefficient through the 17th century (41). The onerous laws and taxes, combined with the appearance of cheap and plentiful sources of Ag in the New World, particularly South America (79, 80), meant that by 1,690 CE Ag production in the region had all but ceased and did not recover until the end of Ottoman rule (41, 77). This is strongly reflected in the Pb$_{Anthro}$ record, with progressive decreases until ∼1,790 CE (Fig. 3*B*), a trend echoed also in the reduction in microcharcoal, and anthropogenic indicator taxa at Crveni Potok (Fig. 4), pointing to region-wide economic stagnation as stated in historical records (41).

The uppermost section of the Crveni Potok record (1,700–1,820 CE, Fig. 4) indicates that the low mining output that characterized later Ottoman Serbia was reversed in the early 19th century, around the time of the two uprisings (1,804–13 and 1,815–17 CE), which eventually led to the establishment of the Serbian state (81, 82). This Pb$_{Anthro}$ upturn likely indicates the first impact of the Industrial Revolution in the Balkan area (Fig. 3*B*).

Comparison with Central-Western European Pollution Records. There are several similarities between Crveni Potok and western European pollution records, suggestive of comparable continent-wide metal production trends at times. Pb enrichment in the Bronze Age has previously been observed in Spain (22, 55), France (83), and Great Britain (84), although not as early as indicated in Crveni Potok (between 3,900 and 2,500 BCE). Furthermore, Roman-related pollution (as observed at Crveni Potok from 150 BCE onward) has previously been documented continent-wide (Fig. 5), from Spain (85, 86) through central Europe (87–89) and as far from centers of occupation as the Faroe Islands (90) and Greenland (91, 92). Finally, the impact of medieval pollution, which is so well expressed in the Crveni Potok record, has been observed previously but primarily close to known mining areas in southern Germany (88, 89) and northern England (21). Further away from such metallurgically active areas, only small-scale pollution is typically observed during the medieval period (Fig. 5) (90).

It is not the similarities with western European records that are the most interesting, however, but the differences. For example, clearly, the Romans had a major influence on the pollution history of the Balkans, echoing a Roman Pb pollution peak observed across much of Europe (Fig. 5) (20). However, as we show in this study, the end of the Roman period in central-western Europe did not bring a cessation of the mining activities in the Balkans (Figs. 3*B* and 5). This is in contrast to western

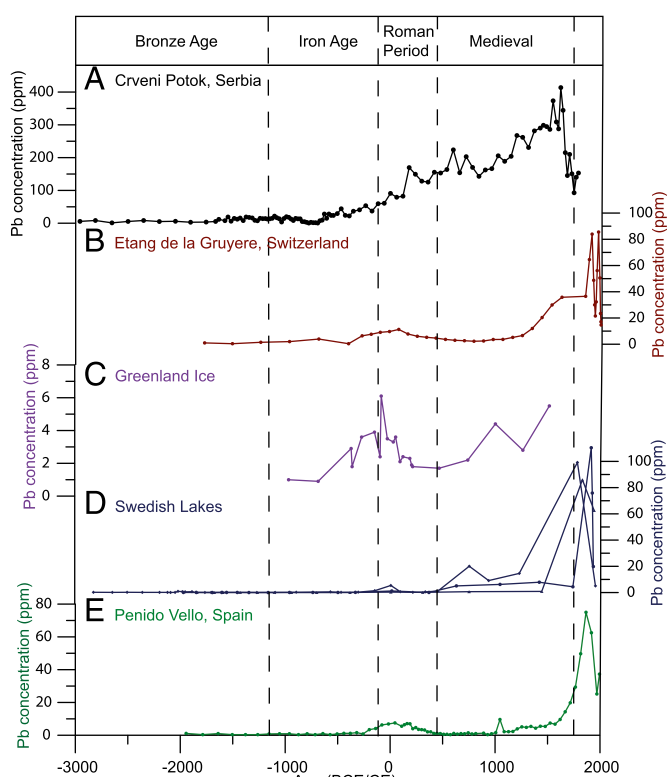

Fig. 5. Comparison of Pb$_{Anthro}$ from Crveni Potok (*A*) with Pb records from western and northern Europe, (*B*) northern Switzerland (86), (*C*) Greenland ice (13), (*D*) southern Sweden (25), and (*E*) northwestern Spain (82).

European records, which indicate major disruptions in metal exploitation and related Pb pollution after 300 CE in both Spain and Switzerland (Fig. 5). The contrast between western and southeastern Europe is evidence for the continued exploitation of Balkan metal ores under the Byzantines, validating previous archaeological indications (71), and confirming the so-called "Dark Ages" of western Europe coincide with significant economic development in southeastern Europe. High levels of metal environmental pollution in the Balkans throughout the medieval period, and after the fall of the Byzantine Empire, indicate that this industry was firmly established in the region (Fig. 3*B*) (41). Thus, we demonstrate here that the Carpathian–Balkans acted as a major source for European metal pollution not only during Antiquity, but also during the early medieval period and later. The timing of the medieval increase in Pb_{Anthro} is in line with the development in Ag mining in Germany (27, 93) and increased Pb pollution in a number of peat records across Europe (20). However, in no other studies does the level of Pb pollution exceed that of the Roman period until after 1,800 CE, with major pollution associated with the inception of the industrial revolution (21, 89). This further confirms the large extent and size of the metalworking industry in the Balkans during the late medieval period.

To allow for direct comparison of the Crveni Potok pollution record with other sites, and to remove intercomparison issues relating to sedimentation rates, Pb accumulation rates (ARs) have also been calculated (Fig. 2*A*). Despite the low sedimentation rates (*SI Appendix*, Fig. S2), and the near-pristine natural local environment at Crveni Potok today (47), Pb ARs are high for the past 2,000 y, peaking during the late medieval period, generally reflecting the Pb_{Anthro} values.

Comparison with the Pb AR records from Etang de la Gruère (25) record in Switzerland's Jura Mountains, and that of Kohlhütte Moor (88) in southwestern Germany provide the most pertinent evaluations (Fig. 1) because similarly to Crveni Potok, these are located in remote mountain areas with relatively low local human pressure during most of the Holocene. Furthermore, geographically they are located close to pollution sources derived from centers of metallurgy: Black Forest medieval mining centers for Kohlhütte Moor, and southeastern France and the eastern Alps, regions with active mining from the Bronze Age onward, for Etang de la Gruère (Fig. 1). The comparison reveals the similarity in the Crveni Potok and Kohlhütte Moor records throughout the Roman period, with both sites indicating Pb AR between 0.5 and 1.5 $mg \cdot m^{-2} \cdot y^{-1}$, suggesting regional smelting activities were similarly extensive. However, in both Kohlhütte Moor and Etang de la Gruère, the Pb ARs do not exceed 2 $mg \cdot m^{-2} \cdot y^{-1}$ until the Industrial Revolution. In contrast, in the Crveni Potok record, this threshold is reached eight centuries earlier (by ∼1,100 CE), rising to a peak of nearly 5 $mg \cdot m^{-2} \cdot y^{-1}$ by ∼1,620 CE (Fig. 2*A*). The latter Pb AR peak is comparable to Pb pollution flux levels reached three to four centuries later in the two central European bogs, which only reach this Pb contamination level by the early 20th century CE (25, 88). Another valid comparison may be made with Lindow Bog near Manchester in northwestern England (21). Here, at a site located within a region of rich mining heritage, Pb ARs comparable to Crveni Potok are observed at roughly similar times, particularly during the medieval period; at Lindow Bog, Pb ARs reach 1.24 $mg \cdot m^{-2} \cdot y^{-1}$ in the period 1,100–1,500 CE, before a peak of roughly 4 $mg \cdot m^{-2} \cdot y^{-1}$ by the 1,450 CE.

The Pb pollution history inferred from the Crveni Potok record is reflective of major mining and smelting activity in the wider Balkan region for the last 5,600 y, which peaks in the 17th century CE. By this time, the mining activity was producing Pb pollution comparable to other known medieval mining centers such as southern Germany and northern England. A major difference, however, is the fact that there is no evidence of proximal mining at Crveni Potok, other than rather uncertain evidence for exploitation along the Drina Valley and at Srebrenica in Bosnia (41). This suggests the high Pb output recorded by this bog is reflective of significant pollution region-wide, and noteworthy underestimation of the extent of Balkan metallurgy and its contribution to the European pollution budget through time.

The Crveni Potok record, therefore, provides evidence that the reconstructed impact of past metal smelting throughout Europe is not robust without considering the Balkans as a major source of metals. Our record shows that overall estimations of historical metal pollution (including Pb production) need improvement, to take into account the varied nature of development across Europe, and to incorporate the previously less considered contribution of Balkan metallurgical history. The fact that southeastern Europe is seldom mentioned as a metal source area in geochemical investigations of past Pb pollution contrasts markedly with the rich base and precious metal ore endowment of the Balkans, and significant field and archaeological evidence of past mining works and metal use.

Disruption of Balkan Metallurgy by Plagues. It has been suggested (8) that economic activities including metal production have been majorly perturbed throughout Europe by the occurrence of deadly plagues such as the Black Death of 1,346–1,354 CE (94). Albeit testing such hypothesis would require a larger number of records from the area, we found evidence to suggest such a linkage is possible with a number of major pestilences that afflicted eastern and southern Europe (Fig. 3). These include the Cyprian Plague (95), believed to be smallpox related, which had a major impact (>5,000 deaths per day in Rome at its height) on the Roman world between 250 and 266 CE, and may be reflected in the decrease in Pb_{Anthro} deposited at this time at Crveni Potok. Other major epidemics that may be reflected in our record include the plagues of Antonine (165–180 CE), Byzantine (746–747), and Vienna (1,679 CE) (96). All are associated with downturns in Pb_{Anthro} at Crveni Potok (Fig. 3). Notable, however, is the lack of apparent influence of the Black Death (1,346–1,354 CE), possibly evidence for its reduced impact in eastern Europe, thus paralleling historical accounts.

Conclusions

The Crveni Potok peat sequence provides an unprecedented continuous record documenting the impact of mining- and smelting-related Pb pollution in the wider Balkan region from the Early Bronze Age to the Industrial Revolution. The first clear signs of anthropogenic Pb enrichment are detected during the Bronze Age, with two main periods of increased Pb pollution (3,900–2,500 BCE and 1,750–950 BCE), corroborating poorly constrained archaeological evidence of regional metal use. The first of these anthropogenic Pb enrichment phases is the earliest such evidence for European Pb pollution in an environmental record.

Pb enrichments correspond to increases in fire activity and early deforestation, pointing to a causal link between mineral resource exploitation and land-use changes. Major Pb pollution is recorded from 600 BCE onward, with gradually increasing values in anthropogenic Pb until a peak at ∼1,620 CE. The record of gradually but continuously increasing levels of environmental pollution is indicative of a long and varied history of exploitation of metals in the area.

The Crveni Potok record highlights a significantly different pollution history in comparison with central-western European records, suggesting that the picture of European environmental impact through such activities is not complete without considering developments in the Balkans, a region very rich in metal ores and a documented long history of mineral resource and land exploitation. No previous studies have displayed constant Pb enrichment increases throughout the medieval period, with most central-western European records peaking only during Roman and later during industrial times. Comparisons of Pb ARs in similar records corroborate the scale of metallurgical activity in the region throughout the medieval period, with values comparable only to sites located close to centers of mining and smelting today, indicative of the size and long-term persistence of the Pb pollution in the Balkans, for several millennia.

Materials and Methods

In total, 270 cm of peat was recovered from Crveni Potok in overlapping cores using a Russian peat corer. The age–depth model was developed using nine AMS ^{14}C dates calibrated using the IntCal 13 dataset (97), and Clam age–depth modeling software (98) (*SI Appendix*, Fig. S2 and Table S2). Subsamples were taken and trace metal analysis was performed on exactly 0.5 cm^3 of peat to allow for density calculations. Each subsample was dried overnight before homogenization and digestion via a mixed acid (HNO_3–HCl–HF) microwave-assisted method (99) (*SI Appendix, Supplementary Text*). These solutions were analyzed via a Perkin-Elmer Optima 8000 ICP-OES system at Northumbria University. Analytical blanks were determined via analysis of a preprepared calibration solution, and all data presented have had this blank subtracted from it. Procedural blanks (digestions carried out with no sample), run at regular intervals, indicate negligible contamination, with the vast majority of analyses being below the detection limit of the instrument. To ensure accuracy, two reference materials were run alongside the samples and indicate reliable recoveries (within 10% of the expected values in the majority of runs) (*SI Appendix*, Table S1). Precision was monitored via measurement of an internal standard (either 1 ppm Sc or In; Dataset S2), and by triplicate measurement of each sample. SDs of each measurement are reported in Dataset S2. To further ensure accuracy, every 10 samples, repeats were run (Dataset S3).

Despite apparently low input from nonatmospheric metal sources including dust and runoff (*SI Appendix, Supplementary Text* and Fig. S1), to derive a reliable picture of past metal loading related to anthropogenic activities it is necessary to extract the pollution-related Pb from the natural background. An approach that distinguishes the lithogenic (natural) heavy-metal component from the anthropogenic component (100) was used. This first calculates the lithogenic component (by comparison with expected values in the upper continental crust) of the heavy-metal contribution, before removal of this signal from the overall metal concentration. The remainder may be considered the anthropogenically related Pb component (Pb_{Anthro}). In addition to calculation of Pb_{Anthro}, we also present the enrichment factor (Fig. 2*C*) (101) and CAAPb (Fig. 2*B*) (100) to better illustrate which periods dominate the Pb depositional history. Finally, to allow for direct comparison with other records (88), the Pb AR (Fig. 2*A*) has been calculated (85) (*SI Appendix, Supplementary Text*). In each case, we use Zr as the conservative lithogenic element.

To robustly determine where statistically significant changes occurred in the Pb data, we have performed change-point analysis. This approach marks each point where the Pb data changes abruptly and shows our findings are not method dependent (see *SI Appendix, Supplementary Text* for details). Three approaches (binary segmentation, Bayesian changepoint analysis, and breakpoints analysis) were used to perform change-point modeling performed on the Pb_{Anthro} (Fig. 2*F*), PbAR (*SI Appendix*, Fig. S4), and raw Pb concentration (*SI Appendix*, Fig. S5). Such approaches rigorously investigate the nature of the time series and, via a selection of methods (*SI Appendix, Supplementary Text*), determine where significant shifts exist. These methods may reliably detect changes in trends (102, 103), circumventing possible overinterpretation of noisy datasets.

ACKNOWLEDGMENTS. We thank Northumbria University for J.L.'s postgraduate studentship and F. Gogâltan for comments on an early draft. Comments and suggestions by two anonymous reviewers greatly improved the paper. This is a contribution to Romanian Research Council Grant PN–II-ID-PCE-2012-4-0530 ("Millennial-Scale Geochemical Records of Anthropogenic Impact and Natural Climate Change in the Romanian Carpathians") and to the French Agence Nationale de la Recherche (ANR) Grant ANR-09-CEP-004-01/OBRESOC.

EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

1. Killick D, Fenn T (2012) Archaeometallurgy: The study of preindustrial mining and metallurgy. *Annu Rev Anthropol* 41:559–575.
2. Muhly JD (1989) Çayönü Tepeşi and the beginnings of metallurgy in the Old World. *Old World Archaeometallurgy, Der Anschnitt, Beiheft 7*, eds Hauptmann A, Pernicka E, Wagner GA (Deutsches Bergbau-Museum, Bochum, Germany), Vol 7, pp 1–13.
3. Radivojević M, et al. (2010) On the origins of extractive metallurgy: New evidence from Europe. *J Archaeol Sci* 37:2775–2787.
4. Radivojević M, Rehren T, Kuzmanović-Cvetković J, Jovanović M, Northover JP (2013) Tainted ores and the rise of tin bronzes in Eurasia, c. 6500 years ago. *Antiquity* 87: 1030–1045.
5. Radivojević M, Rehren T (2016) Paint it black: The rise of metallurgy in the Balkans. *J Archaeol Method Theory* 23:200–237.
6. Pernicka E, et al. (1993) Eneolithic and Early Bronze Age copper artefacts from the Balkans and their relation to Serbian copper ores. *Praehist Z* 68:1–54.
7. Roberts BW, Thornton CP, Pigott VC (2009) Development of metallurgy in Eurasia. *Antiquity* 83:1012–1022.
8. More AF, et al. (2017) Next generation ice core technology reveals true minimum natural levels of lead (Pb) in the atmosphere: Insights from the black death. *GeoHealth* 1:211–219.
9. Csavina J, et al. (2012) A review on the importance of metals and metalloids in atmospheric dust and aerosol from mining operations. *Sci Total Environ* 433:58–73.
10. Dudka S, Adriano DC (1997) Environmental impacts of metal ore mining and processing: A review. *J Environ Qual* 26:590–602.
11. Delile H, Blichert-Toft J, Goiran J-P, Keay S, Albarède F (2014) Lead in ancient Rome's city waters. *Proc Natl Acad Sci USA* 111:6594–6599.
12. Hoffman DJ, Rattner BA, Burton GA, Cairns J (2003) *Handbook of Ecotoxicology* (Lewis Publishers, Boca Raton, FL), 2nd Ed.
13. Hernberg S (2000) Lead poisoning in a historical perspective. *Am J Ind Med* 38: 244–254.
14. Rosman KJR, Chisholm W, Hong S, Candelone JP, Boutron CF (1997) Lead from Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 B.C. to 300 A.D. *Environ Sci Technol* 31:3413–3416.
15. Hong S, Candelone JP, Patterson CC, Boutron CF (1994) Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations. *Science* 265:1841–1843.
16. Bränvall M-L, Bindler R, Emteryd O, Renberg I (2001) Four thousand years of atmospheric lead pollution in northern Europe: A summary from Swedish lake sediments. *J Paleolimnol* 25:421–435.
17. Brännvall ML, et al. (1999) The medieval metal industry was the cradle of modern large-scale atmospheric lead pollution in northern Europe. *Environ Sci Technol* 33: 4391–4395.
18. Renberg I, Bindler R, Brannvall ML (2001) Using the historical atmospheric lead-deposition record as a chronological marker in sediment deposits in Europe. *Holocene* 11:511–516.
19. Novak M, et al. (2011) Experimental evidence for mobility/immobility of metals in peat. *Environ Sci Technol* 45:7180–7187.
20. Hansson SV, Bindler R, De Vleeschouwer F (2015) Using peat records as natural archives of past atmospheric metal deposition. *Environmental Contaminants: Using Natural Archives to Track Sources and Long-Term Trends of Pollution*, eds Blais JM, Rosen MR, Smol JP (Springer, Dordrecht, The Netherlands), pp 323–354.
21. Le Roux G, et al. (2004) Identifying the sources and timing of ancient and medieval atmospheric lead pollution in England using a peat profile from Lindow bog, Manchester. *J Environ Monit* 6:502–510.
22. García-Alix A, et al. (2013) Anthropogenic impact and lead pollution throughout the Holocene in southern Iberia. *Sci Total Environ* 449:451–460.
23. Martinez Cortiza A, et al. (2002) Atmospheric Pb deposition in Spain during the last 4600 years recorded by two ombrotrophic peat bogs and implications for the use of peat as archive. *Sci Total Environ* 292:33–44.
24. Martínez Cortizas A, Peiteado Varela E, Bindler R, Biester H, Cheburkin A (2012) Reconstructing historical Pb and Hg pollution in NW Spain using multiple cores from the Chao de Lamoso bog (Xistral Mountains). *Geochim Cosmochim Acta* 82:68–78.
25. Shotyk W, et al. (1998) History of atmospheric lead deposition since 12,370 14C yr BP from a Peat Bog, Jura Mountains, Switzerland. *Science* 281:1635–1640.
26. Klaminder J, Renberg I, Bindler R, Emteryd O (2003) Isotopic trends and background fluxes of atmospheric lead in northern Europe: Analyses of three ombrotrophic bogs from south Sweden. *Global Biogeochem Cycles* 17:1019.
27. Novák M, et al. (2003) Origin of lead in eight Central European peat bogs determined from isotope ratios, strengths, and operation times of regional pollution sources. *Environ Sci Technol* 37:437–445.
28. Shotyk W (2002) The chronology of anthropogenic, atmospheric Pb deposition recorded by peat cores in three minerogenic peat deposits from Switzerland. *Sci Total Environ* 292:19–31.
29. O'Brien W (2014) *Prehistoric Copper Mining in Europe: 5500–500 BC* (Oxford Univ Press, Oxford).
30. Jovanović B (2009) Beginning of the metal age in the central Balkans according to the results of the archeometallurgy. *J Min Metall Sect B Metall* 45:143–148.
31. Chernyk E (1992) *Ancient Metallurgy in the USSR* (Cambridge Univ Press, Cambridge, UK).
32. Radivojevic M, Kuzmanovic-Cvetkovic J (2014) Copper minerals and archaeometallurgical materials from the Vinca culture sites of Belovode and Plocnik: Overview of the evidence and new data. *Starinar* 2014:7–30.
33. Chernyk EN (1978) *Gornoe delo i Metallurgiya v Drevneyshey Bolgarii* (Izdatelstvo Bolgarskoi Akademii Nauk, Sofia, Bulgaria).
34. Antonović D (2014) *Kupferzeitliche Äxte und Beile in Serbien* (Franz Steiner Verlag, Stuttgart, Germany).
35. Kienlin TL (2014) Aspects of metalworking and society from the Black Sea to the Baltic Sea from the fifth to the second millennium BC. *Archaeometallurgy in Global Perspective: Methods and Syntheses*, eds Roberts BW, Thornton CP (Springer, New York), pp 447–472.

36. Borcoş M, Udubaşa G (2012) Chronology and characterisation of mining development in Romania. *Rom J Earth Sci* 86:17–26.
37. Petković S (2009) The traces of Roman metallurgy in eastern Serbia. *J Min Metall Sect B Metall* 45:187–196.
38. Pernicka E, Begemann F, Schmitt-Strecker S, Todorova H, Kuleff I (1997) Prehistoric copper in Bulgaria. Its composition and provenance. *Eurasia Antiq* 3:41–180.
39. Baron S, Tămaş CG, Cauuet B, Munoz M (2011) Lead isotope analyses of gold-silver ores from Roşia Montanâ (Romania): A first step of a metal provenance study of Roman mining activity in Alburnus Maior (Roman Dacia). *J Archaeol Sci* 38:1090–1100.
40. Paulinyi O (1981) The crown monopoly of the refining metallurgy of precious metals and the technology of the cameral refineries in Hungary and Transylvania in the period of advanced and late feudalism (1325–1700) with data and output. *Precious Metals in the Age of Expansion. Papers of the XIVth International Congress of the Historical Sciences*, ed Kellenbenz H (Klett-Cotta, Nurnberg, Germany).
41. Stojković MD (2013) The influence of Saxon mining on the development of the Serbian medieval state. *Min Hist Bull Peak Dist Mines Hist Soc* 18:35–45.
42. Laznicka P (2006) *Giant Metallic Deposits* (Springer, Berlin).
43. Xun S (2015) The mineral industry of Romania. *U.S. Geological Survey Minerals Yearbook*. Available at https://minerals.usgs.gov/minerals/pubs/country/2013/myb3-2013-ro.pdf. Accessed April 7, 2017.
44. Heinrich CA, Neubauer F (2002) Cu–Au–Pb–Zn–Ag metallogeny of the Alpine–Balkan–Carpathian–Dinaride geodynamic province. *Miner Depos* 37:533–540.
45. Ciobanu CL, Cook NJ, Stein H (2002) Regional setting and geochronology of the late Cretaceous Banatitic Magmatic and Metallogenetic Belt. *Miner Depos* 37:541–567.
46. Janković S (1977) The copper deposits and geotectonic setting of the Thethyan Eurasian Metallogenic Belt. *Miner Depos* 12:37–47.
47. Finsinger W, et al. (2017) Holocene vegetation and fire dynamics at Crveni Potok, a small mire in the Dinaric Alps (Tara National Park, Serbia). *Quat Sci Rev* 167:63–77.
48. Hijmans RJ, Cameron SE, Parra JL, Jones PG, Jarvis A (2005) Very high resolution interpolated climate surfaces for global land areas. *Int J Climatol* 25:1965–1978.
49. Stockhammer PW, et al. (2015) Rewriting the central European early bronze age chronology: Evidence from large-scale radiocarbon dating. *PLoS One* 10:e0139705.
50. Antonović D (2009) Prehistoric copper tools from the territory of Serbia. *J Min Metall Sect B Metall* 45:165–174.
51. Antonović D, Dimić V (2017) Copper ore exploitation at the site of Prljuša on Mali Šturac. *Archaeotechnology Studies: Raw Material Exploitation from Prehistory to the Middle Ages* (Srpsko Arheološko Društvo, Belgrade), pp 117–142.
52. Ling J, et al. (2014) Moving metals II: Provenancing Scandinavian Bronze Age artefacts by lead isotope and elemental analyses. *J Archaeol Sci* 41:106–132.
53. Huska A, et al. (2014) Placer tin ores from Mt. Cer, west Serbia, and their potential exploitation during the Bronze Age. *Geoarchaeology* 29:477–493.
54. McGeechan-Liritzis V, Taylor JW (1987) Yugoslavian tin deposits and the early Bronze Age industries of the Aegean region. *Oxf J Archaeol* 6:287–300.
55. Martínez Cortizas A, López-Merino L, Bindler R, Mighall T, Kylander ME (2016) Early atmospheric metal pollution provides evidence for Chalcolithic/Bronze age mining and metallurgy in southwestern Europe. *Sci Total Environ* 545-546:398–406.
56. Mason AH, et al. (2016) Tin isotope characterization of bronze artifacts of the central Balkans. *J Archaeol Sci* 69:110–117.
57. Pernicka E, Nessel B, Mehofer M, Safta E (2016) Lead isotope analyses of metal objects from the Apa hoard and other early and middle bronze age items from Romania. *Archaeol Austriaca* 1:57–86.
58. Pernicka E, Lutz J, Stöllner T (2016) Bronze age copper produced at Mitterberg, Austria, and its distribution. *Archaeol Austriaca* 1:19–56.
59. Wolters S, Enters D, Bittmann F (2010) Landscape history and land-use dependent soil erosion in central Bosnia from the Bronze Age to medieval times. *EGU General Assembly* 2010:11200.
60. Giosan L, et al. (2012) Early anthropogenic transformation of the Danube-Black Sea system. *Sci Rep* 2:582.
61. Drake BL (2012) The influence of climatic change on the late Bronze Age collapse and the Greek dark ages. *J Archaeol Sci* 39:1862–1870.
62. Dean JR, et al. (2015) Eastern Mediterranean hydroclimate over the late glacial and Holocene, reconstructed from the sediments of Nar lake, central Turkey, using stable isotopes and carbonate mineralogy. *Quat Sci Rev* 124:162–174.
63. Dušanić S (2008) The Valle Ponti lead ingots: Notes on Roman notables' commercial activities in free Illyricum at the beginning of the principate. *Starinar* 107–118.
64. Živković J, Rehren T, Radivojević M, Jevtić M, Jovanović V (2014) Characterisation of Celtic Silver from the Židovar Treasure, Serbia. *Under the Volcano. Proceedings of the International Symposium on the Metallurgy of the European Iron Age (SMEIA) Held in Mannheim, Germany, 20–22 April 2010*, eds Pernicka E, Schwab R (Forschungen zur Archäometrie und Altertumswissenschaft Verlag Marie Leidorf, Rahden, Germany), Vol 5, pp 20–22.
65. Dörfler W (2013) Prokoško Jezero: An environmental record from a subalpine lake in Bosnia-Herzegovina. *Okolište 1–Untersuchungen Einer Spätneolithischen Siedlungskammer in Zentralbosnien*, eds Müller J, Rassmann K, Hofmann R (Dr. Rudolf Habelt GmbH, Bonn), pp 311–340.
66. Dušanić S (2004) Roman mining in Illyricum: Historical aspects. Dall'Adriatico Al Danubio. *L'Illirico Nell'età Greca E Romana. Atti Del Convengo Intenazionale Cividale Del Friuli, 25–27 Settembre 2003*, ed Urso G (Edizioni Ets, Pisa, Italy), pp 247–270.
67. Hirt AM (2010) *Imperial Mines and Quarries in the Roman World* (Oxford Univ Press, Oxford).
68. Westner K (2016) Roman mining and metal production near the antique city of Ulpiana (Kosovo). PhD dissertation (Johann Wolfgang Goethe-Universitat, Frankfurt am Main).
69. Stojanović MM, Šmit Ž, Glumac M, Mutić J (2015) PIXE–PIGE investigation of Roman imperial vessels and window glass from Mt. Kosmaj, Serbia (Moesia Superior). *J Archaeol Sci Rep* 1:53–63.
70. Merkel JF (2007) Imperial Roman production of lead and silver in the northern part of Upper Moesia (Mt. Kosmaj area). *J Serbian Archaeol Soc* 23:39–78.
71. Edmondson JC (1989) Mining in the later Roman Empire and beyond: Continuity or disruption? *J Roman Stud* 79:84–102.
72. Treadgold W (1997) *A History of the Byzantine State and Society* (Stanford Univ Press, Stanford, CA).
73. Fine JVA (1994) *The Late Medieval Balkans: A Critical Survey from the Late Twelfth Century to the Ottoman Conquest* (Univ of Michigan Press, Ann Arbor, MI).
74. Petrovic GG, Petrovic V (2010) Human capital and Serbian mining. *Mining in Central Europe*, eds Engel J, Grujic M, Rybar P (Univ of Belgrade, Belgrade), pp 31–39.
75. Ivanišević V (2001) *Novčarstvo Srednjovekovne Srbije (Serbian Medieval Coinage)* (Stubovi Kulture, Belgrad).
76. Miljkovic E (2014) Ottoman heritage in the Balkans: The Ottoman Empire in Serbia, Serbia in the Ottoman Empire. *Süleyman Demirel Üniversitesi Fen-Edebiyat Fakültesi Sos Bilim Derg* 2009:129–137.
77. Vukovic M, Weinstein A (2002) Kosovo mining, metallurgy, and politics: Eight centuries of perspective. *JOM* 54:21–24.
78. Malcolm N (2002) *Kosovo: A Short History* (Pan, London).
79. Nriagu JO (1994) Mercury pollution from the past mining of gold and silver in the Americas. *Sci Total Environ* 149:167–181.
80. Nriagu J (1996) A history of global metal pollution. *Science* 272:11–12.
81. Stavrianos LS (1958) *The Balkans Since 1453* (New York Univ Press, New York).
82. Mitev P (2010) *Empires and Peninsulas: Southeastern Europe Between Karlowitz and the Peace of Adrianople, 1699–1829* (LIT, Munster, Germany).
83. Monna F, et al. (2004) Environmental impact of early Basque mining and smelting recorded in a high ash minerogenic peat deposit. *Sci Total Environ* 327:197–214.
84. Mighall TM, Foster IDL, Crew P, Chapman AS, Finn A (2009) Using mineral magnetism to characterise ironworking and to detect its evidence in peat bogs. *J Archaeol Sci* 36:130–139.
85. Kylander ME, et al. (2005) Refining the pre-industrial atmospheric Pb isotope evolution curve in Europe using an 8000 year old peat core from NW Spain. *Earth Planet Sci Lett* 240:467–485.
86. Martínez Cortizas A, López-Merino L, Bindler R, Mighall T, Kylander M (2013) Atmospheric Pb pollution in N Iberia during the late Iron Age/Roman times reconstructed using the high-resolution record of La Molina mire (Asturias, Spain). *J Paleolimnol* 50:71–86.
87. Forel B, et al. (2010) Historical mining and smelting in the Vosges Mountains (France) recorded in two ombrotrophic peat bogs. *J Geochem Explor* 107:9–20.
88. Le Roux G, et al. (2005) Recent atmospheric Pb deposition at a rural site in southern Germany assessed using a peat core and snowpack, and comparison with other archives. *Atmos Environ* 39:6790–6801.
89. Shotyk W, et al. (2001) Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 ^{14}C yr BP. *Geochim Cosmochim Acta* 65:2337–2360.
90. Shotyk W, et al. (2005) Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe Islands. *Geochim Cosmochim Acta* 69:1–17.
91. Rosman KJR, Chisholm W, Boutron CF, Candelone JP, Hong S (1994) Isotopic evidence to account for changes in the concentration of lead in Greenland snow between 1960 and 1988. *Geochim Cosmochim Acta* 58:3265–3269.
92. Hong S, Candelone J-P, Patterson CC, Boutron CF (1996) History of ancient copper smelting pollution during Roman and medieval times recorded in Greenland ice. *Science* 272:246–249.
93. Baron S, Le-Carlier C, Carignan J, Ploquin A (2009) Archaeological reconstruction of medieval lead production: Implications for ancient metal provenance studies and paleopollution tracing by Pb isotopes. *Appl Geochem* 24:2093–2101.
94. Byrne JP (2012) *Encyclopedia of the Black Death* (ABC-CLIO, Santa Barbara, CA).
95. Harper K (2015) Pandemics and passages to late antiquity: Rethinking the plague of c.249–270 described by Cyprian. *J Roman Archaeol* 28:223–260.
96. Alchon SA (2004) A pest in the land: New World epidemics in a global perspective. *Americas (Engl Ed)* 61:274–275.
97. Reimer P, et al. (2013) IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* 55:1869–1887.
98. Blaauw M (2010) Methods and code for "classical" age-modelling of radiocarbon sequences. *Quat Geochronol* 5:512–518.
99. Longman J, Ersek V, Veres D, Salzmann U (2017) Detrital events and hydroclimate variability in the Romanian Carpathians during the Mid-to-Late Holocene. *Quat Sci Rev* 167:78–95.
100. Shotyk W, Blaser P, Grünig A, Cheburkin AK (2000) A new approach for quantifying cumulative, anthropogenic, atmospheric lead deposition using peat cores from bogs: Pb in eight Swiss peat bog profiles. *Sci Total Environ* 249:281–295.
101. Weiss D, Shotyk W, Appleby PG, Kramers JD, Cheburkin AK (1999) Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: Enrichment factors, fluxes, isotopic composition, and sources. *Environ Sci Technol* 33:1340–1352.
102. Gallagher K, et al. (2011) Inference of abrupt changes in noisy geochemical records using transdimensional changepoint models. *Earth Planet Sci Lett* 311:182–194.
103. Kylander ME, et al. (2016) Potentials and problems of building detailed dust records using peat archives: An example from Store Mosse (the "Great Bog"), Sweden. *Geochim Cosmochim Acta* 190:156–174.
104. Veron A, Novak M, Brizova E, Stepanova M (2014) Environmental imprints of climate changes and anthropogenic activities in the Ore Mountains of Bohemia (Central Europe) since 13 cal. kyr BP. *Holocene* 24:919–931.