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Geochemical evidence for atmospheric pollution derived from prehistoric copper mining at Copa Hill, Cwmystwyth, mid-Wales, UK

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Abstract

This paper presents geochemical data from a blanket peat located close to a Bronze Age copper mine on the northern slopes of the Ystwyth valley, Ceredigion, mid-Wales, UK. The research objective was to explore the possibility that the peat contained a geochemical record of the pollution generated by mining activity. Four peat monoliths were extracted from the blanket peat to reconstruct the pollution history of the prehistoric mine. Three different geochemical measurement techniques were employed and four copper profiles have been reconstructed, two of which are radiocarbon-dated. The radiocarbon dates at one profile located close to the mine confirm that copper enrichment occurs in the peat during the known period of prehistoric mining. Similar enrichment of copper concentrations is shown in one adjacent profile and a profile within 30 m away. In contrast, copper was not enriched in the other radiocarbon-dated monolith, collected approximately 1.35 km to the north of the mine. Whilst other possible explanations to explain the copper concentrations are discussed, it is argued that the high copper concentrations represent evidence of localised atmospheric pollution caused by Bronze Age copper mining in the British Isles. The results of this study suggest that copper may be immobile in blanket peat and such deposits can usefully be used to reconstruct atmospheric pollution histories in former copper mining areas.

1. Introduction

Pollution caused by Greek and Roman mining and smelting activities between 500 BC and AD 300; High copper and lead concentrations detected in these records demonstrate that the contribution of the Greenland ice cores have been attributed to metalliferous industries to atmospheric pollution by classical civilisations around the Mediterranean and China was significant (Hong et al., 1994, 1996; Shotyk et al., 1997). In northern and western Europe, Roman and subsequent metallurgical activity has also been detected in the records of geochemical deposition in ombotrophic peat (Livett et al., 1979; Martin et al., 1979; Jones et al., 1991; Williams, 1991; Shotyk et al., 1997; Gorres and Frenzel, 1997; Kempter et al., 1997; Kusterand Rehfuess, 1997; Martinez-Cortizas et al., 1997). Less attention, however, has been given to European prehistoric mining and smelting, despite the fact that 'the detection of early mineral exploitation in sediments of this kind is an important step in understanding the extent and nature of mining and smelting in the past' (West et al., 1997). In Britain, prehistoric metal mining sites have been difficult to identify and, until recently, there was a widespread belief that evidence of early mining was destroyed by subsequent activities. This view has been overturned by the discovery

of several prehistoric copper mines in Britain and Ireland. Archaeological excavation, and a programme of radiocarbon dating, has identified a series of Bronze Age copper mines. These include several mines in Wales, notably Copa Hill in the Ystwyth valley, Parys Mountain on Anglesey and Great Orme's Head, Llandudno, in north Wales. In south-west Ireland prehistoric mines have been excavated at Ross Island and Mount Gabriel (Lewis, 1988; Timberlake, 1990a,b; Timberlake and Switsur 1987; Dutton and Fasham, 1994; O'Brien, 1994, 1995; Jenkins, 1995).

One of the pre-eminent issues when using peat archives to reconstruct atmospheric pollution histories concerns the mobility of metals incorporated into the peat bog. Heavy metals are vulnerable to post-depositional transformation in peat via the position and movement of the water table, changes in pH andyor oxidationyreduction status, elemental uptake by surface vegetation, and the degree of humification (Jones, 1987; Urban et al., 1990; Jones and Hao, 1993; Stewart and Fergusson, 1994). Anthropogenically derived metal enrichment may therefore be prone to post depositional transformation in peat and its chronological context obscured (Damman, 1978; Shotyk, 1988; Jones and Hao, 1993; Shotyk et al., 1997). Thus, the mobility of heavy metals must be fully understood before peat bogs can be used reliably to monitor atmospheric pollution. One approach that has been used to assess the mobility of metals is to compare independently dated metal profiles from various sources, e.g. peat bogs and lake sediments or use multiple profiles (Shotyk et al., 1996; MacKenzie et al., 1997; Weiss et al., 1999). An extension of this approach is to compare atmospheric pollution records derived from peat bogs or lake sediments with historical andyor archaeological evidence for industrial activities (Gilbertson et al., 1997; Gorres & Frenzel, 1997). Quite simply, if metals are retained in a chronological sequence, metal enrichment from pollution in the sedimentary deposit should compare favourably with the chronology of past industrial activities.

This paper investigates the extent to which prehistoric copper mining and ore processing activities at Copa Hill, Cwmystwyth, mid-Wales are recorded in proximal peat. Because copper has a good affinity for organic compounds in anaerobic, acidic conditions, it becomes organically bound in stable peat complexes or as insoluble sulfides. Only a small quantity of copper occurs in a soluble ionic form and therefore the majority should be largely unaffected by post depositional processes operating within a peat bog (Jones, 1987; Shotyk, 1988; Stewart and Fergusson, 1994). Therefore we can use this site to test the hypothesis that the record of copper enrichment in the peat should compare favourably with the archaeological and chronological evidence for mining. To do so, the distribution of copper concentrations will be evaluated by (i) replicating copper profiles, at two sites located within 600 m of a prehistoric mine and (ii) comparing these proximal profiles with a relatively distal profile, located 1.35 km from the mine.

2. Site description and materials studied

The bedrock of the Ystwyth valley comprises Silurian gritstones and shales, which constitute part of the Upper Llandovery series. Interbedded within these sediments are a

series of discontinuous ore bodies, predominantly consisting Pb-Zn and some Cu, which have been exploited since the Bronze Age. The prehistoric mining site of Copa
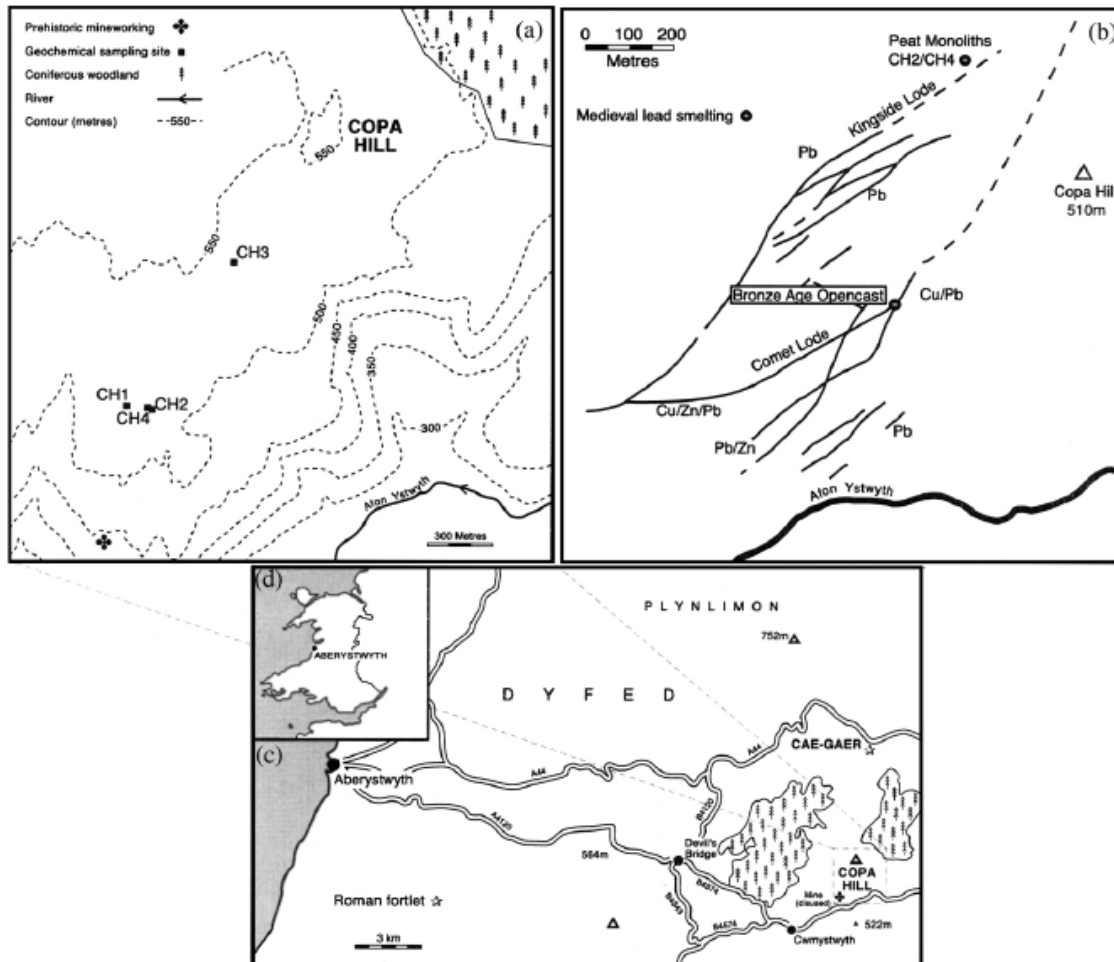

Fig. 1. Location of (a)the geochemical sampling sites; (b)the mineral veins running across Copa Hill; (c)and (d)the sites in mid-Wales.

Hill, Cwmystwyth is situated 30 km ENE of Aberystwyth (SN811751)on a copperylead mineral vein on the northern slopes of the Ystwyth valley at approximately 420 m OD (Fig. 1a–d). Archaeological excavations carried out by Simon Timberlake and the Early Mines Research Group since 1986 have included a programme of radiocarbon dating. Charcoal and wood, recovered from the mineworking debris, have been dated to a period within the early to mid Bronze Age (3690"90 BP (BM-2908; cal BC 2396–1877)and 3210"50 BP (Q-3078; cal BC 1604–1396)(Tim-berlake, 1987, 1990a,b, 1995). An examination of waste material left in the prehistoric opencast mine, on the spoil tips surrounding the mine and of mineral veins worked in prehistory, suggests that the miners extracted chalcopyrite. Small amounts of finely crushed chalcopyrite can be found within the mine entrance and within spoil. Jenkins and Timberlake (1997)interpret this material as small amounts of waste left after chalcopyrite ore was collected and crushed on site. Geochemical anal ysis of material from these contexts confirms that they are relatively copper rich. ICP-MS analysis of crushed material from a prehistoric tip reported a copper

concentration of 680 mg g $_{y1}$; 5200 mg $_{y1}$ of copper was measured in mine sediments, whilst charcoal produced from firesetting was highly enriched in copper, with concentrations ranging from 3700 to 6300 mgg$_{y1}$ (Jenkins and Timberlake, 1997). Metal mining probably resumed in the Ystwyth valley, possibly during Roman colonisation when lead was believed to be the focus of mining activity (Armfield, 1989), and later in Medieval times (Timberlake, personal communication). From the 16th century until the early 20th century, mining continued for lead and zinc (Hughes, 1981, 1994). Thus, this location provides an ideal site to investigate atmospheric pollution histories for mining activities spanning four millennia.

Table 1
Summary of the extraction and measurement methods for the Copa Hill peat profiles

CH1	CH2 and CH3	CH4
Partial Acid digestion (HNO_3) ICP-MS	Acid digestion (HNO_3, $HClO_4$ and H_2SO_4) AAS	Microwave acid digestion (HNO_3, H_2O_2) AAS

3. Methods and materials

3.1. Field sampling

Ideally, ombrotrophic peats, raised above the mineralised water table, are preferred as this environment minimises the risk of post-depositional metal mobility (Shotyk, 1996). However, a raised peat bog was not available for study and, as a result, material was collected from a water shedding, hilltop blanket peat. An extensive area of blanket peat occupies the northern plateau of the Ystwyth valley. *Calluna vulgaris* and *Eriophorum vaginatum* with *Deschampsia flexuosa*, *Eriophorum vaginatum*, *Molinia caerulea*, *Vaccinium myrtillus* and *Sphagnum* spp. dominate the vegetation (Ball et al., 1981). Four peat monoliths were extracted from freshly exposed sections of blanket peat and stored in either 15=15 cm aluminium monolith tins or plastic tubing. They were then wrapped in plastic, sealed and stored in a cold store. In order to detect any atmospheric pollution and to attempt to replicate the data three monoliths CH1, CH2 and CH4 were extracted from the closest, most suitable location, 600 m to the north of the mine. CH2 and CH4 are adjacent to one another, whilst CH1 occurs within 30 m of the others (Fig. 1a). Afourth monolith, CH3 was recovered from a freshly exposed section approximately 1.35 km NE from the prehistoric mine to act as a spatial control (Fig. 1a). Pollen extracted from monolith CH2 was used by Mighall and Chambers (1993) to investigate the impact of prehistoric mining on vegetation.

3.2. Laboratory methods

Three methods were employed to extract and determine metal concentrations. These were, (a) Inductively Coupled Plasma Mass Spectrometry, using a partial acid digestion of the peat; (b) atomic absorption spectrophotometry, using a Kjeldahl digestion method

to produce the aliquot and (c) atomic absorption spectrophotometry, using a microwave digestion method to produce the aliquot (Table 1).

Monolith CH1 was analysed using ICP-MS in the Institute of Geography and Earth Science at Aberystwyth University. The monolith was 180 cm long and the material extracted comprised 170 cm of well-humified *Calluna-Sphagnum* peat underlain by clay. Peat was sampled for analysis by contiguous scrapes of freshly exposed 5-cm sections of the monolith. Each data point on the relevant figures is therefore assumed to represent an average for each 5-cm section. The solution for analysis was prepared using a partial acid digestion technique. Ten-gram samples of wet peat were oven-dried overnight at 105 8C. The resulting oven-dried mass was then disaggregated and treated with 25 ml of 10% vyv nitric acid to digest the organic material. The samples were then placed on a hot plate and heated gradually to 100 8C and left to digest for approximately 40 h. Next, each sample was filtered using Whatman No 1 paper into a 100-ml volumetric flask and made up to 100 ml with milliQ water. The samples were then analysed by ICP-MS. Adetailed account of the use of the ICP-MS may be found in the literature (cf. Fuge et al., 1992; Perkins et al., 1993).

Monolith CH2 was 142 cm long and the material extracted consisted of well-humified *Sphagnum* peat until a depth of 139 cm, where clay was reached, whilst monolith CH3 was 190 cm long and composed of well-humified *Sphagnum* peat (Fig. 2). Samples of 1-cm thickness were cut from both monoliths and oven dried at 40 8C before chemical analysis by HNO -HClO -H SO4 acid digestion and atomic absorption spectrophotometry (AAS), following the procedure outlined in detail by Foster et al. (1987). To digest the organic matter, samples were placed in a Kjeldatherm digest unit for 2 h at 60 8C, followed by1hat 110 8C and then 1 h at 210 8C. Each sample was then filtered through Whatman No 1 paper and made up to a 100-ml solution after the addition of 3 ml of Lanthanum chloride. Monolith CH4 was 142 cm long and the material extracted comprised 139 cm of well-humified *Sphagnum* peat underlain by clay. Copper in the peat of monolith CH4 was extracted using a microwave acid digestion method. One gram of sediment was weighed accurately for each sub-sample; 3 ml of nitric acid and 1 ml of hydrogen peroxide were added, the sample tubes were sealed and placed in a microwave on a set programme of 250 W for 1 min, 0 W for 2 min, 250 W for 5 min, 600 W for 5 min and 400 W for 4 min. Once the microwave digestion was complete, the sub-samples were placed in a water cooler for 10 min, decanted into flasks and made up to 100 ml with deionised water. Copper concentrations were then determined using a Varian model 1472 atomic absorption spectrophotometer, housed in the School of Science of the Environment, at Coventry University.

Three peat samples have been radiocarbon dated. Two samples, one from between 134 and 133 cm and another from 105 to 104 cm, were cut from the CH2 monolith and submitted to the Centre for Isotope Research, Groningen, for radiocarbon dating. One sample, between 178 and 180 cm from monolith CH3 was sent to Beta Analytic, Miami.

4. Results

4.1. Radiocarbon dating

Radiocarbon dating of the basal sample from CH2 provided a uncalibrated date of 3470"35 years BP, whilst the sample extracted from between 105–106 cm provided a uncalibrated date of 2395"35 years BP. The radiocarbon dates are calibrated using a CALIB 4.1 radiocarbon calibration program and IntCal98 (Stuiver and Reimer, 1993; Stuiver et al., 1998) and the calibration age ranges to two sigma are shown in Table 2

4.2. Copper concentrations

Copper profiles from each site are shown in Fig. 3a–d. In all three proximal profiles (Fig. 3a–c) copper distributions followed a similar pattern. Copper concentrations, determined by a partial acid digest, at site CH1 range from 0.3 to 3 mg until 135–140 cm depth. Below this point until 160–165 cm, considerable copper enrichment is evident (Fig. 3a). Asimilar down profile distribution of copper is observed at CH2 and CH4, but concentrations are much higher (Fig. 3b,c). Copper concentrations never exceed 20 mg g until
the basal 15 cm of peat, when significant enrichment occurs as concentrations approach 110 mgg$_{y1}$.In complete contrast, copper concentrations at CH3 (Fig. 3d) appear to be randomly distributed. Concentrations range between the limit of detection and 40 mgg
An estimation of the efficiency of the digestion method and of the accuracy of the analytical measurements for monolith CH4 was obtained by use of replicate sub-samples, spiked blanks and certified reference materials (Ebdon et al., 1998). Replicate sub-samples were taken from one sample of the CH4 monolith to provide an indication as to the accuracy of the microwave extraction method and the AAS. Seven spiked samples of a known
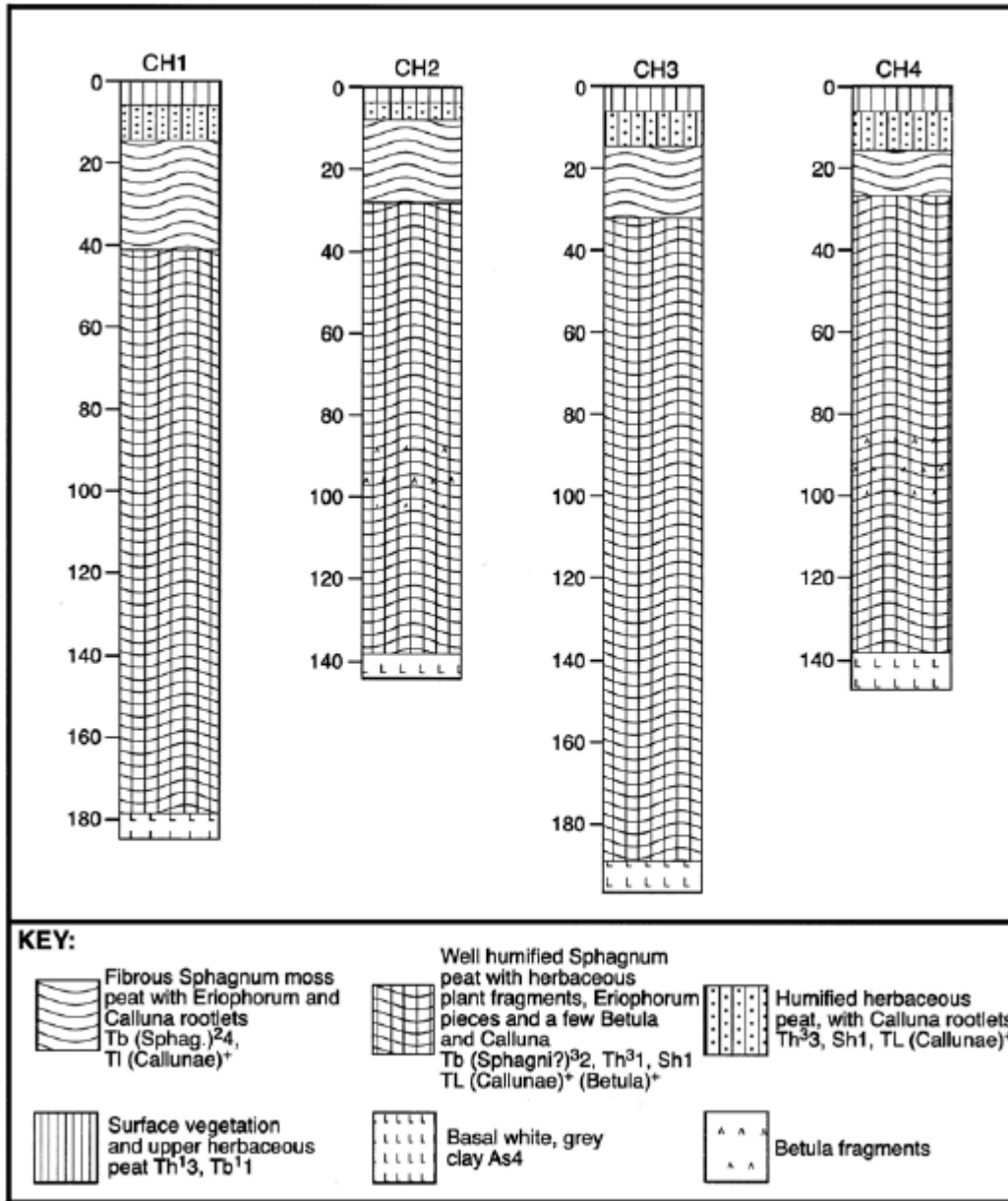
Fig. 2. Stratigraphy of the Copa Hill monoliths.

Table 2 Radiocarbon dates from sampling site CH2 and CH3*

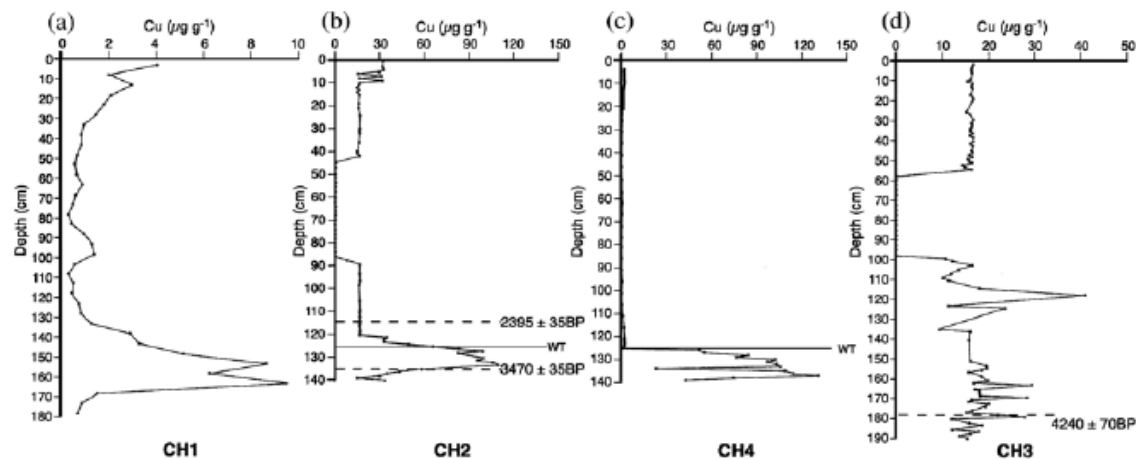| Laboratory no.	Depth (cm)	Uncalibrated date (2 sigma)	Calibrated age range
GrN-17635	105–106	2395"35	cal BC 757–395
GrN-17636	133–134	3470"35	cal BC 1883–1687
*Beta-154444	178–180	4240"70	cal BC 3014–2601

Fig. 3. Copper concentration profiles from (a) sampling site CH1; (b) sampling site CH2; (c) sampling site CH4; and (d) sampling
site CH3.

concentration of 50 mg l $_{y1}$ were analysed and the results produced a percentage mean recovery rate of 113%. Copper concentrations determined from CRM pond sediment (Catalogue number J0-02 from the Laboratory of Government of Chemists) during this study produced an average of 224.42 mg g $_{y1}$, which agrees closely with certified concentration of 210 mg g $_{y1}$. These results suggest that copper recovery using the microwave digestion is very efficient, and the AAS is providing reliable and accurate data.

5. Discussion

It is clear that each of the three proximal monoliths, CH1, CH2 and CH4, record a similar pattern of copper distribution pattern with depth in the profiles, although absolute concentrations do vary slightly. Each of the extraction techniques and analytical methods used has produced broadly similar results. The replication of elevated copper concentrations three times, using three different extraction and analytical methods, suggests that the concentration of copper towards the base of each the proximal monoliths is unlikely to be an artefact of the extraction and analytical method used. However, it is clear that the partial acid digest method used on CH1 dramatically reduced the concentrations detected, though not the pattern of distribution, which limits its comparative value.

Notwithstanding the problems of comparing metal concentrations in soils and peat, the copper concentrations recorded at CH2 and CH4 in the basal part of each monolith are higher than background values. Copper concentrations are higher than 90 mg g $_{y1}$ at CH2 and CH4, exceeding the natural background level for Cu of 25.8 mgg_{y1} in soils, as suggested by Macklin (1992). They all exceed a mean background figure for copper in

local peat, calculated from monolith CH3 at 17.3 mgg_{y1} and the average concentration of the Earth's crust of 50 mgg_{y1} (Wild, 1993). Thus, it is clear that the basal zone of peat is enriched.

Environmental parameters, such as pH, redox potential, the position of the water table, peat humification and surface vegetation, are known to affect the movement of metals in peat (Shotyk, 1988; Van Geel et al., 1989; Jones and Hao, 1993; Stewart and Fergusson, 1994). Whereas this might be the case for certain elements (Damman, 1978; Aaby and Jacobsen, 1979; Pakarinen et al. 1983), experimental data and field determinations attests to the immobility of copper in peat. Bunzl et al. (1974) demonstrated that peat has a strong affinity for copper, whilst Livett et al. (1979) showed that copper was unaffected when using sulfuric acid as a leaching agent. Gao et al. (1993) have also demonstrated that Cu ions form stable humic acid complexes in peat. Based on copper concentrations determined from field studies, Coleman et al. (1956) and Jones (1987) have suggested that the high stability of copper–peat complexes would result in extremely small quantities of soluble ionic copper (Cu$_{2q}$) in most soils, including ombrotrophic peat. Based on the sequential extraction of peat from Ringlow bog in the southern Pennines of England, Jones (1987) found that copper had a strong affinity for both the organic and residual fractions. Further analysis of peat from Ringlow bog led Jones and Hao (1993) to conclude that copper retains its depositional record in peat.

Although there was a statistically significant relationship between copper concentrations and field measurements of pH and redox potential at monolith CH4, producing Spearman rank correlation co-efficient r values y0.6868 and 0.6906, respectively (Mighall et al., 2000); Stewart and Fergusson (1994) argue that the formation of immobile copperyorganic complexes is independent of acid and redox conditions, so neither of these conditions should influence copper concentrations. The position of the water table for monoliths CH1, 2 and 4 is also above the zone of copper enrichment (Fig. 3). Obviously, the position of the water table will have varied as the peat accumulated during the Late Holocene, but it is noteworthy that copper concentrations

are not enriched at the present water table. Equally, the low copper concentrations in the basal clay at site CH4, ranging from 23 to 25 mg g $y1$, suggest that weathering of the underlying bedrock is also an unlikely source. Thus, the balance of evidence strongly suggests copper is unlikely to have been redistributed in the Copa Hill profiles and peat bogs are suitable surrogates for monitoring copper pollution.

Radiocarbon dates obtained from organic deposits, charcoal and wood fragments, collected from the Copa Hill mine and mineworking debris, suggest that mining was taking place for one or more periods between 3690"90 and 3210q50 years BP, although the exact timespan of mining cannot be determined. The basal radiocarbon date of the CH2 peat profile, from 134 to 133 cm depth, provided an age of 3470"35 years BP. Asecond radiocarbon date of 2395"35 years BP was derived from peat between 105 and 106 cm. It is clear that the copper enrichment evident between 125–134 cm in profile CH2 corresponds with the established dates of Bronze Age mining at Copa Hill, 600 m to the south. Bronze Age mining is the most probable source of the enrichment noted. Later mining in the area did not produce any significant quantities of copper ore and therefore pollution that could have been mobilised down the peat cores. Pre-1800 accounts of mining in the Ystwyth valley refer to Copa Hill as a copper mine of great antiquity, with

no great work at present (Wlliams, 1749 and Lewis in approximately 1756, quoted in Hughes, 1981). Historical documents of the amount and type of ores raised between 1800 and 1915, records only lead and zinc (Hughes, 1981).

Unfortunately, only two of the monoliths (CH2 and CH3) have radiocarbon dates to establish their age by an independent method. However, it is possible to correlate CH2 with CH1 and CH4 using peat stratigraphy and down profile patterns of other metals. The copper distribution profile in monolith CH4 is strikingly similar to that of profile CH2. Monolith CH4 was cut from the peat face 65 cm away from CH2. Not surprisingly, they are of the same depth and share similar stratigraphic characteristics (Fig. 2). In particular, a layer of birch macrofossils was found at approximately 1 m depth at both monoliths. The different length of the CH1 monolith, located approximately 30 m to the north-west of monoliths CH2 and CH4, suggests that peat accumulation has occurred at a slightly differing rate. However, the clear similarity of the geochemical profiles and their proximity to each other suggest that it is reasonable to propose, albeit cautiously, that the copper enrichment indicated in monolith CH1 is the result of the same depositional processes occurring at approximately the same time. This assumption is supported when comparing other metal concentrations. Lead concentrations for monoliths CH1, CH2 and CH4 are shown in Fig. 4. Despite differential accumulation rates between CH1, CH3 and CH2y4 peat monoliths, the similarities in the lead concentrations are sufficiently strong to correlate across each profile. Afull interpretation of the lead profiles is outside
Fig. 4. Lead concentration profiles from (a) sampling site CH1; (b) sampling site CH2; (c) sampling site CH4; and (d) sampling site CH3. Pb was determined using the same procedures described for copper. For brevity, detailed descriptions of the Pb profiles are not provided here but can be found in Mighall et al. (2002), forthcoming.

the remit of this paper, but two peaks are noticeable in all the profiles, a near surface peak in the top 15 cm and a second at approximately 81 cm. The peaks are best explained by historical lead mining in the Cwmystwyth valley from the 17th century to the early 1900s and during Roman times, respectively. The stratigraphic and lead profile comparisons

between monoliths CH1, CH2 and CH4 strongly suggest therefore that the copper enrichment determined in the basal part of each profile represents atmospheric pollution from copper mining during the Bronze Age.

The replicated bimodal nature of the copper enrichment in each of the three monoliths may also be important. The peat across the plateau is relatively homogenous and there is

no visible stratigraphic change, which might account for this distribution pattern. Indeed, it could represent two major phases of metallurgical activity.

The basal peak in copper concentrations described at sites CH1, CH2 and CH4 is not evident at site CH3. Assuming that the peat accumulated at a relatively constant rate, the prehistoric mining occurred as peat accumulated between 151 and 134 cm. Copper concentrations remain below 25 mg g $_{y1}$ and show no enrichment in this part of the monolith. One explanation for the absence of high copper concentrations is that the site lies outside the atmospheric dispersion halo of prehistoric mining activity. Studies have shown that the distance over which atmospheric pollutants can be carried varies considerably. For example, Davies (1983) and Davies and Roberts (1978) suggest that the bulk of particulate matter is deposited with 3 km, depending upon its state and the ground pattern of the fallout is largely controlled by prevailing winds. This suggests that the atmospheric pollution particles released from prehistoric mining at Copa Hill were either too large in size to be dispersed any great distance or that the CH3 site is located away from the prevailing wind direction. Alternatively, the scale of mining and processing at Copa Hill resulted in very localised pollution and was of insufficient magnitude to be detected on a larger spatial scale. If peat accumulation did vary at CH3 it is possible that the peak in copper between 130 and 115 cm may have been caused by mining pollution. The copper concentrations are, however, relatively low compared to monoliths CH2 and CH4. It is possible that smelting also contributed to atmospheric pollution at Copa Hill. Whilst evidence for copper smelting has recently been discovered close to the Bronze Age mine on the Great Orme near Llandudno (Chapman, 1997), no archaeological evidence for copper smelting has been found close to Copa Hill. Until such evidence is forthcoming, it is possible that the ore extraction process, including the use of firesetting and the processing of ore on site also contributed to atmospheric particulate pollution that is recorded in the blanket peat north of the mine. Copper concentrations slightly increase at the top of profiles CH1 and CH2, but remain relatively unchanged at CH3 and CH4. The concentrations recorded at CH1 and CH3 are comparable to copper determined in a number of low-background ombrogenous peats in other parts of the British Isles (8–20 mg g $_{y1}$)(Livett et al., 1979). These low concentrations are not surprising given the absence of copper mining in the Cwmystwyth valley since the Bronze Age. Moreover, the site is now located well away from more industrial regions of Wales and England, thus exposure to any form of copper pollution, and subsequent mobility down the peat cores, will have been limited. The surface peaks in copper concentrations in profiles CH1 and CH3 are therefore more likely to be the result of plant bioaccumulation (Shotyk, 1988). The uppermost sample determined for copper at CH4 was only at 4 cm and possibly accounts for the absence of a surface peak.

6. Conclusion

We argue here that the distribution pattern of copper recorded in a hilltop blanket peat reflects prehistoric copper mining activity during the second millennium BC in the remote uplands of central Wales. The multiple-profile approach to replicate the down profile chemical concentrations proved advantageous for detecting localised atmospheric pollution from prehistoric mining. The strong correlation between the known period of prehistoric mining and the enrichment of copper in the peat profiles, irrespective of the sample digestion method used, supports other field and experimental data that copper remains immobile in peat. Having established the existence of this record, it is probable that other geochemical records of ancient mining activity may be detected in upland blanket peat across the British Isles.

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