First comprehensive peat depositional records for tin, lead and copper associated with the antiquity of Europe's largest cassiterite deposits

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ABSTRACT

Tin, as a constituent of bronze, was central to the technological development of early societies, but cassiterite (SnO_2) deposits were scarce and located distantly from the centres of Mediterranean civilizations. As Britain had the largest workable ore deposits in the ancient Western world, this has led to much historical speculation and myth regarding the long-distance trading of tin from the Bronze Age onwards. Here we establish the first detailed chronology for tin, along with lead and copper deposition, into undisturbed ombrotrophic (rain-fed) peat bogs located at Bodmin Moor and Dartmoor in the centre of the British tin ore fields. Sustained elevated tin deposition is demonstrated clearly, with peaks occurring at 100–400 and 700–1000 calendar years AD – contemporaneous with the Roman and Anglo-Saxon periods respectively. While pre-Roman Iron Age tin exploitation undoubtedly took place, it was on a scale that did not result in convincingly enhanced deposition of the metal. The deposition of lead in the peat record provides evidence of a pre-Roman metal-based economy in southwest Britain. Emerging in the 4th century BC, this was centred on copper and lead ore processing that expanded exponentially and then collapsed upon Roman colonization during the 1st century AD.

1. Introduction

With the exception of the Roman use of Spanish deposits (Penhallurick, 1986), the sourcing of tin throughout much of antiquity is largely unknown. Isotopic analysis of the *Himmelsscheibe* (the Sky disk of Nebra) indicates that tin ores from southwest (SW) Britain were being utilized perhaps as early as 1600 BC (Haustein et al., 2010). The recent discovery of tin ingots associated with a 9–10th century BC shipwreck off Salcombe, Devon, also suggests that British tin was mined and traded in the Bronze Age (Archaeology, 2010). Copper ingots found at the wreck are thought not to be of British origin, even though SW Britain was rich in copper ore (Dines, 1956; Northover, 1995). This raises the possibility that the tin was not of SW British origin.

The only substantive written accounts of early tin exploitation in Britain are provided by Strabo (63/64 BC–24 AD) and Diodorus Siculus (90–21 BC), but these were probably compiled from earlier accounts as the authors are thought not to have visited Britain (Penhallurick, 1986). Writing around 440 BC, Herodotus was uncertain about the sources for the tin arriving in the eastern Mediterranean world, but noted "I cannot speak with certainty, however, about the marginal regions which lie towards the west, in Europe... Nor am I certain of the existence of the Cassiterides Islands, from which we get our tin" (Herodotus, 2003). Upon the first Roman incursion into Britain (55–54 BC), Julius Caesar was ignorant regarding the geographical location of British tin lodes, commenting simply that "tin is found inland" (Caesar, 2003); while later classical scholars (Pliny the Elder, Tacitus and Solinus) fail to mention Britain with respect to tin, rather identifying northwest Spain as a primary source (Hatcher, 1973). Pliny the Elder (AD 23–79) goes as far as identifying the mythical Cassiterides as a source for tin (Pliny the Elder, 2004), believing they were "Opposite Celtiberia", but demonstrating that knowledge on this
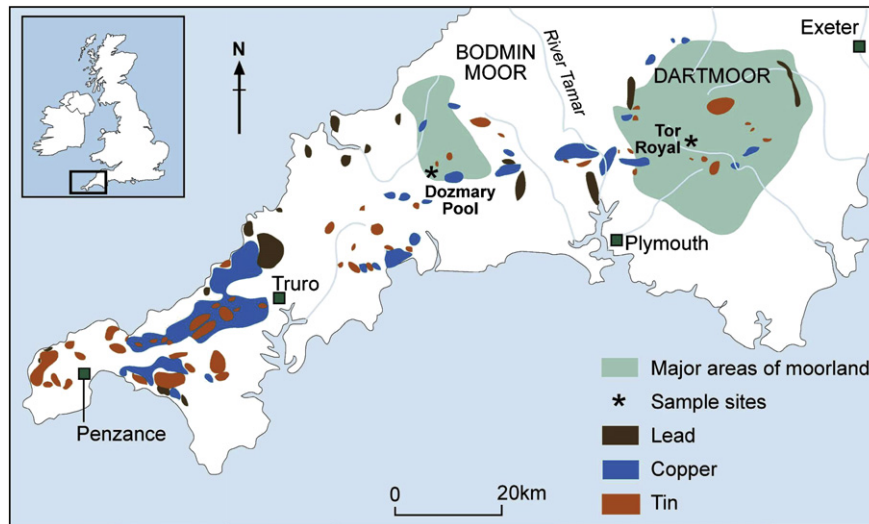
Fig. 1. The locations of Dozmary Pool and Tor Royal Bog relative to base ores of lead, copper and tin in SW Britain (Inset: the study area within the British Isles).

subject had moved forward little since the time of Herodotus (2003). The location of the Cassiterides has exercised modern scholars, with Brittany, the Scilly Isles, St Michael's Mount, Cornwall and the SW peninsula of Britain all variously implicated (Penhallurick, 1986; Cunliffe, 2001). Pliny the Elder quotes a Sicilian historian Timaeus (~352–256 BC), who as a source is thought to have used Pytheas of Marssalia's *Concerning the Ocean* (~310–306 BC), and who states that there is an island named Mictus within six days' sailing from Britain, where tin is found (Penhallurick, 1986; Cunliffe, 2001).

Confusion reigns regarding ancient British tin exploitation, and that of the wider Celtic Atlantic fringe. A chronology for the scale of British tin production during the prehistoric and early historical periods is essential for understanding the development and extent of technology and trading networks throughout Europe and the Middle East (Penhallurick, 1986; Cunliffe, 2001). Tin has a low melting point (232 °C) for a metal and this should lead to atmospheric entrainment and subsequent terrestrial deposition of this element in the same manner as that observed for lead (melting point 327 °C) deposition in undisturbed ombrotrophic peat, lake sediment and ice cores (Kylander et al., 2005; Le Roux et al., 2004; Rosman et al., 1997; Shotyk et al., 2001). The high boiling points for both elements (lead 1740 °C; tin 2270 °C) makes it likely that both metals enter the atmosphere as dusts — oxides, carbonates and sulphides — produced during smelting (Spear et al., 1998), rather than directly as vapour. SW Britain is rich in deposits of copper, lead and silver (extracted from copper and lead through litharge, with lead also used in litharge of copper). The sources of these elements utilized in British prehistory, like tin, remains uncertain (Northover, 1995). Here we establish tin, copper and lead depositional fluxes, along with lead isotopic analysis to characterize sourcing, in radiocarbon-dated cores from two ombrotrophic peat bogs in the centre of the SW British ore fields — Tor Royal Bog on Dartmoor in Devon, and Dozmary Pool on Bodmin Moor in Cornwall (Fig. 1). Both sites have been subject to previous palaeoenvironmental investigation (Amesbury et al., 2008; Brown, 1977; West et al., 1996). Tor Royal has also been characterized with respect to copper, zinc, arsenic and tin deposition in a dated profile, but

Table 1
Radiocarbon dates from Tor Royal Bog, Dartmoor, Devon, UK.

Lab code (SUERC-)	Stratigraphic position (cm)	Nature of sample	Conventional ^{14}C age (yr BP) ± 1σ[a]	±2σ calibrated range (cal yr BC/AD)[b]	δ^{13}C ‰ (±0.1)[c]
27680	51–50	*Sphagnum papillosum*	950 ± 35	1020–1160 AD	−26.8
27681	65–64	*Sphagnum papillosum*	1104 ± 37	830–1020 AD	−25.6
27684	71–70	*Sphagnum papillosum*	1257 ± 37	670–870 AD	−21.0
27685	81–80	*Sphagnum papillosum*	1534 ± 37	430–600 AD	−27.0
27686	91–90	*Sphagnum papillosum*	1193 ± 35	710–950 AD	−25.2
27687	95–94	*Sphagnum papillosum*	1557 ± 37	420–580 AD	−27.8
27688	121–120	*Sphagnum papillosum*	620 ± 37	1290–1400 AD	−24.0
27689	143–142	*Sphagnum papillosum*	941 ± 35	1020–1170 AD	−26.0
27690	146–145	*Sphagnum papillosum*	988 ± 37	990–1160 AD	−26.2
27694	162–161	*Sphagnum papillosum*	1605 ± 35	390–550 AD	−26.7
27695	191–190	*Sphagnum papillosum*	1784 ± 37	130–340 AD	−27.3
27696	204–203	*Sphagnum papillosum*	1993 ± 37	BC 90–80 AD	−27.4
27697	212–211	*Sphagnum papillosum*	2095 ± 52	BC 350–20 AD	−26.4
27698	231–230	*Sphagnum papillosum*	2246 ± 37	390–200 BC	−26.0
27699	235–234	Twig (Ericaceae undiff.)	2134 ± 54	360–40 BC	−28.8
27700	250–249	*Sphagnum papillosum*	2244 ± 37	390–200 BC	−28.4
27701	281–277	Leaves (*Calluna vulgaris* & *Erica tetralix*)	2563 ± 37	810–550 BC	−28.1

[a] Conventional radiocarbon years 'Before Present' (0 BP corresponds to 1950 AD).
[b] End points rounded outwards to the nearest 10 calendar years.
[c] Corrected to standard (δ^{13}C$_{VPDB}$‰ −25).

Table 2
Radiocarbon dates from Dozmary Pool, Cornwall, UK.

Lab code (SUERC-)	Stratigraphic position (cm)	Nature of sample	Conventional ^{14}C age (yr BP) $\pm 1\sigma$[a]	$\pm 2\sigma$ calibrated range (cal yr BC/AD)[b]	δ^{13}C ‰ (± 0.1)[c]
28800	31–30	*Sphagnum magellanicum*	229 ± 35	1530–1960 AD	−20.4
28801	46–45	*Sphagnum papillosum*	207 ± 35	1640–1960 AD	−25.3
28802	61–60	*Sphagnum papillosum* & *Sphagnum* Sect. *Subsecunda*	424 ± 35	1420–1620 AD	−24.1
28805	81–80	*Sphagnum* Sect. *Cuspidata*	382 ± 37	1440–1630 AD	−25.7
28806	102–100	*Sphagnum cuspidatum* & *Sphagnum* Sect. *Cuspidata* (*cf. S. recurvum*)	450 ± 35	1460–1640 AD	−22.8
28807	121–120	*Sphagnum cuspidatum* & *Sphagnum* Sect. *Cuspidata* (*cf. S. recurvum*)	614 ± 37	1290–1410 AD	−23.9

[a] Conventional radiocarbon years 'Before Present' (0 BP corresponds to 1950 AD).
[b] End points rounded outwards to the nearest 10 calendar years.
[c] Corrected to standard (δ^{13}C$_{VPDB}$‰ −25).

sampling and dating was not of sufficiently high resolution to provide robust chronologies, and the sensitivity of the method used (Energy Dispersive X-ray Microanalysis) was not appropriate to adequately quantify the tin (West et al., 1997). The research reported here attends to both these deficiencies.

2. Sites, materials and methods

The SW of England contains the many ore bodies associated with known and inferred extraction of tin, copper and lead in prehistoric and later times (see e.g. Penhallurick, 1986; West et al., 1997; and references therein). Ombrotrophic (rain-fed) mires were required in order to benefit from their ability to retain regional signals of atmospheric metal and minerogenic deposition (*cf.* Shotyk, 1996; Charman, 2002; Mighall et al., 2002).

2.1. Sites and core collection

An 8 cm diameter Russian corer was used to collect peat cores from the raised ombrotrophic mire of Tor Royal Bog (Ordnance Survey grid reference SX 60476 72659), located about 1.5 km southeast of Princetown, central Dartmoor, and from the ombrotrophic mire surrounding Dozmary Pool (SX 19211 74360), around 21.5 km NW of Liskeard at the southern end of Bodmin Moor (Fig. 1). Both are designated Sites of Special Scientific Interest (SSSIs) located at the centre of a region with a history of tin mining. Details of the cores sites and their associated vegetation and stratigraphy may be found in Amesbury et al. (2008) and Brown (1977) respectively. Cores were stored in a laboratory cold room at 4 °C until analysis; sub-sampling was at 1 cm contiguous intervals.

2.2. Geochemistry

Elemental concentrations and lead isotope ratios were determined by high resolution ICP-MS (Element 2, Thermo Scientific, Bremen, Germany) following a modified *aqua regia* digest (1:1 concentrated Aristar grade HCl and HNO$_3$, the standard *aqua regia* digest is 1:3 HNO$_3$:HCl and the modification increases the solubility of tin and other elements) using microwave assisted extraction (MARS, CEM, UK) on oven-dried and ball-milled sub-samples. Full quality control, including reagent blanks and Certified Reference Materials CRM (BCR-700) were used.

Total C contents and ^{13}C:^{12}C isotope ratios of the milled and dried material were determined using a Flash EA 1112 Series
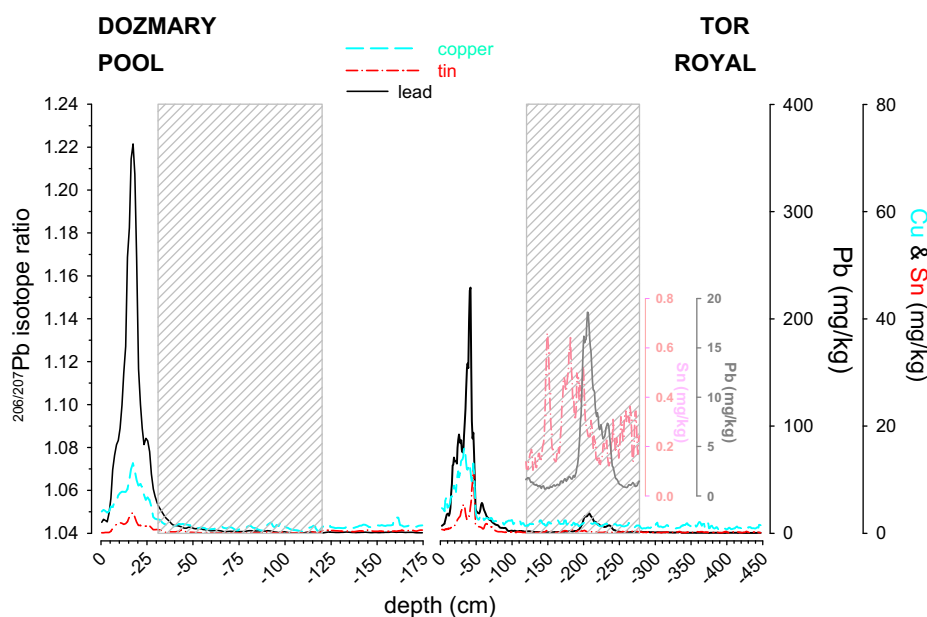

Fig. 2. Copper (Cu), lead (Pb) and tin (Sn) concentrations plotted against core depth for Dozmary Pool (left) and Tor Royal (right). The shaded area is the section of the profile selected for dating.
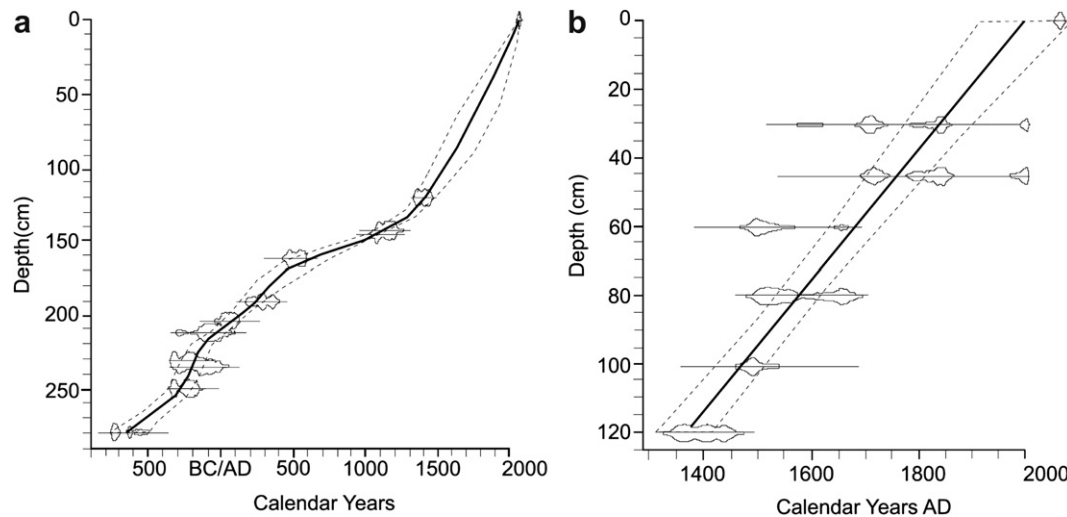
Fig. 3. Age-depth models for (a) Tor Royal (smooth spline) and (b) Dozmary Pool (linear regression) created using *clam* software (Blaauw, 2010). The dotted lines enclose the 95% confidence limits based upon 1000 iterations. The solid line represents the weighted mean. The probability distributions of the calibrated dates upon which the model is based are displayed as hollow silhouettes.

Elemental Analyser connected via a Conflo III to a Delta[Plus] XP isotope ratio mass spectrometer (all Thermo Finnigan, Bremen, Germany). Isotope ratios were calculated with respect to a CO_2 reference gas injected with every sample and traceable to IAEA reference materials USGS40 and USGS41 (both L-glutamic acid). The C contents of the samples were calculated against NIST standard reference material 1547 peach leaves which was analysed with every batch of ten samples.

Bulk densities were calculated by volume displacement per unit weight of wet peat, using the wet to dry weight conversion factor (calculated individually for each sample) to express bulk density on a dry weight basis.

2.3. Radiocarbon dating

Remains of *Sphagnum* spp. were extracted from core sections for radiocarbon dating by AMS (accelerator mass spectrometry). Plant tissues were picked from 500 μm sieve residues following disaggregation from the sediment matrix in cold 10% NaOH. Radiocarbon samples were prepared to graphite at the NERC Radiocarbon Facility, East Kilbride, and measured at the SUERC AMS laboratory (Tables 1 and 2).

Calibrations were performed using OxCal (Bronk Ramsey, 2009) and the IntCal09 calibration curve (Reimer et al., 2009). Radiocarbon dates below 100 cm at Tor Royal present a conformable series and are consistent with the dates reported for this site in Amesbury et al. (2008). Results above 100 cm appear significantly older than expected. The reasons for this are uncertain, but a similar pattern has been observed for a series of ^{14}C dates on *Sphagnum* from Butterburn Flow, a large raised mire in northern England (Charman and Garnett, 2005). The likely explanations for the anomalously old dates observed there were given as contamination by inputs of older carbon (SCPs, spheroidal carbonaceous particles) from industrial emissions, i.e. fossil fuel burning derived deposition.

Clam software (Blaauw, 2010) was used to construct non-Bayesian, 'classical' age-depth models for each site. Smooth spline and linear regression models were found to provide the 'best fit' for the dates from Tor Royal and Dozmary Pool, respectively (Fig. 3). These models allowed the estimation of calendar ages (the cal BC/AD weighted mean) for all depths throughout each peat core.

Table 3
CRM (BCR-700) recovery from analysis process.

| Element	Replicate (μg/g)	Replicate (μg/g)	Replicate (μg/g)	Replicate (μg/g)	Average (μg/g)	SD	Certified (μg/g)	Percentage recovery (%)
Mn	442.14	446.46	459.62	442.47	447.67	8.20	441.00	101.51
Co	13.32	12.60	12.94	12.93	12.95	0.29	13.60	95.20
Cu	30.62	29.20	29.49	28.88	29.55	0.76	32.00	92.33
Zn	79.62	76.76	80.13	82.61	79.78	2.40	100.00	79.78
As	18.32	18.46	19.07	18.69	18.63	0.33	18.00	103.51
Se	0.71	0.35	0.27	0.15	0.37	0.24	0.51	72.57
Mo	1.12	1.08	1.18	1.23	1.15	0.07	1.15	100.09
Cd	0.23	0.23	0.27	0.27	0.25	0.02	0.25	100.00
Sn	4.94	4.94	5.18	5.93	5.25	0.47	12.40	42.33
La	54.98	49.10	51.59	58.12	53.45	3.94	67.00	79.77
Ce	134.54	125.26	131.89	139.83	132.88	6.06	133.00	99.91
Pr	13.94	12.65	13.57	15.01	13.79	0.98	14.60	94.47
Sm	10.36	9.48	10.06	11.13	10.26	0.69	10.40	98.65
Eu	1.70	1.57	1.65	1.79	1.68	0.09	1.66	100.98
Gd	8.36	7.67	8.24	9.27	8.38	0.66	8.50	98.64
Pb	46.09	45.22	47.69	54.59	48.40	4.25	61.00	79.34
Bi	1.14	1.09	1.16	1.30	1.17	0.09	1.44	81.44
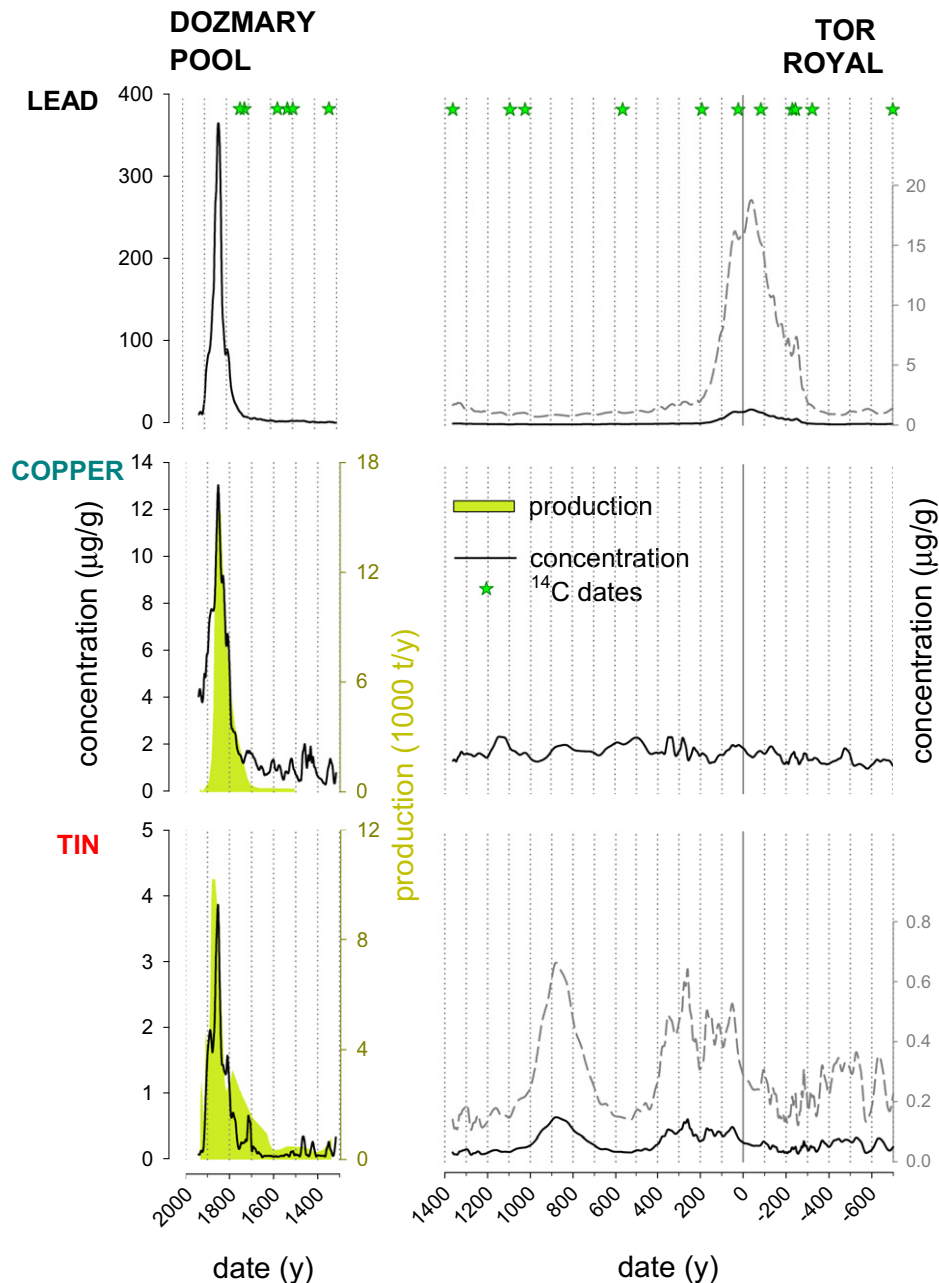
Fig. 4. Lead, copper and tin concentrations plotted against a calendar year timescale. Data are only presented for those ombrotrophic sections of the cores where elevated metal deposition was recorded, and for which the modelled chronology (AMS ^{14}C dating and age-depth profiling) is secure. Positive values along the x-axis reflect years AD; negative values are years BC. Tin and copper production figures are taken from tax records (Dines, 1956; Hatcher, 1973). For Tor Royal, the data are scaled for comparison with Dozmary Pool, as well as having the scale expanded to view detail at lower concentrations, represented by the dotted line.

3. Results and discussion

3.1. General core characteristics

CRM recoveries are reported in Table 3. Recoveries ranged from 79 to 103% with the exception of selenium (73%) and tin (42%). For tin the microwave digestion procedure is only an operationally defined 'extraction', rather than total elemental analysis. The CRM is a minerogenic soil as compared to the peats under study here, but no suitable peat CRM was available. It is likely that metals are more readily solubilized by microwave extraction from an organic matrix as compared to a minerogenic one. For total digest of tin, an alkaline fusion would be required (Allen, 1989), and as the core material was

limited and alkaline fusion procedures (as well as open hot block digestion procedures) are subject to contamination (tin is present at low concentrations in the core material), the operationally defined microwave extraction was used. Also, the high salt content of an alkaline fusion preparation is unsuitable for ICP-MS analysis. It was assumed that extraction efficiency was similar across the cores given the uniformity of the peat, discussed later in the manuscript.

Tor Royal is ombrotrophic throughout the sampled profile while the Dozmary Pool core is only ombrotrophic from a depth of 125 cm up to the ground surface, as was also reported in a previous study (Brown, 1977). The transition from minerotrophic to ombrotrophic peat at Dozmary Pool is reflected by a general decline in metal concentrations, particularly lead and tin (Fig. 2).
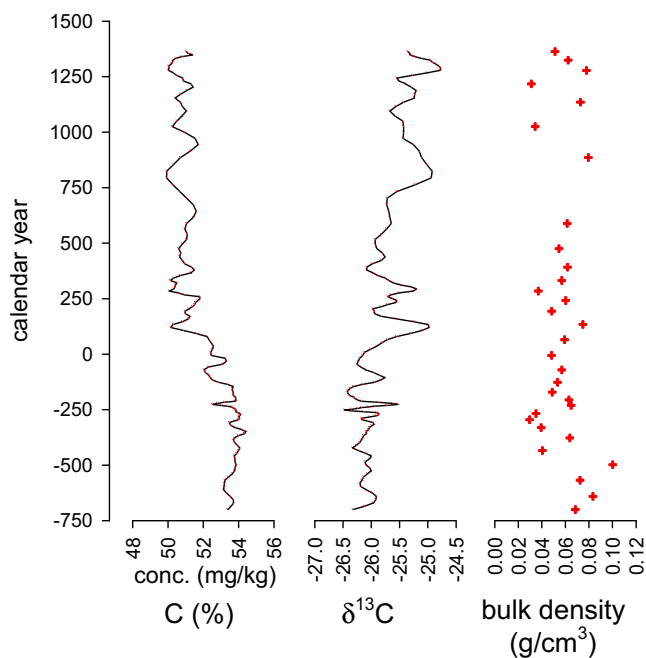
Fig. 5. Percentage carbon, δ^{13}C and bulk density for Tor Royal plotted against calendar year.

Concentrations of tin, copper and lead from the Tor Royal and Dozmary Pool cores are displayed in Fig. 2. AMS ^{14}C dates (Tables 1 and 2) were used to establish a calendar timescale for the geochemical records (Fig. 3). Ombrotrophic sections of the cores can be securely dated over connected time periods: for Tor Royal, from ∼700 cal. BC to cal. AD 1400; for Dozmary Pool, from cal. AD ∼1400 to the present day. Some extrapolated temporal overlap occurs during the 13th century AD and across this interval tin, copper and lead concentrations are directly comparable between the sites (Fig. 4). The geochemical profile for Tor Royal extends back in time to the Bronze Age (before 700 cal. BC), but that core section was not dated owing to a lack of persuasive geochemical peaks. Depositional inputs into each core will be largely reflective of the geographical position of the sampling site relative to ore processing activity at any given time (predominant winds are from the SW).

The magnitude of tin, lead and copper concentration at maximum is similar across the two cores, with lead concentrations

Fig. 6. Percentage carbon regressed against δ^{13}C.

being higher at Dozmary Pool but tin and copper higher at Tor Royal. Peak lead deposition concentrations, corresponding to the 19th century AD for Dozmary Pool (Fig. 4), and by inference for the same period at Tor Royal, are 360 and 220 mg/kg respectively. This is comparable in order of magnitude to other sites in the UK where geochemical records include the Industrial Revolution (cal. AD ∼1800) (Le Roux et al., 2004; Cloy et al., 2005). Dozmary Pool also shows substantial increases in tin and copper deposition associated with the Industrial Revolution (Figs. 2 and 4), with peaks in metal concentration also observed at the top of the Tor Royal profile (Fig. 2). Concentrations of tin and copper in the Dozmary Pool core closely match documented changes in the timing and magnitude of metal production noted in tax records (Hatcher, 1973; Dines, 1956) (Fig. 4), providing strong evidence that these elements are immobile in the bog, and that the depositional record is a good predictor of production magnitude.

As only the Tor Royal core is ombrotrophic in the prehistoric period, the section of the core where this is robustly dated (Fig. 3) is considered in more detail with additional carbon (Figs. 5 and 6) and lead (Fig. 7) isotopic analysis and bulk density calculated (Fig. 5), along with more comprehensive reporting of multi-element analysis (Figs. 8 and 9). Percentage carbon ranges from 50 to 54%, with the lower carbon content predominating at a younger age. The δ^{13}C showed the opposite trend with less δ^{13}C observed towards the upper regions of the dated sections. This negative correlation between percentage carbon and δ^{13}C was confirmed by regression analysis (Fig. 6). The negative correlation indicates that the heavily degraded peat (i.e. lower percentage C) is more enriched isotopically, with each biochemical transformation leading to enrichment. Furthermore, the carbon content is relatively stable post-AD 250 and pre-AD 1, indicating a shift in C cycling. Peat humification is associated with drier and warmer climatic periods. Amesbury et al. (2008) looked specifically at climate change proxies (testate amoebae and peat humification) for Tor Royal and, although the resolution of their data was somewhat limited, they concluded that a shift to a warmer and/or drier phase circa AD 400 occurred, in agreement with our findings. Bulk density was stable down the dated section of the core. This constancy, along with the relative stability of percentage C after AD 200, gives added confidence that any changes in metal deposition patterns during this period are not due to changes in peat properties.

A presentation of 18 elements down the entire extent of the Tor Royal profile (Fig. 8) shows, in the main, dramatic shifts in element profiles towards the surface, as already discussed above for copper, lead and tin. The main exception is selenium which is relatively consistent over the core profile. This can be explained by the fact that selenium deposition is dominated by marine sources (Steinnes, 1997). The rare earth elements show a high degree of consistency in their deposition pattern. Rare earths serve as markers of geogenic inputs (i.e. dust background) (Shotyk et al., 2001). The peak of rare earth deposition occurs at 50 cm depth, probably due to massive dust disturbance in this area around the time of the Industrial Revolution. The fact that zinc and manganese are most elevated at the surface is probably because they are relatively mobile and important plant nutrients, and thus bio-mobilized continuously by the mire surface flora. Interestingly, manganese shows peaks (consisting of 2–3 elevated sections of the core) at 200–150 cm, also matched by cobalt and molybdenum, suggesting as similar source and possibly related to a specific period of discrete pollution, such as exploitation of an ore body rich in these elements. This can be seen more clearly in Fig. 9 where the same 18 elements are plotted against time on an expanded x-axis scale. The spikes in manganese, cobalt and lead occur circa. AD 200–300, during the height of Roman colonization. This plot also shows discrete (i.e. not
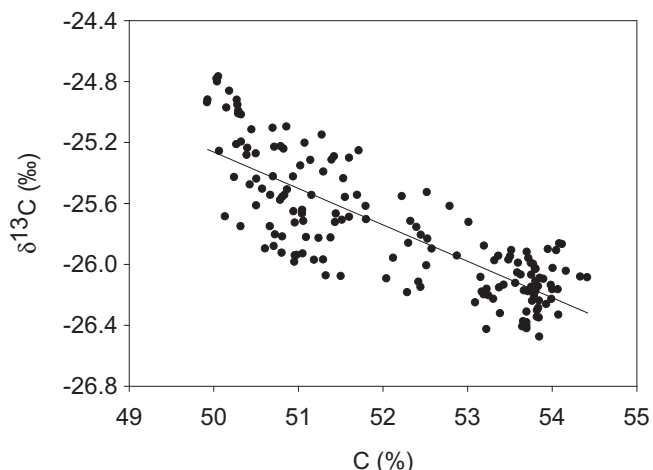
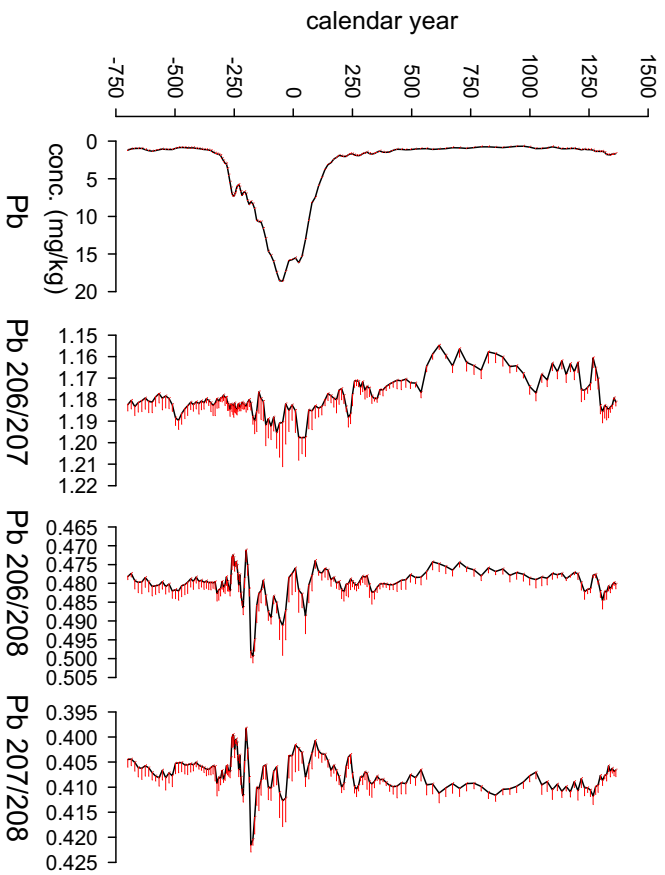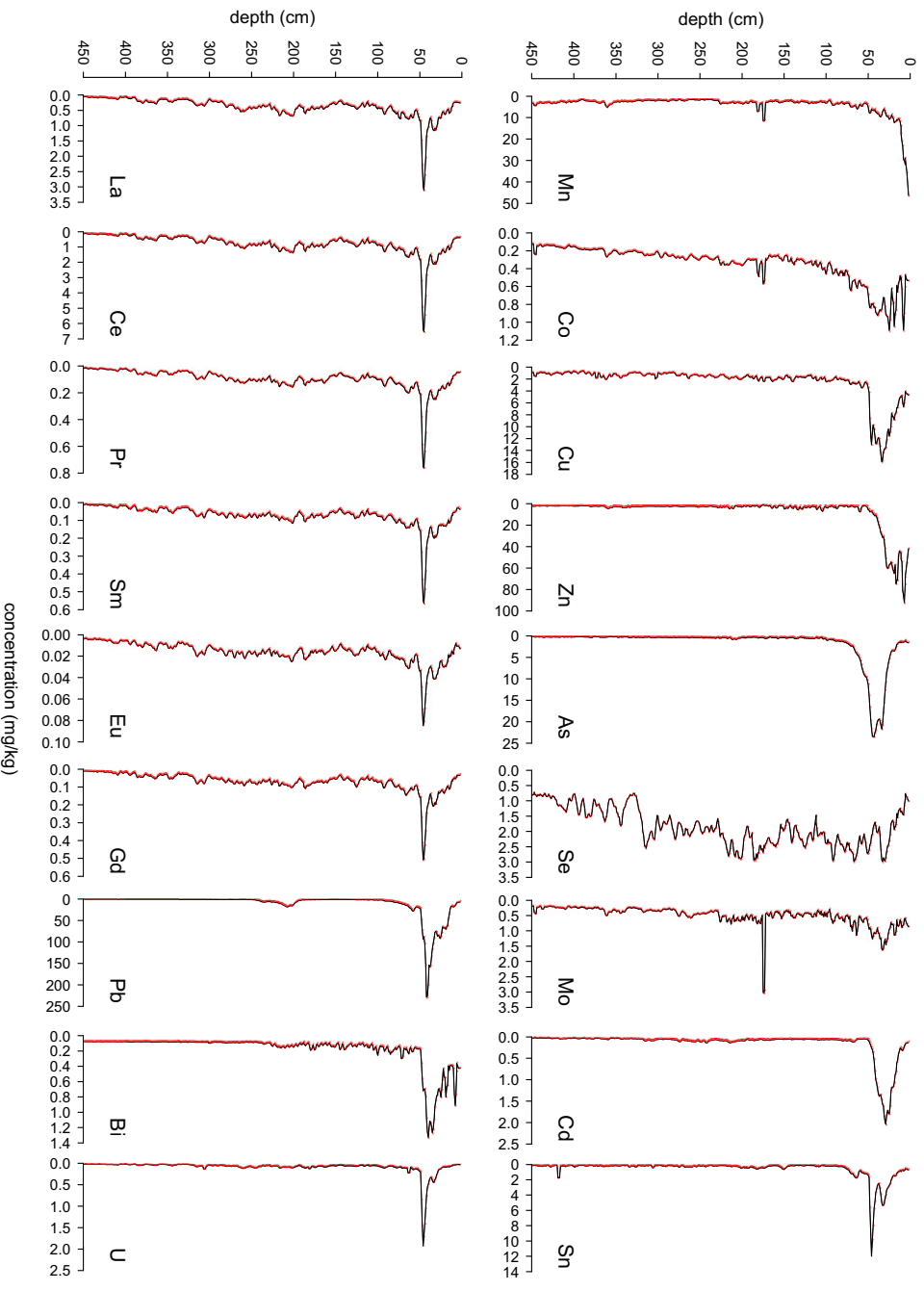**Fig. 8.** Element concentrations for Tor Royal plotted against depth.

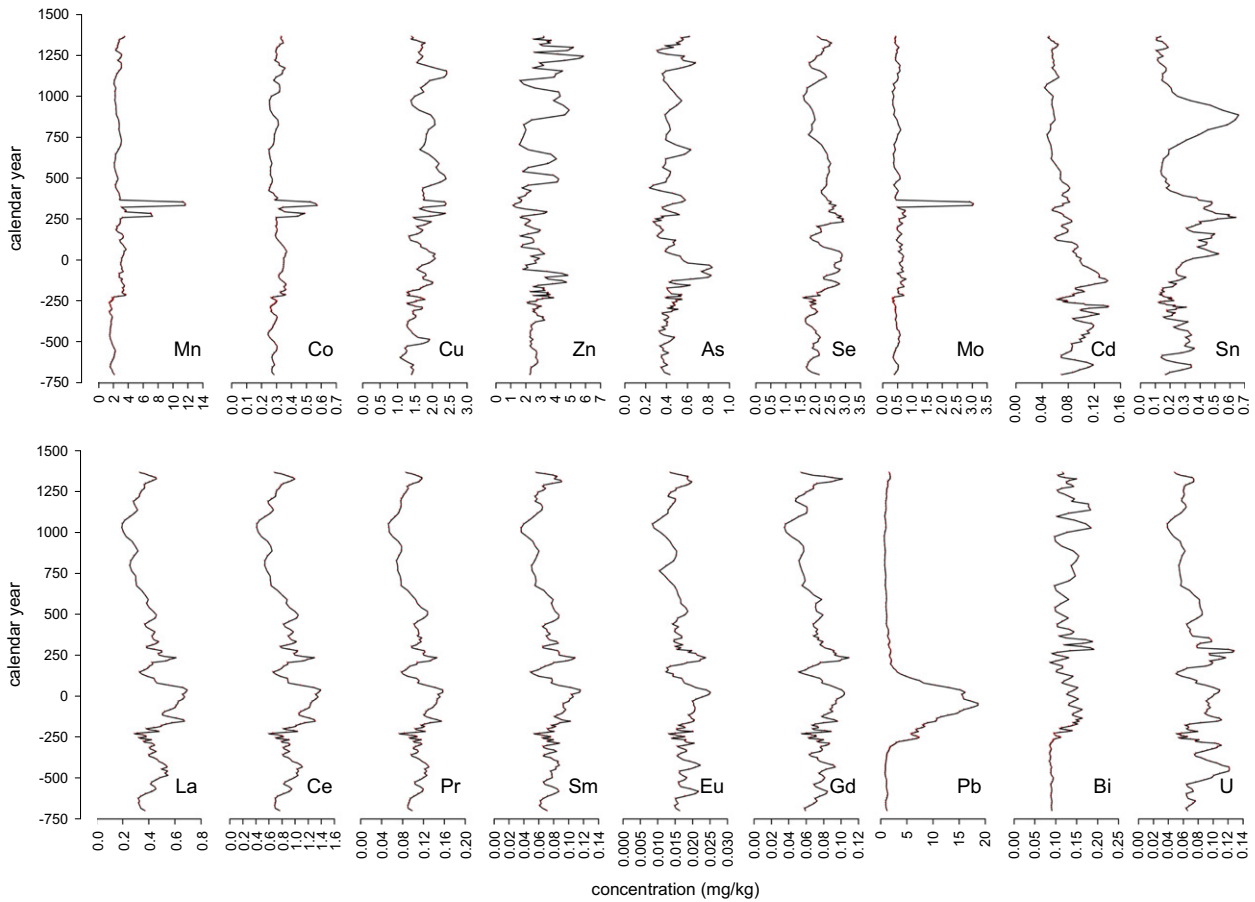**Fig. 7.** Lead isotope ratios for Tor Royal plotted against calendar year.

Fig. 9. Element concentrations for Tor Royal plotted against calendar year.

observed for other elements) and sustained rises in lead and tin concentrations, which will be considered in detail below.

3.2. Tin deposition

Tin observed in the peat cores must be derived from soil/dust deposition resulting from farming or mining activity, or from point or diffuse mining sources. As tin is a rare element with respect to exploitation, it is assumed that any point mining sources must be local. To factor out soil/dust contamination as a source, it is standard practice to normalise the metal of interest, in this case tin, to a metal of predominantly geogenic source, such as Lanthanide Group elements (Shotyk et al., 2001). All the Lanthanides follow the same deposition pattern (Fig. 9), so gadolinium was chosen as a reference as it had a high CRM recovery (Table 3). The tin/gadolinium ratio (Fig. 10) differs little from the tin concentration plot (Fig. 9), so it can be assumed that where tin shows distinct elevation, that this is due to excess tin deposition – i.e. mining sources.

There is no prolonged elevation of tin inputs at Tor Royal before cal. AD 100, although isolated 'spikes' in concentration are evident (Figs. 2 and 4). These spikes may represent sporadic tin smelting activity during the pre-Roman period, rather than 'noise' within the dataset, as lower and more stable tin levels are recorded for cal. AD 400–700 and 1000–1400. A sustained rise in tin deposition is observed from ~cal. AD 100, declining to a smooth baseline ~cal. AD 400 (the latter date would be close to the time of departure of the Roman army from Britain). Material evidence for early Roman exploitation of tin is scarce. Rather, it has been argued that the
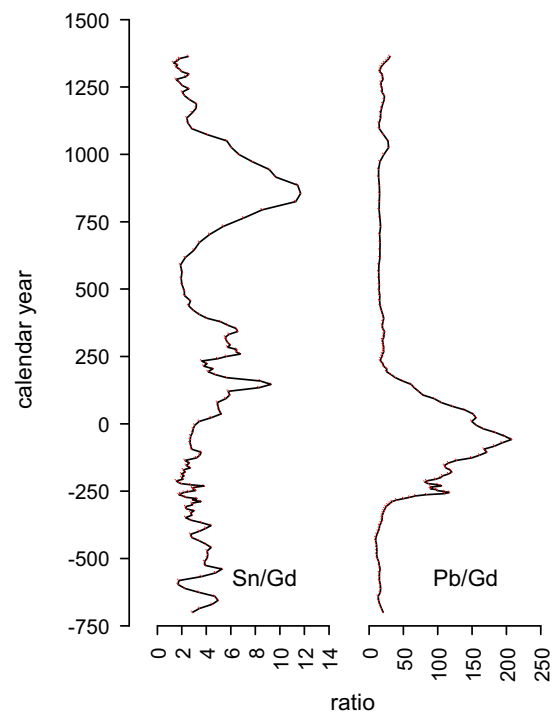

Fig. 10. Tin/gadolinium and lead/gadolinium ratios for Tor Royal plotted against calendar year.

Romans only became interested in British tin following the exhaustion of supplies from Spanish mines by the middle of the 3rd century AD (Hatcher, 1973; Hatcher and Barker, 1974; Penhallurick, 1986). The data presented here suggest that British tin was continuously exploited earlier in the Roman period than has previously been surmised and that smelting was located close to Tor Royal.

From the early 5th century AD onwards, tin inputs into the Tor Royal sediments remained low for ~300 years, a period for which there is very little other evidence for tin production (Hatcher, 1973; Gerrard, 2000). Around cal. AD 700 another significant rise in tin deposition is recorded with influx peaking ~cal. AD 900. Tin values then decline, returning to a baseline by ~cal. AD 1100. Although limited artefactual and environmental evidence has been presented for Anglo-Saxon age tin exploitation (Gerrard, 2000, pp. 23–24), authorities are divided regarding the levels of tin exploitation that occurred during this period (Hatcher, 1973). One view is that production was intermittent and on a small-scale, yet counter arguments have been made that tin was much in demand for tinning (coating with tin) of mirrors, buckles and jewellery, for lining the inside of copper cooking vessels and armour (such as a Sutton Hoo iron helmet decorated with tinned bronze plates), for use in church bells and for the production of small quantities of pewter, Indeed it appears possible that the metal was widely traded throughout Europe, with Britain thought to be the only feasible source of supply (Hatcher, 1973; Hatcher and Barker, 1974; Gerrard, 2000). The results of our study support the latter view.

The deposition of tin in the Tor Royal core may also answer some outstanding questions regarding the lack of documentary records for tin production in the Anglo-Saxon period. Bede's *Historia Ecclesiastica* (*circa* AD 731) does not include tin amongst England's mineral wealth (Hatcher, 1973), while entries in the *Domesday Book* (AD 1086) for Devon and Cornwall list the exploitation by mining of iron and lead, but tin mines are not recorded. The simplest explanation for the absence of tin in these accounts is that they bookend the expansion and collapse of tin production during the later half of the Anglo-Saxon period.

3.3. Copper and lead deposition

Copper was mined from at least the Iron Age in SW Britain (Northover, 1995), but no enhanced copper deposition into the cores is observed until the Industrial Revolution (Fig. 2). The depositional record for copper is much less informative when compared to tin or lead, as copper, with its higher melting point (1083 °C), is less readily entrained atmospherically. Baseline concentrations of copper within the peat are also somewhat higher than those for tin and lead (Fig. 2), which means that anthropogenic inputs above background will only be observable for higher rates of pollution-derived deposition.

The lead deposition record has a very large (~20-fold) and sustained increase above background concentrations starting ~300 cal. BC, reaching a maximum at 50 cal. BC, and declining to a baseline by cal. AD 200 (Figs. 4 and 10). An elevation in Roman period lead deposition has been seen in core studies (Rosman et al., 1997; Le Roux et al., 2004; Shotyk et al., 2001; Kylander et al., 2005; Cloy et al., 2005; Monna et al., 2004). For core study sites distant from ancient mining sources, it has been argued that Roman period lead pollution, inferred from both total concentration and lead isotopes, is due to mining in Spain resulting in continental-wide pollution, a conclusion which has also been inferred from studies of Spanish peat cores (Kylander et al., 2005). However, there is a realization that this scenario may be somewhat simplistic, as British sources of lead pollution, from lead and copper mining, are responsible, at least partially, for an elevated Roman period lead signature (Le Roux et al., 2004). There is a convincing argument that Spanish mining is not the primary source of the increase in lead observed during the Roman period for Tor Royal, where the figures for lead concentrations are as high, or higher, than for other European sites (Rosman et al., 1997; Le Roux et al., 2004; Shotyk et al., 2001; Kylander et al., 2005). When the lead concentrations for Tor Royal are at their highest, the $^{206/207}$Pb ratio reaches 1.22 (Fig. 7) – greater than for any other western European galena (Fig. 11). This is further evidence for local sources dominating the lead deposition, with copper smelting the most probable
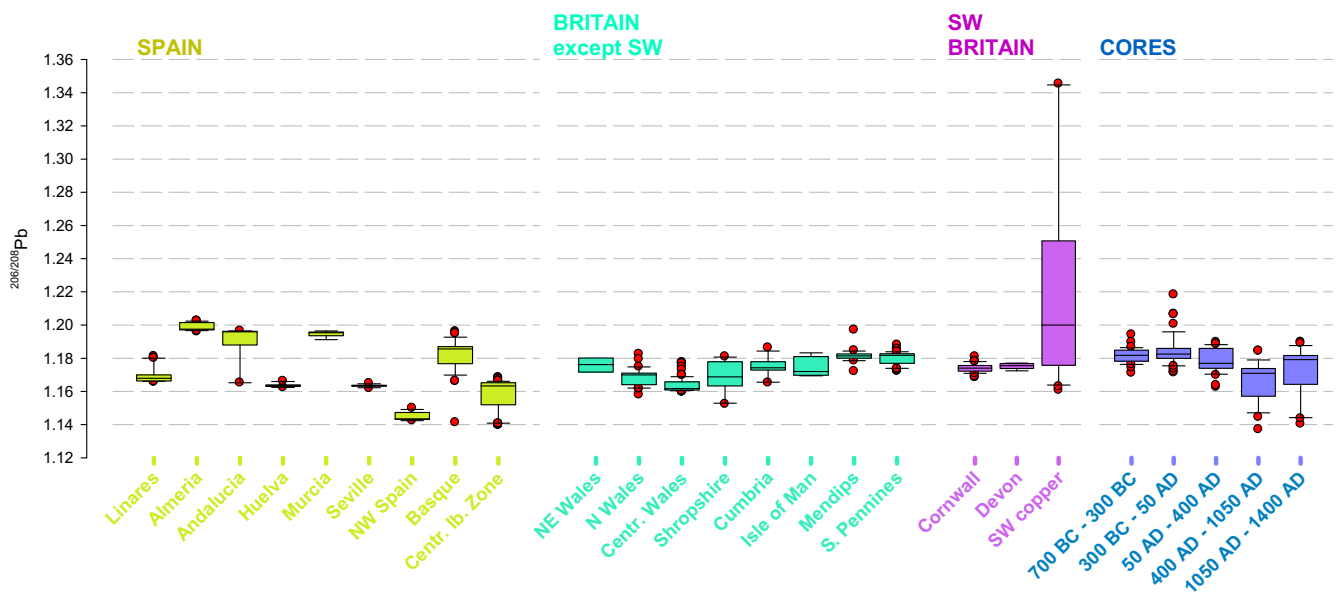

Fig. 11. Comparison of $^{206/207}$Pb isotope ratios for lead and copper ores from different regions of Europe, with additional data for Devon and Cornwall (Arias et al., 1996; Baron et al., 2006; Brevart et al., 1982; Klein et al., 2009; Marcouz and Moelo, 1991; Oh et al., 1989; Rohl, 1996; Rohl and Needham, 1998; Stos-Gale et al., 1995; Tornos et al., 1996; Velasco et al., 1996; Zalduegui et al., 2004) plotted against those for the Tor Royal cores.
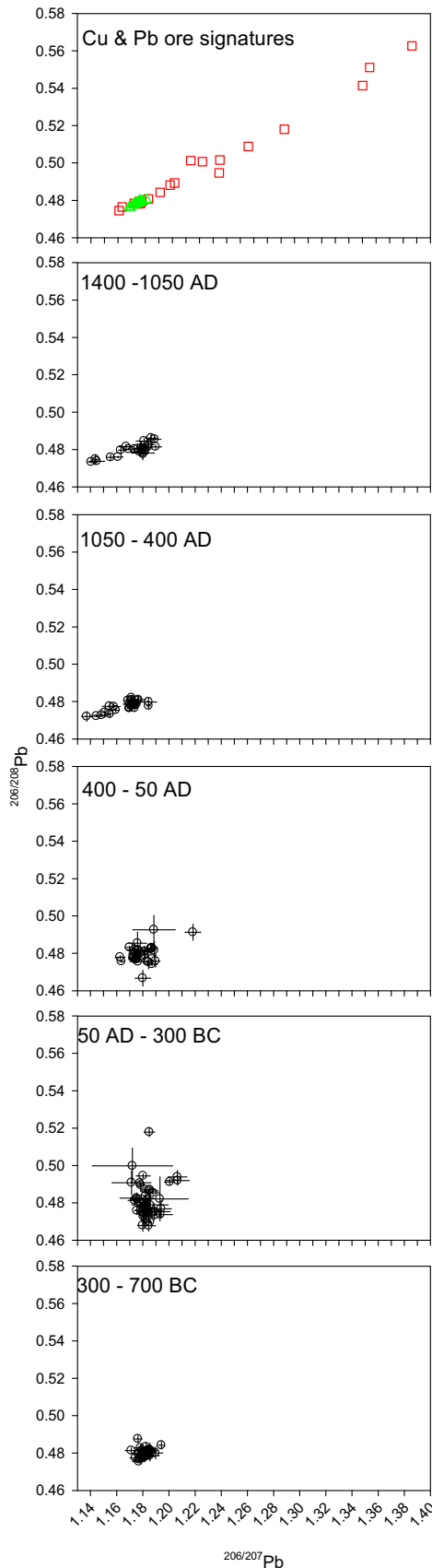
Fig. 12. Comparison of lead isotope ratios for Tor Royal plotted against those for local (Devon and Cornwall) lead (Rohl, 1996), represented on the figure by triangles, and copper ores (Rohl and Needham, 1998), represented by squares.

explanation given that the $^{206/207}$Pb ratio in copper ores from SW Britain ranges from 1.16 to 1.38 (Rohl and Needham 1998). Plots of lead isotope ratios for the Tor Royal core along with local copper and galena ore bodies illustrate that during the Iron Age and Roman periods, lead isotopes match those of local copper and lead ores, but during periods where lead is not elevated (cal AD 400–1050) the core signature partially lies outside the isotope signatures of local ore bodies (Fig. 12). Copper-derived lead has also been hypothesised as a source of elevated lead deposition in northern England (Le Roux et al., 2004). There is strong evidence for the exploitation of copper from SW Britain during the Iron Age for use in bronze (Northover, 1995). Copper and lead ores of this provenance have a high silver content and it may also be possible that these ores were being exploited for silver coinage during the Iron Age (Cunliffe, 1987).

The decline of lead deposition to background levels by ~cal. AD 200 (Fig. 2) suggests that either the Romans were losing interest in copper, lead or silver from Devon or Cornwall during the later stages of occupation, or that the lead deposited into the profile mainly (or perhaps entirely) resulted from indigenous activity which ceased soon after the Roman colonization. The collapse of a metal-based economy in this region is inferred from coin minting, with SW British pre-Roman Iron Age ('Celtic') coinage disappearing during the 1st century AD (Cunliffe, 1987). The Romans widely exploited lead deposits throughout England, as far south as the Mendip Hills in Somerset, but there is no documentary record nor archaeological evidence for them utilizing deposits of galena in Devon and Cornwall (Jones and Mattingly, 1990). Again, this favours an argument for predominantly indigenous rather than Roman base metal mining in the decades following the arrival of the Romans, given that the Roman colonization west of Exeter was slight and occurred late in the period (Cunliffe, 1987).

As the history of copper mining in SW Britain can be traced indirectly through the release of lead from copper ores, the fact that lead influx into the Tor Royal core only rises above an environmental baseline during the pre-Roman Iron Age and in the modern industrial era indicates that any copper mining in this region outwith these periods was not on a substantial scale. Northover (1995) states that while it is "good sense to assume" that there was British copper production during the Bronze age, there is "no direct evidence", with most copper ingots of this period found in the south and east of Britain being of Continental European origin. The archaeology points to an expansion of SW British tin and copper production during the Iron Age only (Northover, 1995) — a hypothesis that is also supported by our data.

4. Conclusions

1. Investigations in SW Britain have provided detailed chronological and geochemical profiles which for the first time enable us to address with confidence many issues surrounding tin in antiquity.
2. The first prolonged elevation of tin influx to a peat profile occurs from ~cal AD 100, declining to a smooth baseline ~cal AD 400. Given dating uncertainties, this would seem to correspond well to the period of Roman occupation in Britain and would conflict with suggestions that the Romans only became interested in British tin following the exhaustion of supplies from Spanish mines by the middle of the 3rd century AD.
3. There was a lull in apparent tin production for the period ~cal AD 400–700 which could reflect a collapse in tin production during the first half of the Anglo-Saxon period. There was then a re-expansion to ~cal AD 1100. British tin may well have been the source of the metal used in wider European trade for this latter period.

4. Apart from in the modern industrial era, the lead inputs into the Tor Royal core only rises above an environmental baseline during the pre-Roman Iron Age (∼300 cal BC), peaking ∼50 cal BC and declining to base level around cal AD 200. The decline of lead suggests that either the Romans were losing interest in copper, lead or silver from Devon or Cornwall, or that much lead deposition had derived from indigenous activity which ceased soon after the Roman colonization — a collapse which is also seen in the records for coinage.

5. Given the lead–copper relationship, this suggests that any copper mining in this region outwith these periods was not on a substantial scale. At their highest, the figures for lead concentration on Dartmoor for the Roman period are as high, or higher, than for other European sites (including Spain). This is further evidence for local SW British sources dominating the lead deposition, with copper smelting the most probable explanation.

6. Our data may provide the first supportive 'direct evidence' for the expansion of SW British tin and copper production during the Iron Age.

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References

Allen, S.E., 1989. Chemical Analysis of Ecological Materials, second ed. Blackwell, Oxford.
Amesbury, M.J., Charman, D.J., Fyfe, R.M., Langdon, P.G., West, S., 2008. Bronze Age upland settlement decline in southwest England: testing the climate change hypothesis. J. Archaeol. Sci. 35, 87–98.
Archaeology, 2010. http://www.archaeology.org/1005/etc/artifact.html.
Arias, D., Corretge, G., Suarez, O., Villa, L., Cuesta, A., Gallastegui, G., 1996. Lead and sulphur isotope compositions of the Ibias gold vein system (NW Spain): genetic implications. Econ. Geol. 91, 1292–1297.
Baron, S., Carignan, J., Laurent, S., Ploquin, A., 2006. Medieval lead making on Mont-Lozere Massif (Cevennes-France): tracing ore sources using Pb isotopes. Appl. Geochem. 21, 241–252.
Blaauw, M., 2010. Methods and code for 'classical' age-modelling of radiocarbon sequences. Quat. Geochron. 5, 512–518.
Brevart, O., Dupre, B., Allegre, C.J., 1982. Metallogenic provinces and the remobilization processes studied by lead isotopes: lead-zinc ore deposits from the southern Massif Central, France. Econ. Geol. 77, 564–575.
Bronk Ramsey, C., 2009. Bayesian analysis of radiocarbon dates. Radiocarbon 51, 337–360.
Brown, A.P., 1977. Late-Devensian and Flandrian vegetation history of Bodmin Moor, Cornwall. Phil. Trans. R. Soc. B 276, 251–320.
Caesar, 2003. The Conquest of Gaul. Penguin Classics, London.
Charman, D.J., 2002. Peatlands and Environmental Change. John Wiley & Sons, Chichester.
Charman, D.J., Garnett, M.H., 2005. Chronologies for recent peat deposits using wiggle-matched radiocarbon ages: problems with old carbon contamination. Radiocarbon 47, 135–145.
Cloy, J.M., Farmer, J.G., Graham, M.C., MacKenzie, A.B., Cook, G.T., 2005. A comparison of antimony and lead profiles over the past 2500 years in Flanders Moss ombrotrophic peat bog, Scotland. J. Environ. Monit. 7, 1137–1147.
Cunliffe, B.W., 1987. Hengistbury Head, Dorset. In: The Prehistoric and Roman Settlement, 3500BC–AD500, vol. 1 Oxford University Committee for Archaeology Monographs 13, Oxford.
Cunliffe, B.W., 2001. Facing the Ocean: The Atlantic and Its People. Oxford University Press.
Dines, H.G., 1956. The Metalliferous Mining Region of South-West England. In: Memoirs Geological Survey Great Britain, vol. 1. HMSO, London.
Gerrard, S., 2000. The Early British Tin Industry. Tempus, Stroud.

Haustein, M., Gillis, C., Pernicka, E., 2010. Tin isotopy — a new method for solving old questions. Archaeometry 52, 816–832.
Hatcher, J., 1973. English Tin Production and Trade Before 1550. Clarendon Press, Oxford.
Hatcher, J., Barker, T.C., 1974. A History of British Pewter. Longman, London.
Herodotus, 2003. The Histories. Penguin Classics, London.
Jones, B., Mattingly, D., 1990. An Atlas of Roman Britain. Oxbrow Books.
Klein, S., Domergue, C., Lahaye, Y., Brey, G.P., von Kaenel, H.-M., 2009. The lead and copper isotopic composition of copper ores from the Sierra Morena (Spain). J. Iber. Geol. 35, 59–68.
Kylander, M.E., Weiss, D.J., Martinez Cortizas, A., Spiro, B., Garcia-Sanchez, R., Coles, B.J., 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. 240, 467–485.
Le Roux, G., Weiss, D., Grattan, J., Givelet, N., Krachler, M., Cheburkin, A., Rausch, N., Kober, B., Shotyk, W., 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.
Marcouz, E., Moelo, Y., 1991. Lead isotope geochemistry and paragenetic study of inheritance phenomena in metallogenesis: examples from base metal sulphide deposits in France. Econ. Geol. 86, 106–120.
Mighall, T.M., Abrahams, P.W., Grattan, J.P., Hayes, D., Timberlake, S., Forsyth, S., 2002. Geochemical evidence for atmospheric pollution derived from prehistoric copper mining at Copa Hill, Cwmystwyth, mid-Wales. Sci. Total Environ. 292, 69–80.
Monna, F., Petit, C., Guillaumet, J.-P., Jouffroy-Bapicot, I., Blanchot, C., Dominik, J., Losno, R., Richard, H., Leveque, J., Chateau, C., 2004. History and environmental impact of mining activity in Celtic Aeduan territory recorded in a peat bog (Morvan, France). Environ. Sci. Technol. 38, 665–673.
Northover, P., 1995. In: Green, M.J. (Ed.), The Celtic World. Routledge, London, pp. 285–309.
Oh, M.-S., Marcoux, E., Calvez, J.-Y., Touray, J.-C., 1989. Anomalous unradiogenic lead from strata-bound Zn-Pb-Cu mineralization in the Saint Georges-sur-Loire synclinorium (Amorican Massif, France). Econ. Geol. 84, 1436–1443.
Penhallurick, R.D., 1986. Tin in Antiquity. Adlard & Son, London.
Pliny the Elder, 2004. Natural History: A Selection. Penguin Classics, London.
Reimer, P.J., et al., 2009. IntCal09 and Marine09 radiocarbon age calibration curves, 0–50,000 years cal BP. Radiocarbon 51, 1111–1150.
Rohl, M.M., 1996. Lead isotope data from the Isotrace laboratory, Oxford: archaeometry data base 2, galena from Britain and Ireland. Archaeometry 38, 165–180.
Rohl, B., Needham, S., 1998. The Circulation of Metal in the British Bronze Age: The Application of Lead Isotope Analysis British Museum Occasional Paper 102, London.
Rosman, J.R., Chishol, W., Hong, S., Candelone, J.-P., Burtron, C.F., 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. 37, 3413–3416.
Shotyk, W., 1996. Peat bog archives of atmospheric metal deposition: geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. Environ. Rev. 4, 149–183.
Shotyk, W., Weiss, D., Kramers, J.D., Frei, R., Cheburkin, A.K., Gloor, M., Reese, S., 2001. Geochemistry of the peat bog at Etang de la Gruere, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Zr, and REE) since 12,730 ^{14}C yr BP. Geochim. Cosmochim. Acta 65, 2337–2360.
Spear, T.M., Svee, W., Vincent, J.H., Stanisich, N., 1998. Chemical speciation of lead dust associated with primary smelting. Environ. Health Perspect. 106, 565–571.
Steinnes, E., 1997. Trace element profiles in ombrogenous peat cores from Norway: evidence of long distance transport. Water Air Soil Pollut. 100, 405–413.
Stos-Gale, Z., Gale, N.H., Houghton, J., Speakman, R., 1995. Lead isotope data from the Isotrace laboratory, Oxford: archaeometry data base 1, ores from the western Mediterranean. Archaeometry 37, 407–415.
Tornos, F., Ribera, F., Shepherd, T.J., Spiro, B., 1996. The geological and metallogenic setting of stratabound carbonate-hosted Zn-Pb mineralizations in West Asturian Leonese Zone, NW Spain. Mineral. Deposita 31, 27–40.
Velasco, F., Pesquera, A., Herreo, J.M., 1996. Lead isotope study of Zn-Pb ore deposits associated with the Basque-Cantabrian basin and Paleozoic basement, Northern Spain. Mineral. Deposita 31, 84–92.
West, S., Charman, D.J., Grattan, J.P., Cherburkin, A.K., 1997. Heavy metals in Holocene peats from South West England: detecting mining impacts and atmospheric pollution. Water Air Soil Pollut. 100, 343–353.
West, S., Charman, D.J., Grattan, J., 1996. In: Charman, D.J., Newnham, R.M., Croot, D.G. (Eds.), The Quaternary of Devon and East Cornwall: Field Guide. Quaternary Research Association, London, pp. 62–80.
Zalduegui, J.F.S., de Madinabeitia, S.G., Ibarguchi, J.I.G., Palero, F.A., 2004. Lead isotope database: the Los Pedroches — Alcudia Area (Spain): implications for archaeometallurgical connections across southwestern and southeastern Iberia. Archaeometry 46, 625–634.