IMPACT OF MINING ON THE SEDIMENT GEOCHEMISTRY AND MINERALOGY OF THE HELFORD RIVER, CORNWALL

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The geochemistry and mineralogy of the intertidal sediments of the Helford River, Cornwall have been examined to assess the potential impact of mining activity on sediment supply. Cores from Polpenwith and Polwheveral creeks show a pulse in Sn (1000-1100 ppm), Cu (800-900 ppm) and Zn (500-600 ppm) at a depth of 30 cm below the present day sediment surface; As and Pb values are typically low and show little down-core variation (<130 ppm As and <78 ppm Pb). Two cores recovered near Gweek have generally low and invariant down-core geochemical signatures, except for a single sample from the base of Core 2 which shows a sudden increase in Sn to >1800 ppm. In addition, two cores were collected from the mouth of Mawgan Creek. Core 4 shows a low but invariant geochemical signature but Core 3 shows a significant down-core increase in Sn (>1900 ppm Sn), Cu (588 ppm) and Zn (1297 ppm). The heavy mineral assemblage is dominated by cassiterite, chalcopyrite and sphalerite, along with less abundant zircon, monazite, ilmenite, rutile/anatase, sphene, wolframite, barite and rare slag products. Diagenetic pyrite, bornite and Fe oxides also occur. The geochemistry and mineralogy are consistent with the historical release of mine waste tailings into the Helford River. ^{210}Pb dating of two cores suggests that the sediments are younger than 1880. Based on these data the most likely sources of the mine waste are from Wheal Caroline and Wheal Vyvyan to the north of the Helford River which are documented as being active between 1827 and 1864.

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INTRODUCTION

Historical mining has had a significant impact upon the environmental geochemistry of SW England. Around the coast, significant siltation as a result of the release and deposition of particulate mine waste tailings has occurred, and where there has been no subsequent disturbance to the sediments, they retain a geochemical and mineralogical signature of the impact of mining (e.g. Pirrie *et al.*, 1997; Pirrie *et al.*, 2000a). Previous work in SW England has focussed on the Fal Estuary (Pirrie *et al.*, 1997; Hughes, 1999, 2000), the Gannel and Camel estuaries (Pirrie *et al.*, 2000a), the Hayle Estuary, the Fowey Estuary (Pirrie *et al.*, 2002) and the Tamar Estuary (Price, 2002). In these estuaries the type and extent of the mining activity is typically reflected by the sediment geochemistry and mineralogy, giving an independant geo-archaeological method of assessing the records of mining activity within the associated fluvial catchment. In this study the mineralogy and geochemistry of the recent intertidal sediments in the Helford River (Figure 1) have been examined. The fluvial catchments to the Helford River drain areas with limited documented mining activity, yet still retain a geochemical and mineralogical signature of the impact of hard rock mining.

METHODS

Six shallow (maximum 54 cm) 6.5 cm diameter cores were manually recovered using 1.5 m-long clean plastic tubes from the intertidal sediments around the Helford River (Figure 2). Following logging, the cores which are dominated by uniform silty-clays, were subdivided into 5 cm stratigraphic intervals for geochemical analysis. 50 g samples were ground to a fine powder in a chrome steel tema mill and prepared as pressed powder pellets using a boric acid jacket with elvacite binder. The samples were then analysed using a Phillips PW1400 X-Ray fluorescence spectrometer (XRF) fitted with a Mo-Sc X-ray tube. In total 41 samples were analysed for Sn, Zn, Cu, Pb and As. Results are expressed as ppm with an analytical error of ± 10 ppm. Based on the geochemical results, 20 representative samples were prepared as polished grain mounts for scanning electron microscopy using a JEOL 840 scanning electron microscope (SEM) with an Oxford Instruments (Link System) AN10000 energy dispersive spectrometer (EDS). On the SEM, minerals containing elements with high atomic number were located in backscatter mode and analysed using the EDS. A beam current of $1x10^{-9}$ amps and an accelerating voltage of 20 kV were used to locate the heavy minerals.

Subsamples from cores 2 and 5 were also analysed for ^{210}Pb, in order to (a) date the sediments, and (b) calculate a sediment accumulation rate. ^{210}Pb (half life 22.3 years) is a naturally-

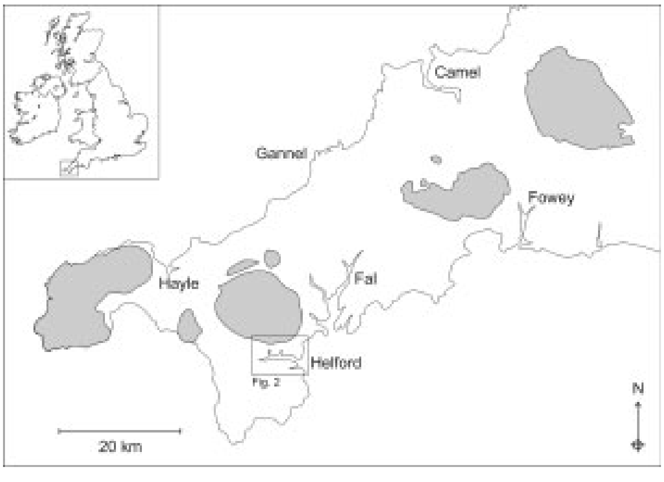

Figure 1. *Sketch diagram showing the location of the Helford River, and other Cornish estuaries mentioned in the paper. Areas in grey are the granites of SW England. The area shown in Figure 2 is indicated.*

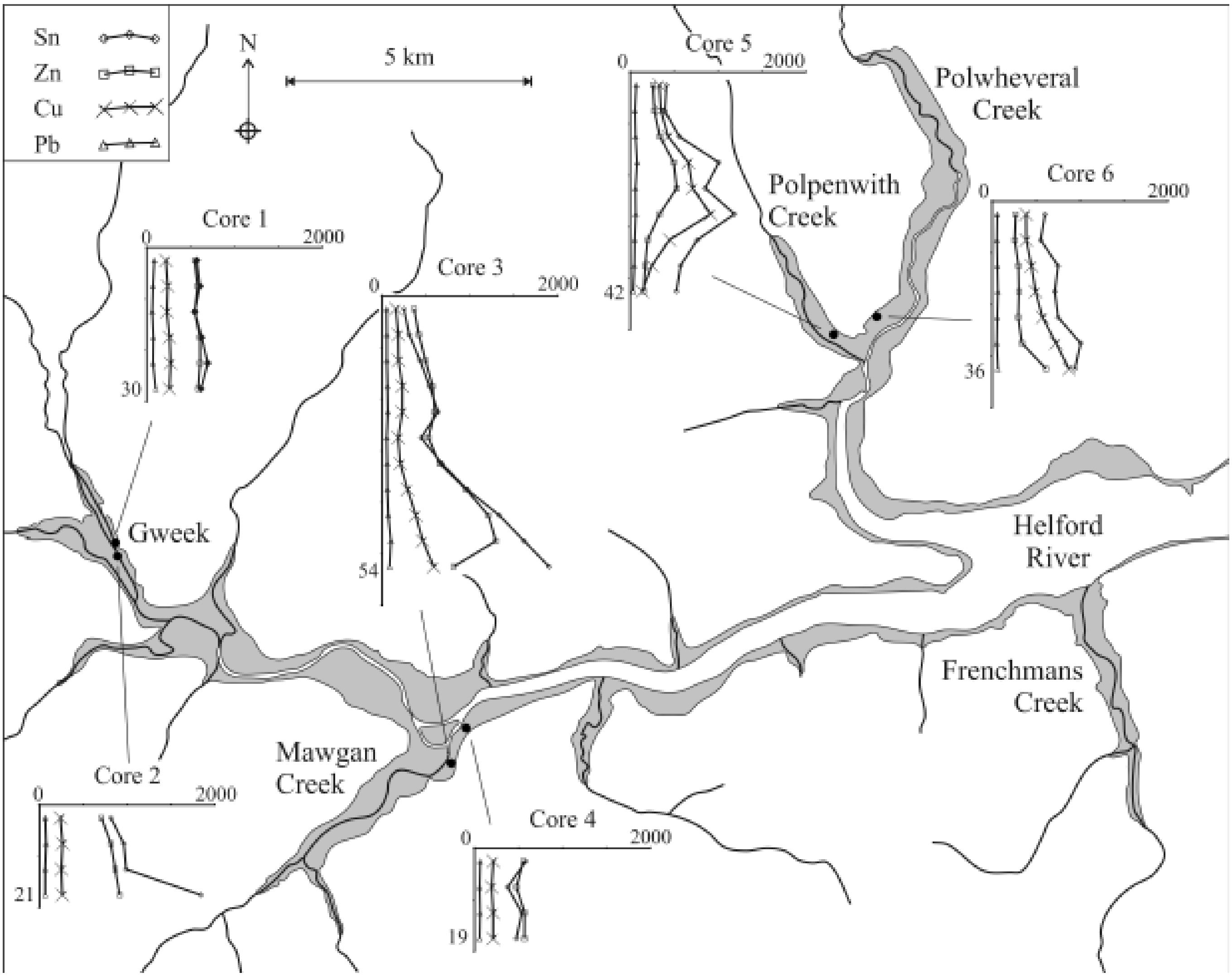

Figure 2. *Map showing the areas of intertidal sediment within the Helford River (areas shaded grey), core locations and down-core geochemical data for Sn, Zn, Cu and Pb (all values are in ppm). Maximum core depths (in cm) below the present day sediment surface are shown.*

occurring radionuclide which has been extensively used in dating recent (less than 120 – 150 years old) estuarine sediments (e.g. French *et al*., 1994; Cundy and Croudace, 1996). Dating is based on determination of the vertical distribution of unsupported ^{210}Pb ($^{210}\text{Pb}_{\text{excess}}$), or ^{210}Pb arising from atmospheric fallout. This allows ages to be ascribed to sedimentary layers based on the known decay rate of ^{210}Pb (see Appleby and Oldfield, 1992 for a synthesis of the ^{210}Pb method). ^{210}Pb was determined through the measurement of its granddaughter ^{210}Po via alpha spectrometry. The methodology is based on Flynn (1968) and uses double acid leaching of sediment and autodeposition of the Po in the leachate onto silver discs. Errors were less than 5%, and detection limits were 0.1 Bq/kg.

Catchment area maps were produced to enable the potential sources of mine waste supply to each creek to be identified (Figure 3). Work on the Fal and Fowey estuaries of Cornwall has shown that the dominant sediment source for the intertidal sediments is from the adjacent fluvial catchments, with marine sediment sources being easily identifiable based on mineralogy and also only important within the subtidal areas (Pirrie *et al.*, 1997; Pirrie *et al*., 2002). A digital elevation model (DEM) (Ordnance Survey, 1999) with a 50 m horizontal and 1 m vertical resolution was used to generate the catchment areas using a raster based geographical information system (GIS). A runoff routine (Jenson and Domingue, 1988) was used to generate the river network patterns. Runoff is allowed to accumulate as it passes from each cell to neighbouring cells at lower elevation. The runoff map was then reclassified to create a Boolean image identifying cells draining catchment areas greater than 400 runoff units (representing 1 km^2 or more). This Boolean image was then used as a target layer in conjunction with the DEM to generate computationally each discrete catchment as a Boolean GIS layer. The focus of each catchment was defined as the point at which each stream reaches the coast at mean sea level. Once defined, the catchment areas can be calculated and the GIS layer used as an overlay filter to determine geological and land use data lying within each catchment.

REGIONAL GEOLOGY AND MINING HISTORY

The regional geology is dominated by Devonian metasediments, the Carnmenellis Granite to the north and the Lizard Complex to the south. The Helford River is located between the Carrick Thrust to the north and the Veryan Thrust and Lizard Thrust to the south (Andrews *et al*., 1998) (Figure 4). To the north of the Carrick Thrust, the Mylor Slate Formation crops out and comprises interbedded low grade metamorphosed mudstones, siltstones and less common sandstones, along with metabasites (Isaac *et al*., 1998). Intruded into the Mylor Slate Formation is the Carnmenellis Granite which is predominantly a coarse, porphyritic muscovite-biotite granite, although seven discrete textural varieties have been mapped (Leveridge *et al.,* 1990). The sandstone-dominant Portscatho Formation crops out between the Carrick and Veryan thrusts and forms the foreshore around the Helford River. To the south of the Veryan Thrust, the Carne and Roseland Breccia formations crop out.

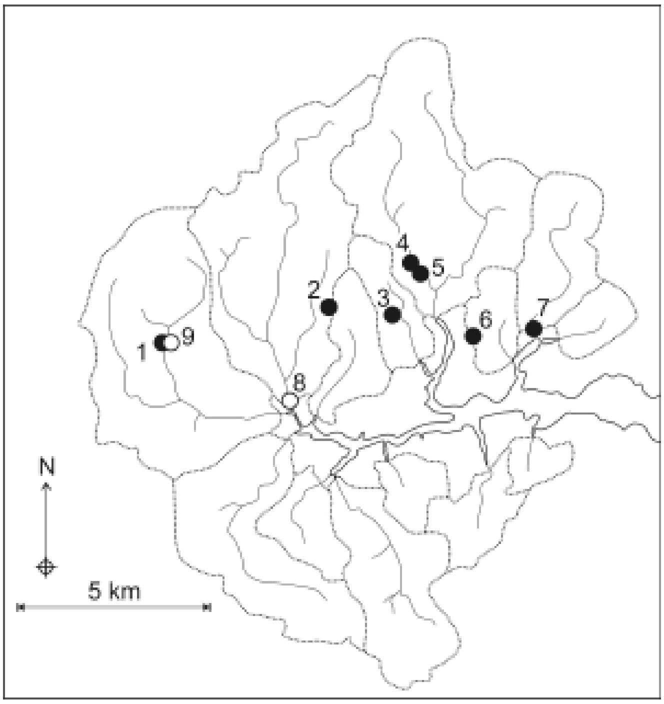

Figure 3. Digital catchment area maps for the Helford River. Individual catchment areas are indicated by the dotted lines. The locations of recorded mines (solid circles) and smelters (open circles) are also shown (data from Dines, 1956; Barton, 1967; Hamilton-Jenkin, 1967; Burt, 1987; Gerrard, 2000). [1]Wheal Freedom, [2]Naffean, [3]Wheal Caroline, [4]Retallack, [5]Wheal Vyvyan, [6]Brogden, [7]Wheal Anna Maria, [8]Gweek Wollas, [9]West Wheal Lovell.

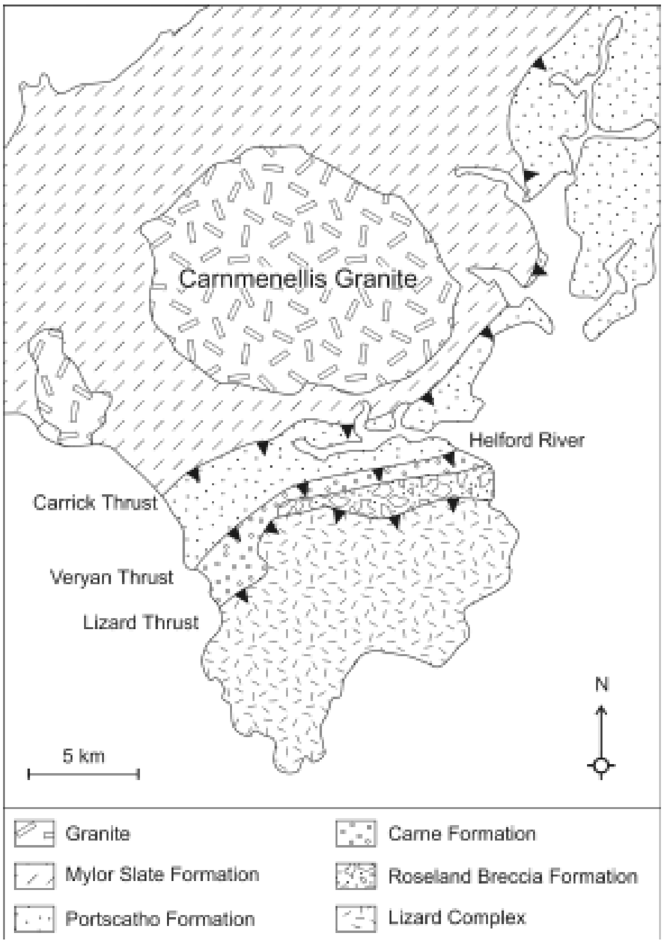

Figure 4. Regional geological map for the area around the Helford River (modified from Andrews et al., 1998).

The Carne Formation is dominated by sandstones, whilst the Roseland Breccia Formation represents a major olistostrome (Isaac *et al.*, 1998). The upper reaches of several streams which flow into Mawgan Creek cut across the Lizard Thrust and drain metabasites and serpentinised peridotites of the Lizard Complex (Figure 4). Sediment may also have been supplied via the reworking of overlying Quaternary Head deposits. In addition, the ?Tertiary Crousa Gravels locally overlie the Lizard Complex (Atkinson, 1998). The Crousa Gravels contain placer cassiterite which was probably reworked from mineralisation initially emplaced into the Carnmenellis Granite and surrounding Mylor Slate Formation metasediments to the north.

Tin - copper mineralisation occurs sporadically within part of the south-western side of the Carnmenellis Granite and within the Mylor Slate Formation (Leveridge *et al.*, 1990). As can be seen (Figure 3), all of the documented mines in the catchment of the Helford River are located to the north of the area, forming a line running close to the contact between the Carnmenellis Granite and the Mylor Slate Formation. Medieval or earlier tin streaming almost certainly occurred within the area, but the earliest well documented mine site within the area is at Retallack, where a well preserved mineral processing complex comprising at least one blowing house, two stamping mills and 4 crazing mills occurs (Gerrard, 2000). This site was probably in use in the early part of the 16th Century (Gerrard, 2000). Seven other mines and two smelters are also recorded in the catchment area of the Helford River (Dines, 1956; Barton, 1967; Hamilton-Jenkin, 1967; Burt, 1987) and are summarised in Table 1. The most important mines in terms of recorded production were the Brogden (Inow) Mine which produced iron ore and Wheal Vyvyan which mainly produced copper and was the largest mine in Constantine parish (Dines, 1956). Other mines within the catchment produced tin, copper, lead, silver, antimony and iron, and were mostly operational in the period 1780 through until 1908. Although no zinc production is documented from the area, sphalerite is a common component of the vein systems and often formed a valuable by product. Two of the mines, the Brogden (Inow) Mine and Wheal Anna Maria have reported occurrences of gold, possibly with mineralisation associated with the Carrick Thrust (Camm *et al.*, 1996). Placer gold is also reported from the streams draining into the Helford River from the southern side (Camm, 1995; Camm *et al.*, 1996) possibly having been reworked from the Crousa Gravels.

Name	Location	Details
Retallack	SW 732298	Mine adit and mineral processing complex. Operational in the early 16th Century
Wheal Freedom (West Wheal Lovell)	SW 681280	Reported Pb-Ag production between 1700 and 1836; Sn production in 1859-1865. Old Sn smelting house noted on site.
Naffean	SW 715287	1780, rich tin lode. Adits and 8 shafts developed.
Wheal Caroline	SW 729285	1850s tin mined, but short lived. 6-7 tons of high grade Cu ore also reported as produced.
Wheal Vyvyan	SW 734294	1827-1864, 8477 tons Cu ore and 92 tons of tin produced. Largest mine in Constantine parish.
Wheal Anna Maria	SW 758282	1907-1908, open. No production records but was worked. Pb, Cu, W and Ag noted.
Brogden Iron Mine (Constantine Mine/ Inow Mine)	SW 746281	1866-1875, 9608 tons of iron ore produced.
Gweek Wollas (smelter)	SW 707267	Pre 1800, closed in 1794. Tin blowing house, Exact location unknown.
West Wheal Lovell (smelter)	SW 681280	Blowing/smelting house for tin. ? Active 1700-1800

Table 1. *Mines and smelters within the catchment of the Helford River (data from Dines, 1956; Barton, 1967; Hamilton-Jenkin, 1967; Burt, 1987; Gerrard, 2000).*

RESULTS

Core sedimentology

The cores ranged from 30 to 54 cm in length. The upper part of each core comprises bioturbated silty-clays, with a mottled orangey-brown to grey colour. Plant debris, shell fragments and *in-situ* thin-shelled bivalves are present. In most of the cores this interval of silty-clays overlies olive grey to black bioturbated mudstones. In cores 2 and 4 the lower part of the cores comprise very poorly sorted sediments with mud intermixed with very coarse sands and clasts of the local Devonian metasedimentary rocks up to 6 cm across.

Geochemistry

The geochemical results are shown in Figure 2 and Table 2. The down-core geochemistry for the shallow sediment cores either shows a flat invariant geochemical profile (e.g. cores 1 and 4) or show an increase in metal concentration with depth below the present-day sediment surface (cores 2, 3 and 6), whilst Core 5 shows a marked pulse in metal concentrations with depth. Core 5 from Polpenwith Creek shows a down-core increase in metals with peak concentrations of Sn (>1100 ppm), As (130 ppm), Zn (531 ppm) and Cu (917 ppm) between 17 and 27 cm below the present-day sediment surface; below this pulse metal values reduce down to values comparable with the present-day sediment surface. Core 6 from Polwheveral Creek shows a general down-core increase in metal values with peak Sn (1007 ppm), As (109 ppm), Zn (614 ppm) and Cu (874 ppm) values 26 cm below the present-day sediment surface. In both cores 5 and 6, Pb values are low and show little systematic down core variation. Two cores (3 and 4) were recovered from the mouth of Mawgan Creek. One of these (Core 4) was only 19 cm long and shows no significant down core geochemical variation. However, Core 3 was 54 cm long and below 34 cm depth, shows a marked increase in Sn (1902 ppm), Zn (1297 ppm) and Cu (588 ppm); As and Pb values also increase but have peak values of <100 ppm. Two cores (1 and 2) recovered from near Gweek have generally low and invariant down core geochemical signatures, except for a single sample from the base of Core 2 which shows a sudden increase in Sn concentration to >1800 ppm. The peak metal concentrations for Sn, As, Pb, Zn and Cu in the Helford River are compared with other SW estuaries in Table 3. As can be seen, the Sn and Cu values are relatively high; Zn values are intermediate whilst the As and Pb values are comparatively low.

Core number & grid reference	Depth cm	Sn (ppm)	As (ppm)	Pb (ppm)	Zn (ppm)	Cu (ppm)
1. SW 7075 2640	0-5	573	29	88	546	220
	5-10	608	26	73	582	241
	10-15	548	34	64	549	232
	15-20	628	32	77	608	262
	20-25	697	34	73	609	272
	25-30	620	39	104	587	260
2. SW 7075 2640	0-6	813	26	65	706	239
	6-11	960	35	75	813	264
	11-16	986	40	64	862	250
	16-21	1839	41	63	913	261
3. SW 7225 2560	0-4	249	13	50	365	157
	4-9	309	10	53	418	184
	9-14	431	15	53	494	188
	14-19	540	19	60	575	230
	19-24	638	23	65	597	229
	24-29	444	24	52	527	184
	29-34	681	27	57	654	206
	34-39	967	30	59	956	289
	39-44	1334	51	71	1209	383
	44-49	1618	58	100	1297	463
	49-54	1902	73	86	813	588
4. SW 7230 2570	0-4	581	18	63	555	212
	4-9	376	21	56	476	193
	9-14	536	22	62	570	210
	14-19	474	25	56	568	209
5. SW 7370 2730	0-2	413	41	68	259	333
	2-7	395	42	53	274	349
	7-12	561	57	60	338	432
	12-17	1010	84	78	497	663
	17-22	855	94	59	531	710
	22-27	1188	130	62	334	917
	27-32	765	77	50	198	448
	32-37	575	58	45	169	246
	37-42	526	38	33	153	137
6. SW 7385 2730	0-6	599	41	56	267	385
	6-11	552	41	52	256	387
	11-16	748	46	57	298	446
	16-21	712	57	63	304	493
	21-26	749	65	56	296	573
	26-31	1007	87	51	338	726
	31-36	942	109	64	614	874

Table 2. *Geochemical data for shallow sediment cores recovered from the Helford River. All values are reported in parts per million (ppm); analytical error for all elements is ± 10 ppm).*

Estuary	Sn (ppm)	Cu (ppm)	As (ppm)	Pb (ppm)	Zn (ppm)	Reference
Helford	1902	874	130	104	1297	This paper
Fal	7852	1562	1864	1843	8146	Hughes (2000)
Fowey	1210	527	144	131	420	Pirrie *et al.* (2002)
Gannel	200	411	975	16,000	3500	Pirrie *et al.* (2000)
Camel	842	241	283	53	207	Pirrie *et al.* (2000)

Table 3. *Peak levels of metal contamination within the Helford River and other Cornish estuaries for comparison.*

Mineralogy

Based on the SEM studies it can be seen that the heavy mineral assemblages present within all of the cores reflect the geochemical results. Cassiterite, chalcopyrite and sphalerite are the dominant heavy mineral phases within all of the cores and typically occur as small (<10 μm) liberated grains. The cassiterite grains are typically angular in shape. Zircon and monazite are also present within all of the samples. Ilmenite, rutile/anatase and rare sphene, wolframite and barite are also present. In contrast to the Gannel and Hayle estuaries (Pirrie *et al.*, 2000a), only minor alteration of the detrital sulphide minerals is present. This is apparently restricted to alteration rims of bornite and Fe oxides around chalcopyrite (Figure 5a). Furthermore, whilst a range of Cu, Pb and Zn diagenetic phases occur in the Gannel and Hayle estuaries (Pirre *et al.*, 2000a; Pirrie *et al.*, 2000b), the only significant diagenetic phase recognised in the Helford River sediments is framboidal pyrite which is abundant throughout, but particularly well-developed in coarser grained laminae (Figure 5b). However, rare Fe oxide cements occur and in some cases contain traces of Cu and Zn (Figure 5c). One small grain of Sn-slag containing blebs of Sn metal was identified from Core 1 (Figure 5d).

Sediment dating and accretion rates

^{210}Pb activity shows a pronounced decline with depth in both Core 2 and Core 5, although in neither core does the activity decrease to a (near-) constant value at depth (Figure 6). In the absence of large-scale compositional variations that might significantly change the supported ^{210}Pb activity, this indicates that $^{210}Pb_{excess}$ is present throughout the cored depth, and consequently that the sediments sampled are younger than 1880 (the period over which $^{210}Pb_{excess}$ decays to undetectable activities, normally taken to be ca. 5 half lives or 120 years). Since the alpha spectrometric method used here only determines total ^{210}Pb activity, and does not discriminate excess from supported activity, it is not possible to determine reliably the supported activity and calculate sediment accumulation rates (using the alpha spectrometric proxy method, supported activity is usually estimated from the value of constant activity with depth in pre-1880 sediment, where excess ^{210}Pb has decayed to negligible activities e.g. Cundy and Croudace, 1996). Based on the premise that $^{210}Pb_{excess}$ is present in all samples analysed, minimum sediment accumulation rates (i.e. assuming the lowest sample analysed in each core corresponds to 1880) of 3 mm/y (Core 5) and 2 mm/y (Core 2) can be determined. The activity values observed at the base of Core 5 are relatively low, and less than those estimated as being equivalent to supported ^{210}Pb activity in similar Cornish estuaries (e.g. Hughes, 2000; Pirrie *et al.*, 2002). This indicates that much of the $^{210}Pb_{excess}$ has decayed away at the base of Core 5, and consequently that 3 mm/y may be a reasonable estimate of the sediment accumulation rate. The relatively high activities of ^{210}Pb observed at the base of Core 2, however, indicates that the true sediment accumulation rate may be much higher in this core.

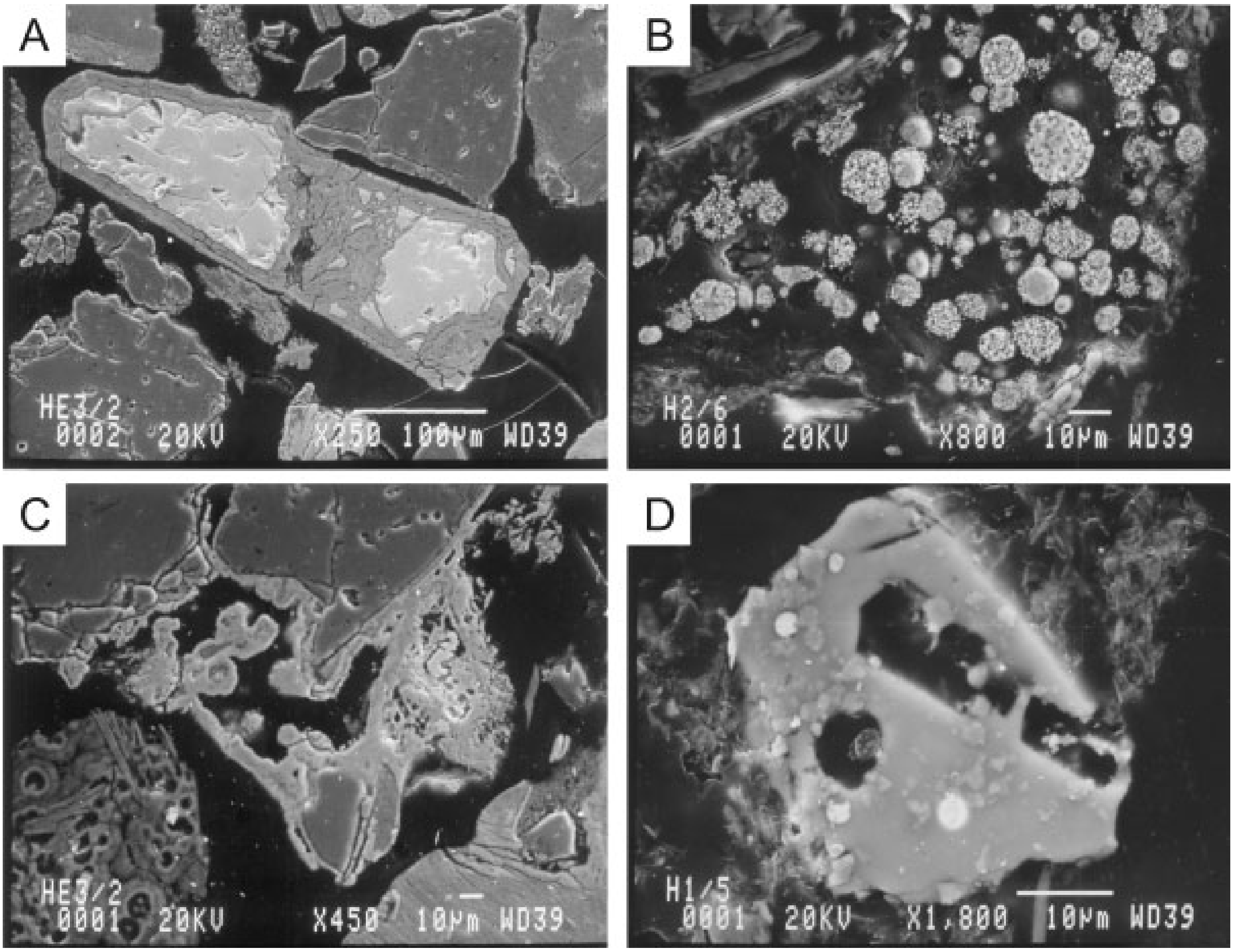

Figure 5. *Scanning electron microscope images of polished grain mounts from the Helford River. (A) Liberated chalcopyrite grain with well-developed alteration rim of bornite and Fe oxides, Core 3, 5-10 cm. (B) Abundant diagenetic framboidal pyrite, Core 2, 0-5 cm. (C) Fe oxide cement containing trace Cu and Zn coating quartz grains. Vuggy quartz in lower left of image, Core 3, 5-10 cm. (D) Smelted grain; bright phase is Sn metal in a Sn-Fe-Al groundmass, Core 1, 5-10 cm.*

INTERPRETATION

The geochemistry of the estuarine sediments in Cornwall is closely related to the sediment input via the adjacent fluvial catchments, with very little sediment mixing within the estuaries (Pirrie *et al*., 1997; Pirrie *et al*., 2002). The geochemical and mineralogical data for the Helford River are consistent with a pulse in sediment supply caused by the release of particulate waste from hard rock Sn and Cu mining activity, along with some sediment supply from smelting. Based on the available data on mining activity within the catchments around the Helford River, the geochemical pulse in the sediments in Polpenwith and Polwheveral creeks probably relates to mine waste input from the Wheal Caroline and Wheal Vyvyan mines which were active between 1827 and 1864 (Dines, 1956). The increase in Sn concentration at the base of Core 2 may relate to mine waste input from Wheal Freedom. The Sn slag in Core 1 at Gweek (Figure 5b) may be from the nearby Gweek Wollas smelter. The source of the pulse in Sn, Cu and Zn in Core 3 from the mouth of Mawgan Creek is less easy to interpret. There is no recorded mining activity or Sn/Cu mineralisation in the fluvial catchments to the south of the Helford River. Although placer cassiterite is present within the Tertiary Crousa Gravels to the south of the Helford River, the grain size distribution and shape of the cassiterite together with the presence of sulphides such as sphalerite within Core 3 precludes an origin from reworking of these placer deposits. Thus, the sediment in Mawgan Creek must have been derived from the hard rock mine sites to the north of the River Helford, with subsequent transport of the contaminated sediments by tidal processes.

Although the peak concentrations of Sn, Cu and Zn reported here for the Helford River are moderately high in comparison with other estuaries in Cornwall they are unlikely to have a significant environmental impact. The Sn is largely present as the stable oxide cassiterite and as such is not bioavailable although rare grains of (potentially bioavailable) smelt waste are present. Abundant chalcopyrite and sphalerite are observed under SEM and a significant proportion of the measured Cu and Zn are

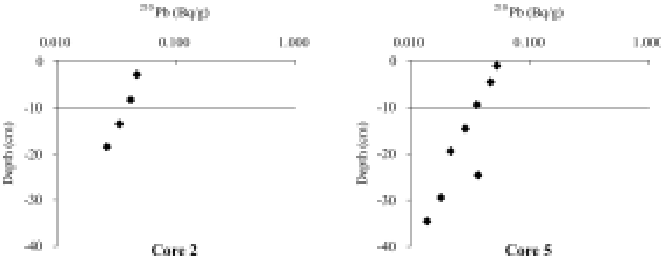

Figure 6. *Diagram showing the decline with depth of ^{210}Pb activity for cores 2 and 5 from the Helford River.*

probably locked within these sulphide phases which show only minor mineralogical alteration. These sulphide minerals will remain stable within the generally reducing conditions in the intertidal sediments as long as they are not reworked into more oxidising areas.

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