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 Polpennowth and Polwheveral creeks show a pulse in Sn (1000-1100 ppm), Cu (800-900 ppm) and Zn (500-600 ppm) at a depth of 50 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, sphen, 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. 210Pb 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 Vyyvan 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 independent 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 elavite 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 1x10-8 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 210Pb, in order to (a) date the sediments, and (b) calculate a sediment accumulation rate. 210Pb (half life 22.3 years) is a naturally-
Pirrie et al.

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 $^{210}\text{Pb}$ ($^{210}\text{Pb}_{\text{excess}}$), or $^{210}\text{Pb}$ arising from atmospheric fallout. This allows ages to be ascribed to sedimentary layers based on the known decay rate of $^{210}\text{Pb}$ (see Appleby and Oldfield, 1992 for a synthesis of the $^{210}\text{Pb}$ method). $^{210}\text{Pb}$ was determined through the measurement of its granddaughter $^{210}\text{Po}$ 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$^{-1}$.

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 metabasics (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 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.
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 serpentinitised 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 5), 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 byproduct. 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.

<table>
<thead>
<tr>
<th>Name</th>
<th>Location</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retallack</td>
<td>SW 732298</td>
<td>Mine adit and mineral processing complex.</td>
</tr>
<tr>
<td>Wheal Freedom (West</td>
<td>SW 681280</td>
<td>Reported Pb-Ag production between 1700 and 1836. 6 Sn production in 1836.  Old Sn blowing house noted on site.</td>
</tr>
<tr>
<td>Wheal Lovell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naffean</td>
<td>SW 715287</td>
<td>1780, rich tin lode. Adits and 8 shafts developed.</td>
</tr>
<tr>
<td>Wheal Caroline</td>
<td>SW 729285</td>
<td>1850s tin mined, but short lived. 6-7 tons of high grade Cu ore also reported as produced.</td>
</tr>
<tr>
<td>Wheal Vyvyan</td>
<td>SW 734294</td>
<td>1827-1864, 8477 tons Cu ore and 92 tons of tin produced. Largest mine in Constantine parish. 1907-1908, open. No production records but was worked. Pb, Cu, W and Ag noted.</td>
</tr>
<tr>
<td>Wheal Anna Maria</td>
<td>SW 758282</td>
<td></td>
</tr>
<tr>
<td>Brogden Iron Mine</td>
<td>SW 746281</td>
<td>1866-1875, 9608 tons of iron ore produced.</td>
</tr>
<tr>
<td>(Constantine Mine/Inow Mine)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gweek Wollas (smelter)</td>
<td>SW 707267</td>
<td>Pre 1800, closed in 1794. Tin blowing house.  Exact location unknown.</td>
</tr>
<tr>
<td>West Wheal Lovell</td>
<td>SW 681280</td>
<td>Blowing/smelting house for tin. 7 Active 1708-1800.</td>
</tr>
<tr>
<td>(smelter)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 motled orange-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 shows 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 3 from Polpenger Creek shows a general down-core increase in metals with peak concentrations of Sn (>1100 ppm), As (150 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. 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 Mawnan Creek. One of these (Core 4) is 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 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.

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 Helford estuaries (Pirrie et al., 2000b), 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 (Pirrie et al., 2000a; Pirrie et al., 2000b), the only significant diagenetic phase recognised in the Helford River sediments is frambooidal pyrite which is abundant throughout, but particularly well-developed in coarser grained laminae (Figure 5b). However, rare oxide cements occur in some samples with small (<10 µm) 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.

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

<table>
<thead>
<tr>
<th>Estuary</th>
<th>Sn (ppm)</th>
<th>Cu (ppm)</th>
<th>As (ppm)</th>
<th>Pb (ppm)</th>
<th>Zn (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helford</td>
<td>902</td>
<td>874</td>
<td>130</td>
<td>104</td>
<td>1297</td>
<td>This paper</td>
</tr>
<tr>
<td>Fal</td>
<td>752</td>
<td>1562</td>
<td>1864</td>
<td>1843</td>
<td>8146</td>
<td>Hughes (2000)</td>
</tr>
<tr>
<td>Fowey</td>
<td>1210</td>
<td>572</td>
<td>141</td>
<td>131</td>
<td>420</td>
<td>Pirrie et al. (2002)</td>
</tr>
<tr>
<td>Gannel</td>
<td>200</td>
<td>411</td>
<td>975</td>
<td>16,000</td>
<td>3500</td>
<td>Pirrie et al. (2000)</td>
</tr>
<tr>
<td>Camel</td>
<td>842</td>
<td>241</td>
<td>283</td>
<td>53</td>
<td>207</td>
<td>Pirrie et al. (2000)</td>
</tr>
</tbody>
</table>

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.
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 Polpenna with 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...
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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