

FEATURE

Mud and metal; the impact of historical mining on the estuaries of SW England, UK

Duncan Pirrie¹ & Robin K. Shail²

¹School of Applied Sciences, University of South Wales, Pontypridd, Wales, CF37 4BD

²Camborne School of Mines, College of Engineering, Mathematics and Physical Sciences, University of Exeter, Cornwall Campus, Penryn, Cornwall, TR10 9FE UK

Visitors and residents alike enjoy the countryside and coast of SW England because of the stunning landscapes and natural environment. Many will also be aware, largely through the industrial archaeological record and world heritage site designation, of the historical importance of mining in this region. Separate mineralization episodes, primarily during the Permian and Triassic, led to the formation of a world-class polymetallic ore field, with major deposits of not only tin (Sn) and copper (Cu), but also iron (Fe), lead (Pb), arsenic (As), zinc (Zn), tungsten (W) and silver (Ag), along with minor occurrences of less common metals such as uranium (U), antimony (Sb), nickel (Ni), cobalt (Co), bismuth (Bi) and gold (Au). Mining of alluvial deposits commenced in the Bronze Age, with hard rock mining commencing by the late thirteenth century and continuing intermittently, as metal prices rose and fell, to the present day. With hard rock mining, came the processing or ‘dressing’ of ores during which they were crushed so that minerals of interest could be recovered. The wastes from this process—mine tailings—were historically released into rivers and transported towards the coast as man-made sediments. Deposition occurred in many of the estuaries around SW England, which consequently preserve a record of the development and historical impact of mining.

Visitors and residents in Cornwall, UK, taking in the views of the estuaries, enjoyed by many for sailing, watersports and fishing, could easily be forgiven for thinking that they were looking over a landscape that has never been significantly affected by industrial activity, other than ship building and agriculture (Fig. 1). Indeed, the estuaries have varying levels of national and international environmental designations, including Areas of Outstanding Natural Beauty (AONB), Special Areas of Conservation (SAC) and Sites of Special Scientific Interest (SSSI). However, the sediments within these estuary systems are directly linked to human activity both within the estuary and its wider catchment. In SW England, estuary sediments provide a unique record of the development and environmental impact of mining on the coastal zone over a period of time from, possibly, the Bronze Age through to the present day. As such they are an invaluable resource for understanding the long-term impact of mining on the environment and are also an independent geo-archaeological record of that industry.

Partially as a result of the highly visual Wheal Jane drainage incident in 1992, when between 25 000 and 50 000 m³ of contaminated waters were discharged into the estuary, the sediments and biota within the Fal Estuary, Cornwall, and its catchment, have been studied by numerous authors in an attempt to understand the impact of mining on the environment. Commonly, such studies assume that much of the metal was discharged in solution during mine water drainage but, in fact, a significant environmental impact was the release of particulate mine waste: tailings. Ore brought to surface was usually crushed during the initial

stage of processing or 'dressing', so that minerals of commercial interest could be more readily separated from each other and the 'gangue' or waste minerals. Historically, density contrasts were often used in 'gravity' separation so that the heavier ore minerals were recovered, and the less dense gangue minerals were released back into the environment. These tailings, inevitably, also contained particles of the ore minerals, which were too small for effective gravity separation and also contained minerals which were not of economic interest at the time of ore processing (what may be considered to be ore or gangue may change with time). In this article we consider the source and fate of these tailings and their long-term environmental impact.

Regional Geology

SW England (in particular the counties of Cornwall and Devon) is an Upper Palaeozoic massif whose bedrock geology is strongly influenced by the Variscan mountain-building event. Its geology is dominated by Devonian and Carboniferous metasedimentary rocks and associated minor mafic intrusive/extrusive igneous rocks into which the Cornubian Batholith was emplaced in the Early Permian (Fig. 2). Devonian and Carboniferous successions are preserved in six east–west trending sedimentary basins which formed during rifting, and the formation of a passive margin and associated oceanic lithosphere (Fig. 2). The oldest successions (Early Devonian) are present in the Looe Basin and include non-marine sandstones and mudstones but, more generally, the basin successions comprise mudstones and sandstones, along with minor limestones and cherts, which were deposited in shallow to deep-marine environments. Rift-related mafic igneous rocks (basalts, dolerites and gabbros) are locally important constituents of the basin fills and sedimentary exhalative (SedEx), and volcanic massive sulphide (VMS) mineralization styles occur locally. The Lizard Complex (Fig. 2) includes partially serpentinized mantle peridotites, gabbros and high-grade metamorphosed mafic igneous rocks; it represents a fragment of the oceanic lithosphere (an ophiolite) formed during rifting along with small areas of pre-Devonian continental crust that have experienced high-grade metamorphism.

Sedimentation in the Gramscatho and Culm basins continued during the early stages of the Variscan continental collision, which brought about deformation and low-grade regional metamorphism of all the basinal successions and, as a consequence, the rocks are variably thrust-faulted and folded. Quartz veins, precipitated from metamorphic fluids, are ubiquitous and are locally associated with Au and Sb metal mineralization. The continental collision continued until the end of the Carboniferous, when it was replaced by a NNW–SSE extensional regime that persisted through most of the Early Permian. This tectonic episode was responsible for the development of post-Variscan Permian 'red-bed' sedimentary basins and voluminous post-collisional felsic magmatism. The principal expression of the latter is the Cornubian Batholith (Fig. 2), which comprises a variety of granite types and is associated with rhyolite/microgranite dykes known in SW England as 'elvans'. Host rocks within 1 km or so of the batholith margins usually exhibit contact metamorphism. The granites, elvans and their Devonian–Carboniferous host rocks are cut by extensional fault systems which host Early-Mid-Permian polymetallic W-Sn-Cu-As-Pb-Zn magmatic-hydrothermal mineralization. A subordinate Mid-Triassic fault-controlled epithermal mineralization episode, associated with the migration of basinal brines from 'red-bed' basins, has resulted in localized Pb-Zn-Ag-barite mineralization. There have also been minor mineralization episodes associated with fault reactivation and fluid flow during Early Cretaceous and Cenozoic uplift and intraplate deformation.

The Quaternary geological history of SW England is dominated by repeated intervals of periglacial climates and warmer inter-glacial episodes. Although some authors have indicated the possibility of small cirque and niche glaciers, the late Quaternary British-Irish Ice Sheet did not extend across the region. Instead, the bedrock geology was influenced by periglacial processes and resultant down-slope mass wasting of bedrock units. These locally derived superficial sediments are referred to in the area as 'head deposits' and typically

thicken into valleys. Along the north coast, marine-derived carbonate blown sand deposits are locally developed as dune sand systems. Flooded steep sided valley systems known as rias, now form the major estuaries which are present both along the south coast, e.g. the Helford, Fal, Fowey, Tamar and Teign estuaries, and as smaller scale systems on the north coast e.g. the Hayle, Gannel and Camel estuaries (Fig. 2).

Mineralization

South west England is internationally renowned as an example of a giant W-Sn-Cu orefield, however, in detail, the history of mineralization is much more complex. The mineralization and related mineral extraction falls into three main groups: (1) polymetallic mineralization dominated by Sn, Cu, Fe, Zn, Pb(-Ag), As and W deposits, along with less important U, Co, Ni and Bi deposits; (2) erosion of exposed areas of mineralization resulted in the formation of extensive fluvial Sn placer deposits and in some areas, there are also transitional and submerged Sn placers (present in 'drowned' river systems); and (3) alteration of the granites led to the formation of extensive kaolin deposits, particularly in the St Austell District. The working of each of these major deposit types led to different types of environmental impact in SW England.

Broadly speaking, there are three episodes/styles of Permian and Triassic polymetallic mineralization: (1) granite-related; (2) cross-course; and (3) unconformity/red bed mineralization. Of these only the first two were significant in terms of impact on the estuaries (Fig. 3).

Granite-related mineralization (Early-Mid- Permian) is largely represented by steeply inclined veins, along with altered wall rocks, that have been worked in both the granites and their pre-Permian host rocks, for a variety of metals, principally Sn, Cu, Zn, Pb, As and W. There is a strong association with the Cornubian Batholith as the mineralization is primarily related to the migration and/or mixing of magmatic-hydrothermal fluids.

Cross-course mineralization (Triassic) is also regional in extent and occurs as steeply inclined veins in pre-Permian rocks and granites. These veins usually cross-cut the granite-related Sn-Cu-Zn-Pb veins, hence the term 'cross-course'. These veins have largely been worked in pre-Permian rocks, primarily for Pb, Zn, Ag, Ag, minor Cu, F and Ba; some Fe veins have similar origins, as do at least some of the rare assorted U and Co, Ni, Bi, As and Ag assemblages. This stage of mineralization is primarily related to the migration of high salinity basinal fluids from overlying and adjacent Permo-Triassic successions. The granite-related and cross-course mineralization events have a regional extent and are most significant in terms of the impact of hard-rock mining on the estuaries of SW England.

There is a very strong association between Sn, W, Cu and As mineralization and the margins of the granite batholith; almost all production has been from areas where the gravity-determined batholith roof zone lies above -2000 m OD and the majority has been from within 500 m of the contact. This mineralization may be hosted by either the granite or its host rock, but most production has been from the host rocks. The dominant trend of lodes hosting these metals is ENE-WSW to E-W, with subordinate ESE- WNW trends. Most Sn and Cu production has been from the western part of the batholith. Tungsten (W) production was historically dominated by the East Pool/South Crofty and Castle-an-Dinas mines but there are also huge deposits in the east at Redmoor (presently being explored by Cornwall Resources Ltd) and Drakelands Mine, whilst operated by Wolf Minerals from 2015 to 2018, produced W-Sn from the Hemerdon deposit, that resulted in the UK being the sixth largest global W producer in 2017. Significant production of As also came from a limited number of mines, almost entirely confined to the Camborne- Redruth-St Day and Callington-Tavistock districts.

In contrast, most Pb-Ag ± Zn production occurred outside the above areas and there is no clear correlation with the granite boundary. The N–S to NW–SE trending lodes around Porthleven, Herodsfoot, Menheniot, Mary Tavy and in the Tamar and Teign valleys host the principal occurrences of crosscourse Pb, Ag ± Zn ± F mineralization. A substantial proportion of the total regional production of Pb and Ag also came from ENE–WSW orientated structures, together with subordinate N–S trending veins in just a few mines in the Perranzabuloe District. A number of mines in areas dominated by granite-related Sn, Cu and As mineralization also produced Zn and Pb ± Ag, whilst in others Zn (as sphalerite) was present in substantial amounts but classed as gangue. The distribution of Zn and, to a lesser extent Pb-Ag, therefore has some affinities with polymetallic Sn-Cu-As as well as cross-course Pb-Ag mineralization. Pb production from N–S veins in the Wadebridge District is in part related to pre-granite Pb-Sb mineralization.

In addition to the major metals, U, Co, Ni, Bi and F have also been produced from a few mines where they are usually hosted in cross-course veins, but also by polymetallic Sn-Cu-As veins. Antimony (Sb) also occurs in cross-course veins although some might reflect pre-granite mineralization. Barite occurs as a minor constituent in cross-course veins but has been worked commercially in the Teign Valley. Gold has been recorded in some cross-course and polymetallic veins and may have been widely recovered by smelters. The variation in the spatial distribution of the mineralization in SW England, along with the location of mineral processing plants, has meant that different river catchments have received different waste streams, such that ultimately the estuaries around the coastline have distinct geochemical and mineralogical profiles (see below).

History of mining and mineral processing technologies

Broadly speaking, the history of mining in SW England can be subdivided into three main stages of extraction and related ore processing techniques: fluvial deposit working, hard rock mining and quarrying.

Fluvial, transitional and locally drowned placer deposits of cassiterite were worked intermittently from the Bronze Age through until the 1980s, although offshore placers are still being commercially evaluated today. Hard rock metal mining can be dated back to at least the late thirteenth century, when it is thought to have already been well established. Deep underground mining continued, again intermittently through until 1998 when South Crofty Mine closed. Quarrying has also been significant throughout Cornwall and Devon. The working of china clay, predominantly in the St Austell District, has historically impacted upon the coastal sediments in the Fal and Fowey estuaries and along the coastline in St Austell Bay. Other quarrying activity, although historically significant, such as the working of granite throughout the region, has had a significant environmental impact, but this has been localized and has not affected the coastal systems.

There is some evidence to suggest that there was a variable, but significant, trade in cassiterite from SW England from the early Bronze Age onwards. However, the evidence for very early placer mining is limited to the recovery of Bronze Age artefacts possibly related to mining activity by miners in the nineteenth century from the 'tin grounds' (alluvial sediments) and geochemical/isotopic analyses of Bronze artefacts suggesting that the cassiterite was sourced from SW England. Some workers have also suggested that the distribution of early settlements on Dartmoor and Foweymore (eastern Bodmin Moor) might be linked to tin working.

The arrival of the Romans in the first century AD did not result in an increase in tin production. However, possibly as a result of reduced supply from Spain, there was renewed production from the mid part of the third century onwards as evidenced by late Roman tin ingots, and a range of artefacts associated with the tin grounds. The working of the alluvial cassiterite deposits through stream works became very extensive throughout the Medieval period. The basic principle of alluvial mining was to separate the grains of cassiterite from the associated sediments by carefully controlling water flow over the sediments as they

were worked. A flow velocity of between 50 and 100 cm/s would enable the clay, silt and sand to be removed whilst leaving behind the cassiterite along with gravel. Stream working had a significant environmental impact with the downstream discharge of large volumes of fine-grained sediment, which would have a lower tin content than the natural alluvial sediments. This release of sediment was recognized in 1356 as causing the possible loss of the port at Lostwithiel as a result of stream working on Foweymore and as a result of this, in 1357 Abraham le Tynnere was charged with having caused 'damage to the prince and haven of Fowey', although these early concerns about the environmental impact of mining did not deter the tin streamers.

The transition from tin streaming to hard rock underground mining was a progressive development of techniques from prospecting pits, through lode-back pits, openworks and then shafts. Lode-back pits were larger than prospecting pits and were shallow shafts sunk into the identified lode to work the cassiterite encountered. These pits are generally aligned along the trace of the lode and are often associated with localized spoil tips. Open works in contrast are where there has been surface mining along the length of the lode. Gradually, these types of working led on to shaft mining. Exactly when this occurred is poorly dated, but there are references to shaft mining, which suggest that this was well established by the late thirteenth century (Fig. 4). The development of hard rock mining was very significant in terms of the environmental impact of mining for two main reasons. Firstly, many of the ores being worked were polymetallic, so the stable tin oxide cassiterite was commonly associated with sulphides—predominantly chalcopyrite, sphalerite, galena, arsenopyrite and pyrite. These sulphides were not generally recovered in early mining operations since cassiterite was the only ore mineral of interest. As a consequence, sulphides and unrecovered cassiterite were released into stream and river systems as tailings. These tailings were significantly enriched in metals when compared with the natural sediments present within the river catchments. Rather than being dispersed to sea, the large volume of tailings being released resulted in rapid siltation throughout the estuaries and narrow sided ria systems throughout SW England.

Unlocking the estuary record

By examining the mineralogy and geochemistry of the sediments, it is possible to: (1) determine where the sediment came from; and (2) assess its potential environmental impact. First one needs a sediment sample. Most of the estuaries of SW England have seen significant sedimentation, particularly over the last 200 years, with the formation of extensive inter-tidal mud banks and areas of salt marsh (Fig. 5). Sampling of the estuarine sediments has included: (1) the recovery of undisturbed cores from the intertidal mudbanks and salt marsh areas of the estuaries (Fig. 6); (2) surface sampling of the intertidal areas; and (3) drop core and surface grab sampling in the subtidal areas of the Fal and Fowey estuaries. Significant care needs to be taken on these inter-tidal sediments due to the very soft 'ground' conditions and rapidly turning tide which together mean that sampling can be hazardous (Fig. 7). Work in SW England has included the recovery of over 150 shallow cores (Fig. 8) along with nearly 2000 individual samples.

Following sediment logging and description, the bulk geochemistry of dried sediment samples was determined using X-ray fluorescence (XRF). All samples were analysed for Sn, Cu, Zn, Pb and As and results are expressed as parts per million (ppm) with an analytical error of ± 10 ppm (note that ppm is equivalent to mg/kg). In some of the studies a wider range of elements were determined. The sediment mineralogy was determined on either: bulk loose sediment samples, with sieved size fractions prepared as grain mounts or thin sections, or undisturbed sediment core plugs prepared as polished blocks following gentle resin impregnation under vacuum. Sediment mineralogy has been determined through: (1) transmitted and reflected light microscopy; (2) bulk sediment X-ray diffraction; (3) manual scanning electron microscopy; and (4) automated scanning electron microscopy and EDS analysis using QEMSCAN technology.

Geochemistry and mineralogy of estuarine sediments in SW England

Published mineralogical and geochemical datasets are available for the Fal, Helford, Fowey and Teign estuaries on the south coast and for the smaller Hayle, Gannel and Camel estuaries along the north coast. A series of papers published in Geoscience in South-West England are open access and free to download from www.ussher.org.uk.

Here we summarize the characteristic shallow (typically ≤ 1 m depth) geochemical profiles present with the estuary sediments, examine data for the surface spatial distribution of metals from the Fal Estuary and examine mineralogical evidence for sediment provenance and mineral reactions (alteration and precipitation) within the recent estuary sediments.

Characteristic changes in geochemistry with sediment depth

Each estuary and indeed each individual river draining into the larger estuaries, have different catchments, and each comprises variable bedrock geology, areas/styles of mineralization and different mining and mineral processing complexes (see Fig. 3). Consequently, the type and abundance of mining-related sediments in each estuary varies. The Fal and Helford estuaries have a signature of significant polymetallic mining with Sn, Cu, As, Pb and Zn contamination. The Fowey has a record of predominantly Sn mining, whilst the Teign Estuary is distinctive with mine wastes relating to the extraction of barite. On the north Cornish coast the major inputs into the Hayle Estuary relate to Cu and Zn mining although the sediments are also enriched in Sn and As, whilst Pb-Zn mining has had a major impact on the Gannel Estuary near Newquay. The Camel Estuary records the input of Sn and W.

Data from ~ 150 shallow sediment cores commonly reveals a very similar profile even though the component elements vary from estuary to estuary (Fig. 9). The sediments at the base of each core usually have the lowest metal abundances. Commonly, there is then a dramatic and sudden increase in metal concentrations, followed by a gradual decline in metal abundance towards the present-day sediment surface, but rarely returning to the lower values recorded at the base of each core. This distinctive upcore geochemical profile is interpreted to reflect: (1) initial estuarine sedimentation with limited mining-related input; (2) a rapid increase in the release of highly contaminated sediment derived from tailings. The release of the tailings into river courses and eventually down to the estuaries, probably reflects the peak in mining; and (3) values then gradually decrease, probably following the cessation of mining, but do not return to the pre-mining levels. This is interpreted as due to both the natural reworking of the highly contaminated sediments through physical erosion and redeposition, and also as a result of burrowing fauna, as well as human activity within the environment causing sediment remobilization.

The recorded maximum values for the analysed elements are shown in Table 1 and are exceptionally high. Overall, the Hayle Estuary on the north Cornwall coast has the highest levels of contamination for Sn (7041 ppm), Cu (29 869 ppm), As (6348 ppm) and Zn (10 571 ppm) whilst the Gannel Estuary has the highest Pb levels at 16 000 ppm, the Teign Estuary has 3360 ppm Ba and the Camel Estuary has 80 ppm W. Note that 10 000 ppm = 1 percent, hence for comparison, some of these estuary sediments are locally more metal enriched than many ore deposits.

Nature of modern surface sediments

Whilst the characteristic down-core geochemical profiles show that the maximum metal concentrations are below the present-day sediment surface, they also show that once the mine waste is released into the environment it can be reworked. The surface sediments are more enriched in metals than the typical concentrations deeper in the sediment profile because even though the mine wastes were typically released over 100 years ago, they still have an impact on the geochemistry of the surface sediments. By analysing the geochemistry of the present-day surface sediments, the spatial distribution of the mine wastes can be visualized. Within the larger estuaries, numerous rivers draining different catchment areas feed into an individual estuary. Depending on the individual catchment area bedrock geology and mineralization, and history of mining and mineral processing, then different rivers may supply different sediments. This is clearly seen in the Fal Estuary (Fig. 10). Restronguet Creek and the Carnon River on the western side of the estuary drained areas with the most significant metal mining and therefore supplied the most metal contaminated sediments. In contrast, the Fal River on the eastern side of the estuary drained areas of china clay workings around the St Austell Granite. Fine grained china clay waste entered this side of the estuary, but this sediment is not enriched in metals or arsenic, hence the eastern side of the estuary is significantly less contaminated than the western. Sediment being supplied along the Carnon River and then Restronguet Creek is then transported south, following the main tidal currents within the estuary.

Evidence for mineral alteration and metal mobility

Given that the estuary sediments of SW England are heavily enriched in metals as a result of historical mining, the question arises as to what the impact of this waste material is on the environment.

Mineralogical studies have demonstrated that the metals recorded within the sediment are predominantly not present as aqueous forms, or adsorbed/absorbed onto the surface of clay minerals or organics but are present as detrital mineral grains (Fig. 11). In fact the sediment mineralogy allows us to identify the potential source areas of the mine waste.

In some cases the elements present are not particularly toxic to organisms living within these environments and are present in minerals that are both resistant to physical erosion and are chemically stable (e.g. the stable oxide ore mineral cassiterite SnO_2). However, much of the polymetallic mineralization occurs as sulphide minerals such as chalcopyrite (CuFeS_2), sphalerite (ZnS), galena (PbS) and arsenopyrite (AsFeS_2). If these sulphide minerals are rapidly buried within the sediment profile, so that they are under reducing conditions, then they are relatively geochemically stable. In contrast, if the sulphides are exposed to oxidising conditions, either through prolonged exposure near the surface, or re-exposure to surface conditions, then they will oxidize and release metals into the surrounding pore waters (Fig. 11). These metals may then reach concentrations which become ecotoxic. In addition, some of the sulphide minerals may be 'carrying' other elements which are potentially hazardous. For example, the mineral sphalerite can often act as a carrier for the hazardous element cadmium.

Mineralogical studies of these sediments are therefore critical as they allow us to identify where the metals are located within the sediments. As different minerals have differing stabilities under near-surface conditions, knowing which minerals are carrying which elements allows the risk of metal remobilization to be determined. Secondly, mineralogical studies may record evidence as to whether alteration has occurred. As in any system where there is a fluid–rock interaction, some minerals may alter, and release metals into solution, but also if the elements become sufficiently concentrated within the pore fluids, new diagenetic minerals can start to grow within the sediments. These new diagenetic minerals indicate the pore fluid and environmental conditions at the time of mineral growth and can also effectively remove elements from the pore waters and lock them up as new stable minerals. Early diagenetic minerals are common in many

sedimentary systems and often include the growth of framboidal pyrite as a result of sulphate reducing bacteria. However, a very wide range of diagenetic minerals are recorded from the estuaries of SW England and many more are still likely to await description. These minerals include those commonly encountered (such as pyrite and siderite) to the rare and exotic including phases such as the Pb-mineral plumbogummite ($\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot (\text{H}_2\text{O})$) and the Zn chloride mineral simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$) (Fig. 11). In some cases, these diagenetic minerals are so common they can be observed in hand specimens. For example, on the southern side of the Hayle Estuary, an area of wetland and saltmarsh is exceptionally contaminated with Cu and Zn. Here the copper chloride mineral atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) can be seen coating and infilling the estuary sediments (Fig. 12). In this case the re-exposure of chalcopyrite and sphalerite mine tailings led to a significant release of Cu, Zn and Cd and the growth of atacamite where the tailings derived pore waters mixed with the saline estuarine pore waters.

Summary

The estuaries of SW England are not only important coastal habitats but they are also attractive landscapes and great settings for leisure activities, whilst also supporting a range of industries. However, the sediments, exposed in inter-tidal areas at low tide, retain a legacy of the once world-class mining industry of this area. Few might realize that these sediments are amongst some of the most metal contaminated sites in Europe. With increasing concern and environmental legislation focussed on water quality, understanding these systems has increasing importance. They can be viewed in many ways as unlined, unmanaged tailings ponds where mine waste has accumulated. Their long-term environmental impact is dependent on a number of factors. Most significantly is the interplay between sediment mineralogy and environmental geochemistry. Under reducing conditions, much of the mine waste is locked in stable minerals within the sediment sequence. However, with oxidation the sulphide minerals may result in metals being released into solution, forming diffuse sources of metal contamination, although under the right set of conditions, the pore water chemistry may lead to the growth of new diagenetic minerals. The sediment mineralogy also strongly influences the potential bioavailability of the metals.

The estuary sediments also provide an important opportunity for research into the long-term impact and fate of mining contaminants in the environment and also as an independent record of the areas industrial archaeology. Mine wastes have been released into the environment for hundreds of years, which has then adapted to cope with these potentially metal-rich systems, with a complex interplay between the sediments, biota and water quality. In addition, the sediments are a geoarchaeological resource, the analysis of which provides an independent test of the mining and mineral processing history in each of the river catchments.

Acknowledgments

This review is based on the previously published studies into the estuaries of south west England led by Duncan Pirrie. Funding for the original research was provided through the CSM Trust, Cory Entrust, European Social Fund, RSPB and Fowey Harbour Commissioners. Cory Entrust funded the production of a CD which provides an introduction to the environmental impact of mining on the Fal Estuary, copies of which are available from Duncan Pirrie. Figure 2 was reproduced with permission from Shail, R.K. & Leveridge, B.E. (*Comptes Rendus Geoscience*, 2009, v.341, pp.140–155) © 2009 Elsevier Masson SAS.

Suggestions for further reading

Pirrie, D., Camm, G.S., Sear, L.G. & Hughes, S.H. 1997. Mineralogical and geochemical signature of mine waste contamination, Tresillian River, Fal Estuary, Cornwall, UK. *Environmental Geology*, v.29, pp.58–65.

Pirrie, D., Power, M.R., Payne, A., Camm, G.S. & Wheeler, P.D. 2000. Impact of mining on sedimentation; the Camel and Gannel estuaries, Cornwall. *Geoscience in south-west England*, v.10. pp.21–28.

Pirrie, D., Power, M.R., Wheeler, P., Cundy, A., Bridges, C. & Davey, G. 2002. Geochemical signature of historical mining; Fowey Estuary, Cornwall, UK. *Journal of Geochemical Exploration*, v.76, pp.31–43.

Pirrie, D., Power, M.R., Rollinson, G., Cundy, A. & Watkins, D.C. 2002. Impact of mining on the sediment geochemistry and mineralogy of the Helford River, Cornwall. *Geoscience in south-west England*, v.10, pp.323–328.

Pirrie, D., Power, M.R., Rollinson, G., Camm, G.S., Hughes, S.H., Butcher, A.R. & Hughes, P. 2003. The spatial distribution and source of arsenic, copper, tin and zinc within the surface sediments of the Fal Estuary, Cornwall, UK. *Sedimentology*, v.50, pp.579–595.

Rollinson, G.K., Pirrie, D., Power, M.R., Cundy, A. & Camm, G.S. 2007. Geochemical and mineralogical record of historical mining, Hayle Estuary, Cornwall, UK. *Geoscience in south-west England*, v.11, pp.326–337.

Simons, B., Pirrie, D., Rollinson, G.K. & Shail, R.K. 2011. Geochemical and mineralogical record of the impact of mining on the Teign estuary Devon, UK. *Geoscience in South-West England*, v.12, pp.339–350.

Thorndycraft, V.R., Pirrie, D. & Brown, A.G. 2004. Alluvial records of Medieval and prehistoric tin mining on Dartmoor, SW England. *Geoarchaeology*, v.19, pp.219–236.

Figures



Fig. 1. Aerial photograph looking west up the Helford River in West Cornwall. The small villages of Helford (left bank) and Helford Passage (right bank) can be seen. Although today a very rural landscape dominated by agriculture and tourism, the estuaries of SW England contain significant amounts of mine waste. (Courtesy of Cornwall Council.)

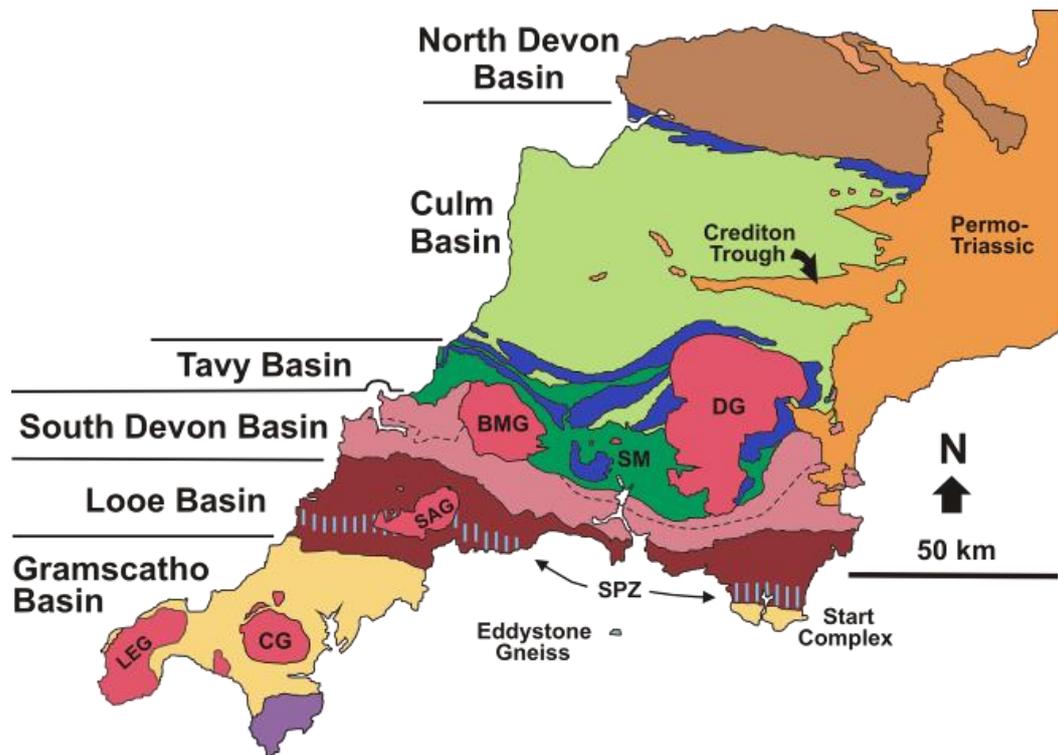


Fig. 2. Summary geological map of SW England. Devonian and Carboniferous sedimentary rocks occur in a series of basins (from west to east, the Gramscatho, Looe, South Devon, Tavy, Culm and North Devon basins). These basins are cross cut by the granites of the Cornubian batholith (LEG, Lands End Granite; CG, Carnmenellis Granite; SAG, St Austell Granite; BMG, Bodmin Moor Granite; DG, Dartmoor Granite). The area shown in purple below the Carnmenellis Granite is the Lizard Ophiolite Complex. To the east, Permian and Triassic sedimentary rocks unconformably overlie the Devonian and Carboniferous sequences below. (From Shail & Leveridge, 2009).

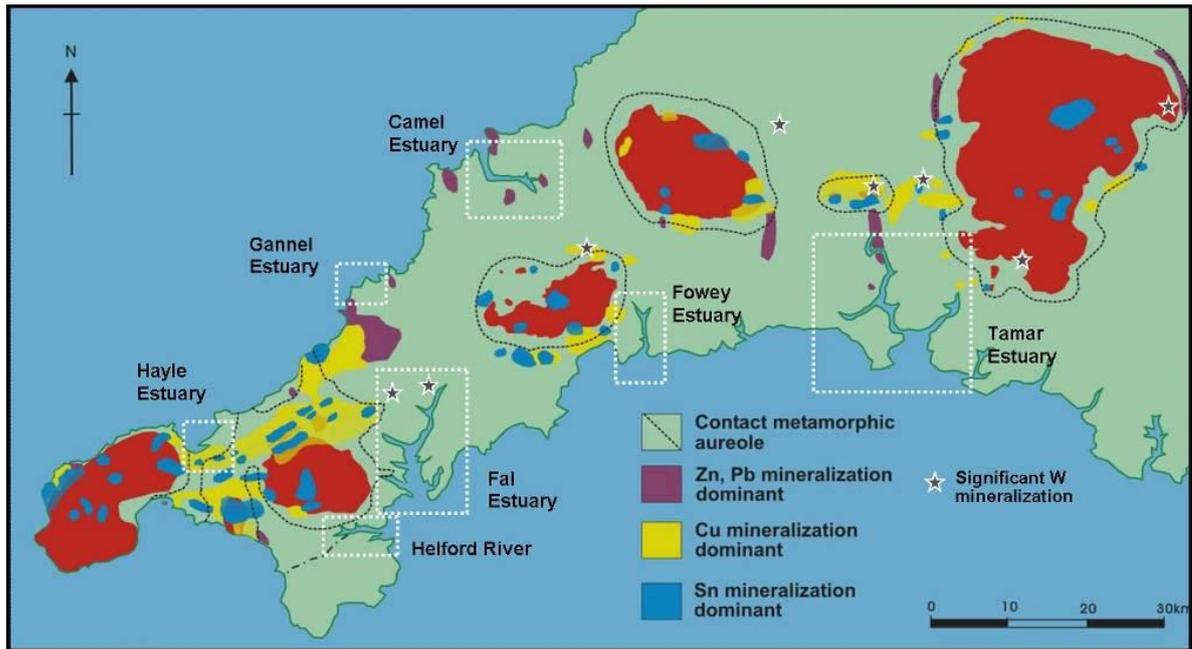


Fig. 3. Simplified geological map of SW England showing the locations of the estuaries described in this paper along with the main areas of metallic mineralization within the region. (Modified after Dines, 1956.)



Fig. 4. For many of the visitors and locals alike, the only visual sign of the past mining activity are the iconic engine houses scattered across the landscape in Cornwall and Devon.



Fig. 5. Rapid rates of sediment supply as a result of the release of tailings led to enhanced siltation in the estuaries of SW England. Here in the Gannel Estuary on the north Cornwall coast, looking towards the east, the saltmarsh and inter-tidal sediments in the upper reaches of the estuary are heavily contaminated with mine waste derived from the Newlyn Downs Pb/Zn mining district. Image courtesy of Cornwall Council.



Fig. 6. Sediment sampling in the intertidal mudflats.



Fig. 7. Within these steep sided river valley estuaries (such as here in the Fowey Estuary), the upper reaches are typically steep sided, with extensive areas of intertidal sediments and active tidal channels. The sediments are commonly very soft and rapidly turning tides mean that care needs to be taken when collecting sediment samples.

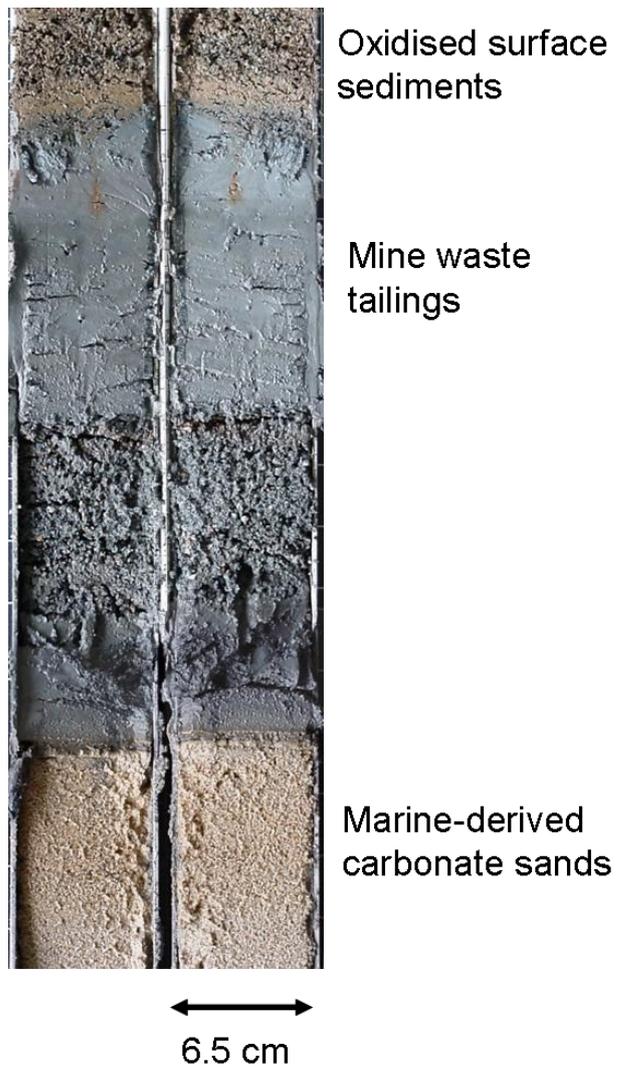


Fig. 8. In many of the recovered cores, the sediments are bioturbated silty mudstones and distinguishing the mine waste from 'natural' sediments can be difficult. However, as seen in this core from the Hayle Estuary, the distinctive grey, mine waste tailings overlie marine derived carbonate sands.

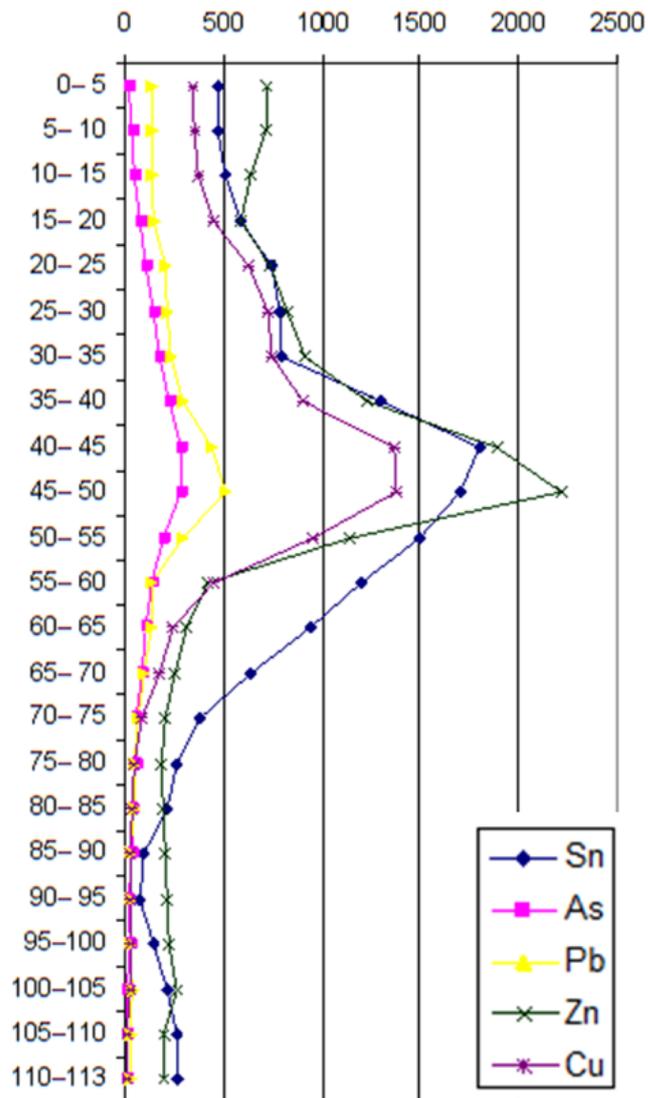


Fig. 9. Downhole geochemical variation, in this case for a core from the Tresillian River, in the Fal Estuary. Vertical scale is in cm; elemental abundance is in ppm (equivalent to mg/kg).

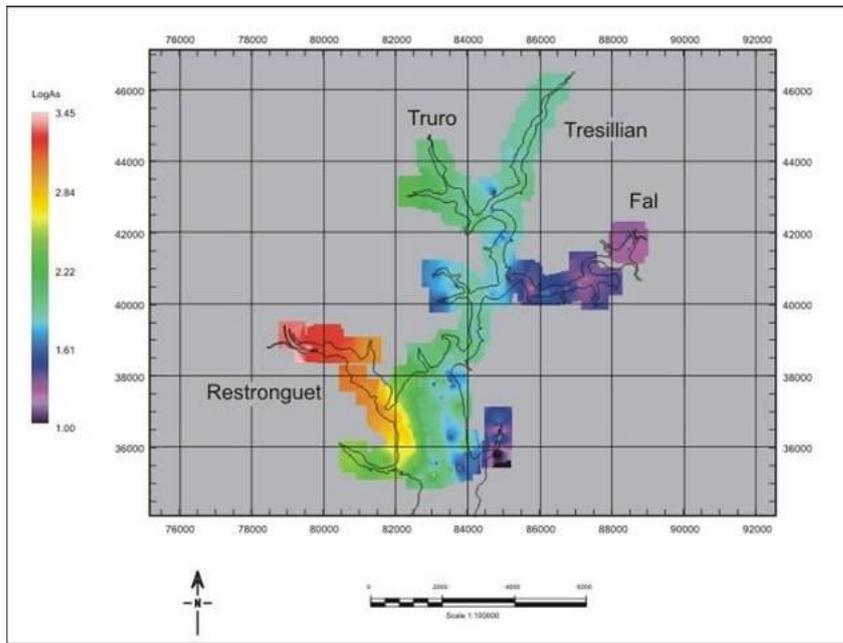


Fig. 10. Example of spatial variation in the abundance and distribution of mine wastes within near-surface sediments, in this case showing arsenic distribution in the uppermost 5 cm of the sediment profile in the Fal Estuary. (Image from Pirrie et al., 2003.)

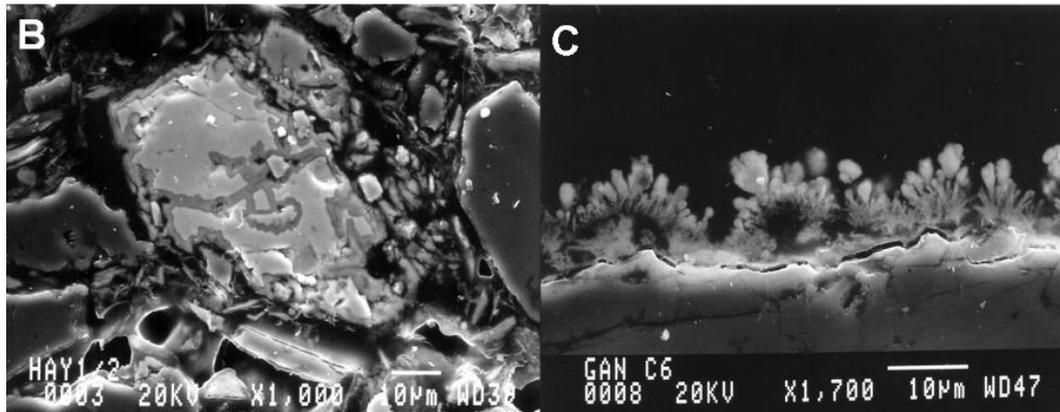
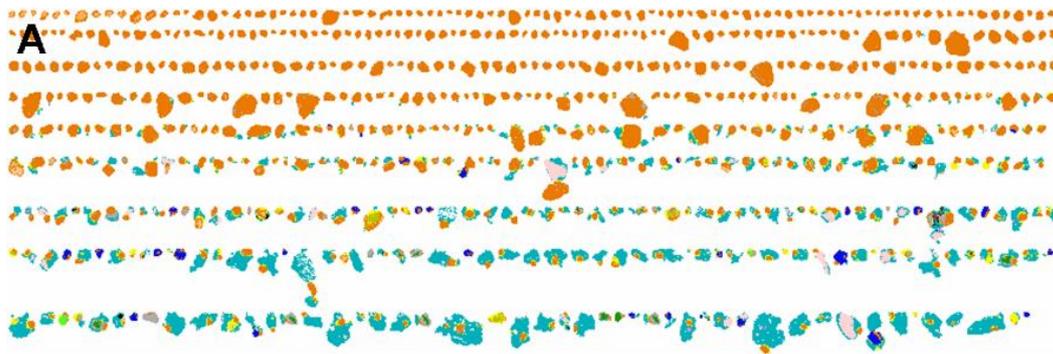


Fig. 11. Mineralogical studies allow the sediment source to be determined as well as allowing a prediction of mineral stability. a. QEMSCAN automated mineral analysis showing particles of chalcopyrite (orange) arranged by area within a single sediment sample from the Hayle Estuary. b. Scanning electron microscope image of a grain of chalcopyrite with a well-developed oxidized rim around the edge of the grain, from which Cu has been leached with a relative increase in the abundance of Fe and O. c. Small crystals of the zinc chloride mineral simonkolleite growing within the sediment in the Gannel Estuary.

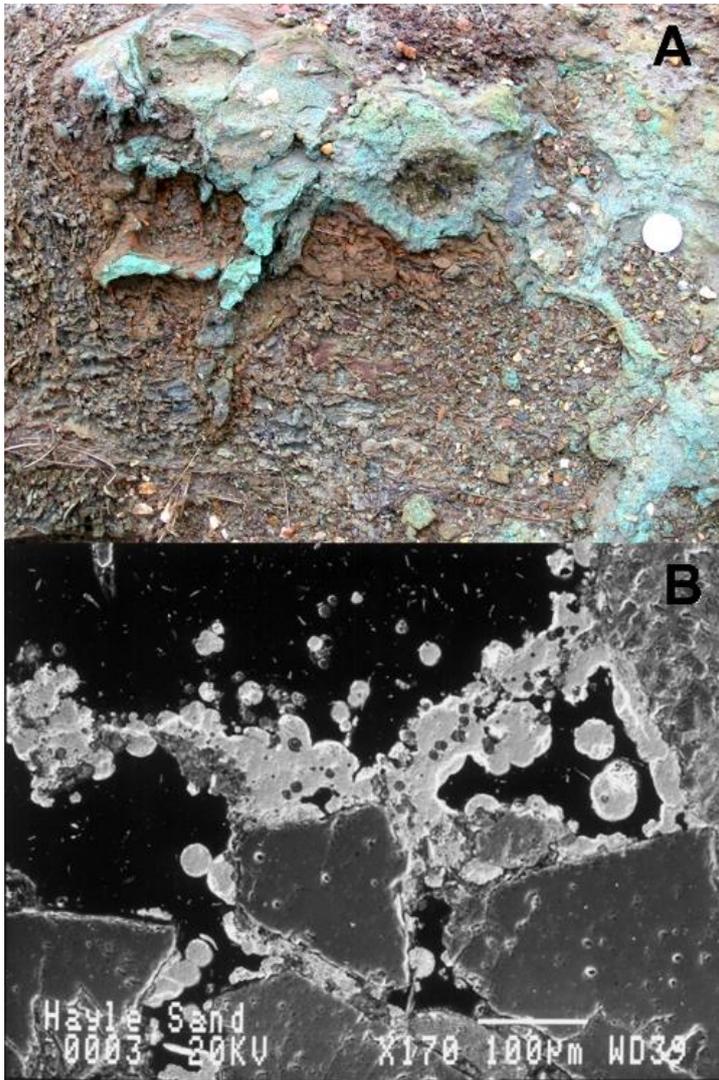


Fig. 12. Diagenetic atacamite growing within surface sediments in the Hayle Estuary, Cornwall, as seen: a. in the exposed sediments— characteristic blue-green areas, and b. as seen under scanning electron microscopy where the bright grey areas are the diagenetic atacamite.