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IMPACT OF MINING ON SEDIMENTATION; THE CAMEL AND GANNEL ESTUARIES, CORNWALL

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The mineralogy and geochemistry of the inter-tidal sediments in the Camel and Gannel estuaries on the north Cornwall coast has been examined to test the importance of mining on sediment supply. In the Camel Estuary there is a clear stratigraphical geochemical anomaly for Sn, W and Zr which corresponds with abundant cassiterite, wolframite and zircon. This sediment was supplied to the estuary as a result of the release of mine waste tailings from hard rock mining of main stage mineralisation, probably from mines such as Mulberry and Wheal Prosper in the area around Lanivet. In contrast the sediments in the Gannel Estuary contain very high concentrations of Pb and Zn. In one core, maximum Pb concentrations are in excess of 8500 ppm, along with over 1600 ppm Zn. This same stratigraphical interval also has very significant enrichment in Zr, Ce, La and Y along with high values for Ag. The geochemistry of the Gannel Estuary sediments is reflected by the mineralogy with abundant galena, sphalerite and plumbogummite (Pb-P-Al phase). In addition to these detrital grains there are abundant diagenetic phases precipitated within the sediments, including authigenic Pb, Zn and Cu-Fe minerals. Early diagenetic calcite-siderite-Fe monosulphide concretions are also present. The likely source for this Pb-Zn-Ag mine waste is from the area around Newlyn Downs. In both cases, the release of particulate mine waste, possibly following mine closure in the latter part of the 19th century or early 20th century, had a significant impact on down stream estuarine sedimentation. However, in the Camel Estuary the presence of abundant cassiterite is unlikely to have had a significant impact on the biosphere, whilst in the Gannel Estuary the presence of significant Pb and Zn and the mineralogical evidence that there is diagenetic mobility of Pb, Zn and Cu, is indicative that these elements were, and may still be, bioavailable.

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INTRODUCTION

Sediment supply to the present day coastal zone is a function of natural sediment transport from either onshore or offshore sources combined with sediment supplied as a result of human activity. Typically changes in land use result in alterations in the rate or type of sediment supply. In Cornwall, the coastal valleys or ria systems were flooded as a result of sea level rise in the early Holocene to form the modern estuary systems. These estuaries have subsequently been infilled with the formation of extensive inter-tidal areas as a result of rapid sedimentation particularly in the last few hundred years. One of the most significant factors leading to rapid siltation was the release of particulate waste from upstream mining operations. Early alluvial tin streaming released very large volumes of sediment that would not have been particularly metal-enriched whilst later hard rock mining, released smaller volumes of particulate waste that was significantly metal-enriched. In addition, smelt waste products were also locally important contributions to the overall sediment budget. This mine waste has been deposited in the inter-tidal areas, and where the sediments have been undisturbed by later human activity, they retain a clear geochemical and mineralogical signature of the impact of mining. Previous work has focused on the Fal Estuary (Pirrie *et al*., 1997, 1999a; Hughes, 1999), Fowey Estuary (Pirrie *et al*., 1999a) and the Hayle Estuary (Yim, 1976; Merefield, 1993; Healy, 1995). In this paper we examine the impact of mining on sedimentation in two of the estuaries on the North Cornwall coast; the Camel Estuary which drains a wide range of mines that principally worked Sb and Sn, and the Gannel Estuary which drains a significant Pb-Zn-Ag mining district. In both estuaries mineralogical and geochemical data clearly indicate the significant role of mining on sediment supply to the coastal zone.

REGIONAL SETTING

Camel Estuary

The catchment area for the Camel Estuary comprises the rivers Amble and Allen that drain Devonian metasediments of the Harbour Cove Slate Formation, Polzeath Slate Formation, Trevose Slate Formation and the Tredorn Slate Formation (Selwood *et al.,* 1998). Basaltic lavas commonly occur within the Harbour Cove Slate and the Trevose Slate formations to the north of the estuary. The River Camel drains the western margin of the Bodmin Moor Granite and overlying head deposits, before flowing south and then west across the Trevose Slate Formation. Less significant rivers drain the Staddon Grit Formation, Bedruthan Formation and the Trevose Slate Formation to the south of the estuary. These Devonian metasediments typically comprise interbedded sandstones and slates with subordinate limestones and volcanic tuffs (Selwood *et al.,* 1998). The most important mineralisation in the area comprises vein hosted Sb-Pb-As-Ag±Au associated with volcanic sequences in the Trevose Slate and Harbour Cove Slate formations. The St Endellion area on the River Amble was the most important area for Sb production in SW England in the late 18th century (Selwood *et al.,* 1998). Although there is minor vein-hosted Sn-W-Cu ±As mineralisation associated with the margins of the Bodmin Moor Granite the presence of extensive Medieval alluvial tin workings on the moor (Gerrard, 2000) suggests that vein hosted Sn mineralisation was originally much more areally extensive (Selwood *et al.,* 1998). Further to the south the catchment to the estuary also drains the area around Lanivet where the major mines of Mulberry and Wheal Prosper (amongst others) worked Sn from stockwork deposits at the edge of the St Austell Granite. The ore from Mulberry was processed in an adjacent valley which drains into the Camel Estuary (Dines, 1956). Production ceased at Mulberry in

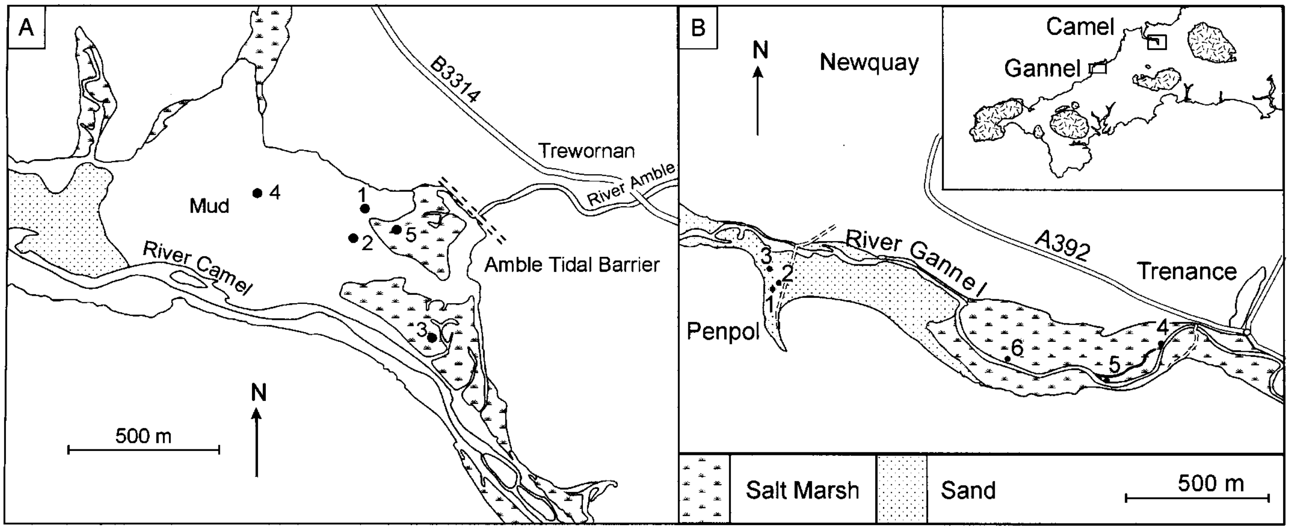

Figure 1. *Sketch map showing the location of the coring sites on (A) the Camel Estuary and (B) the Gannel Estuary.*

approximately 1918 and in 1930 at Wheal Prosper.

Thick (up to 20 m) successions of Holocene sediments occur around the margins of the Camel Estuary. In particular, the extensive alluvial plain on the River Amble at Trewornan, which was originally interpreted as a lake flat due to glacial impounding (Clarke, 1980) has subsequently been interpreted to represent Holocene sediments deposited as a result of mining activity (Scourse, 1985) although no data were presented to support this interpretation. There have been no previous studies on the role of mining in sediment supply to the estuary. Merefield (1982) sampled the coarser-grained inter-tidal sediments in the Camel Estuary and showed the importance of marine derived carbonate, with the sediments containing up to 62% carbonate (predominantly aragonite and low Mg calcite). In a regional survey of the bioavailability of metals in estuaries in SW England, Bryan *et al.* (1980) analysed the soft tissues of the polychaete *Nereis diversicolor* and the deposit-feeding bivalves *Scrobicularia planes* and *Macoma balthica.* They also carried out limited sampling of the surficial sediments. Bryan *et al.* (1980) showed that the surface sediments in the Camel Estuary contained 50-165 ppm Cu, 33-100 ppm As and 330-1000 ppm Sn.

Gannel Estuary

The catchment geology for the Gannel Estuary comprises undifferentiated Devonian metasediments (slates and thin limestones) assigned to the Meadfoot Group along with the Porthtowan Formation to the south. The Meadfoot Group is cross cut by minor lamprophyre and microgranite sheets. Within the catchment to the estuary, the largest mining district was the Pb-Zn-Ag deposits around Newlyn Downs. The most significant mines included East Wheal Rose which was at the height of its prosperity around 1850, working Pb-Zn-Ag lodes (Reid and Scrivenor, 1906) with production in the period 1845-85 of 48,200 tons of 62% lead ore along with 212,700 oz of silver and lesser amounts of copper and zinc ore (Dines, 1956). Other important mines in this area include Wheal Constance, Cargoll, South Cargoll and New Cargoll which predominantlyworked PbZn-Ag lodes along with minor copper ores, with production between 1845 and 1892 (Dines, 1956). The impact of mining on sedimentation in the Gannel Estuary was recognised by Reid and Scrivenor (1906) who comment "The washings from these mines, combined with the shell-sand, drifted in by the sea, have almost silted up the estuary of the Gannel, which can no longer be used for shipping". Although there has been no detailed analysis of the geochemical impact of mining on sedimentation in the Gannel Estuary, Bryan *et al*. (1980) in their analysis of metal uptake by polychaetes and bivalves in SW estuaries showed, that the upper reaches of the estuary were exceptionally Pb contaminated with sediment concentrations in the order of 2000 ppm. Thornton *et al.* (1986) presented the results of work focussed mainly on the water quality in the Gannel River and reported geochemical data for the sediments with 2995 ppm Zn, 2670 ppm Pb and 313 ppm Cu.

METHODS

Eleven shallow (<1 m) 6.5 cm diameter cores have been recovered from the inter-tidal areas in the Camel and Gannel estuaries (Fig. 1). In the Camel, 5 cores were collected from close to the confluence of the rivers Amble and Camel near Trewornan (Fig. la); cores 1, 2 and 4 were from the inter-tidal mud banks, whilst cores 3 and 5 were from saltmarsh areas. In the Gannel Estuary three cores were recovered from inter-tidal sand banks in the small creek at Penpol and three cores were recovered from the saltmarsh areas close to Trenance (Fig. lb).

Following core logging and photography, the cores were split and each 5 cm stratigraphic interval was sampled 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 technique with elvasite binder. The samples were then analysed using a Philips PW1400 X-ray fluoresecence spectrometer (XRF) fitted with a Mo-Sc X-ray tube. All samples were analysed for Sn, Cu, As, Pb and Zn; analytical precision for these elements is ±10 ppm; in total 127 samples have been analysed for this suite of elements. Cores Camel 1 and Gannel 4 were also analysed by XRF for W, Ce, La, Nd, Zr, Th, Co, and V and for Ag, Sb and Bi by atomic absorption spectrometry (AA) following a standard hot aqua regia sample digestion (25 samples in total). The complete geochemical dataset is available on request from the authors. Samples were selected for mineralogical analysis from all 11 cores. Nineteen 3 cm diameter core plugs were carefully collected with minimal sediment disturbance from the Camel Estuary cores along with 13 samples from cores 4, 5 and 6 from the Gannel Estuary. The core plugs were resin impregnated under vacuum and prepared as polished blocks. Cores 1-3 from Penpol were too coarse grained for preparation as core plugs, instead 22 grain mount thin sections were prepared and examined initially by standard light microscopy. All of the core plugs, along with 8 representative thin sections were then examined 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 $1x10^{-9}$ A and an accelerating voltage of 20 kV were used to locate the heavy minerals.

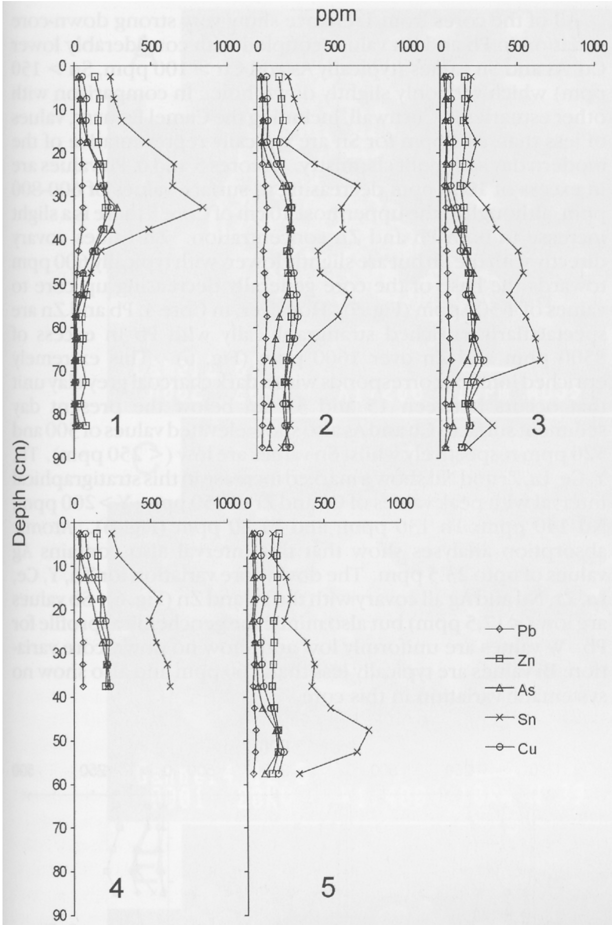

Figure 2. *Sediment geochemical profiles for Pb, Zn, As, Sn and Cu for the 5 cores recovered from the Camel Estuary. Note that in cores 1, 2, 3 and 5 there is a clear geochemical anomaly for Sn, with a sudden increase in Sn concentration followed by a decline towards the sediment surface.*

CAMEL ESTUARY

Sedimentology

The cores recovered from the Camel Estuary are typified by dark grey bioturbated silty very fine to fine grained sands which are either interbedded with silty mudstones or fine up to silty mudstones. *In situ* articulated bivalve shells occur throughout, along with a reworked shell lag deposit (?tidal channel) in Core 1. Core 5, recovered from the active reed beds near the mouth of the River Amble, comprises mottled grey-brown silty clays with very abundant plant debris in the upper 30 cm overlying bioturbated fine grained sands.

Geochemistry

The cores from the Camel Estuary all show a comparable geochemical signature (Fig. 2). In cores 1, 2, 3 and 5 Sn values are all low at the base of the cores but show a rapid increase in concentration to values in excess of 500 ppm (up to 842 ppm in Core 1); the Sn concentration then gradually decreases towards the present day sediment surface. Core 4 only penetrated the upper 41 cm of sediment and shows a profile of decreasing Sn concentration up to the sediment surface. As, Zn and Cu values are less variant than Sn although there is a weak stratigraphical increase in concentration up to approximately 300 ppm that corresponds with the increase in Sn. Although the Pb concentrations are low (typically less than 50 ppm) there are subtle down core variations that appear to mimic the profile displayed by Zn. The down-core profile for W in Core 1 clearly matches that for Sn, with values at the base of the core of approximately 30 ppm suddenly increasing to 80 ppm and then decreasing more gradually to values slightly higher than at the base of the core at the present day sediment surface (Fig. 3).

Core 1 was also analysed for Zr, Ce, La and Y. The geochemical profile for Zr again clearly mirrors that shown by Sn and W with variable values of around 40 ppm at the base of the core rapidly increasing to values in excess of 180 ppm, which then decrease to around 100 ppm at the sediment surface (Fig. 3). Although there is less down core variation, the peak values for Ce, Y and La all co-occur with the peak values for both Sn and W in Core 1 (Fig. 3). Core 1 was also analysed for Ag, Bi and Sb by AA. Ag values are low (less than 2.5 ppm) and show no systematic variation. Sb values are also low (below detection limit up to 18.5 ppm) but gradually

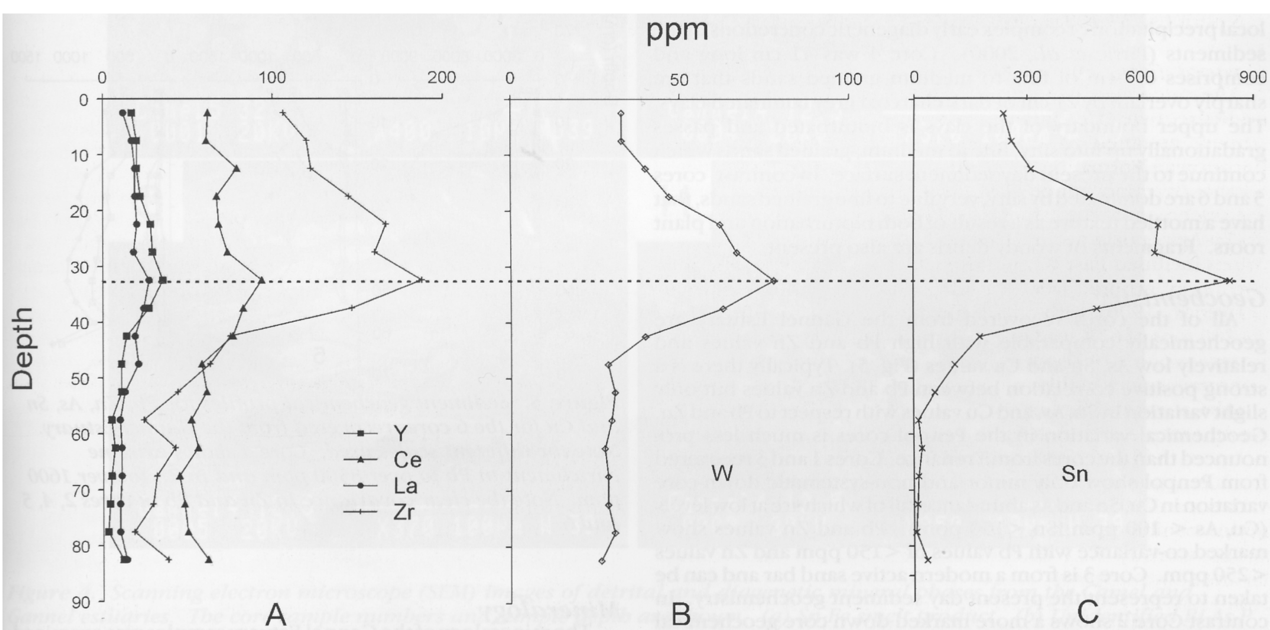

Figure 3. *Geochemical analyses for Core 1 from the Camel Estuary showing (a) Zr, Ce, La and Y, (b) W and (c) for comparison the Sn profile for this core. Note that peak Sn, W and Zr concentrations are all coincident with one another (dashed line). These geochemical data closely match the observed mineralogy, with abundant cassiterite, wolframite and zircon.*

increase up core from values of less than 6 ppm in the lower 40 cm, increasing to values >14 ppm towards the top of the core. In contrast, Bi values are quite invariant at around 180 ppm at the base of the core, decreasing to values around 130 ppm towards the present day sediment surface. There is no correlation between the profile for Sn, W and Zr versus the Bi, Ag or Sb values. In addition, there is no clear correlation between the physical sedimentology and the geochemical data.

Mineralogy

Nineteen representative samples from the Camel Estuary cores were prepared as polished blocks and examined under SEM. The heavy mineral assemblage is dominated by cassiterite which typically occurs as liberated, small (> 30 µm) grains. Wolframite is also present, again as small (< 30 µm) liberated grains. Other common phases include detrital pyrite, Fe oxides/carbonates, zircon and monazite whilst chalcopyrite, sphalerite, ilmenite, rutile and xenotime also occur but in lesser amounts. A small number of grains of an unidentified Bi-As-P phase and Sn smelt products also occur (Fig. 4a, b). There are no significant differences in the mineralogy between the 5 cores examined. Diagenetic minerals are generally not common in the Camel cores, although framboidal pyrite occurs throughout and is locallyvery abundant in some of the more organic-rich sediments (Fig. 4e).

GANNEL ESTUARY

Sedimentology

Six cores were recovered from the Gannel Estuary; cores 13 from Penpol and cores 4-6 from close to Trenance to the west (Fig. lb). Cores 1 and 2 were collected from the intertidal sediments within Penpol Creek close to the location of an old quay, whilst Core 3 was from an active tidal sand bar at the mouth of the creek. Cores 1 to 3 are dominated by well sorted fine to medium grained grey sands that show vague parallel lamination. In addition, in Core 2 there are thin very coarse sand to granule laminae dominated by slate rock fragments along with wood fragments. In Core 1, 15 cm below the present day sediment surface, the sands show a very distinctive charcoal grey colouration; this is interpreted to be due to the presence of abundant diagenetic Fe monosulphides that are related to the local precipitation of complex early diagenetic concretions in the sediments (Pirrie *et al.,* 2000). Core 4 was 41 cm long and comprises 6.5 cm of fine to medium grained sands that are sharply overlain by 21 cm of dark charcoal grey laminated clays. The upper boundary of the clays is bioturbated and passes gradationally up into silty, fine to medium, grained sands which continue to the present day sediment surface. In contrast, cores 5 and 6 are dominated by silty, very fine to fine grained sands, that have a mottled texture as a result of both bioturbation and plant roots. Fragments of woody debris are also present.

Geochemistry

All of the cores recovered from the Gannel Estuary are geochemically comparable with high Pb and Zn values and relatively low As, Sn and Cu values (Fig. 5). Typically there is a strong positive correlation between Pb and Zn values but only slight variation in Sn, As, and Cu values with respect to Pb and Zn. Geochemical variation in the Penpol cores is much less pronounced than the cores from Trenance. Cores 1 and 3 recovered from Penpol show only minor and non-systematic down-core variation in Cu, Sn and As abundance, all of which are at low levels (Cu, As < 100 ppm; Sn <150 ppm). Pb and Zn values show marked co-variance with Pb values of < 150 ppm and Zn values <250 ppm. Core 3 is from a modern active sand bar and can be taken to represent the present day sediment geochemistry. In contrast Core 2 shows a more marked down core geochemical variation for Pb and Zn with peak values in excess of 450 ppm towards the base of the core, decreasing systematically towards the present day sediment surface to values comparable with those which occur throughout Core 3

All of the cores from Trenance show very strong down-core variation in Pb and Zn values coupled with considerably lower Cu, As and Sn values (typically As and Cu > 100 ppm, Sn > 150 ppm) which vary only slightly down-hole. In comparison with other estuaries in Cornwall, including the Camel Estuary, values of less than 200 ppm for Sn are typically representative of the modern day sediment chemistry. In cores 5 and 6, Pb values are in excess of 1000 ppm decreasing to surface values of 600-800 ppm, although in the uppermost 10 cm of Core 5 there is a slight increase in both Pb and Zn concentration. Zn values covary directly with the Pb but are slightly lower, with typically 600 ppm towards the base of the core generally decreasing up core to values of 4-500 ppm (Fig. 5). However, in Core 4, Pb and Zn are spectacularly enriched stratigraphically with Pb in excess of 8500 ppm and Zn over 1600 ppm (Fig. 6). This extremely enriched interval corresponds with a dark charcoal grey clay unit that occurs between 15 and 35 cm below the present day sediment surface. Cu and As also show elevated values of 300 and 520 ppm respectively whilst Sn values are low (< 250 ppm). Th, Y, Ce, La, Zr and Nd show a marked increase in this stratigraphical interval with peak values of Ce and Zr of 250 ppm; Y >200 ppm; Nd 140 ppm; Th 130 ppm; and La 80 ppm (Fig. 6). Atomic absorption analyses show that this interval also contains Ag values of upto 23.5 ppm. The down core variation for Th, Y, Ce, La, Zr, Nd and Ag all covary with the Pb and Zn (Fig. 6). Sb values are low (<17.5 ppm) but also mimic the geochemical profile for Pb. W values are uniformly low and show no down-core variation; Bi values are typically less than 160 ppm and also show no systematic variation in this core.

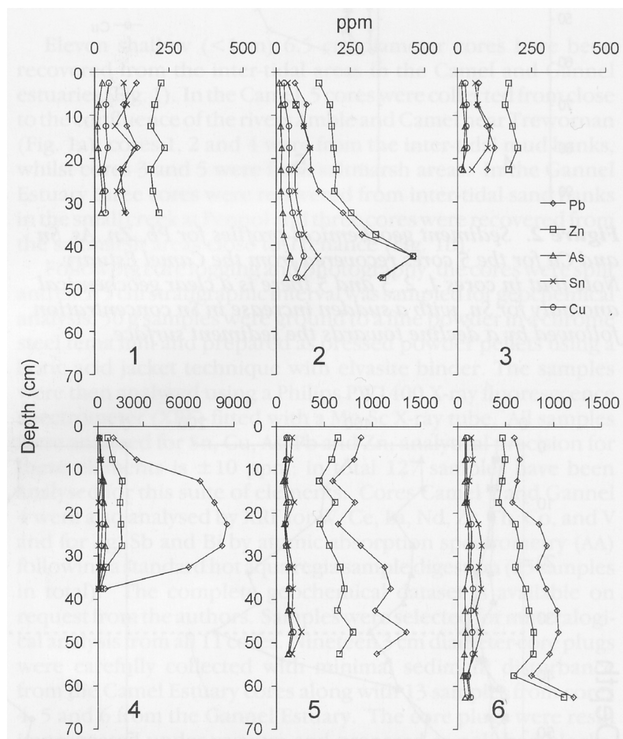

Figure 5. *Sediment geochemical profiles for Pb, Zn, As, Sn and Cu for the 6 cores recovered from the Gannel Estuary. Note the different scales used. Core 4 shows extreme enrichment in Pb to over 8500 ppm and in Zn to over 1600 ppm. Note the clear covariance in Zn and Pb in cores 2, 4, 5 and 6*

Mineralogy

The mineralogy of the Gannel Estuary samples was examined on the basis of 22 thin section grain mounts from cores 1-3 and 13 polished blocks from cores 4-6. The observed detrital mineralogy clearly reflects the bulk sediment geochemistry. Pb and Zn phases are

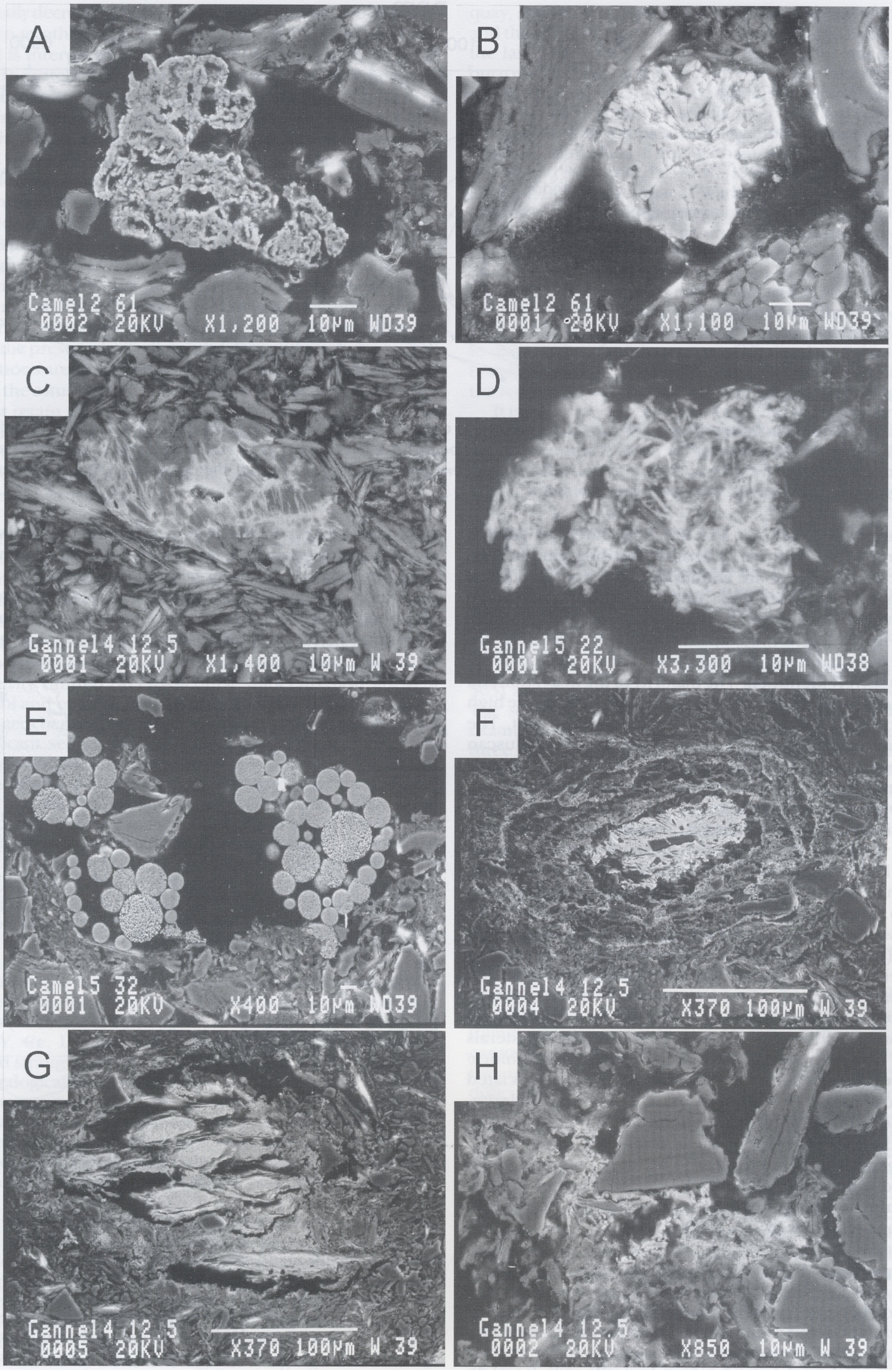

Figure 4. *Scanning electron microscope (SEM) images of detrital and diagenetic mineral phases from the Camel and Gannel estuaries. The core sample numbers and sample depth are shown. (a) Sn-Fe smelt product. (b) Unidentified Bi-As-P phase. (c) Detrital grain of Pb-Al-P (plumbogummite [bright]). (d) Detrital grain of monazite. (e) Abundant diagenetic framboidal pyrite. (f) Detrital grain of galena (centre) with concentric rings of a diagenetic Pb phase (bright) surrounding the grain. (g) Diagenetic Pb phase infilling the cellular structure of plant debris. (h) Diagenetic Pb (bright phase) infilling available porosity between the detrital sediment grains.*

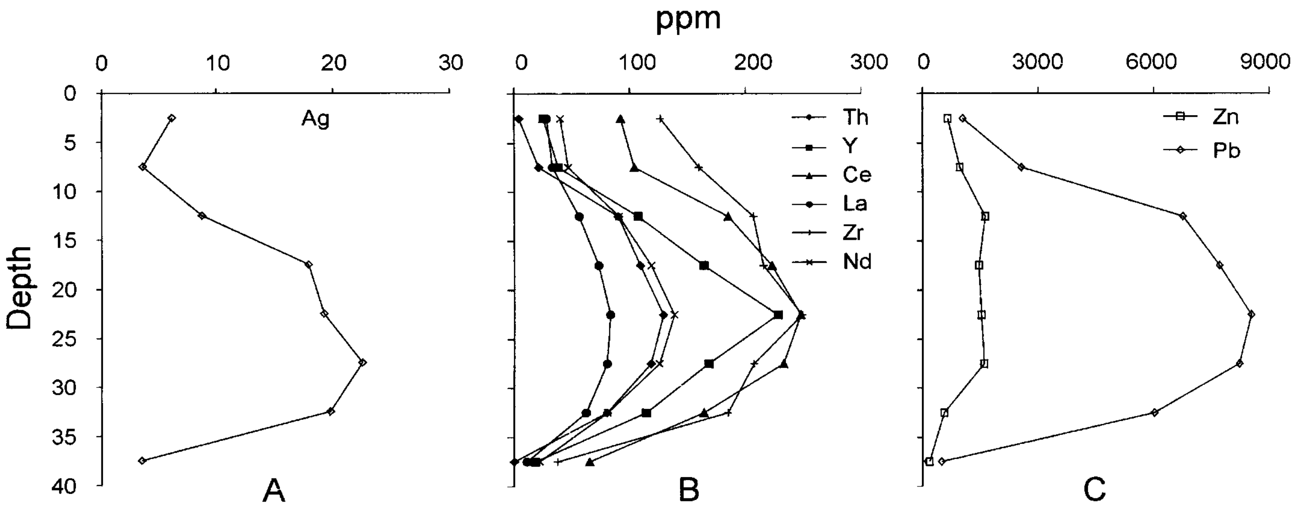

Figure 6. Down core geochemical profiles for Core 4 from the Gannel Estuary for a) Ag, (b) Th, Y, Ce, La, Nd and Zr and (c) for comparison the Pb and Zn profiles for this core. Note that peak Pb, Zn, Ag, Th, Y, Ce, La, Zr and Nd concentrations are all coincident at an interval between 20 and 30 cm. These geochemical data closely match the observed mineralogy, with abundant galena, plumbogummite and sphalerite.

abundant and are dominated by galena, sphalerite and a Pb-Al-P phase, probably plumbogummite (Fig. 4c). Fe oxides/carbonates are common throughout and often exhibit spongey, carious textures. Detrital pyrite and zircon are abundant whilst cassiterite, baryte, arsenopyrite/loelingite, monazite (Fig. 4d), xenotime, apatite, rutile and ilmenite are present in lesser quantities. A small amount of Pb smelt material has been tentatively identified. The majority of the heavy mineral phases occur as small < 30μm, liberated grains. Despite the high concentration of Ce and La, monazite is not very abundant. The coarser grained sands in cores 1-3 are dominated by molluscan skeletal carbonates, foraminifera, quartz and lithic metamorphic rock fragments, alongwith less abundant tourmaline, muscovite, biotite, amphibole and glauconite.

Diagenetic minerals are abundant within the Gannel cores particularly within the Pb and Zn—rich horizons in cores 4-6 near Trenance. Framboidal pyrite is a common diagenetic phase. However, in addition there are abundant diagenetic Pb phases (Fig. 4f, g, h). These commonly occur either within available pore space (Fig. 4h) or as a replacement of organic material, often plant roots (Fig. 4g). Aggregates of diagenetic Pb minerals form clusters over 1 mm in diameter. In one case a grain of detrital galena appears to form a nucleus surrounded by concentric rims of diagenetic Pb minerals which may represent the initial stages of concretion formation (Fig. 4f). Zn sulphide/sulphate minerals also replace organic material. Rare diagenetic Cu-Fe sulphides/ sulphates are present within the sediment, commonly associated with organic material. At Penpol, abundant diagenetic siderite-Mg calcite-Fe monosulphide concretions occur, typically nucleated around either burrows or metal fragments (Pirrie *et al.*, 2000). Diagenetic minerals appear to be more common in the finer-grained sediments. This may be due to a higher organic content within the finer-grained sediments affecting the local Eh-pH conditions (cf. Pirrie *et al.*, 1999b).

INTERPRETATION

Sediment sources in the Camel Estuary

The geochemical and mineralogical data for the Camel Estuary clearly shows a pulse of sediment that is significantly enriched in Sn, Wand Zr. This corresponds mineralogicallywith abundant cassiterite, wolframite, zircon (Zr), monazite (Ce and La) and xenotime (Y). This sediment was clearly sourced from the release of particulate mine waste derived from hard-rock mining activity centred around high temperature Sn-rich main stage mineralisation. Within the estuary catchment there is only one likely source for this mine waste; the open pits of Mulberry and Wheal Prosper (amongst others) in the region of Lanivet which worked Sn stockwork deposits on the edge of the St Austell Granite (Fig. 7a). These mines produced a large quantity of cassiterite processed locally in the Lanivet stream which flows into the Camel Estuary. The geochemical profiles for the estuarine sediments reveal a very rapid increase in mining related sediment supply, which

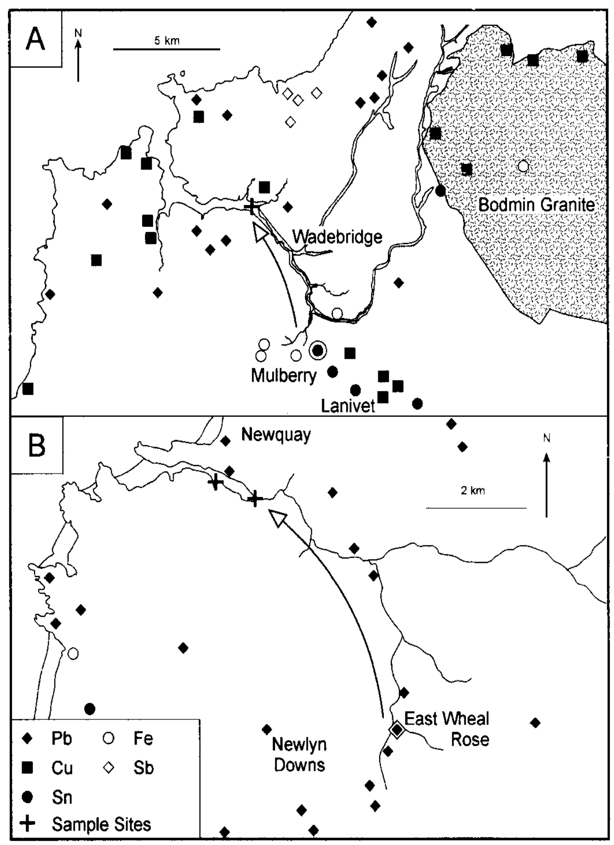

Figure 7. Summary diagram showing the main mining operations in the catchments of (a) the Camel Estuary and (b) the Gannel Estuary (after Jenkin, 1963, 1964). Based on the sediment mineralogy and geochemistry it is most likely that the Sn mine waste in the Camel Estuary was derived from the area around Mulberry and Wheal Prosper. The Pb-Zn-Ag mine waste in the Gannel Estuary was derived from the mines in the Newlyn Downs area such as East Wheal Rose.

then gradually decreases. This is comparable with the geochemical profile seen in other areas such as the Fal Estuary (Pirrie *et al*., 1997) and is interpreted to reflect the sudden release of mine waste into the catchment. This may correspond with either peak production, or more probably immediately after the cessation of mining. The geochemical profile is sharp-based indicating a rapid event, rather than a progressive increase that would reflect continued and increasing tailings supply matching increased mine production. This rapid event most probably reflects mine closure, and a subsequent dramatic release of tailings. Production ceased at Mulberry in approximately 1918 and 1930 at Wheal Prosper.

Although there was a substantial amount of Pb, Zn and Sb mining activity to the west and north of Wadebridge, there is very little evidence of this preserved in the cores recovered from near Trewornan. There is however, an increase in Sb concentrations up core to the present day sediment surface, although the overall concentrations are low. This may reflect the release of Sb mine waste in to the estuary and it is possible that the sediments further to the west retain a clearer signature of this mining impact. In addition, the mineralogical and geochemical data are clearly not related to tin streaming that occurred on Bodmin Moor as this would have released large volumes of sediment that would have had a lower Sn concentration.

Sediment sources in the Gannel Estuary

As previously recognised there has been a significant impact by predominantly Pb mining on sedimentation in the Gannel Estuary. Indeed Bryan et al. (1980) recognised that the Gannel Estuary had the highest Pb contamination of any estuary in the south-west. The geochemical and mineralogical data are indicative that the sediment was sourced from particulate waste from mining activity centred on cross-course mineralisation. Core 2 from Penpol and cores 4, 5 and 6 from close to Trenance show a very clear geochemical signature of mine waste contamination with significant sediment supply enriched in Pb and Zn. The importance of sediment supplied from these sources co-varies and decreases systematically up core, but the surficial sediments still retain very high Pb and Zn concentrations. The mineralogy of the estuary sediments clearly matches the geochemical results with abundant galena, sphalerite and plumbogummite. In contrast, cassiterite is relatively rare in the samples analysed which is consistent with the geochemical results which typically have less than 200 ppm Sn. Cores 1 and 2 from Penpol are from active intertidal sand bars where the dominant sediment supply is from marine carbonate (cf. Merefield, 1982) and therefore show low levels of Pb, Zn, As, Sn and Cu; although Pb and Zn again covary.

Core 4 from the Gannel Estuary reveals the most spectacular down core geochemical variation observed. The extreme enrichment in Pb (in excess of 8500 ppm), Zn (in excess of 1600 ppm), REE (Th, Y, Ce, La, and Nd) and Ag all co-occur and clearly correspond stratigraphically with a dark charcoal grey mudstone unit. Mineralogically this sample is spectacularly enriched in galena and plumbogummite. Although monazite is common, it is not as abundant as might be suggested by the geochemical data. However, plumbogummite is abundant and can contain significant quantities of the rare earth elements (e.g. Morteani and Preinfalk, 1996) which may in part account for the observed abundance of Ce and La.

In addition to the recognised detrital grains there are abundant diagenetic phases present in the Gannel Estuary. Previous work in SW England has recognised diagenetic phases such as chalcopyrite and As sulphides (Thorne, 1983; Pirrie *et al*., 1999b) but as far as we are aware this is the first record of diagenetic Pb phases in estuarine sediments in SW England. These diagenetic phases may represent the local dissolution and reprecipitation of Pb minerals possibly enhanced by mine drainage carrying significant Pb. In addition to the Pb phases, Zn sulphide/sulphate minerals and rare diagenetic Cu-Fe sulphides/sulphates are present within the sediment, commonly spatially associated with organic material. The presence of these diagenetic phases implies that there is considerable metal mobility and hence potential bioavailability of Pb, Zn and Cu. In addition, there are abundant diagenetic concretions within the sediments at Penpol which in the late 19th Century was an active quay, abandoned as a result of siltation. The age of the sediments and therefore when the concretions nucleated must have been in the last 130 years. They are typically either nucleated around burrows or metal artefacts. They are mineralogically very complex; dominant cements include calcite, siderite and Fe monosulphide along with less abundant sphalerite, pyrite and baryte. They are comparable with complex early diagenetic concretions described by Pye and co-workers from Warham Marsh, Norfolk (Pye, 1984; Allison and Pye, 1994; Pye *et al.,* 1990; Coleman *et al.,* 1993). Pye *et al.* (1990) showed that at Warham the precipitation of siderite occurred from marine porewaters at shallow burial depths, within the sulphate reduction zone, in contrast to previous studies that predicted that iron sulphides (either FeS or pyrite) should be the dominant iron minerals precipitated in this zone. The siderite concretions were interpreted as due to the rate of iron reduction exceeding the rate of sulphate reduction within the sediments (Pye *et al.,* 1990; Allison and Pye, 1994). Coleman *et al.* (1993) were able to demonstrate the importance of localised microbial populations in the nucleation and growth of these concretions, particularly by the reduction of Fe (III) to Fe(II) by sulphate reducing bacteria.

It is clear that the Gannel Estuary has received significant mine waste from mines working Pb-Ag-Zn lodes (cf. Reid and Scrivenor, 1906; Bryan *et al*., 1980). The most significant mines in the estuary catchment were in the area around Newlyn Downs, including East Wheal Rose, Wheal Constance, Cargoll, South Cargoll and New Cargoll (Fig. 7b). It is likely that the significant release of mine waste was again either during peak production or immediately following mine closure in the latter part of the 19th Century. The Pb-P-Al phase plumbogummite has only rarely been described from the mines in Cornwall and has not been reported to be present at Newlyn Downs. To confirm the interpretation that this phase was derived from the mines around Newlyn Downs, the present day stream sediments along the course of the River Gannel were sampled at Trewerry Mill [NG 837 580], Mertha Bridge [NG 839 563] and the mine spoil heaps at Newlyn Downs [NG 838 548] . The sediment samples were prepared as polished blocks and examined by SEM, and plumbogummite grains are present at all three sites, supporting the interpretation that this phase was derived from this source, although we know little about the paragenesis of this mineral (Fig. 8). Interestingly, a diagenetic Pb phase is also present at Mertha Bridge, but given the delicate structure of this phase it is unlikely to survive reworking and transportation.

DISCUSSION AND CONCLUSIONS

The mineralogy and geochemistry of the inter-tidal sediments in both the Camel and Gannel estuaries clearly records the release of mine waste tailings into the estuary catchments resulting in enhanced siltation. Comparison with the known regional mining history suggests that the peak geochemical anomalies for Sn in the Camel Estuary probably date to around the start of the 20th century, whilst the peak discharge of Pb, Zn and Ag into the Gannel Estuary was probably in the latter part of the 19th century. It is difficult to assess the historical environmental impact of these mine waste discharges. Certainly contemporary authors suggest that the loss of the quays and shipping trade in the Gannel Estuary was the result of enhanced siltation due to mine waste discharge (Reid and Scrivenor, 1906). In the Camel Estuary the dominant mineral phases present (cassiterite, wolframite and zircon) are geochemically stable and are unlikely to have been bioavailable. In contrast in the Gannel Estuary the mineralogy is dominated by less stable phases and there is clear evidence from the sediment diagenesis that there has been considerable mobility of Pb, Zn and Cu which would potentially be bioavailable. This is supported by the earlier work of Bryan *et al.* (1980) on the metal uptake into the soft tissue of polychaetes and infaunal bivalves in the estuary. The highest metal concentrations correspond with a distinctive dark charcoal grey clay unit within Core 4 from near Trenance; the lateral extent and distribution of this unit should be ascertained and any reworking minimised, to ameliorate any future environmental impact on the estuary by the re-release of this historic Pb-Zn mine waste. However, this area also represents a unique natural laboratory to understand the diagenesis of mine waste contaminated sediments.

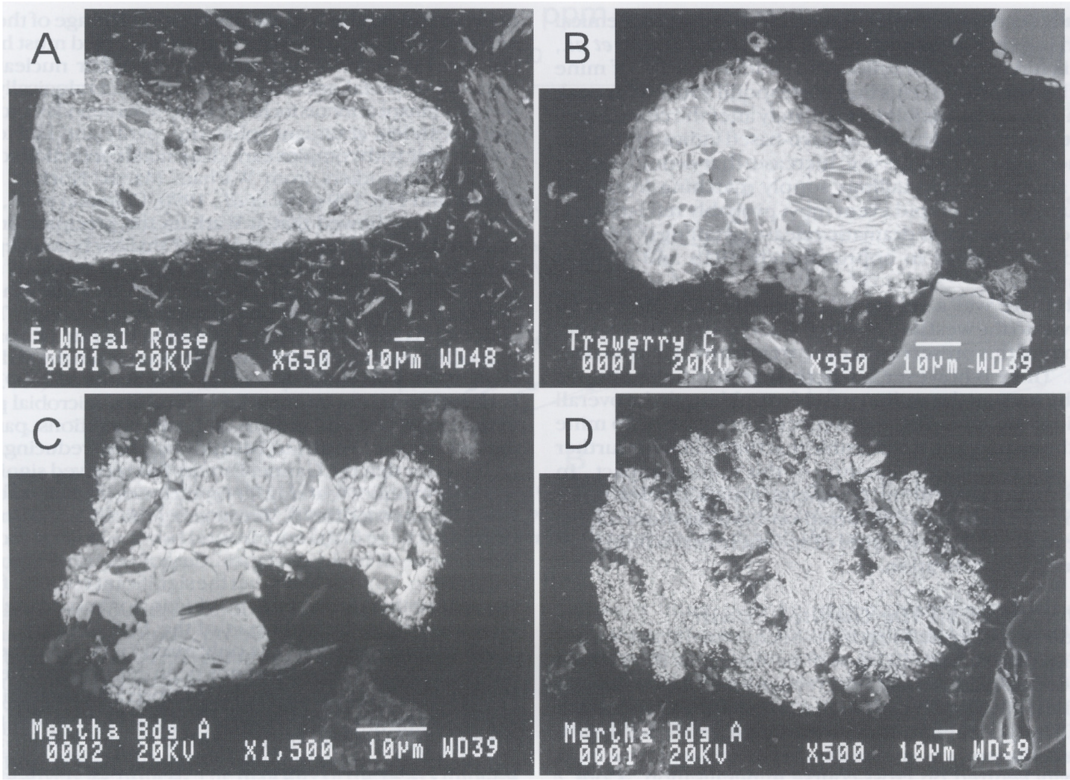

Figure 8. *Scanning electron microscope images of stream sediment samples from the Gannel River and the spoil heaps at Newlyn Downs. Grains of plumbogummite occur at both East Wheal Rose (a) and Trewerry Mill (b). At Mertha Bridge grains of galena showing diagenetic alteration to a secondary Pb phase are observed (c) along with other diagenetic lead minerals (d).*

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