GEOCHEMICAL AND MINERALOGICAL RECORD OF THE IMPACT OF MINING ON THE TEIGN ESTUARY, DEVON, UK

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Previous mineralogical and geochemical studies on the sediments in the Teign Estuary, Devon, UK, have shown that there are elevated levels of barium present within the surface sediments and the river catchment due to historical mining. For this investigation, 8 shallow cores (<1 m) were recovered from various locations in the estuary. These cores were subsequently logged, photographed and divided into approximately 5 cm depth intervals. The geochemistry and mineralogy of 68 samples from the cores were analysed. Bulk sediment geochemistry was determined by XRF and data for Ba, Cu, Pb and Zn are presented here. The mineralogy of the samples was determined by XRD. In addition, the samples from two cores were selected for mineralogical analysis using automated SEM-EDS (QEMSCAN®). The data show a sediment depth related geochemical trend with typically the lowest concentrations of Ba, Cu, Zn and Pb at the bases of the cores. Several of the sampling sites reveal a marked peak in the concentration of Pb and Zn mid-core; however, Cu values are low and invariant throughout. Postdating the Pb-Zn peak, there is a subsequent elevation in Ba in many of the cores studied, at a sediment depth of between 10 and 20 cm. Maximum concentrations of Ba reach 3360 ppm; Pb, 2220 ppm; Zn, 887 ppm and Cu, 258 ppm. Detrital minerals present include: barite, rutile, ilmenite, zircon, monazite, pyrite, cassiterite, sphalerite, galena and chalcopyrite. Framboidal pyrite is the only diagenetic mineral observed. The geochemical results are consistent with the historical mining records in the catchment, with barite mining postdating Pb-Zn mining. Both episodes of mining have released particulate mine waste, which has accumulated within the estuarine sediments.

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INTRODUCTION

The Cornubian Orefield in SW England contains metalliferous mineral deposits that have been mined from the Bronze Age through to the present day (Gerrard, 2000). During the 18th and 19th centuries the orefield was one of the world's most significant producers of tin and copper. Despite 2,500,000 tonnes of tin, 2,000,000 tonnes of copper and 250,000 tonnes of arsenic being produced, contemporary studies suggested that up to a third of the metals were lost during processing (Thomas, 1913). It has been demonstrated that estuarine sediments can retain a record of industrial activity in their catchments (Cundy *et al.*, 2003) with mining waste remaining for millennia, providing the mine waste is not chemically mobile or physically/biologically reworked (Leblanc *et al.*, 2000). Mining has had a huge impact on estuarine sediments throughout the southwest of England with mine waste being released into the environment as particulate waste or in solution through mine drainage. The Fal (Pirrie *et al.*, 1997; Turner, 2000; Pirrie *et al.*, 2003), Fowey (Pirrie *et al.*, 2002a; Friend *et al.*, 2006), Hayle (Pirrie *et al.*, 1999; Turner, 2000; Rollinson *et al.*, 2007; Pirrie *et al.*, 2009a), Camel and Gannel (Pirrie *et al.*, 2000), Helford (Pirrie *et al.*, 2002b) and Erme (Price *et al.*, 2005) estuaries in SW England all retain a record of the type and extent of mining in their respective catchments. This paper presents data that demonstrate the geochemical and mineralogical impact of mining on the Teign Estuary, Devon, UK whose catchment encompasses several historically significant mining districts.

THE TEIGN ESTUARY
Estuarine environments

The Teign Estuary is located on the South Devon coast, with tidal conditions extending from the coastal town of Teignmouth inland to Newton Abbot (Figure 1). It is approximately 7 km long with a width of 0.5 to 0.75 km (Selwood *et al.*, 1984). The area of the estuary is small (3.7 km²) and is dominated by intertidal sub-environments (2.19 km²) along with subtidal and salt marsh areas (Davidson, 2005). Three main rivers drain into the estuary, the River Teign, River Bovey and River Lemon, all of which originate on Dartmoor. The Aller Brook is another major tributary alongside many minor water courses. The discharge of the River Teign is less than 20 m³/s during the summer with peaks of 50-100 m³/s in autumn and winter (Davidson, 2005). The catchments for the rivers Teign, Bovey and Lemon all include areas of past mining activity, including
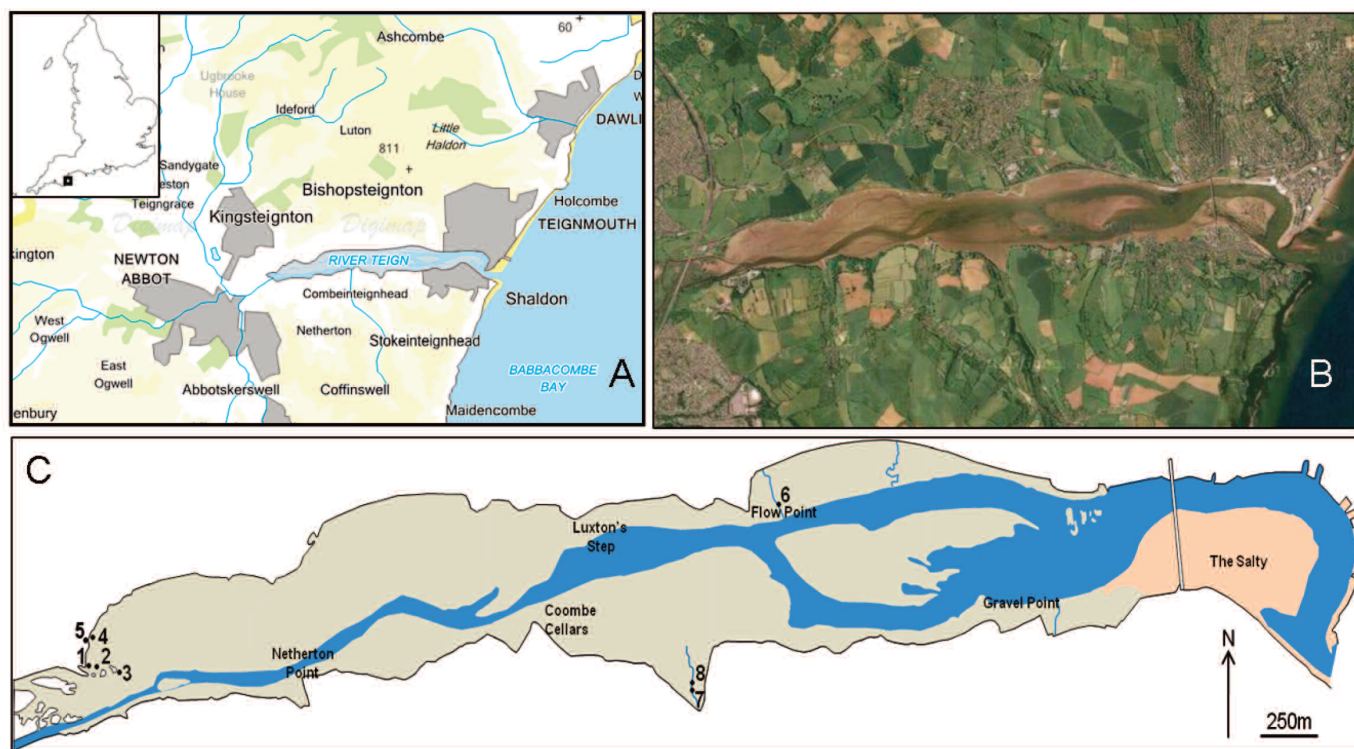
Figure 1. *The Teign Estuary, Devon UK. (**A**) Location map. (**B**) Aerial photograph of the Teign Estuary (from Google maps). (**C**) Map showing the sampling locations for cores T1 - T8 within the Teign Estuary.   Map data retrieved from Multimap, http://www.bing.com/maps/?FORM=MMREDIR accessed 29th November 2010.*

tin streaming operations on Dartmoor. In addition, Teignmouth has a three hundred year old working port and boats are moored in the estuary. A range of activities take place in the estuary including: fishing, sailing, industrial activities related to the harbour, trawling, kayaking and water skiing, but currently other large scale industrial activity is absent other than the export of ball clay.   Dredging has maintained the estuary channels for shipping and has prevented meandering of the main river channel.

Today, the Teign Estuary contains a variety of sediments from muds to sandy gravel. Salt marshes are found around Newton Abbot, one of which, Jetty Marsh, is a local nature reserve. A mixing area between coarser sands bought into the estuary by flooding tides and finer sediments transported down the estuary during ebbing tides is found at the mouth of the estuary in an area called "The Salty" (see Figure 1). The upper estuary is dominantly mud towards the edges with coarser sediments close to the middle of the river where water is faster flowing (Selwood *et al.*, 1984).

Regional geological setting

The bedrock geology of the Teign Estuary catchment is diverse and includes Late Devonian successions of the Tavy Basin, Late Devonian to Carboniferous successions of the Culm Basin, the Early Permian Dartmoor Granite, Permian successions of the lower part of the Exeter Group, Cretaceous Greensand and the Palaeogene sediments of the Bovey Basin (Figure 2).

The Tavy Basin succession is mudstone-dominated, comprising the Upper Devonian Kate Brook Slate and Rora Slate (Leveridge, 2011). The Culm Basin succession spans the Upper Devonian to Mississippian and comprises the Hyner Shale, Trusham Shale, Combe Shale, Teign Chert, Ashton Shale and Crackington Formation (Leveridge and Hartley, 2006). The Teign Chert and underlying Combe Shale host intrusive and extrusive mafic igneous rocks and widespread stratabound manganese mineralisation, typically oxides/oxyhydroxides of probable volcanic-exhalative origin (Beer and Scrivener, 1982).

In addition, the Teign Chert and Ashton Shale Formation host disseminated and stratabound thin veinlet Zn-Pb-Cu mineralisation (primarily sphalerite, galena and chalcopyrite), also of presumed volcanic-exhalative origin; there is also minor pyrite, arsenopyrite and loellingite (Beer *et al.*, 1992). The Tavy and Culm basin successions were deformed and underwent low-grade regional metamorphism during the Pennsylvanian Variscan orogeny (Leveridge and Hartley, 2006).

The Dartmoor Granite was emplaced during the Early Permian and is associated with granite-hosted magmatic-hydrothermal vein mineralisation and localised replacement mineralisation in the host rock (Chesley *et al.*, 1993; Beer and Scrivener, 1982). In the Teign catchment, quartz-tourmaline ± chlorite veins are associated with cassiterite and hematite. Replacement mineralisation, comprising massive intergrown fine-grained magnetite and hornblende is developed in host rocks along the SE margin of the Dartmoor Granite (Le Neve Foster, 1875); the assemblage additionally includes andradite, axinite, siderite, calcite and apatite and traces of arsenopyrite, pyrite, sphalerite and chalcopyrite (Scrivener *et al.*, 1987).

The lower part of the Permian Exeter Group crops out on the eastern side of the Teign catchment and predominantly comprises alluvial/fluvial conglomerates, sandstones and mudstones (Selwood *et al.*, 1984; Edwards and Scrivener, 1999). Crosscourse Pb-Ag-Zn-Ba mineralisation occurs in N-S trending veins hosted by Devonian and Carboniferous rocks and developed during the Middle Triassic as a consequence of the migration of basinal brines from Permo-Triassic successions (Scrivener *et al.*, 1994; Gleeson *et al.*, 2000). In the Teign Valley, Ba mineralisation is dominant and lodes comprise predominantly banded or botryoidal barite along with some quartz, pyrite, galena, sphalerite and tetrahedrite (Selwood *et al.*, 1984).

Cretaceous Upper Greensand and Eocene Flint Gravels crop out in the eastern extremities of the Teign catchment (Selwood *et al.*, 1984). The Bovey Basin developed during the Palaeogene by strike-slip movements along the Sticklepath-Lustleigh Fault and contains a succession of kaolinitic clays, silts, sands, gravels and lignites (Selwood *et al.*, 1984).
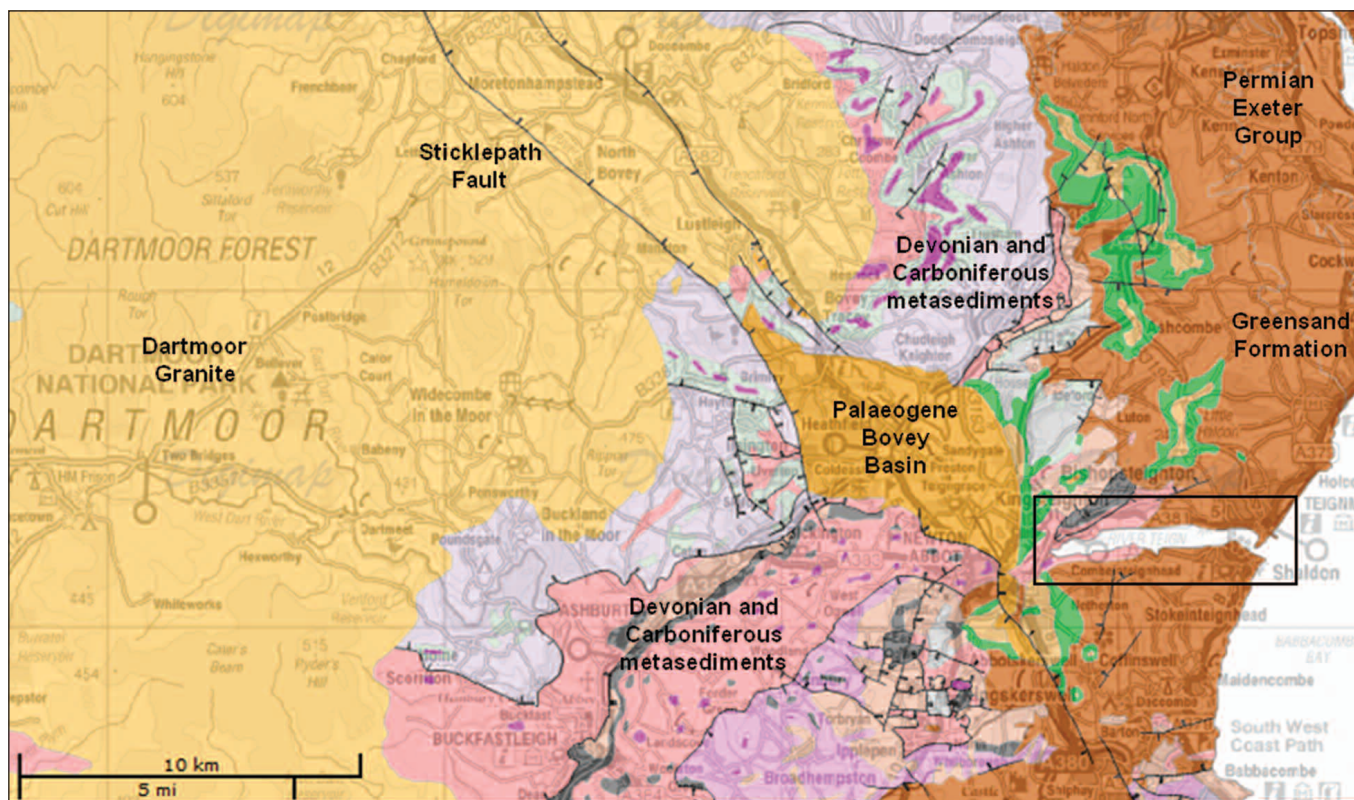
Figure 2. *Geological map of the region around the Teign Estuary. The Teign Estuary is highlighted within the box. Geological map data ©NERC 2011.*

Mining history in the estuary catchment

In the Teign Valley Mining District, which was the most prolific area of mining in the catchment, lead, silver, zinc, micaceous hematite, barium, copper, fluorspar and manganese ores have all been extracted (Dines, 1956; Selwood *et al.*, 1984). The earliest mining in the region was thought to have taken place on Dartmoor, with evidence of tin streaming extending back to the 12th Century although activity is thought to have occurred much earlier than this, possibly back to Roman times (Gerrard, 2000). The Teign Estuary lies downstream of tin streaming sites on Dartmoor and Medieval tin streaming operations resulted in an influx of sediment supply to the rivers (Thorndycraft *et al.*, 2004). The later impact of hard rock mining is also identified within the river terrace sediments along the Teign (Thorndycraft *et al.*, 2004). Although tin streaming in southwest England resulted in the release of large volumes of sediment, it typically had a very minor impact on the sediment geochemistry as it was essentially remobilizing naturally generated and equilibrated sediments. In contrast, hard-rock mining, and the release of crushed ore tailings, was much more significant in terms of its impact on the environmental geochemistry. There are a number of mines on Dartmoor that lie within the catchment for the Teign Estuary that extracted iron and / or tin ores with the earliest recorded activity in the 16th Century (Figure 3, Table 1). In the mid to late 1800s the most significant mining activity was for lead and to a lesser

extent for zinc at mines such as Wheal Exmouth and Frankmills (Table 1). Manganese mineralisation was also worked between *c.* 1810 to 1875 (Beer and Scrivener, 1982) but there are no records that the disseminated Zn-Pb-Cu mineralisation was ever worked. Subsequently, mining for barite was much more significant and continued up until 1958 (Selwood *et al.*, 1984).
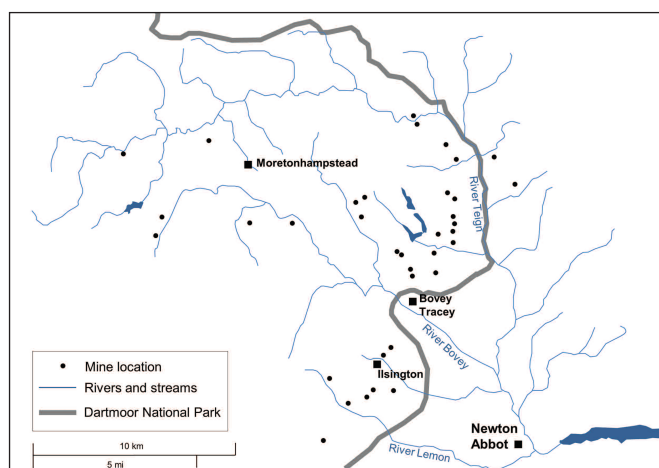
Figure 3. *Mine locations within the Teign Estuary catchment (after Dines, 1956; Beer et al. 1992).*

Mine name	Years active	Output
Smallacombe	1860s-1917	11,959 tonnes Fe ore 1874-9.
Haytor	16th Century - 1921	26,925 tonnes Fe ore 1858-61 and 1869-82.
Great Rock	1902 - 1969	400 tonnes / year Fe ore 1907 - 52.
Yarner	1850s-?	2337 Cu ore tonnes 1858-65.
Owlacombe & Stormsdown	1860s - 1912	354 tonnes Sn ore and 1483 tonnes arsenopyrite both 1854, 1863-6, 1887 & 1909.
Bridford	1855 - 1958	35.6 - 21,337 tonnes / year barite.
South Exmouth (Hennock)	1862 - ?	772 tonnes Pb ore from 1862 - 67, 0.033 tonnes Ag from 1862 - 67.
Wheal Exmouth	1851 - 1874	11,759 tonnes Pb ore, 1589 tonnes Zn ore, 3.345 tonnes Ag.
Frankmills	1857 - 1880	15,037 tonnes Pb ore, 7.045 tonnes silver.

Table 1. *Summary of the main mining operations located within the catchment area of the Teign Estuary. Data are summarised from Dines (1956) and Selwood et al. (1984).*

PREVIOUS WORK ON THE IMPACT OF MINING ON THE TEIGN ESTUARY

Previous work on the environmental impact of mining on the sediments within the Teign Estuary and catchment were carried out by John Merefield in the 1970s and 1980s. Merefield (1974) sampled stream sediments at a number of locations in the Teign Valley Mining District that were analysed by XRF to determine heavy metal concentrations. Merefield (1974) indicated that heavy metals present in the streams were influenced by lithology, weathering and mineralisation/contamination. Metals such as Ba, Pb and Zn were present at high levels due to mining contamination rather than natural weathering and erosion of bedrock mineralisation. The same study was repeated in the following decade (Merefield, 1987a) and the results showed an increase in concentrations of metals such as Ba, Pb and Zn in the river sediments, but little change in concentrations within those of the estuary. This increase in the river sediments was attributed to a higher input of the contaminants due to land change and disturbance of mine waste tips alongside insolubility of the metals, giving an increase and general downstream migration of the metals. Barite build-up in the Teign Estuary was examined by Merefield (1976, 1987b). High concentrations of barium in the rivers were thought to be due to mine contamination, with concentrations decreasing downstream towards the estuary (Merefield, 1976). A follow-up study ten years later showed an increase in the barium concentrations in the river again decreasing downstream (Merefield, 1987b). The British Geological Survey Mineral Reconnaissance Programme undertook two investigations in the Teign Valley for barite (Beer *et al.*, 1977) and base metals (Beer *et al.*, 1992) by carrying out analyses of water and stream sediments, along with geophysical surveys and diamond drilling. The base metal report sought to determine the style of mineralisation that had been mined in the area and to look for further mineralisation. Mineralisation was found to extend beyond the previously mined area in both investigations.

METHODOLOGY

Eight shallow cores ranging between 28 and 79 cm in length were manually recovered from accessible locations on the intertidal areas around the Teign Estuary (Figure 1c) using clean plastic tubes. The location of the cores was recorded both by a handheld GPS with an accuracy of ±10 m and on a base map. Recovered cores were labelled and bagged to prevent contamination. Subsequently, each core was extracted, photographed, logged and then subdivided into 5 cm intervals for geochemical and mineralogical analysis. Bulk dried samples for geochemical analysis were ground using a tungsten carbide Tema Disc Mill and prepared as boric jackets for XRF analysis. Samples were analysed using a Bruker S4 Pioneer X-Ray Fluorescence (XRF) instrument with a rhodium tube with the detection limit set at 10x the background (approximately 5 - 10 ppm). The mineralogy of all of the samples was determined using a Siemens D5000 X-Ray Diffractometer (XRD) with samples scanned at room temperature over 2Θ angles of 2° to 70° with a 0.02° step and 1 sec count per step. The XRD profile produced was smoothed and the JCPDS PDF-2 (2004) database was used to match peaks to known mineral markers. Samples from two of the cores (T4 and T6) were prepared as 30 mm resin impregnated polished blocks and analysed using automated SEM-EDS (QEMSCAN®) technology (Pirrie *et al.*, 2004; Pirrie *et al.*, 2009b). Data processing used the iDiscover software (v.4.2 SR1), and the mineral categories for the QEMSCAN® dataset are shown in Table 2.

RESULTS

Core descriptions

The sediments in all of the cores recovered showed a similar appearance, coarsening downwards through mud, silt and fine sand to gravel. Location T6 was the only core which showed clear colour variations from black to brown/grey at the top of the sediment profile to brown/red back to brown/grey at the base of the profile with all sections approximately 20 cm in length. Core T6 was unusual compared to the others, not only because of the colour variation, but also due to the presence of coarser grained intervals throughout the core, rather than just at the base. At this location a bed at a depth of 18 - 21 cm below the sediment surface comprised a poorly sorted mix of granules, silt and shell fragments. Bivalves, gastropods and bristle worms were found within the sediments at varying depths. The majority of the bivalve shells were disarticulated but articulated shells did occur towards the top of cores T1, T4 and T7. Foraminifera were observed in many of the samples prepared for analysis from cores T4 and T6. All of the sediments appeared homogenous with no evidence for any primary sedimentary structures.

Down core geochemistry

The down core variation in Cu, Pb, Zn and Ba is shown in Figure 4; and these geochemical data are summarised in Table 3. Cores T1, T2, T3, T4 and T5 from the western end of the estuary show the highest levels of Cu, Pb, Zn and Ba, whilst T6 collected from the northern bank of the estuary at Flow Point, the least. Cores T7 and T8 which were collected from the southern side of the estuary have intermediate levels of Cu, Pb, Zn and Ba. In all of the cores, the abundance of Cu, Pb, Zn and Ba is lowest at their base, increasing towards the surface, with the highest concentrations 5 - 15 cm below the present day sediment surface. Barium (Ba) is the dominant metal in the majority of the cores ranging from below detection limits up to 3360 ppm. Lead (Pb) varies from below detection to 2220 ppm. Zinc (Zn) and Cu concentrations are lower, varying from below detection limits to 887 ppm and 258 ppm respectively. Core T3 had double peaks of Ba and Pb and Core T8 has a double peak for Ba. The cores from the western part of the estuary also show a gap between the peak of Ba and the peaks for Zn, Pb and Cu. This gap between the peaks is not present in the cores in the eastern part of the estuary. The concentration of Cu, Zn, Pb and Ba appears to decrease both seaward and also southwards across the estuary, although the available data are too limited to truly assess the spatial distribution of the metals.

Down core mineralogy

The bulk sediment mineralogy of all of the samples was determined using XRD. Results from each sample were similar with major quartz, pyrite, albite, orthoclase and muscovite/illite being present in nearly all of the samples. Halite was also present, and typically decreased in abundance down core, whereas pyrite increased. Several of the samples showed the presence of calcite, which corresponded with the observed abundance of molluscan shells within the logged cores. Minor minerals present include kaolinite, chlorite, titanite, dolomite and hematite.

To determine the mineralogy further, QEMSCAN® analysis was carried out on all samples from cores T4 and T6. Both cores contained the same minerals, except galena and arsenopyrite, which were found in core T4 but not in core T6. Table 4 shows the QEMSCAN® mineralogical data for core T4.

	T1	T2	T3	T4	T5	T6	T7	T8
Cu	b.d. - 258	b.d. - 235	61 - 181	b.d. - 177	b.d. - 181	b.d. - 64	b.d. - 81	b.d. - 81
Zn	91 - 792	75 - 887	190 - 512	85 - 691	116 - 620	95 - 270	141 - 294	148 - 336
Ba	380 - 3210	b.d. - 3020	1000 - 2550	b.d. - 3360	b.d. - 3150	b.d. - 540	b.d. - 957	b.d. - 540
Pb	b.d. - 2220	b.d. - 2050	125 - 1360	b.d. - 1530	b.d. - 1290	b.d.	b.d. - 114	b.d. - 134

Table 2. Minimum and maximum concentrations of Cu, Zn, Ba and Pb (ppm) in each core analysed. b.d. - below detection.
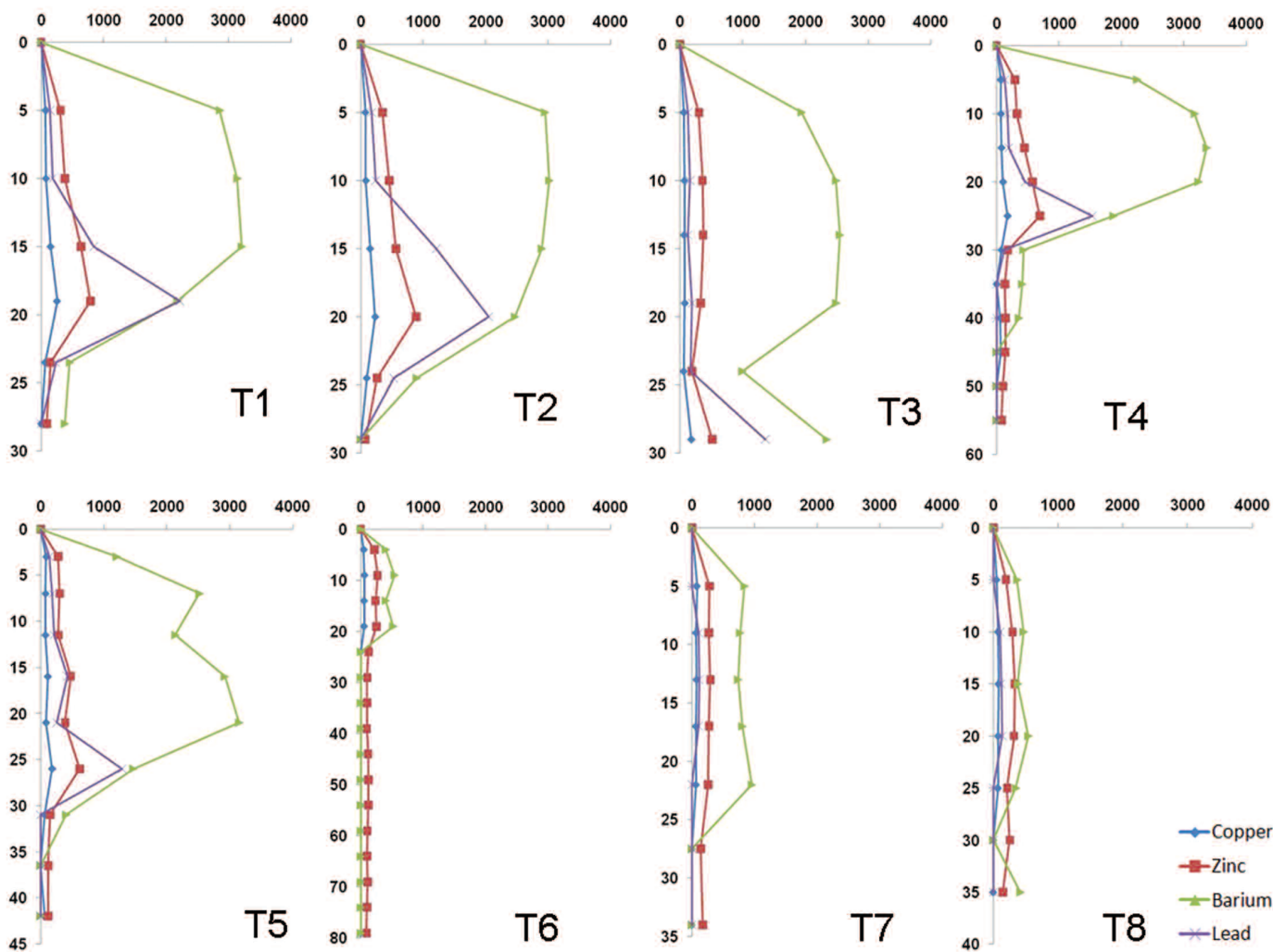
Figure 4. *Graphs showing down core variation in Cu, Zn, Ba and Pb (ppm). All cores show a peak in the top 20 cm, with cores T3 and T8 showing a double peak for Ba. Levels varied, with cores T1-T5 having the highest concentrations of metals. Pb was not detected in core T6. Note the different vertical scales on the graphs (in cm).*

This core had been split into 5 cm stratigraphic intervals, from the present day sediment surface to its base, with eleven samples analysed. The overall mineralogy is dominated by quartz, K-feldspar, plagioclase, muscovite/illite, biotite, tourmaline, kaolinite and chlorite. There are minor variations in overall mineral abundance with core depth (Figure 5a), with for example, decreasing abundance of kaolinite and chlorite, along with an increase in tourmaline, with depth. Sulphide and ore mineral abundance versus core depth is shown in Figure 5b. Pyrite is the most abundant sulphide mineral throughout (0.47-1.71%) and is interpreted to be predominantly diagenetic in origin. Barite is absent from the core samples below 30 cm depth, occurs in trace amounts in the 25-30 cm interval, and then increases in abundance in the sediment samples above that depth to approximately 0.2%. Other minerals present are rutile, ilmenite and Fe oxides, with an increase in rutile abundance in the shallower sediment samples. Chalcopyrite was either absent or had an abundance of less than 0.01%; sphalerite has a maximum abundance of 0.03%, whilst cassiterite forms no more than 0.01% of any of the samples analysed.

The QEMSCAN® mineralogical data for Core T6 are shown in Figure 6. The geochemical results show no significant increase in Cu, Pb, Zn or Ba throughout the core, and the mineralogical data support this, with chalcopyrite and sphalerite being either absent, or having an abundance of up to 0.01%. Barite is present in the uppermost five sediment samples (between 0 and 24 cm core depth) but only with an abundance of between 0.01 and 0.02%. The overall mineralogical profile for Core T6

is however, comparable with the trends shown for Core T4 (see Figures 5a and 6a). Both cores show similar sediment depth-related changes in the overall mineralogy, with a decrease in overall quartz abundance at a depth of 30-40 cm and then an increase in abundance towards the base of the core. Similarly kaolinite and chlorite abundance also decreased with core depth. The most significant difference between cores T4 and T6 is that calcite occurs as a minor component in all of the samples from Core T6 but is absent from Core T4. This may well reflect the position from which the cores were collected with Core T6 being from the most seaward location, also close to the main active channel, such that the increased calcite abundance may reflect the input of marine-derived biogenic calcite.

The QEMSCAN® mineralogical data for Core T4 is compared with the bulk geochemical XRF data in Figure 7, with the down core variation in the abundance of the ore minerals barite, galena and sphalerite plotted along with variations in the measured abundance of Ba, Pb and Zn. It should be noted that whilst the subsamples used for both the XRF and QEMSCAN® analysis were from the same respective stratigraphic interval, they were not homogenised and there may therefore be some variance between the analyses. The overall profile for the measured abundance of barite is directly comparable with the measured variation in Ba abundance throughout. There is a reasonable co-variance between sphalerite and Zn and galena and Pb, except within the 20-25 cm depth core interval, where the geochemical results show considerably more Pb and Zn than would be expected for the corresponding quantities of galena and sphalerite.

Mineral category	Mineral description
Pyrite	Fe Sulphides, pyrite/marcasite and pyrrhotite.
Chalcopyrite	Any phase with Cu, Fe, S, mainly chalcopyrite; other Cu Fe sulphides.
Sphalerite	Any phase with Zn, S, Fe, Mn.
Cassiterite	Any phase with Sn, O.
Rutile	Any phase with Ti,O such as rutlie, brookite and anatase .
Ilmenite	Any phase with Ti,Fe,O and Mn, includes titano-magnetite.
Titanite	Any phase with Ca, Ti, Si, O and minor Al, F, Fe.
Fe-oxides	Includes Fe-oxides such as hematite, magnetite, goethite limonite and carbonates.
Jarosite	Any phase with Fe, O, S, with or without K. May include oxidised pyrite/pyrrhotite .
Al-Fe oxides	Includes Al-oxides, Al-Fe oxides.
Slag phase	Man-made phase with variable composition of Al-Si-Fe-P-As-S.
Chrome spinel	Chrome spinels and chromite.
Mn phases	Mn Fe oxides and Mn silicates .
Barite	Any phase with Ba, S and O.
Galena	Any phase with Pb, S.
Arsenopyrite	Any phase with As, Fe, S.
Ce Phosphate	Ce,La,Th phosphates, such as monazite.
Xenotime	Any phase with Y, P, O.
Zircon	Any phase with Zr, Si and O.
Topaz	Any phase with Al, Si and F.
Quartz	Quartz and other silica minerals/polymorphs.
Carbonates	Calcite, dolomite, ankerite and magnesite. Includes recent bioclast debris.
Plagioclase	Plagioclase feldspars.
K-feldspar	K-feldspars.
Muscovite	Muscovite.
Biotite	Biotite and phlogopite.
Tourmaline	Schorl (Fe rich tourmaline).
Kaolinite	Any Al silicate such as kaolinite.
Gypsum	Any phase with Ca, S, O.
Apatite	Any phase with Ca,P, minor Al.
Chlorite	Chlorite and Nontronite .
Ca Mg Fe silicates	Any phase with Ca, Mg, Fe, Si, such as hornblende, diopside, tremolite, augite and actinolite.
Other silictaes	Any other silicate minerals.
Others	Any other phase not listed above.

Table 3. *QEMSCAN® mineral categories used in this study.*

Sample Code	T4R 19	T4R 20	T4R 21	T4R 22	T4R 23	T4R 24	T4R 25	T4R 26	T4R 27	T4R 28	T4R 29
Depth (cm below surface)	0 - 5	5 - 10	10 - 15	15 - 20	20 - 25	25 - 30	30 - 35	35 - 40	40 - 45	45 - 50	50 - 55
No. X-ray Analysis Points	2148597	2487850	2646083	2349876	2586609	2528972	2424620	2343276	2321338	2432220	2468370
Pyrite	0.47	0.54	0.98	1.43	0.50	0.09	0.71	1.37	1.71	1.26	1.21
Chalcopyrite	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.
Sphalerite	0.01	TR.	0.03	0.02	0.02	TR.	TR.	TR.	0.00	TR.	TR.
Cassiterite	TR.	0.01	TR.	0.01	0.01	TR.	TR.	TR.	0.01	TR.	TR.
Rutile	0.47	0.43	0.41	0.38	0.29	0.22	0.22	0.21	0.22	0.13	0.10
Ilmenite	0.22	0.18	0.17	0.17	0.16	0.16	0.14	0.12	0.11	0.08	0.06
Titanite	0.04	0.03	0.03	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe-Oxides	0.22	0.14	0.15	0.16	0.19	0.14	0.13	0.10	0.07	0.03	0.03
Jarosite	0.01	0.01	0.01	TR.	0.01	TR.	TR.	0.02	0.01	TR.	TR.
Al-Fe Oxides	0.01	0.01	0.03	0.01	TR.	TR.	0.01	TR.	TR.	TR.	TR.
Slag phase	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.
Chrome spinel	0.01	0.01	0.01	0.01	TR.	TR.	TR.	0.01	TR.	TR.	TR.
Mn phases	TR.	TR.	TR.	0.01	0.01	TR.	TR.	TR.	TR.	TR.	TR.
Barite	0.19	0.22	0.21	0.20	0.08	0.01	TR.	TR.	TR.	TR.	TR.
Galena	0.01	0.01	TR.	0.01	0.01	TR.	TR.	TR.	TR.	TR.	TR.
Arsenopyrite	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	0.00	0.00
Ce Phosphate	0.01	0.01	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.
Xenotime	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.
Zircon	0.08	0.07	0.06	0.06	0.04	0.04	0.04	0.04	0.04	0.02	0.02
Topaz	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
Quartz	34.88	30.64	28.19	30.02	26.58	23.54	26.34	29.26	29.45	36.71	41.31
Carbonates	0.81	0.67	0.63	1.21	0.73	0.26	0.21	0.24	0.20	0.06	0.16
Plagioclase	8.81	10.05	11.10	8.92	6.23	6.69	6.62	6.71	7.65	7.27	8.64
K-Feldspar	20.95	23.78	23.45	24.66	26.65	27.49	27.22	26.65	28.75	29.54	29.26
Muscovite	6.64	8.29	9.64	8.60	12.75	15.44	14.79	13.61	11.19	8.37	5.13
Biotite	2.83	2.79	3.14	3.48	5.70	6.53	5.75	5.12	4.68	3.54	2.81
Tourmaline	1.20	1.03	1.02	1.05	1.23	1.79	1.55	1.25	1.50	3.18	3.18
Kaolinite	10.10	11.39	11.82	9.56	7.38	7.19	6.90	6.67	6.93	5.18	4.70
Gypsum	0.29	0.23	0.19	0.13	0.09	0.02	0.03	0.05	0.08	0.03	0.04
Apatite	0.06	0.05	0.05	0.05	0.04	0.04	0.04	0.03	0.03	0.03	0.06
Chlorite	10.57	8.37	7.66	8.78	10.41	9.78	8.74	7.96	6.83	4.26	2.92
Ca Mg Fe silicates	0.21	0.22	0.20	0.22	0.15	0.09	0.08	0.08	0.09	0.05	0.06
Other silicates	0.83	0.75	0.77	0.77	0.67	0.46	0.44	0.44	0.38	0.21	0.25
Others	0.04	0.04	0.02	0.05	0.02	0.01	0.01	0.02	0.02	0.01	0.01

Table 4. *Modal mineralogy results for core T4 based on QEMSCAN® automated mineral analysis. TR - present at an abundance of less than 0.01%.*

Figure 5. QEMSCAN® mineralogical data for Core T4 showing the variation in mineralogy with core depth. (A) Major (>10%) and minor (1-10%) minerals modal abundance. (B) Trace (<1%) minerals including sulphides and barite). Sample T4R 19 is at the top of the present day sediment surface whilst sample T4R 29 is from the base.
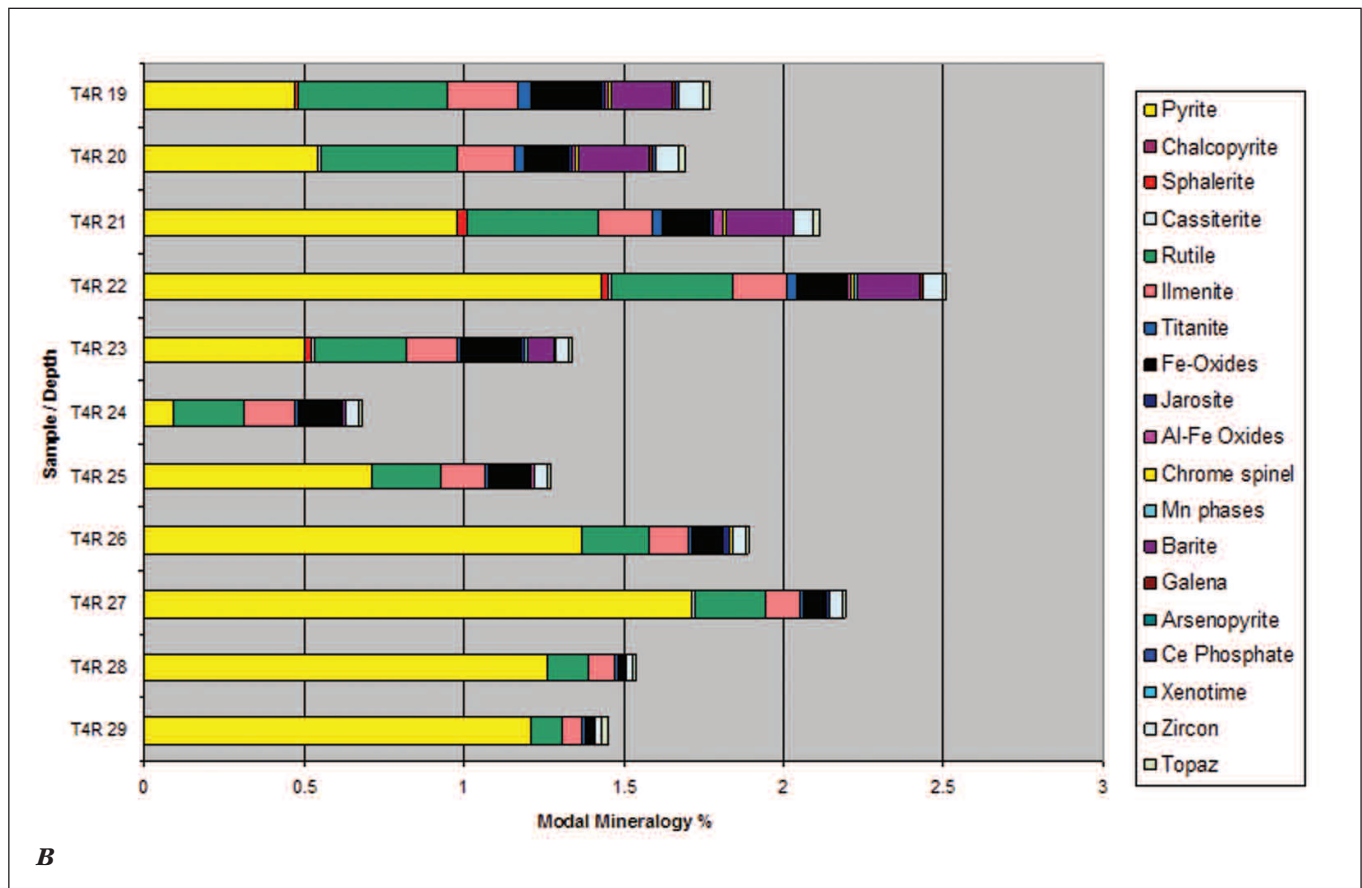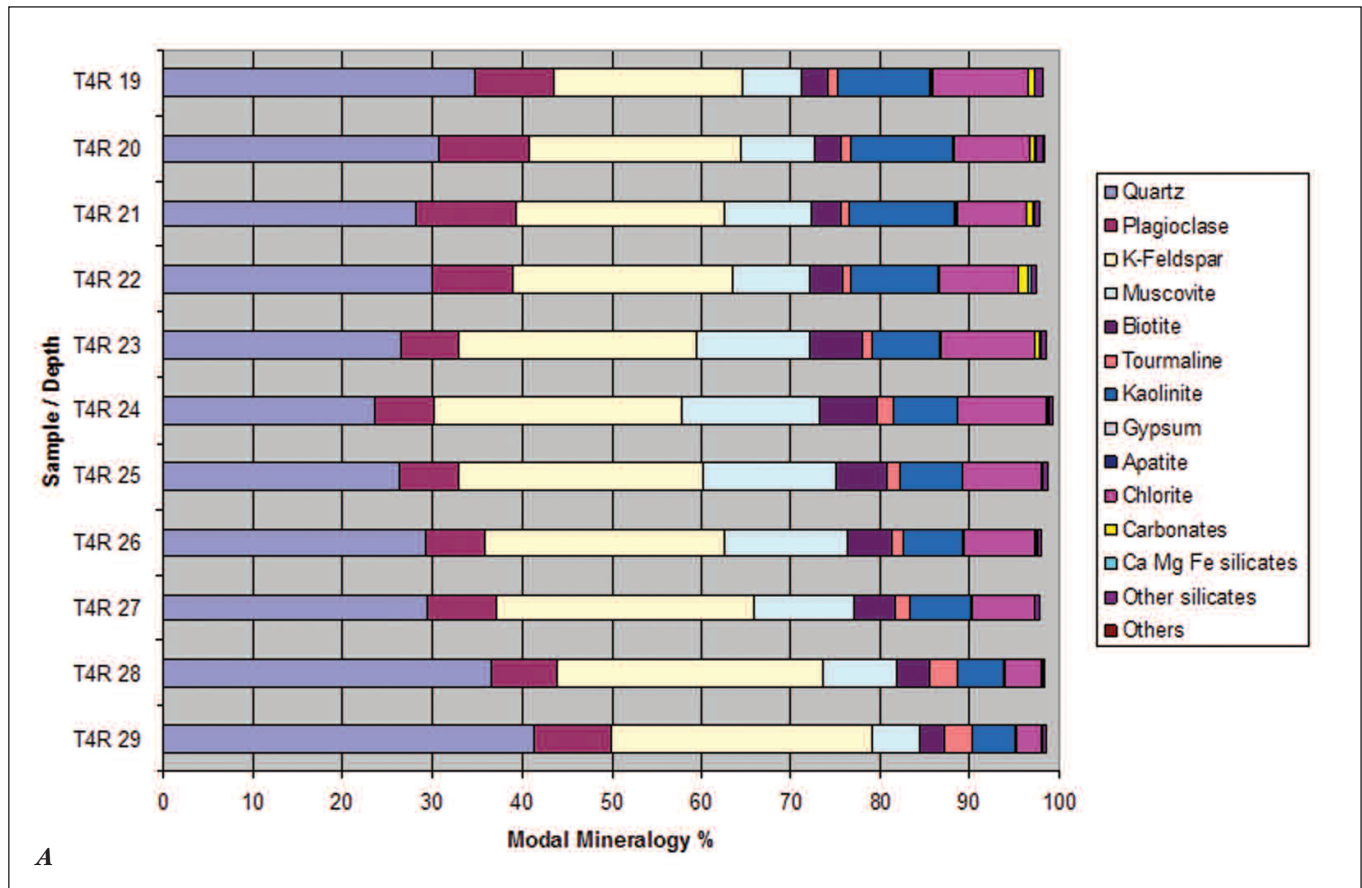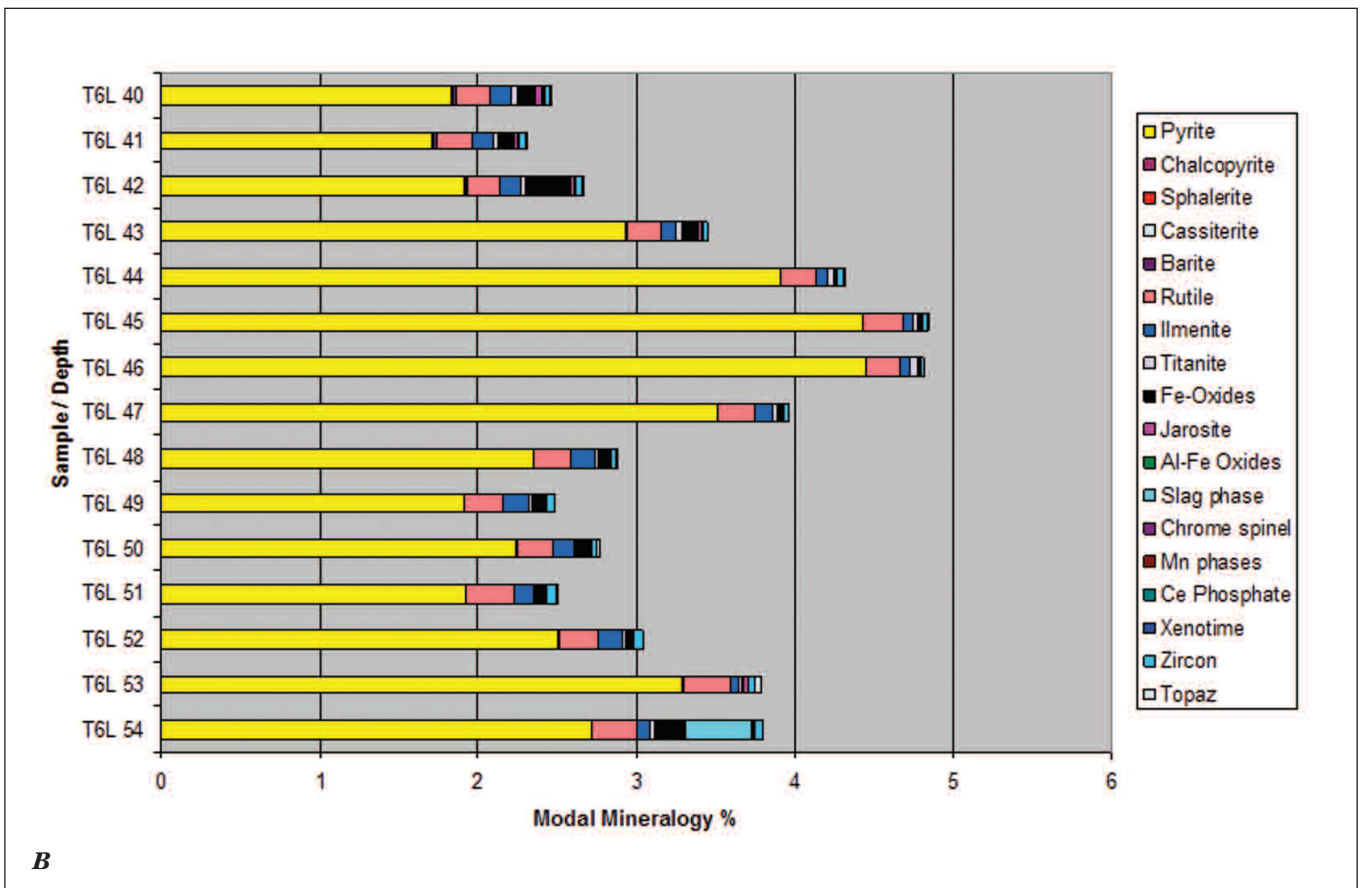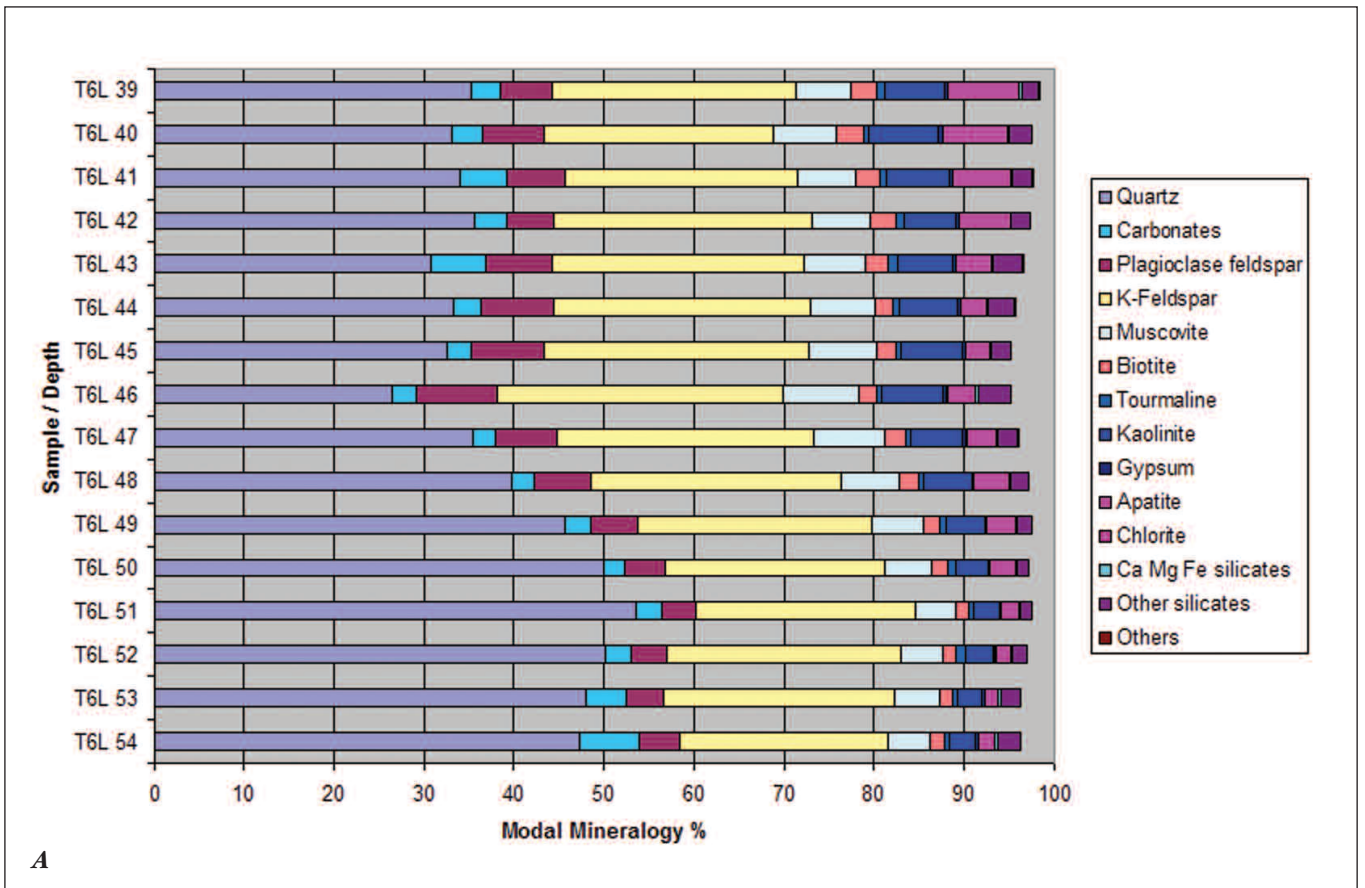
Figure 6. *QEMSCAN® mineralogical data for Core T6 showing the variation in mineralogy with core depth. (**A**) Major (>10%) and minor (1-10%) minerals modal abundance. (**B**) Trace (<1%) minerals including sulphides and barite). Sample T6L 39 is at the top of the present day sediment surface whilst sample T6L 54 is from the base.*
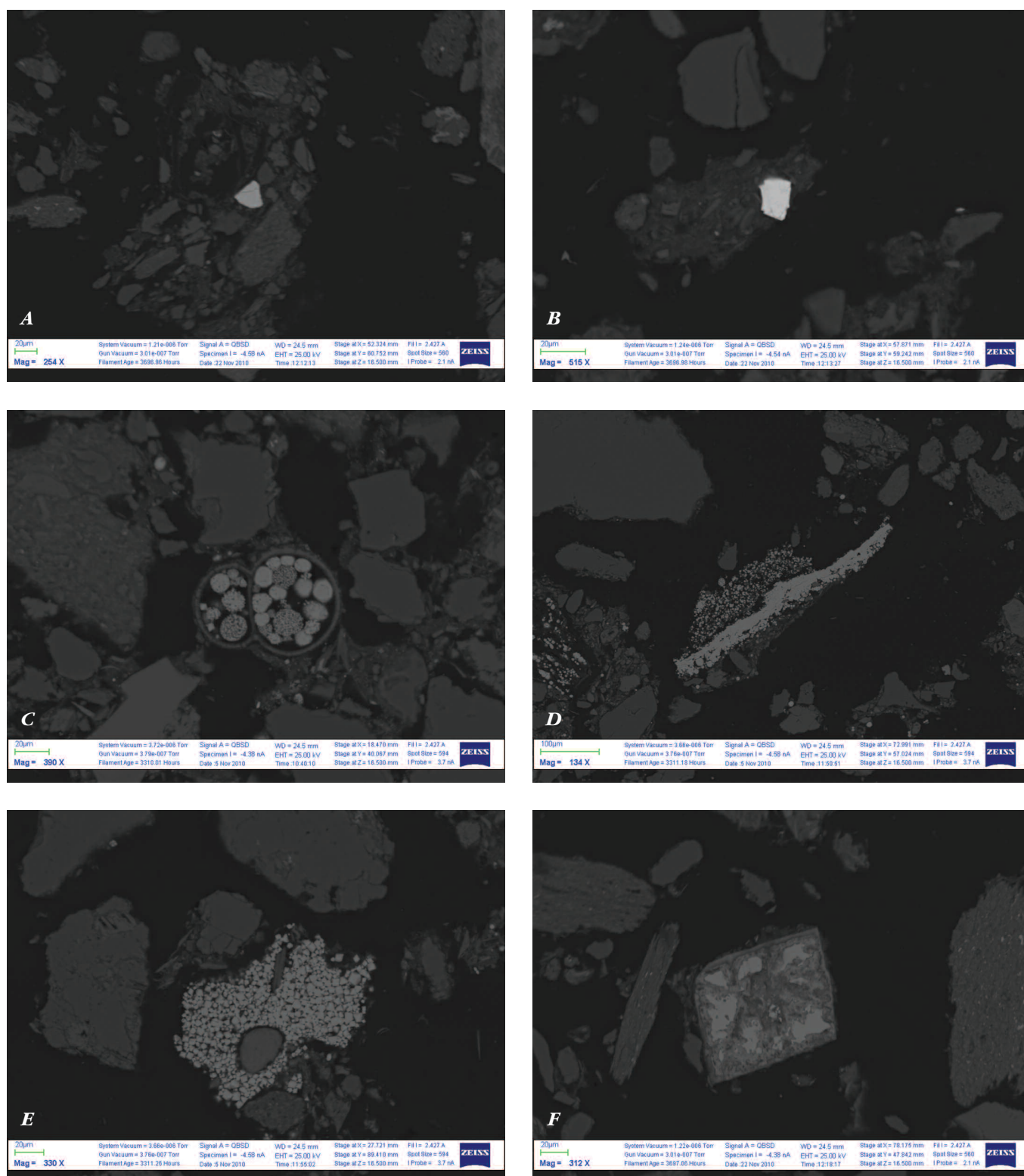
Sample Code	T6L 39	T6L 40	T6L 41	T6L 42	T6L 43	T6L 44	T6L 45	T6L 46	T6L 47	T6L 48	T6L 49	T6L 50	T6L 51	T6L 52	T6L 53	T6L 54
Depth (cm below surface)	0 – 4	4 – 9	9 – 14	14 – 19	19 – 24	24 – 29	29 – 34	34 – 39	39 – 44	44 – 49	49 – 54	54 – 59	59 – 64	64 – 69	69 – 74	74 - 79
No. X-ray Analysis Points	2195102	2174488	2147929	2310374	2445725	2399318	2283156	2614670	2448267	2552451	2441815	2527020	2475423	2631914	2586481	2347361
Pyrite	0.95	1.83	1.71	1.92	2.94	3.91	4.43	4.45	3.51	2.36	1.92	2.24	1.93	2.51	3.29	2.72
Chalcopyrite	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.
Sphalerite	0.01	0.01	0.01	0.01	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.
Cassiterite	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	0.00	TR.
Rutile	0.22	0.22	0.23	0.20	0.20	0.23	0.26	0.22	0.24	0.23	0.24	0.23	0.30	0.25	0.29	0.28
Ilmenite	0.13	0.13	0.13	0.13	0.10	0.07	0.06	0.06	0.11	0.15	0.17	0.13	0.13	0.15	0.06	0.08
Titanite	0.03	0.04	0.03	0.03	0.04	0.04	0.03	0.05	0.03	0.03	0.02	0.01	0.01	0.02	0.02	0.03
Fe-Oxides	0.13	0.12	0.10	0.29	0.10	0.01	0.01	0.02	0.04	0.06	0.09	0.09	0.04	0.04	0.01	0.20
Jarosite	0.03	0.04	0.02	0.02	0.02	0.01	0.01	TR.	TR.	TR.	TR.	0.01	0.01	0.01	0.03	TR.
Al-Fe Oxides	0.02	0.01	TR.	0.01	0.01	TR.	TR.	TR.	TR.	0.01	TR.	TR.	0.01	TR.	TR.	TR.
Slag phase	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	0.42
Chrome spinel	TR.	0.01	TR.	TR.	TR.	TR.	0.01	TR.	TR.	TR.	TR.	TR.	0.01	TR.	TR.	0.01
Mn phases	0.02	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	0.01	TR.	TR.	TR.	TR.	TR.	TR.
Barite	0.02	0.02	0.02	0.01	0.01	TR.	TR.	TR.	TR.	TR.	TR.	0.01	TR.	0.01	0.01	TR.
Ce Phosphate	TR.	TR.	0.01	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	0.01
Xenotime	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.	TR.
Zircon	0.03	0.03	0.04	0.04	0.03	0.04	0.03	0.02	0.03	0.03	0.05	0.04	0.06	0.05	0.04	0.05
Topaz	0.01	0.01	0.01	0.01	TR.	0.01	0.01	TR.	TR.	0.01	TR.	0.02	0.01	TR.	0.04	TR.
Quartz	35.09	33.12	34.00	35.50	30.66	33.27	32.42	26.51	35.28	39.85	45.72	49.93	53.63	50.23	48.00	47.28
Carbonates	3.50	3.22	5.32	3.83	6.04	2.99	2.79	2.57	2.73	2.55	2.83	2.32	2.84	2.73	4.57	6.59
Plagioclase feldspar	5.77	7.02	6.41	5.10	7.56	8.20	8.17	9.10	6.76	6.23	5.22	4.52	3.71	4.02	4.12	4.52
K-Feldspar	26.85	25.44	25.76	28.63	27.83	28.48	29.34	31.72	28.42	27.79	26.03	24.48	24.48	26.01	25.59	23.13
Muscovite	6.24	7.07	6.55	6.66	6.98	7.24	7.66	8.42	7.99	6.39	5.74	5.10	4.48	4.64	5.07	4.80
Biotite	2.85	2.97	2.70	2.82	2.46	2.03	2.15	2.12	2.35	2.14	1.75	1.94	1.47	1.56	1.34	1.48
Tourmaline	0.98	0.63	0.71	0.80	1.15	0.67	0.50	0.39	0.54	0.60	0.75	0.74	0.51	0.91	0.51	0.55
Kaolinite	6.58	7.62	6.86	5.71	6.05	6.42	6.73	6.91	5.79	5.32	4.35	3.67	2.78	3.15	2.83	2.83
Gypsum	0.31	0.52	0.40	0.35	0.37	0.36	0.44	0.38	0.36	0.22	0.14	0.19	0.17	0.21	0.32	0.36
Apatite	0.04	0.05	0.05	0.05	0.03	0.03	0.04	0.03	0.05	0.05	0.04	0.04	0.05	0.05	0.05	0.06
Chlorite	7.95	7.15	6.36	5.64	3.94	2.74	2.57	3.16	3.34	3.86	3.22	2.80	2.00	1.74	1.40	1.84
Ca Mg Fe silicates	0.20	0.19	0.22	0.14	0.21	0.22	0.22	0.24	0.19	0.18	0.16	0.15	0.17	0.18	0.23	0.27
Other silicates	1.91	2.43	2.16	2.03	3.22	2.97	2.06	3.57	2.16	1.90	1.52	1.30	1.19	1.51	2.17	2.47
Others	0.13	0.09	0.18	0.08	0.06	0.03	0.05	0.03	0.05	0.02	0.01	0.02	0.02	0.02	0.02	0.02

Table 5. *Modal mineralogy results for core T6 based on QEMSCAN® automated mineral analysis. TR - present at an abundance of less than 0.01%.*

Figure 7. *Down core variation in barite, galena and sphalerite abundance from the QEMSCAN® data set compared with the geochemical data for Ba, Pb and Zn.*

The polished blocks were also examined interactively using a Carl Zeiss Evo 50 Scanning Electron Microscope (SEM) in backscatter electron mode (BSE). Cassiterite was present in core T4 along with barite and galena. Barite and galena typically occurred as liberated particles less than 20 µm in size (Figure 8a, b) whereas cassiterite occurred as both liberated and locked particles. Framboidal pyrite was the most common diagenetic phase, occurring in every sample from the cores, and was observed infilling shelter porosity within bioclasts (Figure 8c) and replacing organics (Figure 8d) as well as disseminated throughout the sediment samples. Cubic pyrite was also observed in sample T6 54 (Figure 8e). Rarely, larger angular pyrite grains, showing alteration also occurred (Figure 8f); these grains could be detrital in origin.

COMPARISON WITH PREVIOUSLY PUBLISHED WORK

The previously published work on the sediments in the Teign Estuary and its catchment focussed on samples collected at the sediment surface (e.g. Merefield, 1976; 1987b). These data clearly demonstrate the spatial variation in the abundance of Ba throughout the catchment and estuary. The data presented in this paper are based on a series of albeit shallow (<1 m) cores, but they show that there is significant variation in not only Ba, but also Pb and Zn with depth within the sediment profile. There is therefore a difficulty in comparing the data in this study directly with the previous work as there is both a depth related (noted in this work), and a spatial change in the geochemistry as shown by Merefield (1976, 1987b).

The first published account of major and trace element anomalies in stream sediments in the Teign Valley Orefield does not extend down to the estuary (Merefield, 1974). The Mineral Reconnaissance Programme for base metals (Beer *et al.*, 1992) does not extend to the estuary either. Merefield (1987a) reported on heavy metals in the Teign Valley and the sampling did extend to the estuary allowing comparison of results. Levels of Pb in the current study were found to be much higher at 2220 ppm compared to *c.* 300 ppm in Merefield (1987a). Levels of Zn vary greatly from previously published results. The maximum level of Zn in this study is 887 ppm which is greater than the highest concentration of Zn found in the stream

Figure 8. *Scanning electron microscope images of detrital and diagenetic mineral grains. (**A**) Liberated grain of barite (Core T4 25-30 cm core depth). (**B**) Liberated grain of galena (Core T4 25-30 cm depth). (**C**) Framboidal pyrite infilling shelter porosity within a foraminifera (Core T6 44-49 cm depth). (**D**). Framboidal pyrite replacing organic matter (Core T6 74-79 cm depth). (**E**) Cubic diagenetic pyrite (Core T6 69-74 cm depth). (**F**) Alteration of a large angular pyrite grain (Core T4 25-30 cm depth).*

sediments of Merefield (1987a) and significantly greater than concentrations in the estuary which only reached *c.* 240 ppm. Merefield (1987a) only sampled the surface sediments which may account for the differences between the two studies, although spatial variability in the sediment geochemistry could be expected.

Compared to other estuaries in the south west, the Teign Estuary has lower concentrations of Cu, Sn, Zn and As than in the Hayle (Rollinson *et al.*, 2007) or Fal (Pirrie *et al.*, 2003) estuaries. There are also lower concentrations of Cu, Sn and As compared to the Fowey (Pirrie *et al.*, 2002a) and less Sn and As than the Camel (Pirrie *et al.*, 2000) estuaries. However, compared with all of these estuaries the Pb and Ba concentrations are higher in the Teign Estuary. The Gannel Estuary shows higher levels of Zn, Pb, As, Cu and Sn (Pirrie *et al.*, 2000) than the Teign Estuary but no Ba was reported.

INTERPRETATION

The geochemical and mineralogical data presented in this paper allow an interpretation of the impact of mining on the Teign Estuary. Clearly the bedrock within the catchment area is mineralised, and as such sediment supply derived from these areas would naturally be higher in Cu, Pb, Zn and Ba than sediment derived from unmineralised areas. However, if the observed mineralogy and geochemistry is the result of natural erosion and sediment supply from the mineralised areas, then unless there are significant changes in land use, there would be no reason to observe a down-core change in metal abundances.

In contrast, the cores reveal a characteristic down-core geochemical profile similar to that previously documented in the other estuaries of southwest England (Pirrie *et al.*, 1997; Pirrie *et al.*, 2002a, b; Pirrie *et al.*, 2003; Rollinson *et al.*, 2007). The abundance of Ba, Pb, Zn and Cu is typically lowest at the base of the cores. There is then an abrupt peak in Pb and Zn abundance, followed by a decrease in abundance towards the present day sediment surface reaching concentrations similar to those observed at the base of the cores. Post-dating the Pb-Zn peak is a peak in Ba, with elevated Ba concentrations being present above the Pb-Zn peak, but again falling abruptly towards the present day sediment surface. The two pulses in Pb-Zn and Ba are consistent with the record of mining activity within the estuary catchment, with barite not being mined regularly from Bridford mine until 1887 (Dines, 1956) whereas Pb, Cu and Zn were mined at a number of locations from 1836 onwards (Selwood *et al.*, 1984) but their production had ceased before the end of the Nineteenth Century. In contrast, barite production from the Bridford Barite Mine was significant in the first half of the Twentieth Century and did not cease until 1958. A pulse in silts with elevated levels of Pb and Zn are also observed in the River Teign terraces as observed by Thorndycraft *et al.* (2004).

The mineralogical data compliments the geochemical data, with liberated grains of barite observed in cores T4 and T6 and liberated grains of galena observed in Core T4. Liberated cassiterite was also observed in core T4 and T6 although Sn was not detected during the XRF analysis. The double peaks of metals down core could be explained by storm events resulting in an influx of sediments from rivers draining into the estuary or movement of sediments within the estuary or changes in mining in the estuary catchment. There appears to be a variance in the mining of barite, with 35.6 tonnes extracted in 1855 but no regular extraction commencing until 1887 (Dines, 1956). It is not clear how Pb/Zn mining varied.

Environmental impact

The elevated levels of Ba, Pb, Zn and Cu within the estuary sediments are only of concern environmentally if: (a) the elements are present in a mineralogical form which would enable them to be available for biological uptake, and (b) the proportion of Ba, Pb, Cu and Zn present in the bioavailable fraction, are present at a concentration where they may be harmful to plants or animals, or could potentially be bioaccumlated into the food chain. The QEMSCAN® data indicate that the majority of the metals are present as the primary ore minerals such as galena, sphalerite and barite. There is little evidence for either significant diagenetic alteration of the primary sulphide minerals, nor secondary diagenetic minerals other than framboidal pyrite. As the metals remain locked in the minerals, remediation would not be necessary whilst these minerals remain within the estuary sediment profile.

CONCLUSIONS

Sediments from the Teign Estuary retain a record of historical mining in the catchment with maximum values of 2220 ppm Pb, 887 ppm Zn, 3360 ppm Ba and 258 ppm Cu. The maximum

values are not found at the present day sediment surface; Ba peaks in abundance at approximately 10 - 20 cm depth and Pb and Zn abundance peaks at approximately 15 - 30 cm depth within the estuary sediment profile. This depth separation of the peaks in Ba and Pb/Zn abundance is consistent with mining records from the catchment; Ba was mined later than Pb-Zn and would therefore be recorded closer to the sediment surface in the estuarine sediments. Spatially, the highest metal concentrations occur on the western side of the estuary, closest to the river inputs, with the lowest concentrations found at location T6, the furthest seaward. Sampling points on the southern side of the estuary show intermediate concentrations. Heavy minerals in the samples are: barite, chalcopyrite, sphalerite, galena, hematite and zircon. There are minor amounts of cassiterite, xenotime, monazite, chromite, rutile, ilmenite and topaz. Framboidal pyrite is the only common diagenetic phase. There is a good correlation between the geochemistry and mineralogy, and little evidence for significant geochemical mobility of the metals, suggesting that if local environmental conditions remain broadly the same, then there is no likelihood of significant metal bioavailability and therefore no need to remediate the sediment, contaminated as a result of historic mining activity.

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