EARLY DIAGENETIC SULPHIDE MINERALS IN THE HAYLE ESTUARY, CORNWALL

D. PIRRIE, A.J. BEER AND G. S. CAMM

The Hayle Estuary, Cornwall, acted as an effective sediment trap for mine waste tailings and smelt waste released into the river catchments draining into the estuary. The stratigraphy of two 3 m cores recovered from Copperhouse Pool, Hayle comprises interbedded muds (interpreted as mine waste slimes) and sands in the upper 50 cm, passing down into sands composed predominantly of carbonate shell debris. Vacuum resin-impregnated core plugs sampled from more organic-rich intervals in the upper 150 cm of both cores were examined using scanning electron microscopy. Detrital heavy and opaque minerals include abundant grains of cassiterite, chalcopyrite, Fe oxides, arsenopyrite, sphalerite, polymetallic slags, detrital angular pyrite, ilmenite, monazite, zircon, wolframite, ?loellingite (As-Fe), galena, chalcocite/bornite and pyromorphite. Abundant diagenetic sulphide minerals also occur in these samples, and include Cu-Fe-(As) sulphides (probably chalcopyrite), As sulphides and pyrite. The precipitation of chalcopyrite occurred under reducing conditions with the reaction buffered by the Fe system. Possible copper concentrations in equilibrium with the authigenic chalcopyrite are so low that it is likely that there was an influx of more oxidising pore waters carrying higher levels of copper, which was then precipitated on reaching more reducing conditions. The precipitation of the As sulphides occurred from pore fluids with a high arsenic concentration under less reducing conditions than the chalcopyrite.

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INTRODUCTION

Floodplain and estuarine sediments in many mining districts preserve a record of mine waste contamination (e.g. Buckley and Winters, 1992; Dickinson *et al.,* 1996; Swennen *et al.,* 1994; Ridgway *et al.,* 1995; Hindel *et al.,* 1996). In many studies of such systems, whilst the sediment geochemistry is reported, the sediment mineralogy is commonly neglected. This is unfortunate as the sediment mineralogy not only provides clear provenance data in terms of the mine waste contaminants (e.g. Merefield, 1995; Pirrie *et al.,* 1997), but it also in part controls the geochemical stability of the sediments. The possibility of chemical remobilisation of the mine waste tailings is significant as it potentially limits the validity of chemostratigraphy in contaminated floodplain sediments (Hudson-Edwards *et al.,* 1998) and also exerts a control on the bioavailability of heavy metals. Whilst the geochemistry and detrital mineralogy of mine waste contamination in the estuaries of Cornwall is reasonably well known (e.g. the Fal Estuary, Pirrie *et al.,* 1997; Hughes, in press: the Fowey Estuary, Pirrie and Camm 1999: the Hayle Estuary, Yim, 1976), the diagenesis is less well documented and the only commonly described diagenetic mineral is framboidal pyrite. Diagenetic Cu minerals including bornite, chalcocite and chalcopyrite were reported by Thorne (1983) from the Fal Estuary at Restronguet Creek, an observation confirmed by Beer (1992). The aim of this paper is to describe the mineralogy of mine waste contaminated sediments from Copperhouse Pool, Hayle. Diagenetic Cu-Fe-(As) sulphides and As sulphides are described from these sediments, and the necessary sediment pore water chemistry, Eh and pH conditions for the growth of these phases is modelled.

PREVIOUS WORK

Mining and smelting history

From the 18th Century onwards, Hayle was an important site for Cu and Sn smelting, there was an important iron foundry established in 1779, and it was also an active port (Figure 1). The smelting industry of Hayle began in 1721 when a copper smelter was erected at Penpol. In 1758 another copper smelter with a production of about 12 tons of Cu per week was established at Ventonleague on the creek opposite Phillack Church; an area later to become known as Copperhouse (Figure 1). Blocks of black slag from this smelter were used for the construction of local houses and wharves. A tin smelter was active from c. 1816 to 1821, and then continued at the disused copper furnaces at Copperhouse. A new tin smelter started at Mellanear in 1837 finally closing in 1908. Other earlier smelters (presumably initially blowing houses) also once operated in the area such as at Angarrick with smelting from 1704 to 1881 and at Rose-an-Grouse from c.1715 to 1883. Between 1833 and 1838 Hayle was also a coinage town for tin. This industrial activity resulted in the supply of a large volume of mine waste sediment and significant contamination of the estuary sediments around, and in, Copperhouse Pool. In addition to the input of mine waste, the estuary geomorphology has also been modified, with, in the late 1700s, the construction of a canal from the eastern part of Merchant Curnow's Quay to Copperhouse with a tidal pool with sluicing facilities to keep the channel to the sea open completed in 1834. This management of the tidal waterways at Hayle was due to its importance as an industrial port with coal transported from, and copper ore shipped to, Wales.

Mining

The rivers entering both Copperhouse Pool and Hayle Estuary drain old mining areas for Sn, Cu, Zn and Pb (see Figure 1). The immediate area around Hayle is known primarily as a copper mining district (e.g. Wheal Alfred Cu/Pb Mine) and the tailings were released directly into the local streams and rivers. Both Copperhouse Pool and the main estuary have acted as effective heavy mineral sediment traps resulting in rapid deposition. The earliest sedimentation related to mining would have been due to upstream Sn placer mining pre-1700, followed by hardrock mining initially for copper and then tin.

Previous geochemical studies on the Hayle Estuary

Hosking and Ong (1963-64) documented the distribution of Sn in the sediments on Gwithian and Hayle beach and recognised that mine waste tailings had been transported to this area via the Red River. Although the Hayle River drains a significant mining district, it did not supply much sediment to the beach as the estuary acted as an efficient sediment trap. Yim (1976) recovered three cores from the
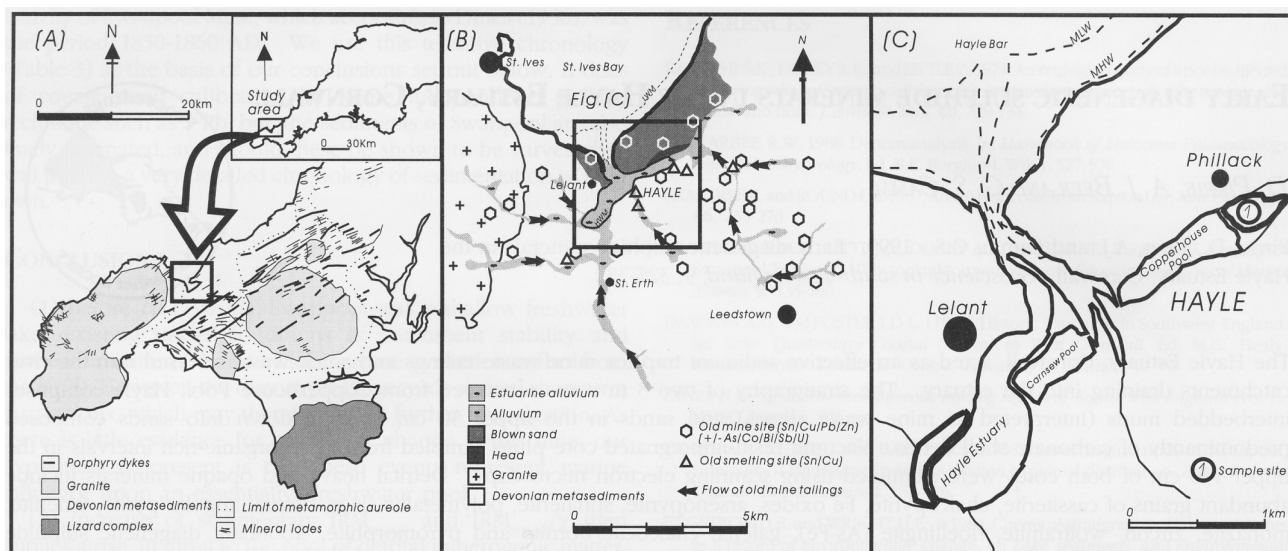
Figure 1. *(a) Sketch geological map showing the location of the Hayle Estuary. (b) Sketch of the Hayle Estuary showing the location of mine sites and smelting sites within the catchment area. (c) Detailed location map showing the position of the two coring sites at the eastern side of Copperhouse Pool.*

Hayle Estuary, Core 1 of which was from Copperhouse Pool. This core comprised alternating clays and sands and geochemical analyses gave maximum concentrations of Sn (~10,000 ppm), As (4080 ppm), Cu (2600 ppm), Fe (96,000 ppm) and Pb (850 ppm) all of which occurred in an interval of alternating black and reddish brown clays at 61122 cm depth (Yim, 1976). This interval was interpreted as due to mine waste contamination in the mid 19th Century. The stratigraphy and micropalaeontology of five cores from Copperhouse was described by Healy (1996). Organic rich deposits in contact with the bedrock at a depth of 1.59 m below O.D. were dated using ^{14}C at 4520± 50 BP. His palaeoecological studies indicated that the cores record a gradual transition from freshwater conditions to wetter, marine-brackish water conditions (Healy, 1996). Healy (1995) examined the geochemistry of the upper 80 cm of a core from Copperhouse, and reported Cu values of 3000 to 4500 ppm, Fe of 20,000 to 30,000 ppm but peaking at 70,000-80,000 ppm in silty clays approximately 40-50 cm below the sediment surface, Pb between 1000 and 3000 ppm, Sn values of less than 1000 ppm throughout, and variable values for Zn but up to 3100 ppm. Merefield (1993) examined the geochemistry of sediments in the River Hayle and its tributaries, and a sample collected from Copperhouse gave 3000 ppm Sn, 483 ppm Pb, 1004 ppm Zn, 1057 ppm As and 1650 ppm Cu.

Diagenetic sulphides within the estuary sediments.

Although framboidal pyrite is a common and abundant phase throughout the estuary sediments (e.g. Pirrie et al., 1997; Hughes, in press), diagenetic Cu sulphides from Cornish estuaries have only previously been reported from Restronguet Creek in the Fal Estuary by Thorne (1983) and Beer (1992). Thorne (1983) described diagenetic chalcopyrite and bornite with garland and atoll textures; their distribution was considered to be due to localised metal supply and sediment permeability and their textures were considered to be indicative of the replacement of original detrital chalcopyrite grains. The chemical conditions necessary for precipitation of authigenic copper sulphide minerals were studied by Beer (1992) and may be due to either the alteration and remobilisation of detrital sulphide grains or to precipitation from pore waters with elevated metal concentrations.

METHODS

In this study two 3 m cores were recovered from Copperhouse Pool, Hayle using a percussion corer.
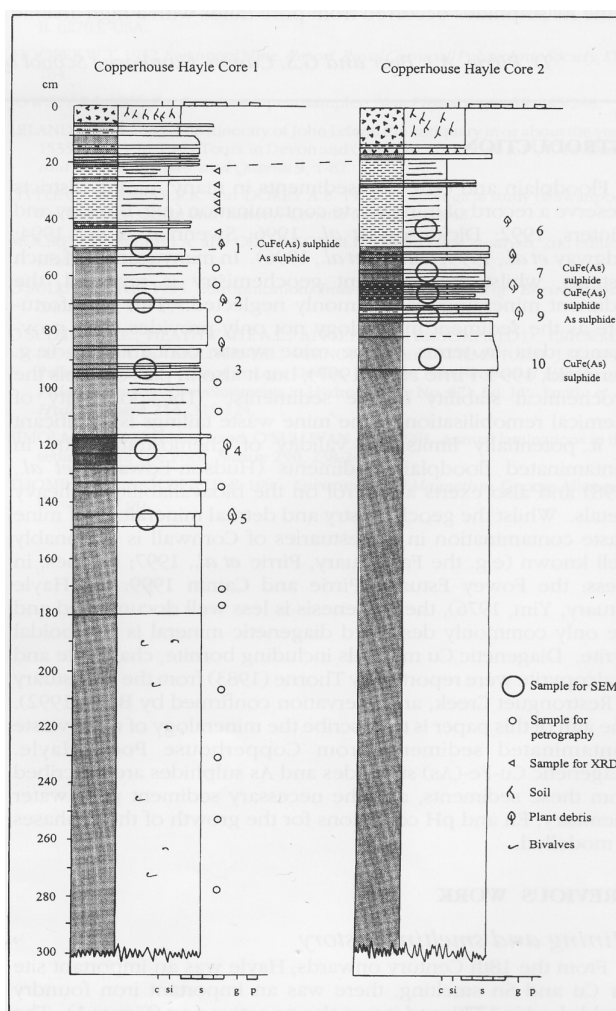

Figure 2. *Graphic sedimentary logs for cores 1 and 2 from Copperhouse. The position of the samples examined by SEM, XRD and standard thin section petrography are indicated. In addition, the distribution of the diagenetic sulphide minerals identified are shown.*
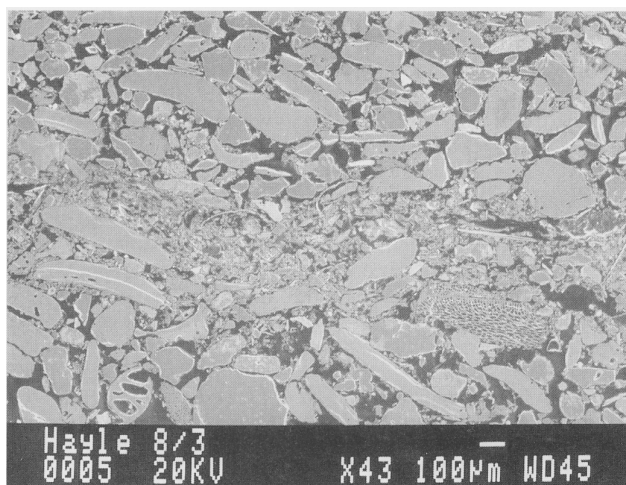
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Figure 3. *Scanning electron microscope image of Sample 8 from Core 2. Note that the primary grain size lamination within the sediment is retained. The majority of the grains are rounded fragments of molluscan shell debris.*

Core 1 was from SW 567 382 whilst Core 2 was from SW 568 382 (Figure 1). Following core description and photography, ten 3 cm diameter core plugs were carefully collected from organic-rich intervals with minimal sediment disturbance. These core plugs were resin-impregnated under vacuum and prepared as polished blocks and examined using a JEOL scanning electron microscope (SEM) with a LINK 10,000 EDS analyser. Eleven samples from Core 1 were prepared as standard covered thin sections for petrographic description and 6 bulk sediment samples were examined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer using CuKα. Sample locations for SEM, XRD and standard petrography are shown on Figure 2.

CORE SEDIMENTOLOGY

The upper part of both cores comprises an active soil zone in the top 10-15 cm, which overlies an interval of fine to medium grained sands, interbedded with orange-brown silty-sands (Figure 2). In Core 1, between 22 cm and 51 cm there is an interval dominated by rusty red-brown finely laminated (mm-scale) clays and silty-clays, with rare 0.5-1.0 cm thick fine to medium grained sand laminae. This same stratigraphic unit occurs in Core 2 between 18 cm and 49 cm. The dominant red-brown colouration is interrupted by dark grey, more organic-rich clays at 50-51 cm in Core 1 and at 44-45 cm in Core 2. It is possible that this clay-dominated interval corresponds to the black and reddish-brown clays described by Yim (1976) as having the highest metal values in the core he recovered from Copperhouse. In Core 1, the clay-dominated interval is underlain by 45 cm of interbedded fine to medium grained thick-bedded, parallel laminated sands and thin, typically 1-1.5 cm thick dark charcoal grey, organic-rich silty clays. In Core 2, a similar interval occurs for 27 cm, with thinly bedded fine to medium grained sands and, 1-2 cm thick organic-rich charcoal grey silty clays. Below 96 cm in Core 1, and below 75 cm in Core 2, the stratigraphy is dominantly fine to medium grained, well sorted sands. The sands commonly show poorly defined parallel lamination (Figure 3).

DETRITAL MINERALOGY

Based on thin section examination of samples from Core 1, the sands between 55 cm and 110 cm typically comprise 60-65% comminuted skeletal carbonate grains (mostly bivalves, foraminifera, bryozoans and calcareous algae) (see also Merefield, 1982). Silicate grains form 30-35% of the sands, and comprise mono- and poly-crystalline quartz, lithic plutonic and lithic sedimentary grains, chlorite,
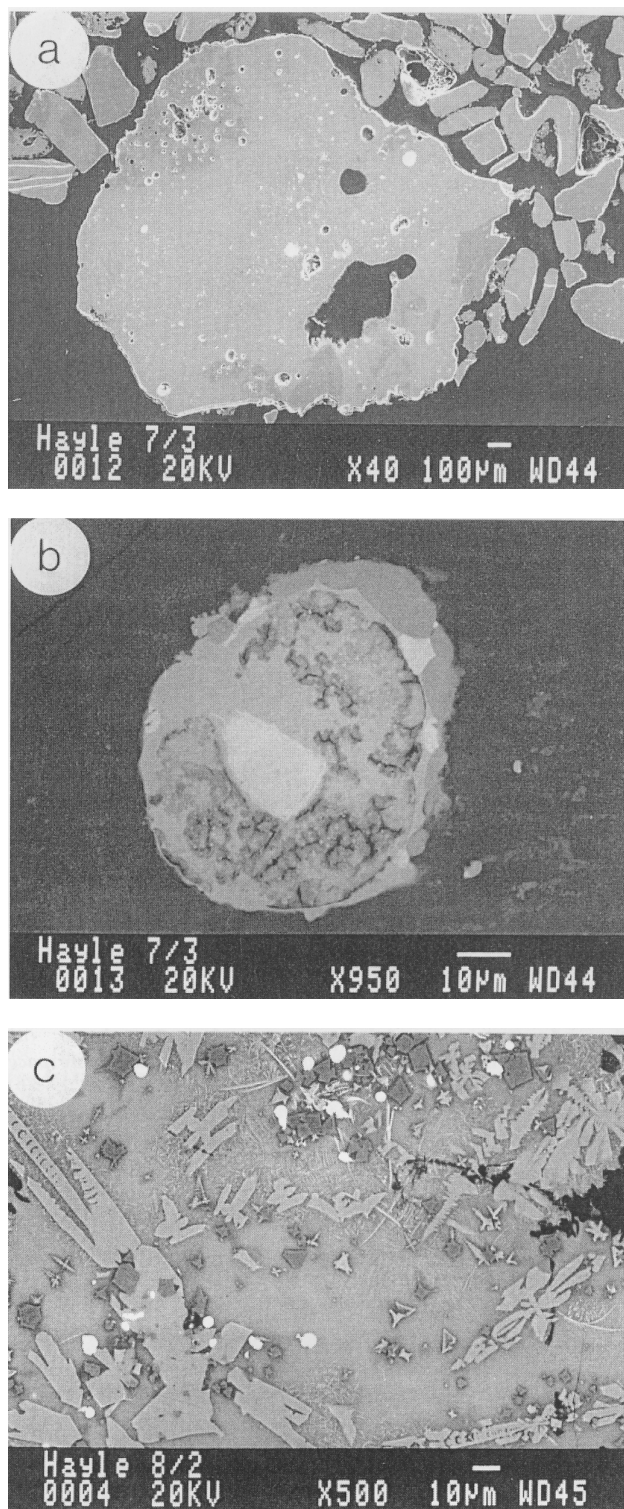

Figure 4. *SEM images of smelt products from Copperhouse. (a) Large smelt waste grain; the groundmass is predominantly Si-Al-Mg, with bright blebs of Cu-Sn alloy and Fe. (b) Close up of the polymetallic smelted metal blebs within this smelt product. (a) and (b) both Sample 7, Core 2. (c) Backscattered electron image (BEI) of a complex smelt product with a Si-Al groundmass, blebs of Sn metal (bright) and angular dendritic zones of Fe-Si.*

tourmaline, muscovite, biotite and hornblende. Opaque grains form 5 to 10% of the sand fraction (see below). Samples below 110 cm are carbonate-rich and silicate/opaque-poor (cf. Merefield, 1982). In thin section, 85-90% of the grains are rounded comminuted skeletal
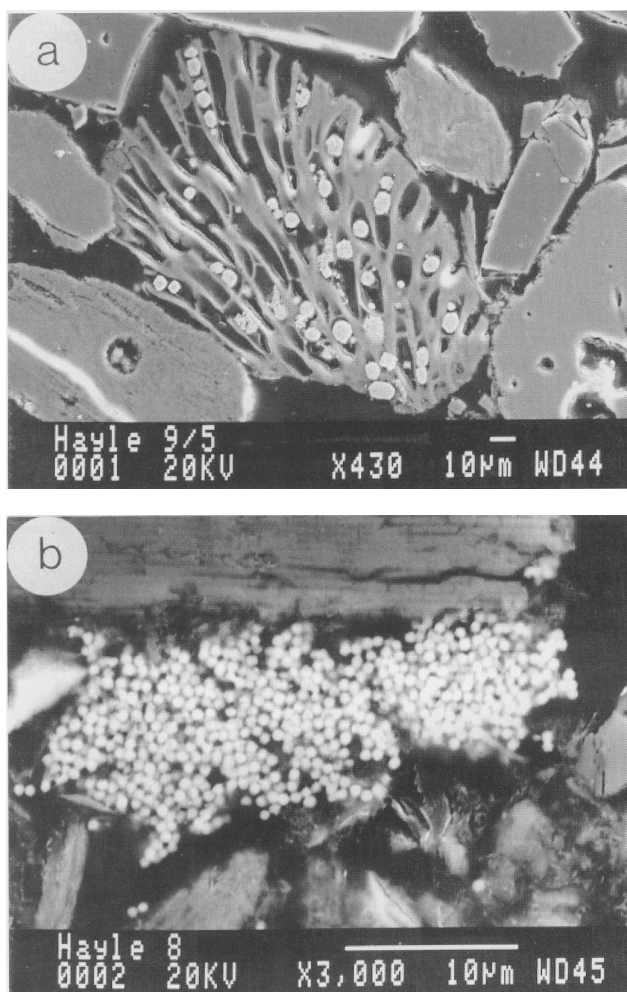
Figure 5. *SEM images of diagenetic pyrite from Copperhouse. (a) Framboidal pyrite (bright areas) precipitated within available pore space in a calcareous skeletal carbonate grain. Sample 9, Core 2. (b) Disseminated pyrite within the fine grained sediment matrix. Sample 8, Core 2.*

90% of the grains are rounded comminuted skeletal carbonate grains (Figure 3). Silicate minerals form 10-15% and comprise mono- and poly-crystalline quartz, muscovite, tourmaline, plagioclase, lithic sedimentary and rare lithic plutonic grains, quartz-tourmaline aggregates and rare angular detrital opaques (~1%). Diagenetic framboidal pyrite occurs throughout this lower interval.

The resin-impregnated polished blocks retain primary lamination defined by grain size variation (Figure 3). The dominant opaque and heavy mineral grains observed under SEM are (in order of abundance), cassiterite, chalcopyrite, Fe oxides, arsenopyrite, sphalerite, polymetallic slags, detrital angular pyrite, ilmenite, monazite, zircon, wolframite, ?loellingite (As-Fe), galena, chalcocite/bornite and pyromorphite. Pyromorphite is a relatively rare mineral; it is however, reported from Wheal Alfred mine. There are no consistent variations in opaque/heavy mineral abundance down core, nor between cores 1 and 2. Cassiterite and chalcopyrite are the dominant heavy minerals in all of the samples studied. Most of the opaque/heavy mineral grains are 10 to 25 µm in size. The chalcopyrite grains are however, coarser grained ranging from 5-80 µm, with a median of 30-35 µm and the cassiterite is typically rather finer grained (median 10-15 µm) often occurring locked within a silicate host. The sulphide minerals most commonly occur as liberated, angular grains, and usually show no evidence for alteration, other than reaction rims around the edge of detrital chalcopyrite grains. Smelted slags occur in every sample; they range in grain size

from 10 to 1800 µm (Figure 4a), and are usually coarser grained than the carbonate sand grains. The smelt products typically have a Si-Al-Mg groundmass, with blebs of Sn, Cu or Fe metals or alloys (Figure 4b) and may show complex dendritic textures (Figure 4c). In comparison with heavy mineral assemblages from either the Fal Estuary (Pirrie et al., 1997) or the Fowey Estuary (Pirrie and Camm, 1999) the Hayle samples contain a larger proportion of sulphide mineral species (e.g. chalcopyrite, arsenopyrite, sphalerite) and smelt waste. The mineralogy of 6 samples of the red-brown finely laminated clays and silty clays from between 22 cm and 51 cm in Core 1 were examined using XRD and comprise quartz, chlorite, mica and cassiterite.

The composition of the heavy mineral fraction within the samples from Copperhouse is entirely consistent with derivation from mine waste tailings and smelt waste. These mining-related grains become a major component of the sediments in the upper 110 cm of the cores diluting the background carbonate sediment supply. The only interval where carbonate grains are lacking is the clay-dominated interval interpreted to represent mine waste slimes. A similar stratigraphic unit is described by both Yim (1976) and Healy (1995, 1996) and corresponds with the highest metal values in their geochemical analyses. Yim (1976) suggested that the deposition of the sands overlying this clay was related to a major storm event in 1869, and that the age of the clay interval corresponded with a peak in mining in the mid part of the 19th Century.

DIAGENETIC MINERALOGY

Diagenetic sulphide minerals occur in eight samples examined under SEM. Their distribution is shown in Figure 2. No diagenetic sulphide minerals have been observed in samples 4 or 5, both of which are coarser grained and contain less opaque heavy minerals than the other samples. Three main diagenetic sulphide minerals are observed: pyrite; a Cu-Fe sulphide that also contains trace levels of As: this phase is probably chalcopyrite (see below); and AsS (either realgar (As_2S_2) or orpiment (As_2S_3)). Pyrite occurs in all eight samples usually as framboidal crystal aggregates, commonly precipitated within shell fragments (Figure 5a) and woody plant debris, but also as more disseminated pyrite (Figure 5b). Diagenetic Cu-Fe-(As) sulphides occur in four of the samples studied, and are found predominantly within the upper part of both cores, associated with the more organic-rich dark charcoal grey clays. They occur as relatively amorphous masses clearly enveloping detrital grains (Figures 6a, 6b) or as botryoidal masses disseminated within the sediment (Figure 6c). One grain with a clearly framboidal texture is chalcopyrite (Figure 6d). These sulphides are ~10 µm in size and occur most commonly within the finer-grained intervals. Arsenic sulphides occur in samples 1 and 9 and have a fringing, garland-type texture (Figure 7).

Although framboidal pyrite has been described frequently from estuarine sediments in Cornwall, diagenetic copper minerals have only previously been described from Restronguet Creek on the Fal Estuary (Thorne, 1983; Beer, 1992). The diagenetic Cu sulphides at Hayle are larger and more abundant than those previously described and we are not aware of any previous reports of diagenetic As sulphides within the Cornish estuaries. Diagenetic sulphides appear to be more common at Hayle than in the Fal Estuary. This may in part be due to the increased supply of detrital sulphides at Hayle when compared with either the Fal or the Fowey estuaries. However, it is important to note that careful sample preparation is critical for the preservation of these delicate authigenic sulphides, and they may be more abundant in Cornish estuaries than previously thought.

INTERPRETATION

Chemical conditions necessary to form diagenetic sulphides

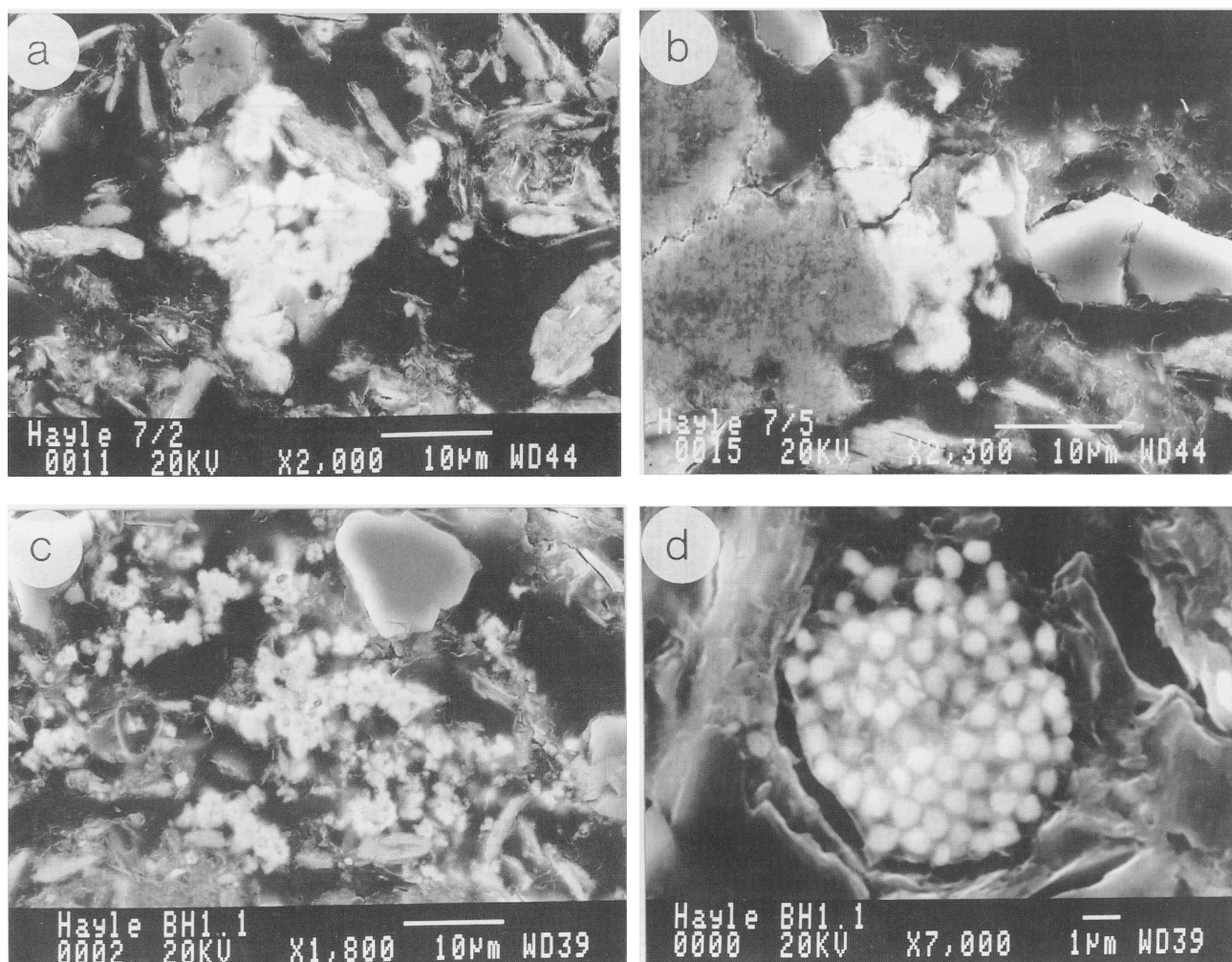The chemical conditions necessary for the precipitation of

Figure 6. SEM images of diagenetic Cu-Fe-(As) sulphides from Copperhouse. (a, b) Amorphous Cu-Fe-(As) sulphides clearly enveloping detrital silicate grains, Sample 7, Core 2. (c) Disseminated botryoidal masses of Cu-Fe-(As) sulphide precipitated within fine grained sediment matrix, Sample 1, Core 1. (d) Diagenetic framboidal grain composed of chalcopyrite; note that there is no evidence for alteration of pyrite to chalcopyrite. Sample 1, Core 1.

authigenic copper sulphide minerals in the Fal Estuary were studied by Beer (1992) using a simple computer model based on the Nernst equation:

For a reversible chemical reaction:

$$aA + bB + eH_2O <=> cC + dD + hH^+ + ne^-$$
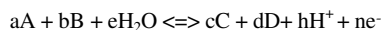
the oxidation potential (Eh) is given by:

$$eh = E^\circ + \frac{0.059}{n} \log_{10} \frac{[C]^c[D]^d[H^+]^h}{[A]^a[B]^b} \text{ - the NERNST EQUATION}$$

where:

E° is the standard electrode potential for the reaction
[A],[B] etc. represent the concentration of compound A, B, etc in

solution a, b etc. represent the molar proportions of the compounds involved in the reaction

The Nernst equation can be rearranged so that it represents the equation of the equilibrium conditions for a particular chemical reaction with respect to quantities such as pH, the Eh of a geochemical system, and ions in solution. This allows chemical stability diagrams to be plotted for minerals and ions within a particular chemical system against a variety of parameters. In this study, the parameters chosen

are dissolved sulphur concentration, Eh and pH. As both diagenetic copper and arsenic sulphide minerals are observed at Copperhouse, diagrams have been plotted for both the Cu-Fe-S-O-H and the As-Fe-S-O-H geochemical systems.
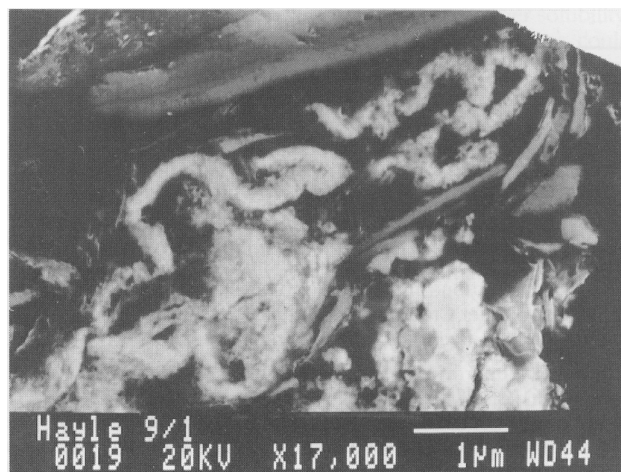

Figure 7. SEM image of diagenetic As sulphide farrowed) showing garland textures. Sample 9, Core 2.
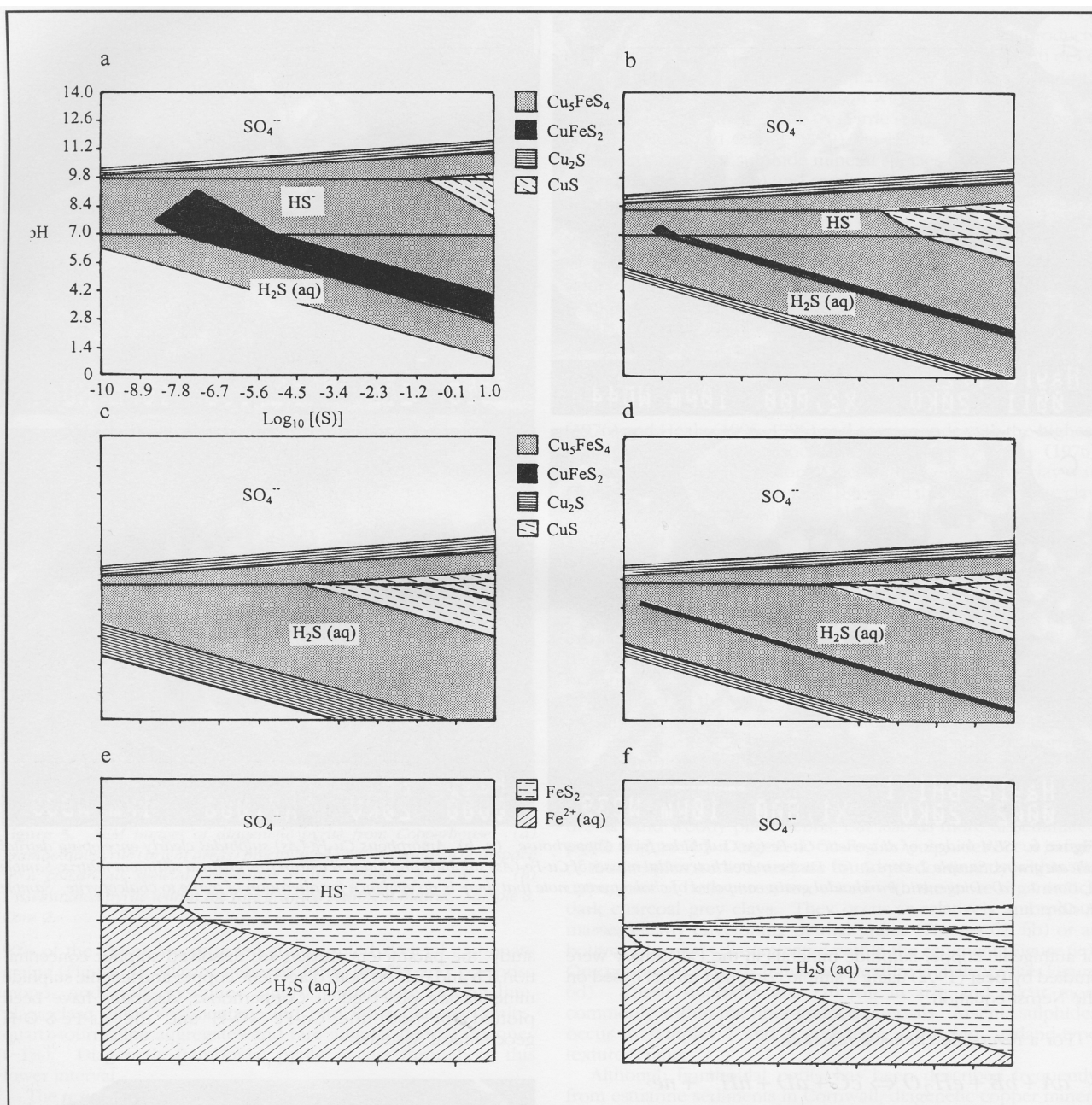
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Figure 8. a-d. Stability of copper sulphide minerals with respect to pH and dissolved sulphur concentrations for a range of oxidation potentials (Eh) and dissolved metal concentrations. (a) Eh = -0.4v, metal concentration 10^{-6} m, (b) Eh = -0.3v, metal concentration 10^{-6} m, (c) Eh = -0.2v, metal concentration 10^{-6} M, (d) Eh = -0.2v, metal concentration 10^{-3} M. e-f. Stability of dissolved iron (II) and pyrite with respect to pH and dissolved sulphur concentrations. (e) Eh = -.04v, $[Fe^{2+}] = 10^{-6}$ m, (f) Eh = -0.2v, $[Fe^{2+}] = 10^{-3}$ M.

Thermodynamic data for the calculation of these diagrams are taken from Garrels and Christ (1965) and Kubaschewski and Alcock (1983). As data regarding the concentrations of chemical species in solution in the samples taken is not available, limits to these concentrations are assumed to be similar to those recorded from Restronguet Creek by Beer (1992), with Cu concentrations of 11-65 ppb (1.6×10^{-7} to 10^{-6} M) in the interstitial pore waters.

Diagenetic copper minerals

Although the authigenic copper minerals observed in the Hayle Estuary sediments contain arsenic, they have not been analysed quantitatively. The yellow colour of the polished minerals under reflected light, together with analyses of similar minerals observed in

Restronguet Creek (where the arsenic content of the diagenetic copper minerals was typically around 4% - Beer, 1992) suggests that arsenic is most likely present as an impurity in the copper minerals, rather than representing a copper-arsenic-sulphide phase such as enargite. For these reasons the minerals are treated in this section as copper-ironsulphide minerals only.

Stability diagrams have been plotted for a range of likely conditions (Garrels and Christ, 1965) in reducing sediments for the Cu-Fe-S-O-H system (Figure 8a-d). These indicate that diagenetic copper minerals are stable under a range of reducing (Eh = -0.2v to Eh = -0.4v) and generally acidic conditions, with the mineral bornite (Cu_5FeS_4) having the widest stability range. In contrast, chalcopyrite has a much lower stability range, and at an Eh value of -0.2v is not stable with a dissolved metal ion concentration of 10^{-6}M (the
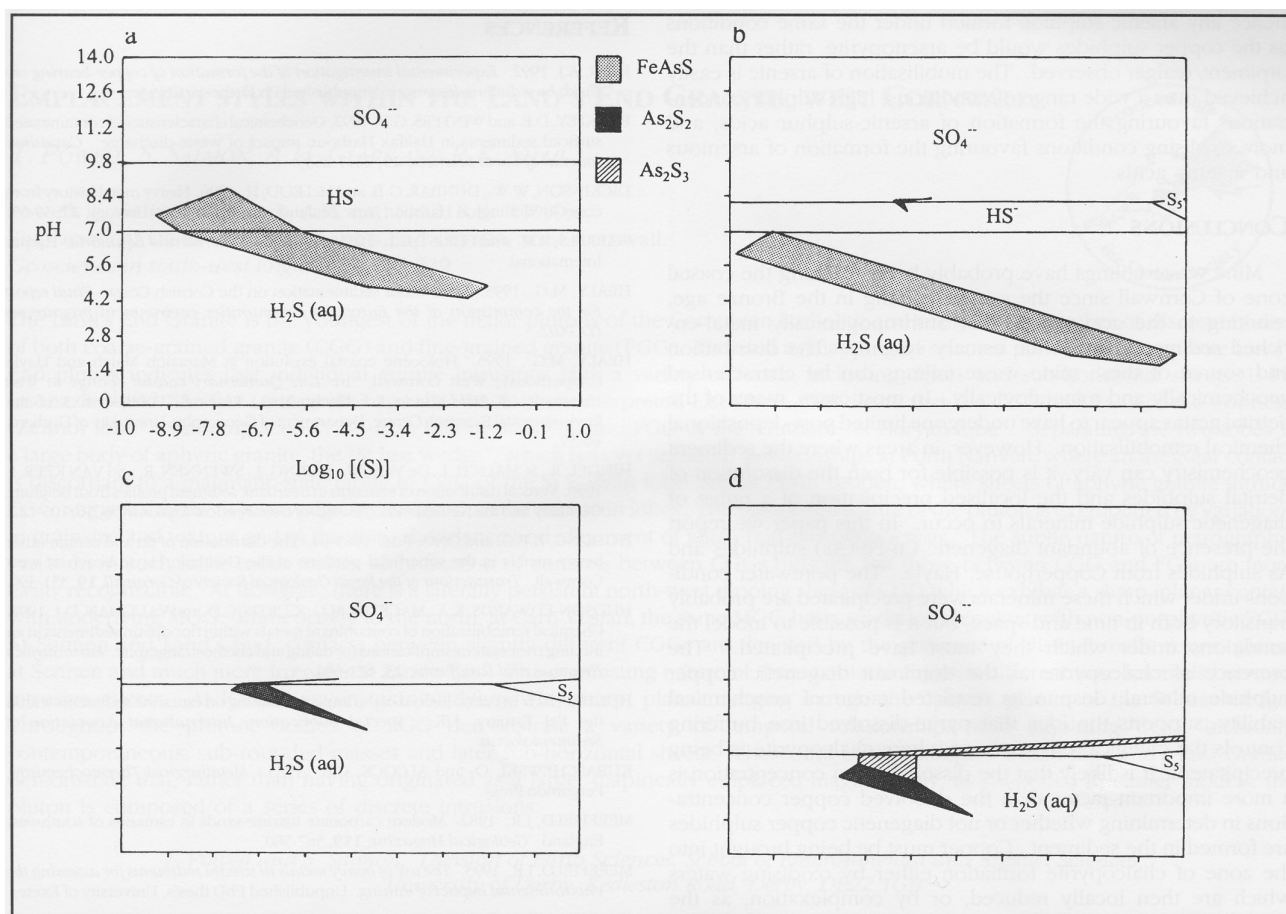
Figure 9. *Stability of arsenic sulphide minerals with respect to pH and dissolved sulphur concentrations for a range of oxidation potentials (Eh) and dissolved metal concentrations. (a) Eh = -0.4v, metal concentration 10^{-6} M, (b) Eh = -0.3v, metal concentration 10^{-3}M, (c) Eh = -0.2v, metal concentration 10^{-3} g (d) Eh = -0.0v, metal concentration 10^{-3} M.*

maximum concentration of dissolved copper observed in Restronguet Creek porewater by Beer (1992)). Thus we may therefore have expected to observe bornite, rather than chalcopyrite as the dominant authigenic copper mineral. However, the copper sulphide minerals must not be considered in isolation, because iron is present (in the form of pyrite and iron oxides) in much greater quantities than copper, and the effect on geochemical conditions in the sediment of reactions in the Fe-S-O-H system must be much greater than copper reactions. If the diagrams for the Fe-S-O-H system and the Cu-Fe-S-O-H system are compared (Figure 8a with Figure 8e, Figure 8d with Figure 8f), it can be seen that the stability conditions for chalcopyrite are 'locked' to the line representing equilibrium between Fe^{2+} ions in solution and pyrite (FeS_2). The iron system reactions are buffering geochemical conditions in the sediments, favouring the formation of chalcopyrite.

It is also important to note the role of the dissolved metal concentration on authigenic copper sulphide formation. Under less oxidising conditions (Eh = -0.2v) chalcopyrite is only stable with higher dissolved metal concentrations (10^{-3}M as opposed to 10^{-6}M - Figures 8c and 8d) than are likely for copper in the sediments (the maximum copper concentration in porewaters of the highly contaminated Restronguet Creek is measured as 10^{-6}M (Beer, 1992)). It should be noted that the copper compounds present in these diagrams are all in the solid state, the dissolved copper concentration under the conditions of Eh and pH necessary for authigenic sulphide mineralisation are less than 10^{-10}M. The only metal whose concentration will actually change will be iron; thus it is an increase in the concentration of dissolved iron rather than copper which favours the formation of chalcopyrite. The copper concentrations which can be generated under equilibrium conditions

with authigenic chalcopyrite are so low that there must be an influx of more oxidising waters carrying higher levels of copper into the reducing sediments, which can then be precipitated with dissolved iron and sulphur to form chalcopyrite when they reach a zone with a greater reducing potential. This is supported by the observation that the authigenic minerals are not forming as overgrowths on pre-existing chalcopyrite, but are nucleating as new crystals, and by the observation that the diagenetic sulphides are limited to the dark, organic-rich layers in the sediment which will provide reducing conditions. What is not considered here is the effect of complex ion formation on copper solubility. Beer (1992) demonstrated that chloride ion complexes could greatly increase copper solubility, but at Eh values where chalcopyrite is stable, a high concentration of chloride (twice seawater concentration) and a high degree of acidity (pH less than 3) are necessary to solubility even 1ppm copper.

Diagenetic arsenic minerals

Stability diagrams for the As-Fe-S-O-H system are given in Figures 9a and b. The minerals observed are either realgar (AsS) or orpiment (As_2S_3). The diagrams indicate that these minerals are stable under less reducing conditions (Eh between -0.2 and 0.0v - Figures 9c and d) than chalcopyrite, and require a high arsenic concentration ($>10^{-3}$M) to form. These minerals are also not 'locked' to the Fe^{2+} - pyrite buffer, but form under less acidic conditions. The presence of arsenic-only sulphides rather than arsenopyrite, which is stable under more reducing conditions (Figures 9c and d), indicate an environment in the sediments of greater overall oxidising potential than is necessary for the formation of diagenetic copper sulphides. The formation of arsenopyrite is 'locked' to the dissolved iron - pyrite buffer, hence any arsenic sulphide formed under the same

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as the copper sulphides would be arsenopyrite, rather than the orpiment/realgar observed. The mobilisation of arsenic is easily achieved over a wide range of conditions, high sulphur concentrations favouring the formation of arsenic-sulphur acids, and more oxidising conditions favouring the formation of arsenious and arsenic acids.

CONCLUSIONS

Mine waste tailings have probably been reaching the coastal zone of Cornwall since the start of mining in the Bronze age, resulting in the accumulation of anthropogenically metal-enriched sediments within the estuary systems. The distribution and source of these mine waste tailings can be characterised geochemically and mineralogically. In most cases, many of the detrital grains appear to have undergone limited post-depositional chemical remobilisation. However, in areas where the sediment geochemistry can vary, it is possible for both the dissolution of detrital sulphides and the localised precipitation of a range of diagenetic sulphide minerals to occur. In this paper we report the presence of abundant diagenetic Cu-Fe-(As) sulphides and As sulphides from Copperhouse, Hayle. The porewater conditions under which these minerals were precipitated are probably transitory both in time and space, but it is possible to model the conditions under which they must have precipitated. The presence of chalcopyrite as the dominant diagenetic copper sulphide mineral, despite its restricted range of geochemical stability, supports the idea that pyrite-dissolved iron buffering controls the chemical environment where chalcopyrite is being precipitated. It is likely that the dissolved iron concentration is a more important factor than the dissolved copper concentrations in determining whether or not diagenetic copper sulphides are formed in the sediment. Copper must be being brought into the zone of chalcopyrite formation either by oxidising waters which are then locally reduced, or by complexation, as the solubility of copper under the conditions required for chalcopyrite formation is so low as to be insufficient to allow for the formation of diagenetic minerals in sediments which were probably deposited only 100-150 years ago. The diagenetic arsenic minerals observed must have formed under different geochemical conditions to the copper sulphides and cannot form where the dissolved iron - pyrite buffer system controls the geochemistry. There must be a variety of geochemical microenvironments present within the estuary sediments, both to allow the mobilisation and re-precipitation of copper and to permit arsenic sulphides and chalcopyrite to precipitate.

If we are to understand the distribution of the mine waste tailings throughout the Cornish estuaries, then it is important that we can constrain their geochemical mobility. In addition, the presence of diagenetic sulphide minerals documents the changing porewater/sediment geochemistry through time and/or space. It also highlights the importance of integrating mineralogy with geochemistry in the understanding of mine waste impact on sedimentary systems.

ACKNOWLEDGEMENTS

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