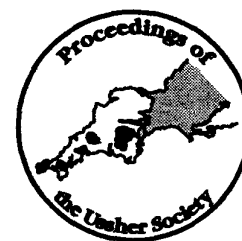


## A NEW OCCURRENCE OF DIAGENETIC SIMONKOLLEITE FROM THE GANNEL ESTUARY, CORNWALL

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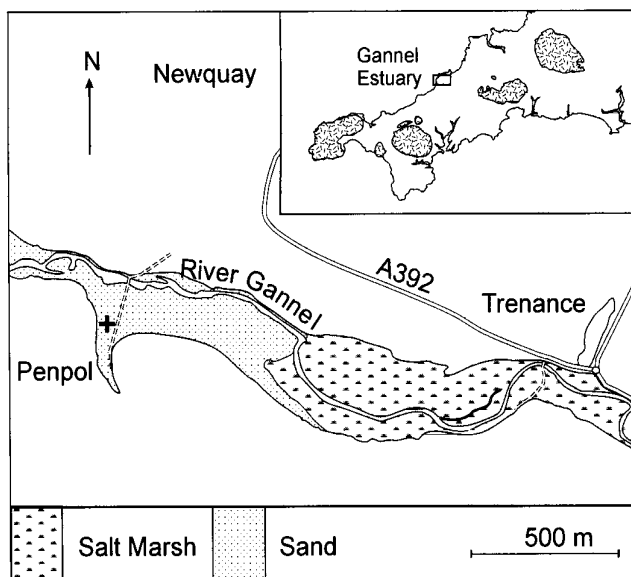


Early diagenetic concretions, that have grown in the last 130 years are common at Penpol in the Gannel Estuary. They are mineralogically complex, being dominated by calcite-siderite-Fe monosulphide cements. Commonly, they are nucleated around discarded metal artefacts. In one of the concretions, diagenetic simonkolleite ( $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ ) has been identified along with zincite and an unnamed Zn phase; this is the first record of simonkolleite in the UK. The diagenetic simonkolleite probably formed as a result of the corrosion of a Zn plate artefact within the estuary, either from shipping or possibly mine waste slag.

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### INTRODUCTION

Early diagenetic concretions are common at Penpol in the Gannel Estuary (Fig. 1). The concretions are diagenetically complex, being dominated by siderite, calcite, Fe monosulphide and Zn sulphide/sulphate cements. They appear to have nucleated around either *in situ* invertebrate burrows or metal artefacts discarded within the estuary. One of the concretions from Penpol has a sheet-like morphology, and occurs at a depth of 15 cm in an active inter-tidal sand bar composed predominantly of skeletal carbonate grains (cf. Merefield, 1982). This concretion, is mineralogically complex, but includes diagenetic simonkolleite ( $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ ); this phase is described from the UK for the first time here.



**Figure 1.** Location map showing Penpol on the Gannel Estuary; the concretion described here was collected from the intertidal sediments within the creek, 5 m from a loading quay that was active in the late 19th century (+ on Fig.).

### REGIONAL SETTING

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. There was also a significant Pb-Zn-Ag mining district in the estuary catchment in the area around Newlyn Downs. Sediment supply to the estuary was from both marine carbonate sources (Merefield, 1982) and from the release of Pb-Zn-Ag mine waste tailings (Pirrie *et al.*, 2000).

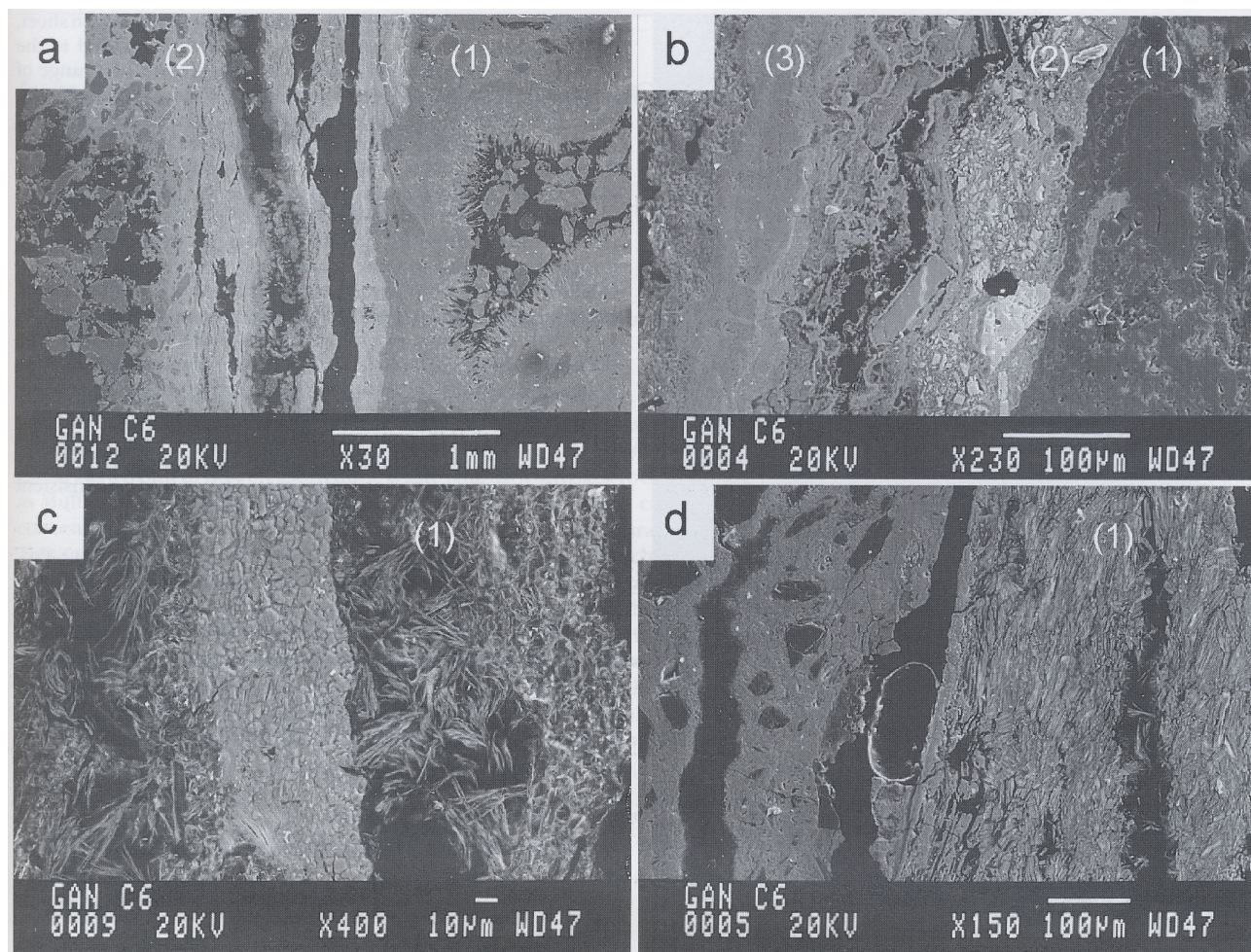
In this study, we have sampled the sediments adjacent to a small quay at Penpol, where small (typically a few cm across) early diagenetic concretions have grown in the sediments (Fig. 1). The concretions occur within fine to medium grained carbonate sands which cannot be more than a 130 years old based on the age of abandonment of the adjacent quay as a result of siltation. Being adjacent to an old quay, a large number of both wooden and metal artefacts have been discarded into the estuary sediments. These artefacts have commonly formed the nuclei for the growth of complex early diagenetic concretions the shape of which, in part, mirrors the shape of the host artefact. One particular concretion within the intertidal sediments has a sheet-like morphology with irregular upper and lower surfaces surrounding a composite sheet-like layer 1 mm thick. This concretion contains a complex range of diagenetic minerals described below.

### METHODS

The early diagenetic concretions were carefully resin impregnated and then prepared as polished thin sections. Following standard petrographic examination, the samples were examined using a JEOL 840 scanning electron microscope (SEM) with an Oxford Instruments (Link System) AN10000 energy dispersive spectrometer (EDS). Representative subsamples were also analysed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer using CuK $\alpha$  radiation. The thin sections were also examined using a Technosyn cold cathodo-luminescence microscope.

### CONCRETION DIAGENESIS

The concretionary sheet within the Penpol sediments is dominated by non-luminescent acicular isopachous calcite fringing cements

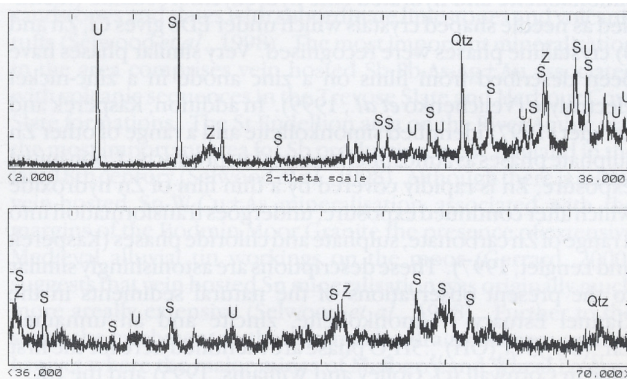


**Figure 2.** Scanning electron microscope images of diagenetic phases from the Gannel Estuary concretion. (a) Diagenetic phases within the sheet-like concretion. The apparent vertical zonation was horizontal in the field. The dull phase (1) is diagenetic calcite cements whilst the brighter areas (2) are Zn, Zn-Cl and Pb phases. (b) Calcite cemented sediment (1) with a fragmental zone comprising a Ba phase with Zn cements (2) in turn overlain by zoned Zn and Zn-Cl-S cements (3). (c) Fibrous Zn cements (1). (d) Blocky book-like Zn-Cl simonkolleite cements (1).

precipitated around detrital bioclasts and siliciclastic grains (Fig. 2a) and bright orange luminescent microsparry calcite cements. Also present is a sheet-like layer, 1 mm thick, that is composed of a much more complex array of diagenetic phases dominated by a wide range of Zn-bearing minerals, identified using the SEM and XRD, and including a Zn sulphide/sulphate, a Zn-Fe sulphide/sulphate and a Zn-Cl mineral. In addition, a Ba phase and a Pb phase also commonly occur. The overall small size, composition and complexity of these diagenetic phases makes their mineralogical identification difficult. Detrital carbonate and elastic sediment grains with abundant calcite cements occur adjacent to a layer dominated by angular grains of the Ba phase, cemented by Zn sulphide/sulphate (Fig. 2h) which appear encrusted by complex zoned Zn cements. Elsewhere, needle fabric Zn cements dominate (Fig. 2c) Under SEM this phase is dominated by Zn with common small (1-2 mm) blebs of Pb; a Zn-Cl-S phase also occurs. Finally, there is a common cement phase that is dominated by a rather book-like morphology that under SEM is a Zn-Cl phase (Fig. 2d). A subsample of this sheet structure was carefully powdered in an agate mill and analysed by XRD. The resultant XRD trace confirmed the presence of simonkolleite ( $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ ), along with Pb metal, and possibly zincite ( $\text{ZnO}$ ) and an unnamed  $\text{Zn}_{12}(\text{SO}_4)_3\text{Cl}_3(\text{OH})_{15} \cdot 5\text{H}_2\text{O}$  phase (Fig. 3). The XRD and SEM data are consistent with the original description of simonkolleite by Schmetzer *et al.* (1985). These diagenetic Zn sulphide/sulphate cements also occur 3 mm away from the sheet-like structure where they are nucleated upon, and line detrital quartz and calcite grains (Fig. 4).

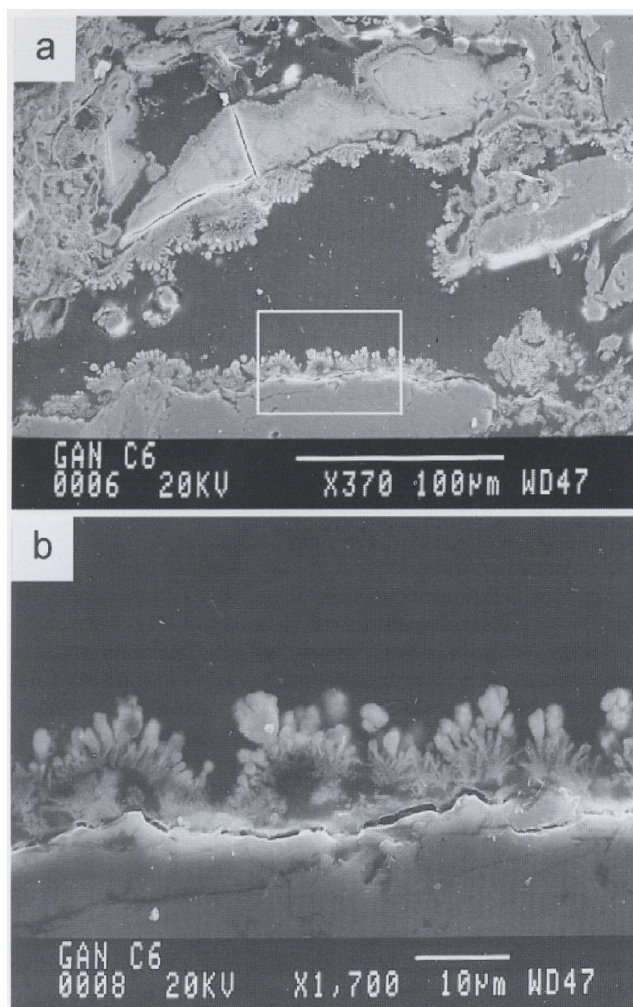
## DISCUSSION

Simonkolleite was first described and named by Schmetzer *et al.* (1985), from Richelsdorf, Germany where it occurs as a natural weathering product of Zn-bearing mine slags. Schmetzer *et al.* (1985) identified wulfingite ( $\text{Zn}(\text{OH})_2$ ), along with native Zn, zincite and hydrozincite. Most reports of simonkolleite are in the



**Figure 3.** XRD profile for the sheet-like structure within the concretion, clearly indicating the presence of simonkolleite (S), zincite (Z) and an unnamed  $\text{Zn}_{12}(\text{SO}_4)_3\text{Cl}_3(\text{OH})_{15} \cdot 5\text{H}_2\text{O}$  phase (U). Quartz is also present (Qtz).





**Figure 4.** Scanning electron microscope images of diagenetic Zn sulphide/sulphate cements. (a) Zn sulphide/sulphate cements nucleated on detrital quartz and carbonate grains. (b) Close-up showing the structure of these cements rimming a detrital quartz grain; these cements are located 3 mm away from the sheet-like structure.

understanding of surface atmospheric corrosion products on Zn plate. Both simonkolleite and zincite were described following the experimental corrosion of electrolytic Zn plates in a marine test site in the Yucatan Peninsula of Mexico (Quintana *et al.*, 1996). Quintana *et al.* (1996) placed electrolytic Zn plate in a marine test site and analysed the corrosion products formed after 1, 3, 6, 9 and 12 months using XRD and SEM; zincite, simonkolleite and hydrated zinc hydroxylchlorosulfate (identified as needle shaped crystals which under EDS gives Cl, Zn and S) crystalline phases were recognised. Very similar phases have been described from films on a zinc anode in a zinc-nickel electrolyte (Velichenko *et al.*, 1999). In addition, Kasperek and Lenglet (1997) identified simonkolleite and a range of other Zn sulphate phases as atmospheric corrosion products. Upon initial exposure, Zn is rapidly covered by a thin film of Zn hydroxide which after continued exposure, undergoes transformation into a range of Zn carbonate, sulphate and chloride phases (Kasperek and Lenglet, 1997). These descriptions are astonishingly similar to the present observations of the natural sediments in the Gannel Estuary. Simonkolleite, zincite and an unnamed  $\text{Zn}_{12}(\text{SO}_4)_3\text{Cl}_3(\text{OH})_{15}\cdot 5\text{H}_2\text{O}$  phase are identified here for the first time in Cornwall (cf. Golley and Williams, 1995) and the UK.

There are two possible interpretations for the observed diagenetic minerals in the Gannel Estuary. Firstly, several of the concretions at Penpol are nucleated around clearly identifiable metal artefacts. It is possible that the sheet-like structure present in the concretion

described here was originally part of a Zn sheet, common in shipping construction, that was discarded in the estuary and has corroded *in situ* with the growth of a range of diagenetic Zn phases. This is entirely compatible with the experimental data from the Yucatan Peninsula in Mexico (Quintana *et al.*, 1996) and also the work of Velichenko *et al.* (1999) and Kasperek and Lenglet (1997). Subsequently, following corrosion of the Zn artefact and growth of the Zn phases, continued concretion growth occurred, with predominantly, the precipitation of calcite cements. However, aspects of the concretion mineralogy are not consistent with this interpretation. Firstly, it is important to note that the Gannel Estuary sediments are extremely enriched in both Zn and Pb, with up to 1600 ppm Zn as a result of the release of mine tailings (Pirrie *et al.*, 2000). The dominant detrital Zn phase is sphalerite. The concretion hosts a sheet-like structure dominated by Zn cements; however, there is also a layer dominated by fragments of a Ba phase and Pb metal. It is possible that this paired layered structure may represent a composite slag product that has undergone alteration following deposition in the estuarine sediments. This would be consistent with the previous work by Schmetzer *et al.* (1985).

## ACKNOWLEDGEMENTS

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## REFERENCES

- GOLLEY, P. and WILLIAMS, R. 1995. *Cornish mineral reference manual*. Endsleigh Publications, Truro.
- KASPEREK, J. and LENGLET, M. 1997. Identification of thin films on zinc substrates by FTIR and Raman spectroscopies. *Revue de Metallurgie - Cahiers de Informations Techniques*, **94**, 713-719.
- MEREFIELD, J.R. 1982. Modern carbonate marine-sands in estuaries of southwest England. *Geological Magazine*, **119**, 567-580.
- PIRRIE, D., POWER, M.R., PAYNE, A., CAMM, G.S. and WHEELER, P.D. 2000. Impact of mining on sedimentation; the Camel and Gannel estuaries, Cornwall. *Geoscience in south-west England*, **10**, 021-028.
- QUINTANA, P., VELEVA, L., CAUICH, W., POMES, R. and PEÑA, J.L. 1996. Study of the composition and morphology of initial stages of corrosion products formed on Zn plates exposed to the atmosphere of southeast Mexico. *Applied Surface Science*, **99**, 325-334.
- SCHMETZER, K., SCHNORRER-KÖHLER, G. and MEDENBACH, O. 1985. Wulfingite,  $\text{e-Zn}(\text{OH})_2$ , simonkolleite,  $\text{Zn}_5(\text{OH})\text{Cl}_2\cdot\text{H}_2\text{O}$ , two new minerals from Richelsdorf, Hesse, F.R.G. *Neues Jahrbuch für Mineralogie Monatshefte*, **4**, 145-154.
- VELICHENKO, A.B., PORTILLO, J., SARRET, M. and MULLER, C. 1999. Surface analysis of films formed on a zinc anode in a Zn-Ni electroplating bath. *Applied Surface Science*, **148**, 17-23.