Littleham Cove native copper (UK)

Description: The Devon natural analogue site is an occurrence of metallic copper segregations in a mudstone formation. The site is situated in Devon, SW England, at Littleham Cove near the mouth of river Exe (Figure 1). Geologically the formation belongs the Permian-Triassic sedimentary rock sequence, accumulated more than 200 Million years ago in a large-scale geological depression (the Wessex Basin). The depositional environment was non-marine, rather dry (arid – semiarid), as indicated by the typical red colour caused by oxidized iron ('red-bed' deposition). As well as in many other 'red-bed' formations, accumulation of uranium-vanadium and Cu (+ other heavy metals) is a typical feature of this sedimentary sequence.

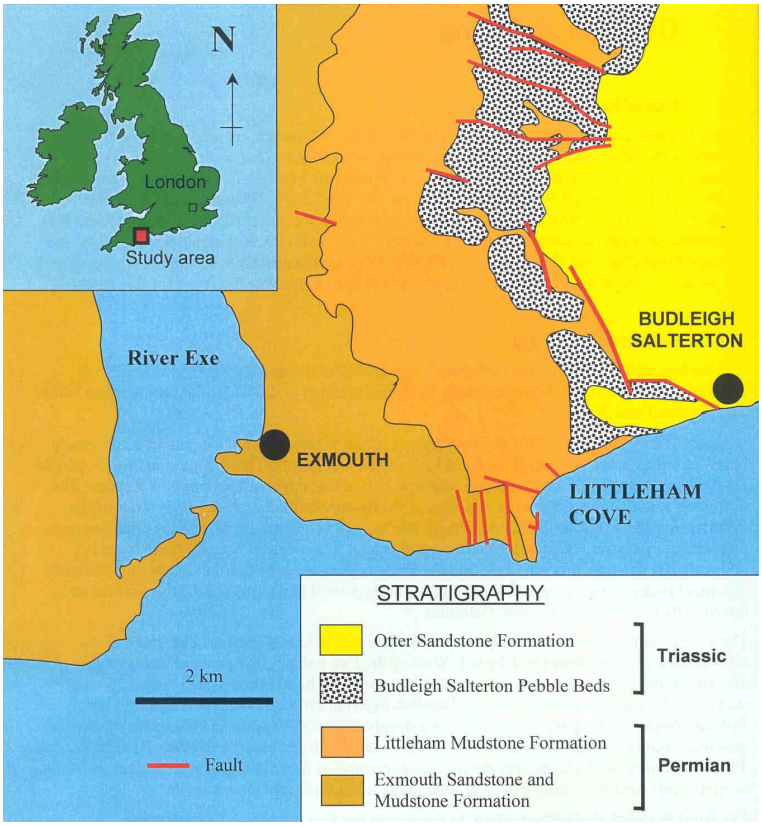

Figure 1: Location and geology of the Littleham Cove area (Milodowski et al. 2002)

Figure 1 shows the geology of the site, displaying a gently eastward dipping sequence: the formations get gradually younger from the Lower Permian around river Exe to Triassic around Budleigh Salterton. The Pebble bed has been interpreted to represent the lowermost Triassic sedimentation (about 250 Ma ago). The Upper Permian Littleham Mudstone Formation is the specific target of the Devon copper-analogue study.

Metalliferous concretions are typical to the Littleham Formation, and are studied in details by Harrison 1975, Milodowski et al 2000, Milodowski et al 2002. Uranium-vanadium rich concretions are most common. The concretions, occurring in localized horizons, are best exposed in cliffs and low-tide shoreline. Often these segregations consist of a U-V-clay mineral core with a surrounding bleached reduction spheroid, giving a 'fish-eye' appearance to the concretion. At large however, morphology, mineralogy and chemical composition of these segregations is very complex.

Sheet-like native copper concretions accompanied by traces of native silver have been found in certain strata of Littleham Formation (Figure 2). Copper segregations appear to be stratigraphically associated with the more common uranium-vanadium concretions. The biggest copper plates have a maximum diameter of about 16 cm, but they are thin (up to 4 mm). The plates seem to be aligned with the bedding planes of grey marl horizons, and to be located in the uppermost section

of the Littleham Formation, stratigraphically some meters (about 10 m) below the Triassic Pebble Beds.

Figure 2: Native copper plate. Field of view = 140 mm [Milodowski et al., 2002]

Copper, as well as other concretions in the formation are authigenic, i.e., formed after deposition of the sediment, but the processes of formation are not understood in detail. Evidently, redox processes play a critical role: concretions are typically associated with a restricted reduced mesoscopic environment (bleached halos), where predominant Fe(III) has been reduced to Fe(II). The reduction may have been initiated by and around organic nuclei, which could have caused the development of reduction front.

During accumulation of the sediment pile, concretions were then gradually buried and were subjected to increasing pressure and, for the most of time, a water saturated environment. Maximum burial was attained during Lower Jurassic (about 170 Ma ago). During burial, copper surfaces were partly altered, mainly to cuprite (Cu_2O) and minor tenorite (CuO), which are associated with pitting of the surfaces. There is evidence for limited migration and retardation of Cu in the surrounding mudstone-matrix. After the maximum burial, sediments were subjected to erosion until they were exposed to the atmosphere and secondary copper carbonate and sulphate minerals were formed. However, significant proportion (30 – 80 %) of the original thickness of plates has been preserved during 170 million years time.

Surroundings of the uranium-rich (≈1 wt % as U_3O_8) cores of 'fish-eye' concretions were studied for the effects of α-radiolysis. Harrison 1975 measured the lengths of 1000 α-tracks. Most of the tracks were about 15 – 25 μm long, being due to ^{238}U and ^{226}Ra. Milodowski et al. (2002) point out that natural radiolysis has not significantly oxidized surrounding reduced species (Fe(II) and sulphides). Oxidant (H_2O_2) production of one large nodule during 240 Ma time is of the order of 2.5 g.

***Relevance*:** The existence of native copper at the Devon site demonstrates the longevity of metallic copper in clay environment through geological times (hundreds of million years) in a ferric iron-dominated 'red bed' type of system. The site also provides information on the behaviour of natural uranium, with a special reference to the effects of radiolysis.

Position(s) in the matrix tables: Mechanical integrity of barriers=>corrosion=>copper package

Limitations: Due to the highly oxidized 'red bed' conditions, copper stability in reducing, sulphidic conditions cannot be demonstrated in straightforward way. Copper samples from undisturbed 'in situ' conditions not available.

Quantitative information: Reach of α-radiolysis in clay. Estimation of copper corrosion depth.

Uncertainties: Hydrogeological conditions of the formation not reported.

Time-scale: Geological.

PA/safety case applications: Demonstration of copper canister longevity in bentonite buffer system. Long-term effect of α-radiolysis in buffer.

Communication applications: None identified.

References:

Harrison KE. 1975. Concretionary concentrations of the rarer elements in Permo-Triassic red beds of south-west England. Bull. Geol. Surv. Great Britain 52. 1 – 26.

Milodowski AE, Styles MT, Hards VL. 2000. A natural analogue for copper waste canisters: The copper-uranium mineralised concretions in the Permian mudrocks of south Devon, United Kingdom. SKB Technical Report TR-00-11.

Milodowski AE, Styles MT, Horstwood MSA and Kemp SJ. 2002. Alteration of uraniferous and native copper concretions in the Permian mudrocks of south Devon, United Kingdom. SKB Technical Report TR-02-09.

Added value comments: None identified.

Potential follow-up work: None identified.

Keywords*:* near-field, copper, corrosion, radiolysis, redox front

Reviewers and dates: Lasse Ahonen, GTK (April, 2004)