

The use of polarography in geochemical studies of anoxic sediments

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Polarography is a powerful experimental electrochemical technique for determining chemical speciation in solution at low concentrations. Conventionally it is carried out with a mercury drop electrode, which provides a continually renewed electrode surface. However, the mercury drop electrode is limited in its application in natural systems since it cannot be introduced to the measuring site and it is difficult to use in the field. Solid state electrodes were developed by Brendel and Luther (1996) which, in combination with the availability of more sensitive, computer-controlled voltammeters, allow field measurements to be made. In this preliminary study, we were interested to determine if a voltammetric signal could be obtained from direct electrode insertion into anoxic, sulphidic muds and if the signal could be interpreted.

An electroactive FeS species has been reported from water columns in lakes (Buffle *et al.*, 1988; Davison *et al.*, 1988) and marine waters (Theberge and Luther, 1997). Buffle *et al.* (1988) first suggested that the electroactive FeS species was sub-colloidal. The electroactive properties of the species place constraints on its size since reactive current is proportional to the square root of the diffusion coefficient, which, in turn, is proportional to the inverse of the particle radius. They put an upper size limit of 5 nm (50 Å) on the size of the species. The size limitation suggests that this aqueous FeS is in the form of quantum-sized particles or clusters which contain indefinite numbers of FeS molecules but are small enough to behave as dissolved species. If these soluble FeS clusters are important intermediaries in pyrite formation, they should be present in natural systems where iron sulphides and pyrite are forming. In this paper we report evidence for abundant FeS clusters in the pore waters of an intertidal estuarine mud.

Study area and methods

The Loughor Estuary is a W–E trending macrotidal, diurnal, ebb-dominated funnel-shaped estuary situated at lat 51° 39' 23''N long 04° 07' 24''W on the west coast of the UK. Historically, the hydrodynamics of

the estuary have been significantly altered by the coal, iron and steel industries. Six 50 cm-long push cores were recovered from a small mudflat located on its northern shores just to the south of the British Steel Works at Trostre and the Tir Morpha saltmarsh. The cores were taken from a small tidal channel incised into the mudflat.

An Analytical Instruments® Model DLK-100 Electrochemical Analyser was used for the voltammetry. A reference saturated calomel electrode and a platinum wire counter electrode were inserted at the top of the core, where they remained throughout the experiment; while the working 125 µm gold-amalgam microelectrode, prepared by the method of Brendel and Luther (1995), was inserted through the holes in the plastic liners. In square wave voltammetry (SWV), a pulse height of 24 mV was used with a scan rate of 200mV/s. Scans were run from 0 to –1.7 V which allowed the Fe(II), H₂S/HS[–] and [FeS]_{aq} peaks to be collected. A conditioning step of 30 seconds at a potential of –1.0 V was used to remove sulphide from the electrode surface.

Pore waters were analysed with a Perkin-Elmer® 5000 ICPMS, sediments with a Phillips® PW1710 diffractometer with Cu-Kα radiation. Pyrite volatile sulphur and acid volatile sulphur (AVS) were determined by the method of Bottrell *et al.* (1994).

Results

Total iron sulphide-S increases with depth from 22 to 30 mmol S.100 g.sed^{–1}. Pyrite-S increases with depth from c. 6 to 25 mmol S.100 g.sed^{–1} whereas AVS decreases from ca 16 to 6 mmol S.100 g.sed^{–1}. ICPMS analyses only revealed normal seawater with trace Mn and Cu in solution in ppb concentrations. In contrast, the dissolved Fe concentrations decrease with depth from 6 to 4 mM. The plug-in pH varies between 7.8 and 8.1.

Typical SWV traces are complex with a double peak appearing below 25 cm downcore. This peak shows the characteristics of [FeS]_{aq}; viz. a double peak around –1100 mV which is irreversible. The

voltammograms to indicate a systematic change with downcore depth. Down to -10 cm hexaquoiron(II) is the only species seen. At -10 to -15 cm HS⁻ appears and hexaquoiron(II) is absent. An intermediate situation is observed at 20 cm downcore with two peaks being recorded: a shift in the HS⁻ peak to -810 mV and the appearance of a small peak at -1140 mV. This possibly represents some bisulphide complexing as well as the first appearance of [FeS]_{aq}. Below -25 cm, [FeS]_{aq} dominates the pore water and neither HS⁻ or hexaquoiron(II) is observed. The electrode only samples an extremely small volume. Samples taken 5cm apart (on opposite sides of the core) show good reproducibility. Comparison of 2 cores taken at different locations 3 m apart also show similar results.

Discussion

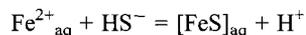
Excess Fe(II) is detected in the porewaters at all depths. However, below 30 cm it is possible that a significant proportion of dissolved Fe(II) is in the form of [FeS]_{aq} since no hexaquoiron(II) wave is detected on the SWV scan. The electrode response for hexaquoiron(II) in the upper sediment sections is approximately 40 nA per mM. The detection limit on the SWV scans in this measuring situation appears to be around 20 nA, suggesting that free hexaquoiron(II) is present in sub-micromolar concentrations in the [FeS]_{aq} zone. That is, [FeS]_{aq} constitutes >75% of the dissolved Fe(II). In contrast, [FeS]_{aq} does not make any major contribution to the total sedimentary sulphide content.

The pyrite concentration increases and the AVS decreases with depth from the sediment-water interface in the lower bank sediments. AVS in these freeze-dried samples mostly consists of solid amorphous FeS (FeS_{am}). The total iron sulphide-sulphur content increases gradually with depth suggesting continuing bacterial sulphate reduction. On the timescale of the Loughor mudflats, FeS_{am} formation and pyrite formation via H₂S oxidation of FeS_{am} are instantaneous. The decrease in FeS_{am} and increase in FeS₂ and [FeS]_{aq} with depth are therefore not a function of their chemical reaction rates.

The mass balance between pyrite and FeS_{am} does not appear to satisfy the overall equation FeS + S⁰ = FeS₂. The average, depth integrated rate of pyrite-S production in the section shown is 0.36mmolesS 100g sed⁻¹ whereas AVS-S (i.e. FeS_{am}-S) is disappearing at 0.2 mmoles S 100g sed⁻¹. Both the increase in pyrite concentration and the disappearance of FeS_{am} are correlated with depth, but this correlation does not necessarily imply that these

processes are directly genetically related.

The observed replacement of Fe²⁺_{aq} and HS⁻ in the sediments by [FeS]_{aq} is consistent with a simple protonation reaction: e.g.



However, this is expected to be a fast reaction if it proceeds by conventional Eigen-Wilkins kinetics as proposed for FeS formation by Rickard (1995) and implicated by Theberge and Luther (1997) for [FeS]_{aq}. Likewise the possible equilibrium between FeS_{am} and FeS_{aq} appears inconsistent with the observation of the existence of FeS_{am} 30 cm upcore from the first appearance of [FeS]_{aq}. It is possible that, if [FeS]_{aq} is involved as an intermediary in fast pyrite formation, its standing concentration might be kept low until the bulk of pyrite forms, as observed in these cores.

Conclusions

Solid state microelectrode polarography can be used directly in anoxic, sulphidic, fine-grained sediments to determine sulphide speciation. The SWV response is both significant, with currents up to 1000 nA, and interpretable with few distinct peaks. The seawater matrix appears not to affect the scans above around -1500 mV where sodium begins to provide a significant electrode response. The results appear relatively reproducible.

The iron and sulphide speciation in these sediments is depth dependent. Micromolar concentrations of free hexaquoiron(II) are present in the upper parts of the section. HS⁻ appears at depth and [FeS]_{aq} dominates in the deepest sections. [FeS]_{aq} appears to replace hexaquoiron(II) as the dominant dissolved iron species.

The appearance of [FeS]_{aq} in these sulphidic sediments seems to be related to the pyrite formation process: [FeS]_{aq} appears after the bulk of the pyrite has been formed. The stability of [FeS]_{aq} has been shown to be closely related to the solubility of amorphous FeS. Buffle *et al.* (1998) concluded that [FeS]_{aq} was only present at > 0.25KFeS_{am} whereas Theberge and Luther (1997) found that $K([\text{FeS}]_{\text{aq}}) \sim K(\text{FeS}_{\text{am}})$. Both results suggest that amorphous FeS must be present for the [FeS]_{aq} to form. This is consistent with the results of this study which show that amorphous FeS (as AVS) is present wherever [FeS]_{aq} occurs. However, this study demonstrates that the reverse is not true: [FeS]_{aq} is not detected wherever amorphous FeS is found. In the upper parts of the sedimentary section [FeS]_{aq} is replaced by hexaquoiron(II) and HS⁻ or even iron(II) bisulphide complexes such as FeSH⁺.