Micro-scale biogeochemical heterogeneity in sediments: A review of available technology and observed evidence[1]

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Abstract

The hypothesis that reducing conditions exist in localized zones of high organic matter, termed microniches, was first suggested over a century ago, but only relatively recently have high-resolution techniques been available to investigate them. In any sediment containing benthic fauna, bioturbation affects the distribution of a number of redox-sensitive components. Direct faecal deposition and the death of fauna may be expected to cause particles of labile organic matter (microniches) to be distributed heterogeneously within the sediment. This review discusses the significance and future direction of microniche studies by considering, exclusively, data obtained on a sub-mm scale that provide significant evidence for the existence and properties of microniches. Microelectrodes and planar optodes have shown the significant effect of burrowing organisms on localized O_2 distributions and revealed distinct depletions in O_2 due to microniches. Localized increases in pCO_2 and decreases in pH measured by optodes were attributed to elevated activity at microniches. Diffusive gradients in thin-films have shown isolated supersaturation of metals and sulphide, providing evidence for possible simultaneous oxidation of organic matter by sulphate and iron oxides. The stochastic nature of these data and the lack of information for the same precise location hinders interpretation in terms of sediment diagenesis. If microniches are known to account for a significant proportion of organic matter degradation, re-examination of the current understanding of sedimentary diagenesis may be needed. Further investigation on the distribution and frequency of microniches is required, including a wider range of analytes, in order to estimate their cumulative effect on element diagenesis, immobilisation/remobilisation processes and ultimately pollutant fate.

Keywords: microniche, planar optodes, faecal pellet, burrow, DGT, bioturbation, early diagenesis

1. Introduction

Analysis of porewaters of sediments has, until relatively recently, been largely based on measurements at resolutions of one centimetre or greater. Porewater concentrations for many components were routinely determined by squeezing or centrifugation of core slices and analysis of the supernatant or exuded solution from typically 20-80 ml of sediment. Sorbed species were determined by selective treatment of the bulk sediment. These procedures provide spatially averaged vertical profiles of sediment chemistry. Heterogeneities, both vertically and horizontally, at scales of less than a cm, are averaged within the volume of each sediment slice.

Observed heterogeneity/homogeneity of sediment systems will depend upon the resolution of the measurement. Figure 1 shows a schematic of how the physical parameter porosity may vary depending on the scaling of the measurement. At the grain scale, porosity will fluctuate sharply as mineral grains, organic matter and porewater are encountered. At the microenvironment scale, background values will be close to the average, however, distinct features such as burrows, shell fragments and organic matter microniches will also be apparent. Figure 2 shows an image obtained by slicing a resin embedded sediment core, in which both grain scale and microenvironment features are evident. Scaling issues relevant to early diagenetic processes are examined further by Morse et al (2003).

Aller (1982; 2001) has reviewed and assessed the roles and significance of burrowing, tube construction, irrigation and faecal pellet microenvironments, introduced by macrobenthos. Measurements using core sampling are likely to miss the chemical heterogeneity at such features. Several critical limitations to the established core slicing method were reviewed by Brendel and Luther (1995). As the average concentration for each section is determined, any steep concentration gradients, either vertical or horizontal, within a section will be missed. Mixing of extracted porewater from within the section causes any localized zones of species at high concentrations to be diluted, potentially by an order of magnitude or more. Where the section is composed of different redox regimes, mixing of extracted porewater can allow chemical reactions to alter the concentrations of some of the redox reactive species, also potentially resulting in an apparent overlap of redox species where none exists (e.g. Luther et al, 1998; 1999).

Measurements made on cores may not accurately reflect the in situ concentrations, due to retrieval artefacts. Previously observed differences between O_2 measurements in benthic chambers and from retrieved cores have helped to identify these artefacts (e.g. Pamatmat and Fenton, 1968; Rowe et al, 1997). Discrepancies in O_2 measurements from microprobes deployed in situ and in retrieved cores demonstrate the problem directly (Figure 3). The sediment chemistry of cores may be modified in several ways, such as by pressure (decompression) and temperature changes, elevation of labile organic matter due to death of sensitive organisms, disruption of natural flow conditions over the sediment during coring operations and redistribution of surface material, with consequential effects on near-surface, concentration gradients (e.g. Reimers et al, 1986; Reimers, 1987; Glud et al, 1994). Specific sampling artefacts associated with the carbonate system have also been identified (e.g. Murray et al, 1980; Emerson et al, 1982). Difficulties associated with specific coring techniques are reviewed by Blomqvist (1991).

Although the problems and phenomena identified above have been recognized for some time, our ability to study or overcome these issues has been limited by technical constraints. More recently, analytical techniques have provided measurements of solutes directly in situ and at a high resolution. Microsensors, including electrodes, optodes and micro-biosensors, have been developed to analyse many species at resolutions of one millimetre or higher (see Kühl and Revsbech, 2001; Reimers, 2007, for recent reviews). Optodes have been used routinely to provide two-dimensional images of O_2 and pH concentrations at high resolution (e.g. Glud et al, 1999; Hulth et al, 2002). Measurements of sulphide and metals on the sub-mm scale have been made with diffusive gel techniques, including some limited analysis in two-dimensions (see Davison et al, 2000).

Interpretational difficulties can arise when sediments are analysed at centimetre and millimetre resolution. Numerous articles have reported data that reveal features identified by only a single data point (see Grundmanis and Murray, 1977; Docekalova et al, 2002; Leermakers et al, 2005 for examples). Method comparisons using sub-mm techniques have demonstrated that micro-features in profiles are often missed altogether by measurements at lower resolutions (see Wenzhöfer et al, 2001; Mortimer et al, 2002 for examples). Such apparently erratic data can not be used to predict fluxes to and from microenvironments and across diffusive boundary layers, as, to define gradients well, the resolution must be sufficient to provide multiple data points. Where only ‘bulk’ data are required or where spatial trends in concentrations are linear, measurement techniques with inherent averaging (e.g. benthic chambers or core slicing) may be more appropriate. Microscale data may adequately define gradients, but any flux obtained only strictly applies to the narrow column of sediment that the measurement encompasses. It may not be representative of the larger scale flux, particularly where few probes have been deployed and averaging cannot be applied. However, microscale measurements may be useful in explaining the variability that may arise in multiple chamber measurements, as particular localized processes can be identified.

1.1. Historical concepts in sediment microheterogeneity

There is a long history of scientific interest in sediment microheterogeneity. Examples from the mid 1800’s include, a study on coprolites (fossilized faeces) by Buckland (1835) and a comprehensive survey of benthic fauna by Dalyell (1853), which includes observations of habitat features such as mucus secretions in burrow structures. Many studies in the late 1800’s focused on the tube building and habitats of specific benthic biota (e.g. Cunningham and Ramage, 1888; Watson, 1890; M’Intosh, 1894). Dapples (1942) reviewed a selection of early literature examining sediment turnover rates by benthic biota, in terms of debris ingestion, faecal pellet formation/decay and burrow processes. The studies cited above are largely zoological surveys, investigating the fauna present and their habitat. However, it has also been long recognised that the presence of benthic fauna must have a significant effect on overall diagenesis (and thus by implication sediment chemistry; e.g. Buchanan, 1890). The hypothesis that localized reducing conditions exist in restricted areas of high organic matter was suggested by Emery and Rittenberg (1952). The idea was invoked to explain both the existence of pyrite in zones of positive redox potential and the morphometry of the pyrite, which took the form of internal casts of radiolarian and other shells. This concept of localized reactive organic matter was developed further by modelling reducing microniches within ambient oxidized sediment (e.g. Jørgensen, 1977). Further references in relation to historical concepts are cited in Aller and Yingst (1978).

1.2. Rationale for microscale studies

In any sediment containing benthic fauna, it is likely that bioturbation will affect the distribution of a number of redox components. Direct faecal deposition and the death of benthic fauna may be expected to cause particles of labile organic matter to be distributed heterogeneously in the sediment column. The formation of feeding tubes and burrows affects the distribution of solutes, including those diffusing from or to the sediment. Aller (1983) observed that diffusion of solutes across the mucus linings of burrows was retarded, resulting in the rate of diffusion across this boundary being only 10-40% of the value in free solution. Several studies have revealed enrichment in bacterial populations at these burrow walls (Aller, 1988 and references therein). Papaspyrou et al (2006) observed that in some burrows the bacterial communities of the linings and walls resembled those in ambient anoxic sediment rather than oxic sediment. The stochastic distributions (life positions) of benthic organisms may therefore indirectly affect mineralization pathways by amending the distribution of oxidants and labile organic matter. The changing redox conditions (redox oscillations) induced by bioturbation may lead to more rapid decomposition of organic matter than simple unidirectional redox changes (Aller 1994). Jørgensen (1977) suggested that the interface between oxidized and reduced sediment could be substantially increased if reduced microniches are mixed into the oxic zone. He calculated a theoretical lower limit of particle size for the formation of an anoxic spherical microniche to be approximately 100 µm, assuming a low ambient O_2 concentration and higher respiration rates than the average sediment. The nature of the microniche will also have a direct influence on the porosity and will affect the diffusion coefficient of solute oxidants (see also the scaling effects in Figure 1). This will in turn affect the apparent O_2 consumption rates. Diffusion coefficients within faecal pellets may be altered due to some or all of the following factors: a smaller average particle grain size than the ambient sediment, higher density (compacted nature), and existence of peritrophic membranes (e.g. Aller, 1982). Conversely, water content in faecal pellets has been observed to be higher than the ambient sediment (80% compared to 49-58%; Kristensen and Pilgaard, 2001). High-resolution images of particles within and surrounding faecal pellets have been presented (Figure 2; from a larger compilation of high resolution sediment imaging by Watling, 1988). The texture of faecal pellets is discussed in more detail by Rhoads and Boyer (1982). Other microniches such as aggregates of algae (e.g. Widerlund and Davison, 2007), may have a much higher porosity (due in part to a lack of mineral particles). In oxic sediments this higher porosity will theoretically require consumption rates to be much higher for anoxia to occur.

1.2.1. Early diagenesis and pollutant fate

Studying sediment processes at the sub-mm scale will expand knowledge of early diagenetic processes and further our understanding of the relationships between the microbiology, macrobiology and chemical processes. This will in turn allow us to better understand the fate of anthropogenic pollutants and potentially enable a better predictive ability through more accurate modelling of the system.

To date, most estimates of reaction rates within sediments have been calculated using concentration profiles derived from spatially averaged sliced sediment or whole cores. Aller and Mackin (1989) describe several whole core incubation methods for determination of reaction rates in sediment. Methods such as these may not yield data that can be used to model microenvironment processes. A model, at the pore-scale, of reactive transport (Meile and Tuncay, 2006) has shown that estimates of reaction rates based exclusively on localized pore-scale heterogeneity can be significantly different to those estimated when these localized areas are upscaled and incorporated into a macroscopic heterogeneous system. This suggests that at localized reaction sites the average concentration in a typical sampling volume may not be representative of the concentration at the site of the reaction. The effect of benthic biota on conditional rate constants, spatial heterogeneity, and reaction order were reviewed and assessed in relation to processes such as excavation, burrowing, feeding and ventilation activities, by Aller (2001) and Aller et al (2001). Müller and Stierli (1999) highlighted the importance of accurate in situ reaction rates for understanding and modelling early sediment diagenesis. As the volume of data from micro-scale studies of sediments increases (particularly for microniches), and the data are interpreted using 3D models, there will be an increasing need for the determination of reaction rate constants of processes occurring at the localized scale. Use of constants estimated using spatially averaged data is unlikely to be applicable to three-dimensional reaction and transport models that include microenvironments. To date the few models that have attempted to simulate the effect of discrete microenvironments on sediment systems (Jahnke, 1985; Brandes and Devol, 1995) have only investigated limited components in one or two dimensions. Where conditions around a microniche vary over space and time only three-dimensional models give full validity. Such models of whole systems (e.g. Sochaczewski et al, 2008) will allow estimates of changes to the system due to external influences (for example sudden anoxia or an input of a pollutant) to be better predicted. Use of only a single rate constant for the whole of the system excludes the likelihood that reactions occurring at microniches will have a higher rate constant than those occurring in the rest of the sediment matrix, due to elevated microbial populations that are more likely to be in the exponential growth phase. Using multiple rate constants will allow examination of the effect of microniches on the system and estimations of their significance.

At microniches of relatively high concentration (compared to ambient conditions) the kinetic order of reaction may also be important when predicting diagenetic behaviour. An analysis of Mo speciation by Erickson and Helz (2000) showed that a three-fold change in sulphide concentration could produce a 100-fold change in the rate of conversion of molybdate (MoO_4^{2-}) to tetrathiomolybdate (MoS_4^{2-}). Such an observation suggests that the assumption that reactions used in most diagenetic models are first order may not always be appropriate. Supersaturation of metals and sulphide at a microniche was observed by Motelica-Heino et al (2003), suggesting that their rates of resupply at these locations may exceed reaction rates for consumption processes. This additional complexity needs to be considered when modelling sediment systems in 3D.

1.2.2. Role of microniches in accumulation and scavenging processes

When trace metals in sedimentary rocks are used to characterise paleoenvironments potential effects caused by microniches must be considered, to allow accurate prediction of past deposition environments. For example, Mo is converted in sulphidic environments from a weakly binding hard base to a soft base that is easily scavenged by Fe-bearing sediment constituents (Erickson and Helz, 2000). If this process occurs at sulphidic microniches within the oxic zone, the sediment's ability to enhance accumulation of Mo is increased. This is probably an extreme example, as the reduced form of Mo is less easily oxidized than other reduced metal species

(Shaw et al, 1990). Given the critical role of sulphide concentrations in Mo reduction, microniches may play an important role in these accumulation/scavenging processes.

1.2.3. Analysis of solute distributions

Another benefit of sub-mm studies is the more accurate analysis of solute distributions, such as O_2 penetration depth. O_2 microprobes allow the immediate environment around burrows and feeding tubes to be investigated at high resolution. Investigation at these locations is important if fluxes estimated from diffusion gradients are to be compared to directly measured fluxes. However, if data relating to large-scales are required, such as an average flux for a large area of ocean sediment, multiple benthic chamber measurements may be more appropriate. Equivalent results could only be obtained using microsensors by making many, time-consuming, deployments. Glud et al (2005) demonstrated the need to use multiple deployments at the same site to predict accurately fluxes using microscale techniques. They calculated an O_2 penetration depth of a Sagami Bay (Japan) sediment along a 175 m transect to be 3.9 ± 1.5 mm based on 347 profiles. Microelectrodes provide the best option for the study of solute concentrations across the sediment-water interface on a local scale, as they have the least influence on the hydrodynamic conditions. Compression of the diffusive boundary layer (DBL) by electrodes has been assessed quantitatively (Glud et al 1994a). While recently developed planar optodes will allow the solute distributions below the sediment surface to be described in two dimensions for several analytes (O_2, pH, CO_2, NH_4^+), they have a greater effect on the DBL than microprobes because of the greater physical dimensions of the device and the introduction of a wall through the sediment at the plane of measurement.

1.3. Scope of this review

This review provides a unifying framework for literature where measurements have been made on a sub-mm scale and microscale features have been identified. This embraces O_2 probes (microelectrodes and needle/2D optodes), other planar optodes, diffusive gel probes (DET and DGT) and three high-resolution biological studies. The basic principles of these techniques are identified and performance characteristics of the chemical methods reviewed. The features revealed by the procedures are then assessed for each type of probe. With the aim of discussing the significance and future direction of microniche studies, the review considers exclusively sub-mm data that reveal microenvironments. It is not intended to be exhaustive and does not cover data that reveal local features using mm or lower scale analysis. Sub-mm scale analysis has the advantage of consistently providing multiple data points that define solute gradients at, and in the vicinity of, microenvironments, particularly when the data are available in two dimensions. When only one or two data points represent peak concentrations, features, and their diameters, are not well established.

In order to focus exclusively on processes occurring within the subsurface sediment, this review will exclude microscale measurements of photosynthetically active sediments. This well-studied subject has been recently reviewed by Revsbech (2005) and Kühl (2005). These reviews are, in part, focussed on commercially available probes, but the cited references provide a good catalogue of previous research.

Several other microsensors have been developed that cover a range of components and are capable of making measurements at sub-mm resolution, but these techniques are not covered in this review, as published data do not include micro-features. Table 1 contains examples of these probes, including the maximum resolution obtained and the maximum depth to which they have been deployed. A range of microelectrodes for sediment analysis are reviewed in Kühl and Revsbech (2001), Taillefert et al (2000), and Hanrahan et al (2004). See also Buffle and Horvai (2000), and Viollier et al (2003) for broader views of recent technologies.

1.4. Definitions

In this review, a microenvironment is defined as a small-scale location within the 3-dimensional sediment matrix where the geochemical behaviour is significantly different from the average for that depth. This may be a gas bubble, a burrow or feeding tube from a benthic organism, or a particle of reactive organic matter or other component that has biogeochemical reaction rates which are higher (or lower) than the surrounding environment. We reserve the term microniche for the microenvironments associated with reactive organic matter. In a microscopic study of marine sediments, Johnson (1974) identified possible food sources of diameters ranging from five µm to 1.9 mm. Jørgensen (1977) estimates a detrital particle scale range of one µm to several millimetres or centimetres. There may be particular conditions where such particles can be considered as microniches. Based on measurements from the studies reviewed here, a characteristic observable microniche scale range is from 400 µm to ~1 cm diameter.

2. Oxygen microprobes

2.1.1. Microelectrode

O_2 microsensors were first used to study marine sediment at high spatial resolution by Revsbech et al (1980; 1980a). They used a modified Clark type electrode (Clark et al, 1953) where a current is generated by O_2 reacting at an electrode (cathode) after diffusing through a membrane. The tip of a 0.1 mm platinum wire, encased in glass so that only the tip was exposed, was electrolytically etched in saturated KCN to a diameter of 1-4 µm. A recess was then etched into the wire at the tip, and covered with a membrane of collodion and polystyrene, to give a final tip diameter of 2-8 µm. The anode was a separate Ag/AgCl electrode. In the first environmental studies using this electrode the measurements were made at 0.5 mm intervals (Revsbech et al, 1980a). The method was improved by firstly electroplating the tip with gold and using silicone rubber for the membrane (Revsbech and Ward, 1983) and secondly incorporating an internal guard cathode to quench O_2 diffusing toward the sensor from the internal electrolyte (Revsbech, 1989).

Until the development of O_2 optodes, the microelectrode methods developed by Revsbech and co-workers were used for the vast majority of studies investigating sediment O_2. As the general principles of electrode measurements are widely reported, they are not addressed in this review (see e.g. Mendham et al, 2000; Reimers, 2007).

2.1.2. Performance characteristics

O_2 electrodes have good response times, with 90% of the maximum signal being reached typically within 0.2 s. Due to the very low O_2 consumption and the micro-scale, near-spherical geometry, the measurement was found to be almost independent of stirring while responding linearly to the concentration of O_2. Although, current drift can be experienced at high and low O_2 tensions and in the presence of sulphide (Revsbech et al, 1980), Reimers (1987) showed that current drift could be overcome by in-situ pre-equilibration in a powered state for 15-20 mins before commencing measurements. Reimers (1987) also demonstrated that the changes in electrode behaviour as a result of pressure variations are thermodynamically predictable. The operational lifetime of commercially available O_2 microelectrodes made using similar techniques to those described above, is two months to one year (Revsbech, 2005).

Microelectrode tips have diameters in the range of 2-10 µm. This small size has the advantage of minimising disturbance of the surrounding media and, because spherical diffusion is promoted in solution, a steady-state current is generated. However, the minimum tip size tends to be restricted by the necessity of maintaining optimum rigidity. Flexing of the electrodes can occur when pushed towards particles, resulting in erratic signals (Revsbech et al, 1986). Nodules of Mn near the sediment surface and sharp grains can cause additional stress on the electrode tips, which have been reported to break in several of the studies reviewed (e.g. Reimers, 1987). This fragility limits deployment depths within sediments. Glud et al (1994a) investigated the effect on the DBL imposed by the deployment of microelectrodes and concluded that the deployment of electrodes from above the sediment surface reduced the DBL thickness by 25-45%.

The majority of studies using O_2 microelectrodes have been carried out in marine environments. However, some studies have deployed these probes in freshwater sediments (e.g. Sweerts et al, 1989; Wang et al, 2001; Stief et al, 2005).

2.2.1. Needle-type optodes

Oxygen optodes, largely utilising phosphorescence based methods, have long been used in the fields of clinical science and environmental monitoring. Photochemical and physical properties of probes and polymers were recently reviewed by Amao (2003). Fibre-optic O_2 microsensors (microoptodes) were first developed for use in sediments by Klimant et al (1995). Oxygen optodes use the ability of O_2 to dynamically quench fluorescence. An O_2 sensitive dye, immobilized in a polymer, is formed at the tip of an optic fibre. The dye, which consists of a molecule containing ruthenium, absorbs light at a wavelength of 450 nm and maximally emits light at a wavelength of 610 nm. The fluorescent light, that is returned through the fibre optic and measured, is inversely related to the concentration of O_2. The practical advantage of optodes over microelectrodes is their robustness and relatively easy fabrication (Klimant et al, 1995). The optode is typically constructed from a multimode silica/silica step index fibre with a core diameter of 100 µm surrounded by a cladding of 125 µm thickness. The fibre is placed into an injection needle to improve mechanical stability. The system can be optically isolated by the application of a black silicon layer over the polymer dye layer. Final tip diameters are within the range 30-50 µm, with the size being limited by the minimum required intensity of the excitation light (Klimant et al, 1995). Strongly tapered fibres reduce excitation light to unacceptable levels (Glud et al, 1999). The optoelectrical system that is coupled with the device is described in Klimant et al (1995) and Glud et al (1999).

2.2.2. Performance characteristics

As O_2 optodes do not consume the analyte, the signal does not depend upon the flow velocity. However, response times are in the range 5-30 s, depending upon the thickness of the optically active and insulating layers. Microelectrodes are the preferred choice where a response time of <2 seconds is required (Glud et al, 1999). Interference tests by Klimant et al (1995) showed further advantages compared to microelectrodes. Optode signal strengths are unaffected by electromagnetic fields, high concentrations of sulphide and CO_2, changes in salinity, pH variations, or high concentrations of heavy metals. Optodes also provide long-term signal stability and a good shelf- life (typically >6 months) (Klimant et al, 1995). High pressures can have the effect of decreasing the quenching efficiency of the optode. O_2 sensitivity at 200 atm was found to be 8% lower than at 1 atm and 20% lower at 600 atm pressure (Glud et al, 1999).

Unlike O_2 microelectrodes, the needle optode gives a non-linear calibration. However, the calibration can be linearized by means of a modified Stern-Volmer equation (Klimant et al, 1995). The intensity of luminescence is strongly temperature dependent and changes with water depth. Therefore, calibration should ideally be performed under deployment conditions (Glud et al, 1999). Generally, a two-point calibration is implemented by performing a Winkler titration on sampled bottom waters and using the optode data from the anoxic zone within the sediment (Wenzhöfer et al, 2001).

Both Wenzhöfer et al (2001) and Glud et al (1999) obtained consistent O_2 profiles in marine sediments using both microoptodes and microelectrodes deployed in situ using benthic landers. Variability between optode and electrode profiles at these sites was no greater than the variability during multiple deployments of microelectrodes at a single site (e.g. Reimers et al, 1986). Wenzhöfer et al (2001) deployed microoptodes at 0.5 cm intervals, to sediment depths of up to 40 cm, demonstrating that the depth to which these sensors can be deployed is significantly greater than the maximum for fine-tipped microelectrodes.

2.3.1. Planar (2D) optodes

Planar O_2 optodes, that were first used in sediments by Glud et al (1996), use similar optical principles to those for the needle type optodes, except that the O_2 quenchable fluorophore dissolved in the polymer is applied as a thin layer (10 µm) onto a transparent 175 µm thick support foil. The total optode thickness after application of an optical insulation layer is 205 µm. These dimensions are relatively arbitrary and a range of thicknesses of the optical sensor layer and support foil can be used. In the early work, the planar optode was then mounted onto a small frame of transparent Plexiglas, which was in turn mounted with transparent silicon onto the interior glass of an aquarium (Glud et al, 1996). Illumination can be provided by a halogen lamp (Glud et al, 1996) or an LED array (Wenzhöfer and Glud, 2004), coupled with an excitation filter. The luminescent light is collected by a charged coupled device (CCD) camera after being filtered to remove any reflected light from the excitation source. Measurements can be based on either fluorescence intensity or lifetime (time-domain) measurements. The measuring signal using the fluorescence lifetime approach is independent of the absolute fluorescence and thus is a more robust parameter (König et al, 2005). Frequently the ‘shark-fin’ approach to fluorescence lifetime of Hartmann et al (1997) is applied. Using this approach the ratio between the sensor signal in excited and nonexcited states is calculated during well-defined pulsing of the excitation light (Glud et al, 2001). Spatial resolution of the technique was 26 µm after data processing (Glud et al, 1996). Sediment profile imaging (SPI) photographic cameras housed in wedge-shaped Plexiglas chambers, for the in-situ study of organism-sediment interactions, were presented by Rhoads and co-workers in the early 1970’s (Rhoads and Young, 1970; Rhoads and Cande, 1971). Optodes using a similar construction have been successfully deployed (e.g. Glud et al, 2001).

2.3.2. Performance characteristics

The performance of the planar optode, in terms of interferences and optical behaviour, is similar to that of the needle optode, as the design chemistry and physics are the same. However, the 2D nature of the system introduces some unique limitations. Large variations in the response between different locations within the plane can be caused by both non-uniformity in the thickness of the polymer/fluorophore layer and the distribution of the silicon sealant used to affix the assembly to the aquarium glass. Steady fluorescence response measurements are most sensitive to sensor heterogeneity. Fluorescence lifetime or ratiometric approaches can minimise or eliminate such problems. Calibrating all pixels individually, which can be performed automatically, overcomes sensor heterogeneity and greatly improves the fidelity of the 2D images (Oguri et al, 2006). It is also recognized that the planar surface may affect the hydrodynamic conditions at the sediment-water interface (Glud et al, 1999). The thickness of the DBL may be increased and horizontal diffusion into or from the depth plane may result in the observation of a non-linear DBL gradient (Glud, personal communication). A modelling based assessment of the effect of DBL thickness on benthic mineralization and O_2 distributions has recently been undertaken (Glud et al, 2007). Viollier et al (2003) recommend avoiding the use of planar optodes for DBL studies in hydrodynamically active systems. Wenzhöfer and Glud (2004) have recognized that there is a possibility that invertebrate fauna may prefer to establish themselves adjacent to a solid surface in order to reduce O_2 consumption and to gain protection against predators. While this characteristic simplifies studies of the effects of fauna on O_2 distributions, it suggests that caution should be exercised in relating the information to faunal populations.

The system has been adapted for incorporation into both on-line (Glud et al, 2001) and autonomous (Glud et al, 2005) benthic landers. Oguri et al (2006) have successfully deployed a planar optode system using a UV sensitive fluorophore incorporating platinum, which enables higher resolution analysis in low pO_2 environments. Planar O_2 optodes have been used to measure uptake rates associated with burrows (Polerecky et al, 2006) and to study photosynthetic sediments (Frederiksen and Glud, 2006; Fenchel and Glud, 2000).

Glud et al (2001) assessed the potential effect of particle smearing, during deployment of the wedge shaped probe, on the O_2 distribution. Fluorescent particles were deposited at the sediment surface before insertion. No fluorescence from this source was detected at depth in the sediment, indicating that any smearing effect was of minor importance in the silty sediment tested. However, the study recognized that smearing is likely to be sediment specific and exacerbated in sediments where mechanical forcing of obstacles, such as shell fragments, occurs.

2.4. Evidence for microenvironments from microscale O_2 studies

The majority of microscale studies of O_2 in sediments are not aimed at investigating the geochemistry of microniches. Rather, the focus is usually on measuring diffusive fluxes and identifying O_2 behaviour due to biological activity, particularly in microbial mats and around feeding tubes and burrows. Evidence for the widespread existence of burrows in sediments, both in the oxic zone and at greater depths, is provided by numerous microelectrode profiles (Glud et al, 1994; Reimers, 1987; Wenzhöfer et al, 2001; and Jørgensen et al, 2005). Studies at the 100-µm scale usually identify burrows with 10-100 data points, demonstrating the usefulness of microsensors in clearly quantifying solute patterns at and around such structures.

In some cases, where several microsensors have been deployed together at one site, they have demonstrated the heterogeneity of the sediment by showing a significant variability between the profiles, both in terms of the penetration depth and profile gradients (e.g. Reimers et al, 1986). However, due to the continuous flux of O_2 into the sediment, it may be difficult to identify microenvironments that comprise an organic matter particle with an anoxic centre. The identification of such niches would require the electrode to penetrate close to the centre of the particle during the measurement. Anoxic niches within the oxic zone, created by dead organisms within shells (due to reduced O_2 penetration by decreased diffusion), will not be measured, as the shells will break the electrode or at least be displaced by it. Anoxic microniches have been observed using O_2 planar optodes in the oxic zone (Glud et al, 2005).

Profiles of microelectrode measurements illustrated in Wenzhöfer et al (2001) at Southern Atlantic sites (Figure 4) and in Koschorreck et al (2003) in a German acidic mining lake, show several sharp O_2 minima within otherwise regular profile shapes.

This suggests that there may be microniches of reactive organic matter that locally deplete O_2 due to higher oxidation rates.

According to a spherical model of O_2 consumption under deep-sea conditions (Jahnke, 1985), depletion of O_2 within the centre of a microniche of reactive organic material will require one or more of the following conditions: a large diameter (≥5 cm), a fast O_2 consumption rate or a slow internal diffusivity. As, in deep-sea sediments, particles of diameters greater than 5 cm are unlikely to exist, microniches characterized by O_2 minima are likely to arise through a combination of the latter two conditions. The particle size necessary to create an anoxic microniche will not only be dependent upon the above factors, but also on the O_2 concentration surrounding the particle (e.g. Jørgensen, 1977). Sochaczewski et al (2008) modelled, in 3D, the behaviour of O_2, NO_3^- and sulphide at spherical microniches with a range of diameters, positioned just below the sediment surface (centre of niche positioned at 2.5 mm below the sediment water interface). Sulphide was generated in niches as small as 2.5 mm diameter under the modelled conditions.

The nature of the particle may also affect microniche formation. Alldredge and Cohen (1987) found that O_2 depletion in a large crustacean faecal pellet (6.2 mm long) could occur just 100 µm below the surface of the pellet when the peritrophic membrane remained intact. The bacterial population per volume was also found to be significantly larger within this environment than in marine snow particles. O_2 depletion in marine snow and other faecal pellets ranged from 6-45% in dark conditions. Settling particles, particularly in shallow seas and continental margins, may also deplete O_2 from the sea floor (Alldredge and Cohen, 1987). Biological mixing of these particles into the sediment, together with direct faecal deposition within the sediment oxic zone, is likely to lead to the production of sub-oxic or anoxic microniches. The duration of the anoxia within microniches occupying the oxic zone may be unlikely to exceed 2.5 days, as Alldredge and Cohen (1987) found little or no O_2 depletion in faecal pellets of this age or older.

Sub-surface features should be considered in any calculations of sedimentary O_2 budgets and mineralization rates. Diffusion across burrow walls, which can be considered as secondary interfaces (e.g. König et al, 2005), can significantly affect these estimates. The O_2 distribution and temporal scales in burrow microenvironments and associated distributions of protozoa have been investigated in a marine sediment using microelectrodes (Fenchel, 1996; 1996a). Planar optodes were used by Wenzhöfer and Glud (2004) to show that O_2 penetration depths of 2-3 cm in the presence of fauna, compared to a few millimetres in their absence, were attributable to irrigation by polychaetes. This study and that of König et al (2005) observed plumes of suboxic waters just above the sediment surface because of expulsion of water from burrows by benthic fauna. Within the sediment Oguri et al (2006) identified sporadic depletion and recovery of O_2 concentrations at the oxic-anoxic interface, which may be caused by respiration of benthic foraminifera. These features had peak apparent O_2 consumption rates of ~20 µM min^{-1} and were observed over minute time-scales. Methods of estimating O_2 fluxes, incorporating faunal burrow O_2 concentration data from optodes, have been developed (Wenzhöfer and Glud, 2004). Peak uptake rates of ~5.3 mmol m^{-2} h^{-1}, observed at the onset of darkness, decreased to less than half the peak rate just before sunrise. These observations were attributed to a distinct diel pattern in faunal activity.

Cameras incorporated onto benthic landers have, for decades, identified significant microtopography in oceanic sediments (see the excellent compilation of images by Heezen and Hollister, 1971). Many of the study sites reviewed here have employed benthic cameras (e.g. Wenzhöfer et al, 2001; Jørgensen et al, 2005). This imaging can allow better estimation of the sediment-water interface when deploying sediment-penetrating probes.

3. Other optodes

The construction of optodes to measure components other than O_2 usually only differs in the frequency of the excitation light and the chemical used as the fluorophore. The measurement approach (ratiometric or time-domain) is usually dictated by the available fluorophore. This section will therefore only report the analyte specific detail of other optodes.

Microelectrodes for pH and pCO_2 have been used extensively in the study of sedimentary geochemistry. A significant proportion of pH electrode use in sediments has been dedicated to co-analysis with another component to determine a species not directly measurable, such as carbonate for calcite saturation and calculation of total sulphide from S(-II) (e.g. Cai et al, 1995; Müller and Stierli, 1999; respectively). As studies of microenvironments with pH and pCO_2 probes have exclusively used optodes, microelectrodes for these components are not considered further in this review.

3.1.1. pH optode

A planar pH optode was first reported by Hulth et al (2002). It used a HPTS (8-hydroxypyrene 1, 3, 6, trisulphonic acid trisodium salt) fluorophore immobilized by sorption onto a cellulose acetate optode foil. HPTS has the advantage of operating in the visible range and having a large Stokes' shift separating the excitation (405/450 nm) and emission (520 nm) frequency maxima. The dual excitation nature of the fluorophore was used to calculate pH ratiometrically. The fluorescence response of the immobilized HPTS to increased sample pH is sigmoidal, reflecting the titration of this weak organic acid. This ratiometric detection largely eliminates any signal variation caused by non-uniformity in the distribution of HPTS on the foil (Hulth et al, 2002). Zhu et al (2005), who used an alternative membrane for the support foil (covalent immobilization onto PVA membrane), established that the ratiometric response is independent of temperature changes. Excitation and emission frequency maxima of their alternate foil were found to be 506/428 nm and 540 m respectively. An optode with an alternative fluorophore, utilising time domain dual-lifetime referencing (Liebsch et al, 2001), was developed by Stahl et al (2006) and deployed in a photosynthetic marine sediment. The spatial resolution for the pH optode measurements in all studies is approximately 50 × 50 µm, using sensors with areas up to 225 cm^2.

3.1.2. Performance characteristics

The sensor response time for the cellulose acetate supported HPTS was estimated to be less than five seconds. Zhu et al (2005), using a PVA support, measured the response time for a two unit pH change to be <5 mins to reach complete stability. Optodes using both support materials were deployed for a period of over 50 days without any significant changes to the calibration. Shelf life is up to three years when the sensor membrane is refrigerated (Zhu et al, 2006). The sensor foils are transparent, allowing visual inspection or photography of the sediment and any burrow structures, but care must be taken to ensure optical isolation, which is normally accomplished by measuring under dark or low light conditions.

Due to the sigmoidal calibration, the sensor has the greatest sensitivity close to the pK_a of the immobilized HPTS (Hulth et al (2002), pK_a of 6.4; Zhu et al (2005) pK_a of 7.06). The more the pH deviates from this value the greater the uncertainty, due to reduced signal to noise ratios, illustrating the advantage of the fluorophore used by Zhu et al (2005) for measurements in marine sediments. However, the sensor developed by Hulth et al (2002) has been deployed at pH ranges typical of marine environments without problems, consistent with the pK_a of HPTS being more suited to the lower pH ranges found in sediments as opposed to overlying seawater. Measurements agreed well with those obtained using pH electrodes and response is maintained in the presence of NH_4^+, Fe^{2+}, Mn^{2+} and sulphide in both oxic and anoxic conditions. The time-domain sensor developed by Stahl et al (2006) has a somewhat higher pK_a of ~8.3. Photobleaching of the area of pH indicator that was above the sediment-water interface reduced the sensitivity of that area of the probe by 7% (at pH 8.1) compared to pre-incubation calibrations. However, the calibration curve for the area of the sensor in the sediment remained constant for over three days. This probe was recommended for studies within pH ranges of 7.3 to 9.3 (Stahl et al, 2006).

3.2.1. pCO_2 optodes

The recently developed pCO_2 optode film uses the pH fluorophore HTPS combined in a cocktail with tetraoctylammonium cation (TOA^+) and tetraoctylammonium hydroxide (TOAOH). The sensor film is coated with a gas permeable silicon membrane (Zhu et al, 2006a). As with the pH optode, the pCO_2 system uses the ratio of fluorescence intensities (emission maxima 515 nm) following dual excitation (maxima 405/475 nm). Resolution is comparable to the pH optode. The sensor in this initial study was optimized for concentrations up to 20 matm. Typical concentrations from the Long Island Sound (USA) site were ~0.8 matm for overlying water and ~18 matm for the peak sediment value.

3.2.2. Performance characteristics

The 90% response time of the optode for an increase from zero to five matm was 1.5 mins. Response was found to be consistent over hundreds of pCO_2 transition cycles.

When the sensor foil is stored refrigerated and sealed, response remains stable for at least several months. Response was unaffected by pH (over the range 2-12), NH_3, or O_2. Interference from hydrogen sulphide at concentrations of less than 20 µM was negligible. Due to the reversible properties of these sensors, prolonged deployment times can be achieved, allowing measurement of temporal changes occurring over days or weeks. Zhu et al (2006a) deployed a pCO_2 optode for several weeks with no degradation in sensor foil properties. Deployment of pH and pCO_2 optodes either in-situ or in freshwater sediments has yet to be reported.

3.3. Evidence for microenvironments from pCO_2 and pH optodes

The 2D planar nature of optodes makes these sensors ideal for the study of solute distributions around polychaete worm burrows in sediments. Sharp pH gradients have been observed across burrow-wall/sediment interfaces (Figure 5), with a drop of 1.5 pH units over 1.1 mm observed by Hulth et al (2002) for a active *Nemertea* burrow. Data from occupied burrows of *Nepthys incisa* and *Nereis succinea* showed that the pH at the body surfaces of the worms can have large interspecies variations, with the pH adjacent to *N. incisa* having a typically lower pH (>1 pH unit) than the overlying water, while for *N. succinea* it was indistinguishable from the pH of the overlying water (Zhu et al, 2006). The large pH and redox gradients across irrigated burrow walls may affect the distribution of sorbed sediment components. The effect of sediment disturbance (including bioturbation and resuspension) on the sorption and partitioning of metals, organic and organometallic contaminants has been recently reviewed (Eggleton and Thomas, 2004).

Zhu et al (2006) observed that a region of lower pH (compared to the burrow and the surrounding sediment) began to form almost immediately adjacent to the area irrigated by *N. succinea*. This region of lower pH may be due to the supply of O_2 generated as a consequence of irrigation by the worm. The zone of low pH re-equilibrated to that of the surrounding sediment within approximately two days when the animal vacated the burrow. In contrast, abandoned burrows of *N. incisa,* which were subsequently infilled or collapsed, exhibited a substantially lower pH and elevated pCO_2 than the surrounding sediment. These features dissipated within approximately one week (Zhu et al, 2006; 2006a). They were attributed to elevated microbial activity associated with the possible introduction of reactive organic matter to the burrow, such as mucus secretions or faecal material, and the formation of energetically favourable oxidants (Fe and Mn oxides) within the burrow wall or introduced as the burrow becomes infilled (Hulth et al, 2002; Zhu et al, 2006a).

The decay of a *N. Succinea* body at 10 cm depth was examined over a one-week period (Zhu et al, 2006). On day one a region of low pH (≤ 5.9) was centred on the body. On day two the pH at the centre of the body increased slightly and rapid diffusion of protons into the surrounding sediment was observed. By day five the pH distribution had equalized with the surrounding sediment. These data suggest that microniches created by decaying fauna in anoxic sediment may be short lived. Localized decreases in pH associated with microniche activity were also identified by Hulth et al (2002).

4. Diffusive gel based devices for microscale measurements

Techniques that allow in situ sampling of porewaters, while limiting the disturbance of the overall system, have been developed over past decades. Peepers (dialysis samplers; e.g. Hesslein, 1976) have been used for many years as an alternative to core extrusion/centrifugation or whole core squeezing. Resolution is generally constrained by the dimensions of the sampling windows. The highest resolution peeper used to date was a system deployed to study, in 2D, the effects of burrows on filterable reactive phosphorus fluxes within and from sediment porewater. However, spatial resolution was limited to 9 mm, due to the diameter of the cell (7 mm) and the distance between cells (2 mm; Lewandowski et al, 2002; 2007). Improving the resolution will be limited by the challenges of small scale fabrication. Developments in gel-based techniques, have allowed the high-resolution analysis of many solutes in sediment porewaters at mm and sub-mm scale.

4.1.1. Diffusive equilibration in thin-films

Diffusive equilibration in thin-films (DET; Davison et al, 1991) utilises a polyacrylamide hydrogel (95% water) typically less than one mm thick, housed in a plastic assembly with a window on one side. A 0.45 µm membrane filter acts as a protective cover for the gel. The device allows solutes in the water of the gel to equilibrate with the adjacent porewater so that concentrations in the gel and porewater become equal. Equality of concentrations has been confirmed experimentally for major components and nutrients, but not for all trace metals. Deployment times are typically ≥ 24 hrs. Davison et al (1994) suggested that leaving the probe in place for this length of time may minimise the effect of disturbances caused by deployment (such as particle smearing). Although, depending on the diffusion layer thickness, times approaching a day are usually required to assure complete equilibrium (>95%), the concentrations measured by DET in sediments reflect most faithfully the concentration within the porewater during the final few hours of deployment (Harper et al, 1997).

This technique was first used in sediments for measuring dissolved iron (Davison et al, 1991). After deployment, the iron was immobilized through oxidation and hydrolysis by immersing the probe in sodium hydroxide solution. The gel was then dried and analysed directly by proton-induced x-ray emission (PIXE). Other workers have used quick slicing of the gel, followed by back equilibration of the slices into Milli-Q water or NaCl solution (e.g. Mortimer et al, 1988). Fones et al (1998) used 2M nitric acid as the eluent. The technique has been applied at one millimetre resolution for a large range of major ions and trace elements (in order of earliest use), Mn and Fe (Davison et al, 1994), NO_3^-, SO_4^{2-}, (Krom et al, 1994), NH_4^+, alkalinity, $\sum CO_2$, Ca, Cl, Br (Mortimer et al, 1998), Mg, K (Zhang et al, 1999), Cd, Cr, Cu, Pb, Zn (Yu et al, 2000), U, Re, Mo (Morford et al, 2003), Fe(II) (colorimetric; Jezequel et al, 2007) . Docekalova et al (2002) showed in laboratory tests that DET probes could be used for the simultaneous determination of many different analytes using the same probe (at least 19 elements).

4.1.2. Performance characteristics

The spatial resolution at which DET provides an accurate record of porewater chemistry is a function of both the diffusional relaxation during equilibration in the sediment and of the diffusional relaxation time between removal of the probe and fixation. Diffusional relaxation, which refers to the tendency of ions in the gel to diffuse from regions of high to low concentration (Davison et al, 1991), is the most significant limitation to DET resolution. The resolution at which fidelity of measurement is preserved when a single piece of 1 mm thick gel is used cannot be improved appreciably beyond the one millimetre used in many of the above studies. The time dependence of diffusional relaxation has been modelled by Davison et al

(1994) and Harper et al (1997). For example, the apparent concentration at a one millimetre wide peak, measured using a 0.4 mm thick (unconstrained) gel, will be reduced to ~75% of the actual peak porewater concentration after a relaxation time of ten minutes (Harper et al, 1997).

To improve resolution by preventing lateral diffusion, a DET probe where the gel was constrained within small compartments was developed (Fones et al, 1998). The constrained probe consisted of a ladder of laser cut 200 µm wide compartments, each 2 mm long. Gel compartments were spaced at 200 µm vertical intervals, giving a vertical resolution of 400 µm. Three 'ladders' were cut onto the single probe, with the centre column being offset by 200 µm depth to the other columns. This allowed the entire depth range of the probe to be analysed at 200 µm intervals. Polyacrylamide gels with a non-swelling composition were used to fill the thin compartments.

DET has been successfully deployed in freshwater, estuarine and marine sediments (see above references), 2D data has also been achieved by fixing analytes within the gel (e.g. Shuttleworth et al, 1999) and using colorimetric approaches (e.g. Jezequel et al, 2007).

4.2.1. Diffusive gradients in thin-films

Diffusive gradients in thin-films (DGT) was first developed by Davison and Zhang (1994) as a method to determine trace metal concentration in solutions, but was soon used for the measurements of metals in sediments (Zhang et al, 1995). Fick's First Law of Diffusion is used to calculate the concentration in the exposure solution from the measured mass of analyte bound to a binding layer placed behind a layer of polyacrylamide diffusive gel of known thickness. Several binding layers have been developed for a large range of analytes (see recent reviews by Davison et al, 2007; Warnken et al, 2007).

Binding layers are formed by either adding a solid component to a gel before casting and curing, or precipitating a solid directly in the gel. Two binding layers have been used for sub-mm resolution analysis. Suspended particulate reagent iminodiacetate (SPR-IDA) has a bead size of 0.2 µm and has a high affinity for many metals and divalent cations. Gels that contain homogeneous distributions of binding components can be analysed at high-resolution by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) or PIXE. This approach was first used by Davison et al (1997) to provide a 2-dimensional image of Zn, Fe, Mn and As(III) in a microbial mat and underlying sediment. The other binding phase used for sub-mm analysis is silver iodide (AgI) embedded in a gel (Teasdale et al, 1999). This initially pale yellow layer becomes grey-black when the AgI reacts with sulphide to form black silver sulphide (Ag_2S). The density of the colour change, which can be related to concentration, can be analysed using a flat bed scanner and computer software. Further advancements of this technique have yielded a more homogeneously distributed binding phase precipitated within the gel (Devries and Wang, 2003), and analysis by LA-ICP-MS has been performed (Widerlund and Davison, 2007). Jezequel et al (2007) have successfully used a reaction with a PVC film within a DGT-type device to estimate dissolved sulphide species.

4.2.2. Performance characteristics

If porewaters are effectively buffered by rapid resupply from a local source, such as a desorbing solid phase, the DGT measured flux can be quantitatively interpreted as a concentration (Davison et al, 1997). Quantitative interpretation in terms of the concentration in the porewaters is also possible if there is no supply from solid phase to solution. In practise there is usually some solid phase resupply and quantitative interpretation in terms of concentration is more complicated. The differences between DET and DGT data is illustrated by profiles from Fones et al (2001), where Fe and Mn peaks measured by DGT were three times more pronounced than the peaks at the same depth measured by DET. Dynamic models of the DGT–sediment system that incorporate the kinetics of metal exchange induced by the DGT device have been developed (Harper et al, 1998; 1999; 2000; Sochaczewski et al, 2007). Although these models were verified for saturated soils (Ernstberger et al, 2002), they have yet to be tested fully in sediments. However, the dependence of the resupply on diffusive gel thickness has been experimentally examined (Zhang et al, 1995; Naylor et al, 2006) and cases of deficient supply were considered (Zhang et al, 2002). Generally the DGT measurement is best treated as an assessment of the solute that can be locally supplied in response to a perturbation. A local peak in the signal indicates a local elevation in the concentration in the porewaters or a locally increased supply from the solid phase.

Lack of localized DGT maxima at depth in homogenized sediment, suggests smearing effects are not significant (Zhang et al, 2002; Tankere-Muller et al, 2007). The effects of solution composition and deployment times on the measurement of trace metals have been investigated (Gimpel et al, 2001) and specific performance characteristics for the SPR-IDA binding phase have been assessed (Warnken et al, 2004).

4.3. Evidence for microenvironments from diffusive gel studies

Measurements with the constrained DET probe revealed a double maxima for Fe(II) in a freshwater lake sediment (Fones et al, 1998). Potential biogeochemical explanations are that the feature is caused by microbially mediated reduction of nitrate by Fe(II) or that there is horizontal banding of labile organic material. However, the possibility that the features are a sampling artefact is not ruled out. The doublet was resolved by multiple data points at 400-µm resolution, but the smaller of the two maxima was only resolved by one data point at one millimetre resolution. The data clearly illustrated that coarser resolution has a tendency to overestimate peak width and underestimate peak height.

Metals were measured at 100-µm resolution in a contaminated freshwater sediment overlain by a microbial mat using DGT with an SPR-IDA binding layer that was analysed by PIXE (Davison et al, 1997). Peak mobilisation of Zn, Mn and As occurred at 0.8, 2.0 and 3.6 mm respectively below the interface with the mat, clearly showing their control by different mechanisms. It was suggested that the Zn was released primarily from organic matter, while As release occurred with the reductive remobilisation of Fe.

Motelica-Heino et al (2003; 2003a) observed simultaneous release of metals and sulphide in a freshwater sediment. An SPR-IDA binding layer was placed behind a silver iodide gel in a DGT sediment probe. Below the sediment water interface, dark, irregular spots of Ag_2S were observed on the AgI gel, indicated local centres of elevated sulphide concentrations above a uniform background. These centres were attributed to the clustering of sulphate reducing bacteria, but this was not confirmed by biological analysis. By scanning a laser across the trace metal binding layer underlying the sulphide binding gel and measuring the ablated material by ICP-MS, trace metal concentrations were analysed at 100 µm resolution in a transect corresponding to one of the sulphide spots. Localized remobilisation of metals (Ni, Co, Fe and Mn) was observed at the site of elevated sulphide (Motelica-Heino et al, 2003). Saturation indices (SI) of metal sulphide species were calculated for microniche concentrations. At the peak concentration, the SI indicated supersaturation for all metals except Mn. Motelica-Heino et al (2003) proposed that supersaturation at the site of the peak concentrations may be caused by the rate of production exceeding the rate of removal by precipitation. Elevated trace metal concentrations associated with sulphide may be due to simultaneous remobilisation associated with both sulphate and iron acting as electron acceptors for the oxidation of the microniche organic matter. Koretsky et al (2005) observed coexistence of aerobic, Fe-, Mn- and sulphate-reducing bacteria within the upper 10 cm of a salt marsh sediment that is subject to a large supply of organic matter and intense bioturbation. Coexistence of these bacteria suggests that within localized environments, oxidants may become limited, allowing processes with lower free energy yields to occur successively.

The study by Motelica-Heino et al (2003) provides evidence for the simultaneous release of metals and sulphide from microniches, and for the coexistence of local excesses of labile organic matter, iron and sulphate reducing bacteria. This technique has considerable potential to yield useful geochemical information, particularly as 2D mapping of sulphide and metal concentrations can be undertaken in the same combined gel. In their evaluation of techniques for 2D imaging of trace metals by laser ablation (LA)-ICP-MS, Warnken et al (2004a) showed, using a 500 µm spaced analysis grid, that Co was heterogeneously distributed in two dimensions in a freshwater sediment, whereas slicing into 1 x 15 mm strips averaged the data to a featureless line of almost constant concentration (Figure 6). Fones et al (2004) showed localized centres (1-2 mm diameter) of Zn mobilisation in a marine sediment in their 2D images of Zn obtained using LA-ICP-MS at a resolution of 100 × 300 µm. In these last two examples the DGT probes were deployed in situ using landers.

Other high-resolution studies using DGT have exploited Teasdale et al’s (1999) development of a simple procedure for measuring sulphide in one or two dimensions by simply scanning the image. 2D images of sulphide obtained by Motelica-Heino et al (2003) and Devries and Wang (2003) in freshwater sediments showed dark spots of elevated sulphide from 1 mm to >1 cm diameter superimposed on background sulphide signals. These sulphidic microniches were attributed to spatially discrete aggregates of reactive organic matter with associated high populations of sulphate reducing bacteria. In microniche faecal pellets where the peritrophic membrane is intact, reduction may occur in the order O_2, NO_3^- and SO_4^{2-}, as Fe and Mn oxides are effectively excluded. This may result in some microniches in the anoxic zone being reduced almost exclusively by sulphate. Localized sulphide release was also evident in linear high-resolution profiles (Naylor et al, 2006). 2D data for DGT deployments in undisturbed freshwater cores, obtained by Widerlund and Davison (2007), showed the proportion of microniche-related sulphide flux was ≥1-8% of the total net porewater flux of sulphide. Figure 7, illustrates data that can be extracted from DGT sulphide binding probes.

5. Sub-mm biological surveys

Many methods, covering a range of scales and within different environments (marine and freshwater), have been used to assess the influence of benthic organisms (i.e. bioturbation and bioirrigation) on physical and chemical characteristics of sediments (a large body of this work was reviewed by Krantzberg, 1985). Developments in analytical techniques (as detailed in previous sections) have led to the ability to study chemical behaviour at the exact location of defined features (e.g. inhabited or relic burrows). Other technological advancements have led to additional techniques with the specific ability to visualise biological features at high-resolution. This section will cover three such techniques, mapping of relative enzyme activity, a resin based method for investigating sub-mm life positions and axial tomography of sediment cores for 3D visualisation of benthic structures.

5.1. Azo dye mapping of relative enzyme activity

Rogers and Apte (2003) presented a unique method for the sub-mm analysis of relative enzyme activity in sediments. Enzyme substrates (naphthol AS) were loaded onto filter membranes that were attached to a plastic card to provide rigidity. Enzymes in contact with the membrane hydrolyse the substituted naphthol. This exposed membrane can then be developed in a diazonium salt solution, resulting in a coloured precipitate where substrate hydrolysis occurs (Rogers and Apte, 2003). A deployment time of 24 hrs was chosen to minimise the effects of any potential disturbance during probe insertion. In common with DGT AgI probes, the resulting image can be analysed by computer-imaging densitometry. The scanned images can provide high-resolution information (such as those shown in Figure 7 for the DGT sulphide binding phase), although numerical data extracted from these scans in the initial study were one-dimensional and at the mm scale. Previous one-dimensional studies using core slicing have been undertaken at one millimetre resolution or lower (e.g. Craven et al, 1986). How well measurements of relative esterase activity are able to predict general microbial activity is still unknown (Rogers and Apte, 2003). Further work is therefore needed to establish whether microniches observed using this technique are related to zones of higher overall microbial activity.

5.2. Sub-mm life positions of benthic biota using the fluorescently labelled embedded core (FLEC) technique

Bernhard et al (2003) presented a new technique to determine the life-positions of benthic fauna, which combined the life position method developed by Bernhard and Bowser (1996) with hot-knife microtomy (McGee-Russell et al, 1990). The FLEC technique involves perfusing several solutions/liquids through a small core (1.5 cm diameter and <10 cm long) as a pre-treatment, before a final perfusion of a liquid resin through the core, which is subsequently cured for a period of 12 hours to obtain a solid core suitable for cutting (Bernhard and Bowser, 1996). Bernhard et al (2003) suggest that the perfusion of several liquids through the core does not significantly affect the life positions of the biota of interest. The hot-knife method allows sectioning of cores into ~100 µm slices without sample loss. Depth profiles that were 11 mm long were examined. Sections were analysed using a laser scanning confocal microscope (LSCM). Benthic fauna were then visually identified from the images. Studies of microbioirrigation have been undertaken using similar techniques (Pike et al, 2001)

5.3. Axial tomography of intact sediment cores

X-radiography of sediments was first performed several decades ago (e.g. Hamblin, 1962; Calvert and Veevers, 1962; Axelsson and Händel, 1972). Using this technique with thin aquaria, animal burrows have been studied (e.g. Rhoads and Young, 1970; Schaffner et al, 2001). Perez et al (1999) established procedures for using axial tomography (computer-aided tomography; CT) for the study of benthic communities in intact cores. The minimum axial slice thickness in this initial study was 1.5 mm. A rotating array of x-ray transmitters and receivers scans from all angles around a sample. Each voxel (pixel with a depth dimension) value will depend on x-ray attenuation related to material density, atomic number, and the principles of radiation matter (Dufour et al, 2005). Thus, attenuation of x-rays can differentiate between sediment and water in benthic structures. Data from these scans have been used to determine the percentage space occupied by biogenic structures, gravel and organic matter (Michaud et al, 2003; Mermillod-Blondin et al, 2003; Dufour et al, 2005; Rosenberg et al, 2007). Linear (pixel) resolution in the above studies was in the range 0.2 mm to 0.5 mm.

5.4. Microenvironments revealed by biological studies

Two-dimensional scans of esterase activity clearly showed niches of elevated activity in a sediment mesocosm at both sub-mm and mm scale (Rogers and Apte, 2003), but the relationship between esterase activity and general microbial activity still requires evaluation.

CT scans of cores can show the production and destruction rates of biogenic microenvironments. Depth characteristics of such structures can be assessed and spatial distributions can be determined. The data can be used to assess the effect of these structures on solute distributions and fluxes, both within, and from and to the sediment. An example of the images available is shown in Figure 8A. These techniques also give the potential for assessing the impact of preferential burrowing of biota at planar surfaces by quantifying its significance. This type of information may allow better quantification of solute patterns obtained by planar optodes and may give more insight the mechanisms of microniches formation at the surface of DGT devices.

Bernhard et al (2003) investigated the sub-mm life positions of bacteria, protists and metazoans in a Santa Barbara Basin sediment that contains a high bio-volume in the surface centimetre. The study revealed much heterogeneity in both horizontal and vertical distributions of benthic fauna (shown in Figure 8B). Several features related directly to microenvironments. Large flagellate communities (flagellate swarms), which are zones of elevated carbon cycling, are thought to exist exclusively in anoxic environments. They were observed at a depth of 0.2 mm where a weakly oxic environment is expected. It was estimated that there may be as many as 14 of these swarms per cm^3, suggesting that they may exert a significant influence on whole sediment geochemical processes in surface sediment, in terms of turnover rates/volumes, and yet still contribute to structuring chemical heterogeneity. Some metazoans were found to occur in close proximity to anaerobes, which is unexpected due to the opposing survival conditions of each organism (oxic and anoxic). Bernhard et al (2003) suggest that this proximity may occur due to the niche conditions having sufficient O_2 for respiration but not enough for O_2 toxicity. The sporadic temporal O_2 depletion/recovery cycles observed by Oguri et al (2006) using a planar optode, may potentially be associated with the life-positions of such biota. The possibility that there is a symbiotic relationship between the organisms is not ruled out (Bernhard et al, 2003).

6. Assessment of progress and geochemical implications

Results from the limited number of studies undertaken at the microscale suggest that our understanding of sedimentary diagenesis has been somewhat oversimplified by analysis at a larger, spatially averaged, scale. All of the probes reviewed have, to varying extents, revealed microniches. For example planar optodes have revealed niches of lower pH and depleted O_2, DGT has revealed points of elevated trace metal and sulphide activity, and a life positions study has demonstrated that some biota may exist in heterogeneously distributed communities. However, interpretation of these data in terms of sediment biogeochemistry is often difficult, as specific chemical or biological ‘drivers’ of these processes are not identified and the processes can generally only be related to one or two analytes. Microsensor techniques have enabled more precise measurements of diffusive boundary layers and when combined with data from secondary interfaces, will provide a more accurate understanding of variations in solute fluxes across the sediment-water interface. DGT data have revealed double maxima in key redox components that would not have been resolved by lower scale measurements, suggesting that in many systems biogeochemical processes may be more complex than previously considered.

6.1. Effects of benthic fauna

Data from planar optodes and O_2 microprobes provide more details of the effects that benthic biota exert on solute distributions in surface sediments, both in terms of spatial and temporal influences. This influence extends into the anoxic zone in the majority of studies. The overall effect of burrows (the secondary interface) is largely to increase the effective interface between the sediment and the overlying water. The amount of O_2 available for organic matter (OM) degradation and reoxidation of reduced species is increased, and irrigation facilitates a more rapid efflux of solutes such as CO_2 from the sediment. The large gradients of solutes across the secondary interface have implications for high-order, pH-dependent processes, such as hydrolysis, or dissolution reactions. These large solute gradients may lead to extreme, spatial variations where localized chemistry will have little resemblance to mean values (Zhu et al, 2006).

6.2. Interpretation of microniche data

6.2.1. Microniche distributions

Heterogeneity within sediments is increased as a result of increased inter microniche distance, slow transport and fast sinks (Harper et al, 1999a). Microniches can be regarded as finite zones where organic matter degrades at elevated rates, so if they are very numerous their individual effects may not be observed. The sediment could be considered laterally homogeneous if the following conditions were met: no concentration peaks exist in the horizontal plane, an even distribution of oxidants occurs across the plane and where benthic fauna are absent. In this case, the averaging scale represented in Figure 1 would be sufficient to describe the system. In practice, in sediments with significant populations of benthic fauna and an input of organic carbon, microniches are likely to exist, with their density and distribution depending upon the faunal populations and the volume and spatial distribution of the organic matter.

6.2.2. Assessment of compatibility of microniche data

So far, data revealing microniches are not always complementary. Optodes have identified microniche activity attributed to elevated OM decomposition within the oxic zone (e.g. Hulth et al, 2002; Glud et al, 2005), while DGT profiles identified elevated niches of trace metal activity within the same zone, but not at the sub-mm scale (e.g. Fones et al, 2004). Published evidence of microniches using DGT has either not described the O_2 conditions associated with the niche or has focussed on the simultaneous release of sulphide and metals in anoxic environments. The lack of congruent analysis makes it difficult to interpret these data in terms of specific geochemical processes. If the data reviewed here were shown to be compatible, the depleted O_2/lower pH observed by optodes and the elevated sulphide and trace metals observed by DGT may allow calculation of the expected metal sulphide formation and indicate if these environments are important for long-term mineral formation. However, synthesis of the current data, obtained from deployments in a range of sedimentary environments, would be speculative at best.

There is convincing evidence, from both the techniques reviewed here and other studies at lower resolutions, that microenvironments caused by burrowing biota have significant effects on local solute distributions and fluxes to overlying water. However, evidence that discrete particles of organic matter (microniches), introduced into the sediment by biota, affect large-scale or longer-term diagenetic processes or reaction rates is inconclusive. Further investigation on the distribution and frequency of microniches is required in order to estimate their cumulative effect on element diagenesis and immobilisation/remobilisation, including pollutant fate.

6.3. One- or two-dimensional data?

Two-dimensional data have the advantage of providing information about variations in processes occurring in both the horizontal and vertical planes simultaneously, allowing direct measurement of the dimensions of a feature where the chemical component being measured differs from its background. If there is an associated physical manifestation, such as a burrow, it can also be directly observed visually when transparent optodes are used. Planar probes are generally left in situ for extended periods (hours to weeks) to provide temporal data from optodes, to ensure equilibration with solutes in the porewaters when using DET and to allow analysis of low concentrations of trace metals by DGT. This deployment time may be longer than the typical lifespan of a microniche, so observation of microniche activity may only be possible if bioturbation introduces fresh organic matter at the planar surfaces. As there is a possibility of planar surfaces preferentially attracting burrowing organisms, the prevalence of microenvironments may be over-estimated, with their observed distribution being unrepresentative of the bulk sediment. It is difficult to quantify the effect of benthic organisms on observed DGT or DET profiles, as no direct visual record is available. Needle type probes with short response times have the advantage of providing a measurement at a precise spatial location without (i) affecting the geochemical nature of the surrounding sediment (ii) moderating the concentration of the analyte or (iii) providing a surface substrate for biota. In theory, then, their repetitive deployment to provide a grid of data should overcome some of the problems of planar probes. However, needle probes are unlikely to give precise data on the size of features, as they are unlikely to penetrate repeatedly their centres, or intersect edges at a precise 90º angle. As distributions of microniches are likely to be stochastic, many multiple deployments will be required to characterise them, potentially introducing substantial disturbance. Furthermore, needle probes may directly damage living organisms.

6.4. Future direction of microniche studies

There is a need for further data that covers a wider range of analytes. Given the ‘toolbox’ of high-resolution techniques, which have been used for studies that have not reported microenvironments (Table 1), the capacity to expand knowledge in this area already exists. If microniches are known to account for a significant proportion of organic matter degradation, re-examination of the current understanding of some aspects of sedimentary diagenesis (e.g. trace metal behaviour and fate) may be required. Reaction rates for processes occurring in microniches may be much greater than comparable rates estimated for ‘whole sediment’. Moreover, DGT data have demonstrated that the dynamics of processes occurring in microniches can cause localized supersaturation. The multi-G model for organic matter decomposition may have its physical embodiment in microniches. If microniches were to account for only one percent of the total available organic matter, but had rates 50 times that of the bulk material, the microniche activity would account for one-third of the C turnover of the whole system.

Use of probes capable of measuring only a single element increases the complexity of elucidating diagenetic behaviour. When there is small scale heterogeneity, data from separate probes, even deployed as close as 1 cm apart, cannot be directly compared. To provide a full picture of the biogeochemical processes operating at a micro scale, probes capable of simultaneous multi-species analysis will be required. Future developments in probe design will need to incorporate this requirement. A number of tools already exist that fulfil these criteria but where microniches have not been identified (Table 1). One such device, the multi-element voltammetric microelectrode developed by Brendel and Luther (1995), has been deployed at high-resolution. A microbial mat was examined over ~2 mm at intervals up to 50 µm (for O_2, Fe(II) and Mn(II); Trouwborst et al, 2007). Deployment in intertidal salt marsh sediments at mm resolution has revealed small scale features (~cm scale). In this study the electrode was used for quantifying O_2, Fe(II), Mn(II), $\sum H_2S$, and detecting $FeS_{(aq)}$, and dissolved organic complexes of Fe(III) (Taillefert et al, 2007). The ability to provide speciation information for some elements is an additional benefit of this technology. Although this probe will be subject to the same disadvantages as any electrode (discussed above), it is clearly a tool capable of providing useful geochemical information about microniches.

The need for further studies of sediment systems at high resolution is clear. However, to date analysis tends to have focussed upon a limited number of analytes at specific geographical locations. In order to gain fully from the methods reviewed here, other existing technology and future developments, it would be beneficial if a range of techniques were deployed at future investigation sites. This more complete information, coupled with co-analysis of multiple analytes at precisely the same location, may allow interpretation in terms of specific chemical or biological diagenetic processes.

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Table 1. Sensors capable of measurement of sediment components at high resolution.

Sensor type	Maximum resolution (µm, µm^2 for planar)	Tip diameter (µm)	Sediment deployment depth (mm)	References
Amphoteric				
CH_4 biosensor	100	20	14	Damgaard and Revsbech, 1997
NO_x^- biosensor	200	70	8	Meyer et al, 2001
H_2S	100	<20	~35	Kühl et al, 1998
O_2/N_2O	100	20	6	Glud et al, 1995
Potentiometric				
NH_4^+	10	1	~17	de Beer et al, 1991; 1993
S(-II)	100	600	23	Müller and Stierli, 1999
pCO_2	500	160	70	Cai et al, 2000
pH	500	15	70	Cai et al, 2000
Ca^{2+}	100	10-20	~100	Wenzhöfer et al, 2001a
NO_3^-	100	1	2	Jensen et al, 1993
Voltammetric				
Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}	50	n/r	~2.5	Daniele et al, 2007
O_2, Mn, Fe, I^-, S(-II)	50	n/r	≥100	Brendel and Luther, 1995 Anschutz et al, 2000
Optical				
pCO_2 (needle)	200	<30	150	Wenzhöfer et al, 2001a
NH_4^+ (planar)	210 × 210	−	−	Strömberg and Hulth, 2005
pCO_2/pO_2 (planar)	78 × 78	−	−	Schroeder et al, 2007

n/r = not reported.

Figures

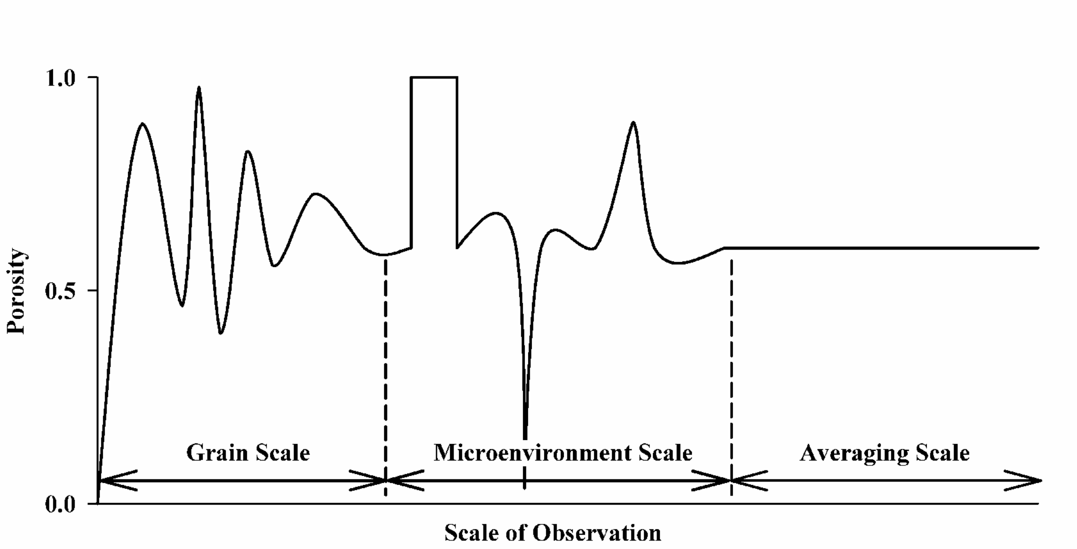

Fig. 1. Expected variations in porosity if measured at the specified scales (where scale refers to the size of the sediment parcel being observed). The observations go from the scale of a grain to that of an average measurement of a larger sediment sample. In the central section variability is caused by sediment features such as burrows, benthic organisms, faecal pellets or ‘hard-parts’ such as shells (the frequency of the features in this section will vary depending not only on the sediment properties but also the depth within the sediment). The porosity begins at zero as the starting point is arbitrarily set within a sediment grain. Modified from Boudreau (1997).

Figure 2: Copyright controlled

Fig. 2. Intact faecal pellets at 3–4 cm depth observed by slicing of a resin embedded sediment sample. Scale bar is 50 μm. Reproduced, with permission, from Watling, L., 1988, Marine Ecology-Progress Series, 47, 135–144.

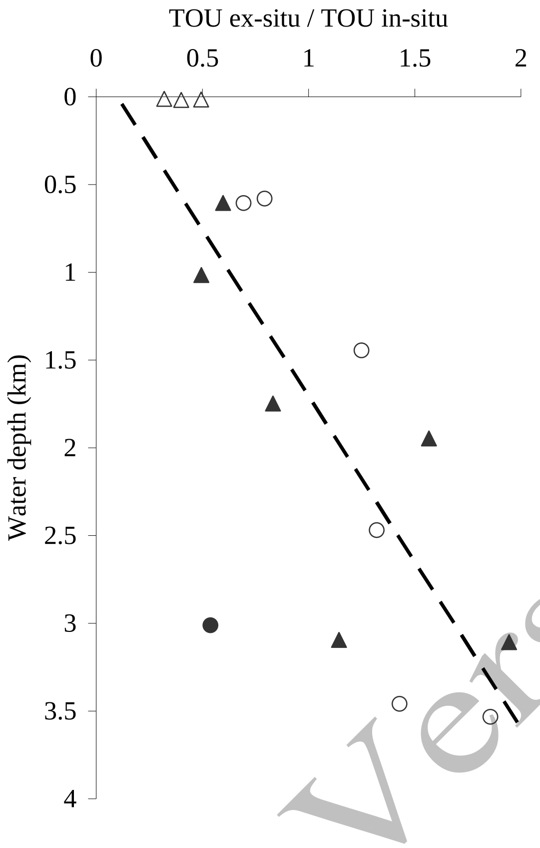

Fig. 3. Comparison of the sediment total oxygen uptake (TOU) ratio (ex-situ/in-situ) against the depth of overlying water. The dashed line indicates the best fit with an r^2 of 0.59, this increases to 0.78 when the outlier (filled circle) is excluded. Data from; Glud et al. (1994a; closed triangles), Glud et al. (1999b; circles) and Jørgensen et al. (2005; open triangles). TOU is the measure of the flux of O_2 taken from the overlying water by the sediment with units of mmol m^{-2} d^{-1}.

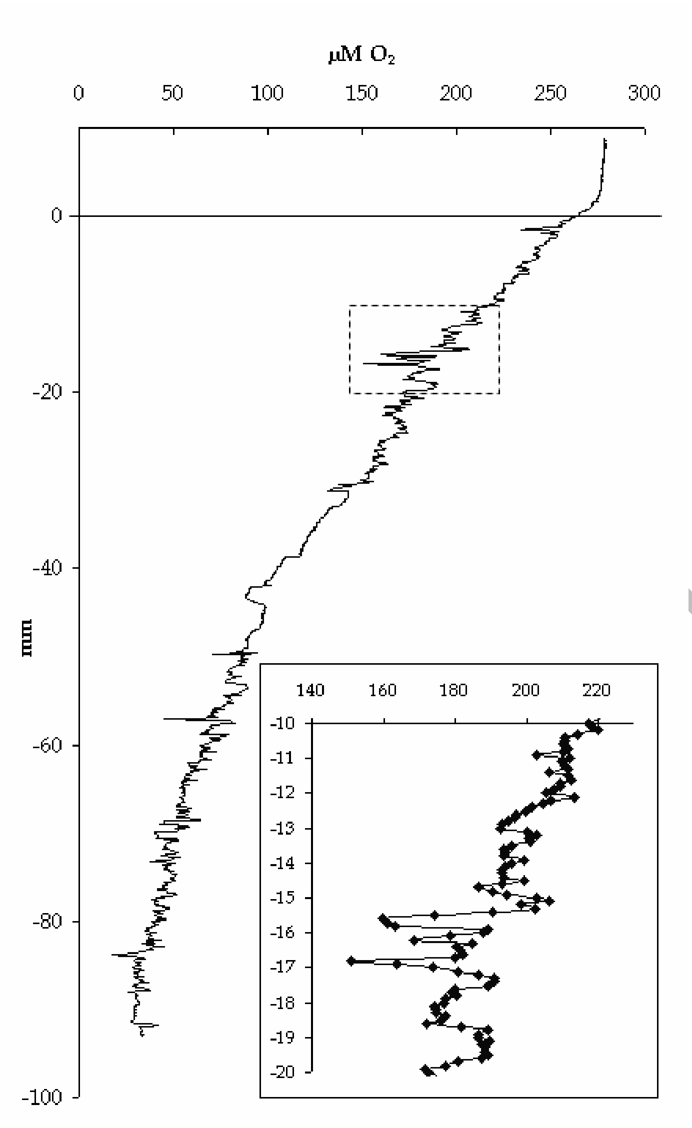

Fig. 4. In situ microelectrode oxygen profile for an Atlantic Ocean sediment. The inset represents the data in the dashed box and shows that heterogeneity is identified by multiple data points. Modified from Deep-Sea Research I, 48, Wenzhöfer, F., Holby, O., Kohls, O., Deep penetrating benthic oxygen profiles measured in situ by oxygen optodes, 1741–1755, Copyright 2001, with permission from Elsevier.

Figure 5: Copyright controlled

Fig. 5. Example data from planar optodes. (A) represents a visible image, with the white arrows identifying occupied burrows and (B) shows 2-dimensional pH distributions in the same sediment plane pH across the 1D plane at the black arrowvaries from ~6.2 to 8, representing variability in the proton concentration of a factor of ~63, over a distance of less than 1 cm. Reprinted from Geochimica et Cosmochimica Acta, 70 (19), Zhu, Q.Z., Aller, R.C., Fan, Y.Z., Two-dimensional pH distributions and dynamics in bioturbated marine sediments, 4933–4949, Copyright 2006, with permission from Elsevier.

Figure 6: Copyright controlled

Fig. 6. (A) High-resolution Co distributions (time averaged interfacial DGT derived concentrations) in a Priest Pot (UK) sediment determined by LA-ICP-MS. (B) Results for a similar 1 cm of sediment using slicing and aqueous elution techniques. Reproduced from Warnken et al. (2004a). Reproduced with permission from Anal. Chem. 2004, 76, 6077–6084. Copyright 2004 American Chemical Society.

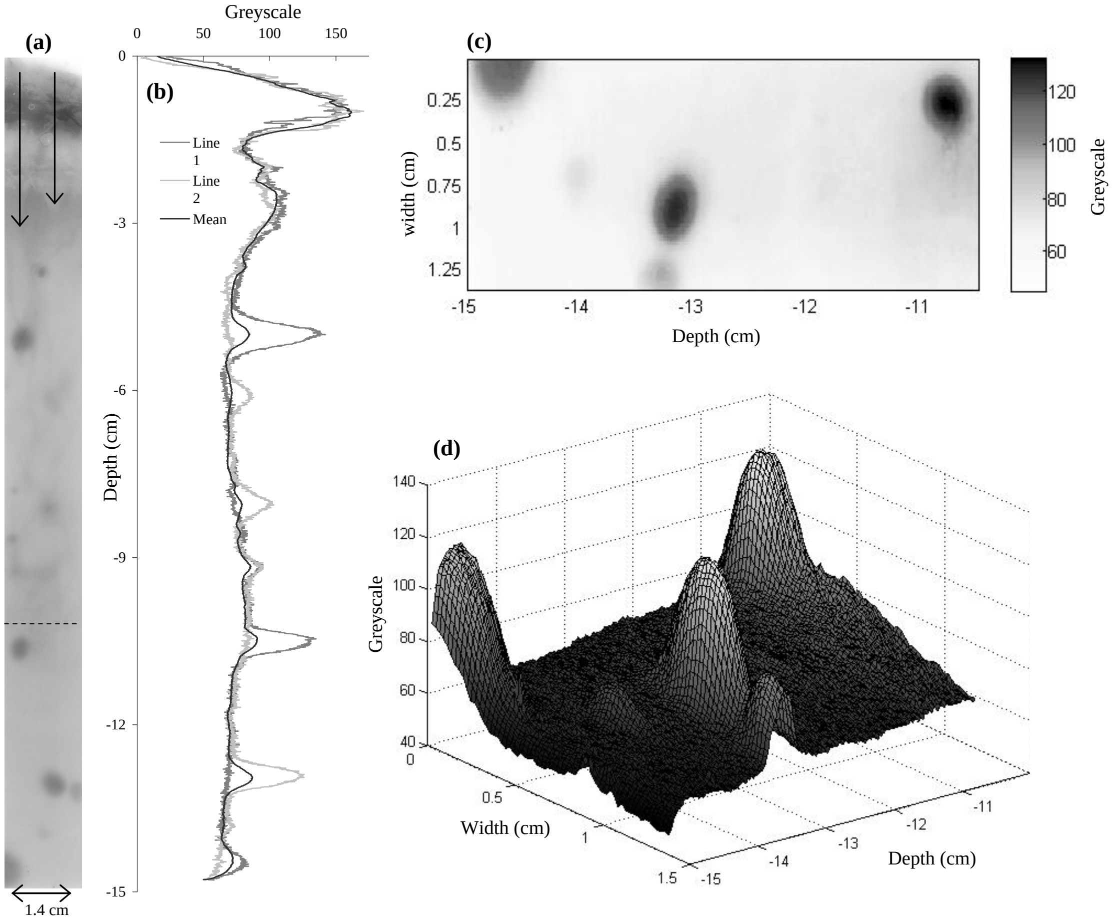

Fig. 7. Data visualisations available from colourimetric probes. (A) A AgI DGT probe deployed in an Esthwaite Water (UK) mesocosm, showing niches of elevated sulphide. The two arrows represent the two vertical cross sections plotted in the line graph (B). The mean data represent the averaged value for each horizontal row of pixels. Using Matlab, the area below the dotted line in (A) is plotted as a surface plot (C) and a contour plot (D). The scale in the data represents the assigned value of the pixel, based on an inverted 8-bit greyscale (values from 0 to 255, white to black). Vertical distances are relative to the top of the probe, horizontal distances represent the position relative to the left hand side of the probe.

Figure 8: Copyright controlled

Fig. 8. 2D data from biological studies. (A) axial tomodensitometry image (CT scan) of air filled structures in a sediment core from Baie du Ha! Ha! Canada. Ma and Mb identify pallial cavities of the bivalves *Mya arenaria* and *Macoma balthica* respectively. (B) LSCM image of life positions of benthic biota in a Santa Barbara Basin sediment, following application of the FLEC technique. Depth scale is in mm. Reproduced with permission, from Dufour et al., 2005 (A); and Bernhard et al., 2003 (B). Copyright 2005 (A) and 2003 (B) by the American Society of Limnology and Oceanography, Inc.