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Reactivity of pyrite and organic carbon as electron donors for biogeochemical processes in the fractured Jurassic Lincolnshire limestone aquifer, UK

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ABSTRACT

In this study, the weathering profiles of limestone blocks in the Jurassic Lincolnshire limestone (UK) are used to determine the spatial variation in concentration of electron donors (organic carbon and pyrite) that might drive subsurface microbial respiration, including denitrification. Organic carbon concentrations were found to be constant throughout the block transects. In contrast, sulphur and pyrite–iron concentrations were significantly higher in the unweathered zones in comparison to the weathered zones. Moreover, acid-extractable iron concentrations were significantly higher in the weathered zones in comparison to those of the unweathered zones. This suggests that pyrite is operating as the main electron donor in this system and that organic carbon is unreactive. Therefore, potentially beneficial microbial processes such as denitrification of agrochemically-contaminated groundwater will be limited, not by availability of organic carbon, but by availability of pyrite.

1. Introduction

Biogeochemical redox processes play an important role in elemental cycling (Borch et al., 2010). A key element of these complex intertwined reactions is elemental exchange between geological and modern reservoirs by oxidative weathering of organic carbon and minerals in near-surface environments. These processes influence global environmental conditions, such as the Earth's atmospheric composition, through geological time (Appenzeller, 1992; Hedges, 1992; Petsch et al., 2005; Falkowski et al., 2008). Moreover, biogeochemical processes are integral to alleviating current societal problems including contamination related to human activity (Hiebert and Bennett, 1992).

The major microbial respiration processes in the outcrop zone of the Lincolnshire Limestone are oxic respiration and denitrification (Lawrence and Foster, 1986; Wilson et al., 1990; Moncaster et al., 2000). Denitrification has been highlighted as an important mechanism for attenuating diffuse inputs of nitrate into subsurface waters, commonly resulting from intensive fertiliser application during agriculture (Hiscock et al., 1991; Korom, 1992). The electrons required to drive respiration reactions can be derived from a variety of sources including humic substances and other organic compounds (Lovley et al., 1996; Rivett et al., 2008). The bioavailability of organic carbon (OC) is generally accepted as rate-limiting (Petsch et al., 2005; Hiscock et al., 2007; Rivett et al., 2008; Schwientek et al., 2008; Hiscock et al., 2011). This is particularly important in closed environmental systems (e.g. low permeability rock matrices) where potential for OC utilisation often exceeds supply (Hill et al., 2000). However, although most microorganisms are heterotrophic (using organic carbon as electron donor to produce CO_2), many are lithotrophic, utilising inorganic, mineral-associated electron donors (Korom, 1992; Petsch et al., 2000; Schwientek et al., 2008; Korom et al., 2012).

It is widely accepted that reduced sulphur species and iron (II) found in pyrite and iron mono-sulphide are integral to lithotrophic biogeochemical processes, particularly in anoxic groundwater contaminated with nitrate derived from fertiliser inputs (Schippers and Jorgensen, 2002; Korom et al., 2005; Jorgensen et al., 2009; Zhang et al., 2009; Hiscock et al., 2011). As abiotic pyrite oxidation is often kinetically slow and dependent upon the exposure of reduced subsurface geological formations to highly-oxidising conditions, the microbial catalysis of pyrite oxidation coupled to denitrification is reported as the main process influencing sulphur release in anoxic, nitrate-rich environments (Kölle et al., 1985; Stumm and Morgan, 1996; Petsch et al., 2005; Jorgensen et al., 2009).

Such weathering processes have important wider significance. Pyrite oxidation rapidly depletes saturated zone groundwaters of oxygen, producing anoxic conditions that favour denitrification. However, the reduction of both oxygen and nitrate by pyrite oxidation leads to large increases in sulphate concentrations (e.g. Moncaster et al., 2000; Korom et al., 2005). Similarly, drawdown of groundwater levels due to abstraction can also promote significantly increased pyrite oxidation and increased

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sulphate concentrations (Schuh et al., 2006; Bottrell et al., 2008; Samborska and Halas, 2010). After nitrate has been consumed, this accumulation of high sulphate concentrations in anoxic groundwater increases the relative significance of bacterial sulphate reduction, leading to enhanced sulphide production (Korom, 1991; Bottrell et al., 2000). If the aquifer provides baseflow to surface waters, the accumulation of sulphides could prove toxic to surface water and wetland ecosystems (van der Welle et al., 2006). Moreover, high concentrations of sulphide interfere with the iron-phosphate cycle, releasing phosphates that increase eutrophication, exacerbating the effect of high nitrate concentrations from fertiliser inputs (Lamers et al., 2002; Smolders et al., 2010). Ultimately, the changes in groundwater chemistry in aquifers containing significant fractions of pyrite can render important drinking water resources unfit for use and can damage local ecosystems (Lowson, 1982; McMahon and Chapelle, 2008). Conversely, heterotrophic denitrification does not increase sulphate concentrations in groundwater, but releases climate reactive gases (N_2O, CO_2) as metabolic products (Mandernack et al., 2009; Koeve and Kähler, 2010). Therefore, understanding the controls on denitrification is of considerable importance for the management of nitrate-polluted aquifers to ensure optimal outcomes that balance the benefits of lowered nitrate concentrations against these potential adverse effects. Over 25% of the world's population relies on groundwater from carbonate aquifers (Ford and Williams, 1989); however, due to the health risks associated with nitrate exposure, many groundwater supplies contaminated with nitrate are deemed hazardous (Pawar and Shaikh, 1995).

The Lincolnshire limestone forms a regionally important aquifer in eastern England, UK, and has been impacted by agricultural nitrate pollution. It is a Middle Jurassic limestone formation up to 40 m thick. It is composed of an upper unit dominated by oolitic limestones with only a small proportion of thin (<100 mm thick) marls and clays, and a lower, more clay-rich, unit of carbonate mudstones, wackestones and packstones. It crops out in a N–S band and dips to the east at 1 to 3°; the upper units of the Lincolnshire limestone thus crop out over a wide band on the dip slope and are quarried for building stone at several locations. The oolitic limestones are porous but have low primary permeability; the high transmissivity of the aquifer in the outcrop zone (commonly $>1000\ m^2\ day^{-1}$; Peach, 1984) is provided by a near-rectilinear network of fissures associated with two well-developed sets of vertical fractures of tectonic origin and fissure development along bedding planes (Downing and Williams, 1969; Berridge et al., 1999). This divides the aquifer matrix into a series of porous "blocks" whose low permeability ensures that the pore water they contain is effectively immobile (Lloyd et al., 1996). These blocks are surrounded by fissures containing mobile west-to-east flowing groundwater (i.e. a classic "dual porosity" system — see Bear et al., 1993; Lloyd et al., 1996). In the unweathered core, all lithologies in the Lincolnshire limestone range from pale to dark bluish-grey in colour, while at the outcrop the rock is weathered to a rich yellow-buff colour that is prized as a building stone (Greswell et al., 1998). During quarrying, blocks are often fractured and many reveal remnant bluish-grey cores surrounded by weathered buff-coloured rims (Fig. 1). Petrographic analysis of core samples taken from Longwood Quarry, Lincolnshire, show that the weathered, buff samples are composed of ooids, bioclasts, whilst the unweathered grey material is composed of a greater proportion of micritic mud (Greswell et al., 1998). Also, the weathered buff fissure material was found to have a higher hydraulic conductivity ($7.3\times10^{-8}\ m\ s^{-1}$) than the unaltered grey material ($6.4\times10^{-9}\ m\ s^{-1}$) (Greswell et al., 1998).

Groundwater chemistry in the Lincolnshire limestone is dominated initially by carbonate dissolution reactions and sulphide oxidation becomes progressively more important towards the confined zone (Bishop and Lloyd, 1990; Moncaster et al., 2000). Nitrate contamination has been identified as a significant water quality problem in this aquifer and the beneficial effects of denitrifying bacteria have been identified (Lawrence and Foster, 1986; Wilson et al., 1990). Moncaster et al. (2000) pointed out that large increases in sulphate concentration were in excess of those that could be driven by observed dissolved oxygen concentrations and were spatially coincident with declining nitrate concentrations. Thus they concluded that pyrite-driven nitrate reduction could be a significant process. Pore-water in the rock matrix contains concentrations of dissolved organic carbon (DOC) of 10 to 30 $mg\ L^{-1}$ (Lawrence and Foster, 1986) and this has been proposed as the electron donor that might drive nitrate reduction (Griffiths et al., 2006; Hiscock et al., 2011). However, accumulation of high concentrations of reactive DOC can be indicative of a lack of consumption due to suppression of microbial activity (Bartlett et al., 2010). Indeed, Bottrell et al. (2000) found that the majority of matrix pore-waters in the deep confined Lincolnshire limestone had very different chemistry to the contemporary fissure waters. Fissure waters had very low sulphate concentrations due to the effects of microbial sulphate reduction. By comparison, matrix waters had elevated sulphate. Thus, the matrix pore waters were immune to the effects of microbial activity influencing the fissure waters and effectively isolated from them. Thus high concentrations of DOC in the matrix pore-waters may persist simply because DOC is not consumed in the matrix blocks and does not diffuse outward at a significant rate toward zones of microbial activity adjacent to fissures.

In this paper, we investigate weathering profiles between fissure surfaces and the unweathered cores of limestone blocks in the Lincolnshire Limestone. These data provide insights into processes operating during weathering and the use of kerogen organic carbon and pyrite as electron donors for biogeochemical processes. Specifically, the objectives are:

1. To assess the spatial variation in concentration of OC, S and Fe species in transects that cross the visual interface between the weathered (buff) and unweathered zones within limestone blocks;
2. To deduce the relative importance of pyrite and OC as electron donors during microbial respiration (and thus denitrification) in this aquifer.

2. Methods

2.1. Sample collection

Samples were selected from large blocks of limestone that had become fractured during quarrying to reveal clear weathered rims adjacent to natural fissures and unweathered cores (e.g. Fig. 1). Suitable sections were prepared in the field with hammer and chisel and subsequently cut with diamond saw to a square prism with long axis normal to the plane defined by the weathered/unweathered interface. This was then subsampled into blocks by cutting parallel to the weathered/unweathered interface, the first cut being along the interface itself and working into the adjacent weathered and unweathered zones.

2.2. Rock preparation and analysis

Each block was crushed and the powder dried at 105 °C. Weighed aliquots of each powder were treated with an excess of 1 M HCl to remove carbonate and residual solid recovered on pre-weighed glass fibre filters, dried at 105 °C, and reweighed to determine weight loss and analysed for C (= OC following carbonate removal) and S using a Carlo Erba 1106 elemental analyzer (Bartlett et al., 2010). The carbonate-free solid was also analysed for: i) acid extraction with boiling 12 M HCl and determination of HCl-soluble Fe by Atomic Absorption Spectrometry (Raiswell et al., 1994); and ii). Where total S was of sufficient concentration (approx. >0.1 wt.%), pyrite-S was determined by chromous chloride extraction (Newton et al., 1995). All analyses are recalculated to the original sample mass. Where pyrite was analysed specifically, pyrite-Fe is calculated from the analysed pyrite content; where this was not done (i.e. low-S samples) pyrite-Fe was calculated from the total S analysis, which gives a maximum estimate assuming all S to be in pyrite.