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SHORT COMMUNICATION

Centimeter-long electron transport in marine sediments via conductive minerals

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Centimeter-long electron conduction through marine sediments, in which electrons derived from sulfide in anoxic sediments are transported to oxygen in surficial sediments, may have an important influence on sediment geochemistry. Filamentous bacteria have been proposed to mediate the electron transport, but the filament conductivity could not be verified and other mechanisms are possible. Surprisingly, previous investigations have never actually measured the sediment conductivity or its basic physical properties. Here we report direct measurements that demonstrate centimeter-long electron flow through marine sediments, with conductivities sufficient to account for previously estimated electron fluxes. Conductivity was lost for oxidized sediments, which contrasts with the previously described increase in the conductivity of microbial biofilms upon oxidation. Adding pyrite to the sediments significantly enhanced the conductivity. These results suggest that the role of conductive minerals, which are more commonly found in sediments than centimeter-long microbial filaments, need to be considered when modeling marine sediment biogeochemistry.

The ISME Journal (2015) 9, 527–531; doi:10.1038/ismej.2014.131; published online 22 July 2014

To evaluate the conductivity of coastal anaerobic marine sediments, gold electrodes separated by a 50-μm nonconductive gap were inserted at different depths in intact sediment cores collected from Nantucket Bay, Massachusetts (Figure 1a). Conductivity of the sediments was measured with techniques comparable to those previously used to document the conductivity of microbial pili networks and biofilms (Malvankar et al., 2011, 2012a). This approach to measure in situ dc conductivity is substantially different from previous attempts to probe the conductivity of soils and sediments that either used self-potential monitoring (Ntarlagiannis et al., 2007) or measurements over small timescales (<1 s) (Regberg et al., 2011), which primarily measure the ionic contribution and not electron conductivity (Du et al., 2009; Patra et al., 2010). Direct conductivity measurements revealed values that were low in oxidized surficial sediments (<1 μS cm⁻¹); however, conductivities were significantly higher (P<0.05, t-test) in deeper, highly reduced sediments (Figure 1b). Along with intact sediment cores, experiments were also performed with mixed sediment subsamples. Comparable values of 7 ± 0.15 μS cm⁻¹ (mean ± s.e.; n=3) were obtained using this alternative approach, in which reduced sediments were placed on a four-probe electrode array under anaerobic conditions (Figure 1c) and conductivities measured over the 1-cm span of the electrodes.

In previous studies (Nielsen et al., 2010) that led to the concept of long-range electron transport via conductive microbial filaments (Pfeffer et al., 2012), electric currents in the sediment were not actually measured, but rather inferred from rates of sediment oxygen consumption that were estimated from oxygen concentration profiles (Nielsen et al., 2010). In Aarhus Bay, estimated rates of oxygen consumption were 9.7 mmol O₂ per m² per day with 31% of this oxygen consumption attributed to electric current from deeper sediments (that is, 3 mmol O₂ per m² per day) and in Aarhus Harbor sediments 42% of the estimated 46 mmol O₂ per m² per day was attributed to the inferred electric currents (Nielsen et al., 2010). Thus, given that four moles of electrons are required for each mole of oxygen reduced to water (O₂ + 4H⁺ + 4e⁻ → 2H₂O), the estimated electron flux through the sediments was 12–77 mmol of electrons per m² per day. This electron flux through each m² of sediment can be converted to electric current as follows (calculations shown for maximum estimated flux): ((7.7 × 10⁻² moles of electrons per day) × (1.16 × 10⁻⁵ days s⁻¹) × (Amp/1.036 × 10⁻⁵ moles of electrons...
The current (thus I) of long-range electron transport (Pfeffer et al., 2012; Malkin et al., 2014) because the hypothesized conductivity and the mechanisms for conduction have not been documented (Reguera, 2012).

An abiological mechanism for electron transport through sediments that could potentially be eliminated with oxidation is conduction through iron–sulfur minerals. Dense assemblages of conductive iron–sulfur minerals in ore bodies (Sato and Mooney, 1960) or hydrothermal vents (Nakamura et al., 2010) may be capable of conducting electrons over distances of centimeters (Nakamura et al., 2010) to meters (Sato and Mooney, 1960). To determine whether lower abundances of an iron–sulfur mineral, comparable to those that might be found in reduced marine sediments, could contribute to conductivity, finely ground pyrite (10–100 μm diameters) was added to the reduced sediment. There was a significant increase in conductivity at higher pyrite concentrations (Figure 2c). The conductivity of freshwater sediment also increased upon addition of pyrite (Figure 2d).

Although it has been suggested that filaments of cells closely related to Desulfovibulbus species accounted for conductivity to reduced marine sediments from Aarhus Bay, it is, in fact, unknown whether this is possible because the conductivity of the filaments was not demonstrated (Pfeffer et al., 2012; Reguera, 2012; Malkin et al., 2014). No long bacterial filaments were observed in the Nantucket sediments used in these studies. The findings reported here, based on direct measurements of sediment conductivity, demonstrate that conductive...
minerals can confer substantial conductivity to anaerobic marine sediments and could potentially have an important role in sediment biogeochemistry. The simple method described here for assessing sediment conductivity is expected to be a useful tool for future studies of long-range electron conduction in a diversity of soils and sediments.

Materials and methods

Sediment collection and maintenance

Near-shore sediments were collected from the previously described (Holmes et al., 2005) study site in Nantucket, Massachusetts, USA in PVC cores (15.24 cm diameter; 53.34 cm long). Both ends of the cores were sealed with rubber stoppers for transport. The sediment cores were incubated at 15°C to mimic in situ temperatures. For pyrite addition experiments, 6–60 mg (dry weight) of finely ground pyrite (10–100 μm particle size) was added to 3 g of reduced sediments, which were then homogenized under anaerobic conditions. The sediment cores were collected from upper 50 cm depth zone. For other sediment experiments, reduced sediment was collected from the top 2 cm. Sediments were homogenized only for the experiments that involved the addition of pyrite. All other experiments were performed on intact sediment cores or undisturbed sediments.

Electrode fabrication

Gold electrode fabrication was performed as described previously (Malvankar et al., 2011, 2012c). Glass slides (2.54 cm × 2.54 cm) were cleaned ultrasonically using successive rinses of trichloroethylene, acetone and methanol, and then blown dry with nitrogen. To achieve an insulating gap in the anode, a 50-μm diameter tungsten wire was placed on the glass substrate as a deposition mask. For four-probe measurements, electrodes were fabricated using standard photolithography processing. A 40-nm Au film atop a 10-nm Cr adhesion layer was thermally evaporated on these substrates, at 10–6 mbar, at a deposition rate 0.1 nm s⁻¹, thus producing gold split electrodes with a 50-μm nonconductive spacing. Optical microscopy was used to confirm that the gap was uniform, and resistance measurements were employed to assure that the electrodes were well insulated from each other with \( G_{\text{gap}} < 10^{-10} \) S.

DC conductivity measurements

Sediment conductivity was measured using an approach similar to that described previously for measuring the conductivity of microbial biofilms and pili nanowires (Malvankar et al., 2011). A voltage ramp of −0.05 to 0.05 V was applied across gold electrodes in steps of 0.025 V for two-probe measurements using a source meter (Keithley Instruments, Cleveland, OH, USA; Model 2400). For each measurement, after allowing the exponential decay of the transient ionic current, the steady-state electronic current for each voltage was measured every second over a minimum period of 100 s using a Labview data acquisition program (National Instruments, Austin, TX, USA). Time-averaged current for each applied voltage was calculated to create the current–voltage (I–V) characteristics. For four-probe measurements, a source meter (Keithley Instruments, Model 2400) was used to apply a fixed current between outer of the four electrodes and to measure the potential drop between...
two inner electrodes (Lange and Mirsky, 2008), by measuring the voltage for each current every second over a period of 100 s, after reaching the steady state (Figure 1c). An additional high-impedance voltmeter (Keithley Instruments, Model 2000) was used to record the output voltage of the current source to calculate conductance (Lange and Mirsky, 2008) as described previously. For both two- and four-probe measurements, linearity of I–V characteristics was maintained by applying appropriate low voltage/current. The dissipative power was kept under 10⁻⁶ W to eliminate self-heating effects.

Conductivity calculation
Conductivity was calculated using the methods described previously (Malvankar et al., 2011). Conformal mapping (the Schwarz–Christoffel transformation) (Kankare and Kupila, 1992) was employed to calculate sediment conductivity from measured conductance (G) according to the following formula

\[ \sigma = \frac{G \pi}{L} \ln \left( \frac{8g}{\pi a} \right) \]

where \( L \) is the length of the electrodes (\( L = 2.54 \) cm); \( a \) is the half-spacing between the electrodes (\( 2a = 50 \) \( \mu \)m); and \( g \) is the sediment thickness. This formula is valid for the case \( a < g < b \) where \( b \) is the half-width of the electrodes (\( 2b = 2.54 \) cm). Sediment thicknesses were individually measured for each experiment except for sediment cores where a sediment thickness of 1 mm was used for all comparisons.

Sediment oxidation using air and electrochemical gating
For oxidation of sediments, 1 g of sediments was placed on the electrode arrays. For electrochemical gating, a source meter (Keithley Instruments, Model 2400) was used to apply voltage (\( V_g \)) between gate (Ag/AgCl, 3 M KCl reference electrode, BAS, West Lafayette, IN, USA) and the source–drain electrodes to create the electrolyte-gated field effect as described previously (Malvankar et al., 2011, 2012b). Another source meter (Keithley Instruments, Model 2400) was used to apply voltage between source and drain to measure conductance. IGOR Pro software (WaveMetrics Inc., OR, USA) was used for data fitting and analysis. Experiments involving air-oxidation of sediments were performed in an incubator maintained at 4 °C and sediments of 3 mm thickness were exposed to air. Conductivity was measured periodically to evaluate the effect of air-oxidation (Figure 2a).

Conflict of Interest
The authors declare no conflict of interest.

Acknowledgements
We thank Prof. Kelly Nevin and Prof. Mark Tuominen for helpful discussions and experimental assistance. This research was supported by the Office of Naval Research (grant no. N00014-12-1-0229 and N00014-13-1-0530), the Office of Science (BER), US Department of Energy (award no. DE-SC0006790) as well as the NSF Center for Hierarchical Manufacturing (grant no. CMMI-1025020). Nikhil S. Malvankar holds a Career Award at the Scientific Interface from the Burroughs Wellcome Fund.

References


