Fluctuation Analysis of Oxidation-Reduction (Redox) Potential As a Method of Distinguishing Chemcial and Biological Iron Oxidation. A. M.L. Enright[1], and F. G. Ferris, Department of Earth Sciences, University of Toronto, 22 Russell St. Toronto, Ontario, Canada. M5S 3B1. [1]enright@es.utoronto.ca

Introduction: Iron metabolism is thought to be one of the most ancient on Earth[1]; Fe^{2+} -oxidizing bacteria (FeOB) are thought to have played a key role in the Great Oxidation Event (GOE)[1], and iron metabolism has been suggested as a possible candidate for life outside of Earth[2].

The redox state of any aqueous environment is the quotient of the chemical activity of the relative concentrations of dissolved oxidized and reduced chemical species, according to the Nernst equation:

$$E = E^0 + \frac{RT}{nF}\ln Q$$

where E is the electrochemical potential of the cell in mV, R is the universal gas constant, T is absolute temperature, n is the number of electrons participating per atom, F is Faraday's constant, and Q is the reaction quotient, $\frac{[oxidized\ species]}{[reduced\ species]}$. Redox potential is determined by the diffusivities of oxidized and reduced chemical species in solution[2,3]; these give rise to small amplitude fluctuations due to bulk diffusion limitations on electron transfer reactions at the working electrode surface.

As microbial metabolic activity is exclusively based on oxidation-reduction (redox) reactions, all metabolically active organisms directly influence the relative abundance of redox active species in their environment[4,5]. As such, they play an important role in regulating the redox state of iron in their environment[4] and the diffusion of chemical species into and out of their cells. To date, fluctuations of redox potential have been attributed to instrument noise, and characterization or classification of these fluctuations had not been attempted. Perhaps the fluctuations contain information about the nature of the processes contributing to redox potential. Moreover, perhaps this information could serve as a physical basis for distinguishing biologically-driven redox processes.

Methods: Time series fluctuations in redox potential were analyzed with detrended fluctuation analysis (DFA)[6] to determine whether small-scale fluctuations in this system property could distinguish chemical and biological oxidation.

Results: Two different geochemical settings were studied: a bioreactor fed by reduced anoxic groundwater, and a reduced, anoxic groundwater seep. Both host thriving communities of bacteriogenic iron-oxide (BIOS)-producing FeOB.

The Bioreactor: Oxidation rate and fluctuations were compared for the bioreactor and its (abiotic) inflow pipe. The biological Fe^{2+}-oxidation rate constant, $k'_{BIOS} = 0.089\ min^{-1}$ was six times the calculated value, $k'_{CHEM} = 0.015\ min^{-1}$[7]. The scaling exponent for redox potential fluctuations in the bioreactor was 1.89 compared to 1.67 for the inlet[7]. In one-sided *t*-tests, the inlet and BIOS α values were significantly different at a level of $p < 0.01$[7]. The difference in scaling exponents parallels the difference in rate constants determined for chemical and bacterial Fe^{2+}-oxidation suggesting that measured redox potential fluctuations are related to Fe^{2+}-oxidation rates.

The Groundwater Seep: A series of four microcosms evaluated the effects of microbial activity, oxidation rates, and presence of BIOS as a substrate on fluctuation behaviour. Two live systems with maximal (MAX) and typical (AVG) amounts of biomass, an abiotic control (AUTO) with killed BIOS, and a chemical control (CREEK). The pseudo-first order rate constants for the four systems are $k'_{MAX} = 0.1425\ min^{-1}$, $k'_{AVG} = 0.0575\ min^{-1}$, $k'_{AUTO} = 0.0225\ min^{-1}$, and $k'_{CREEK} = 0.0036\ min^{-1}$. Scaling exponents were calculated for several windows of time, and plotted against calculated oxidation rates. The values of the initial scaling exponents are similar in range to those from the bioreactor. More compelling is the relationship between oxidation rate and scaling values. The regression slopes of the biological and chemical system are consistently orders of magnitude apart.

Significance: The consistent differences in fluctuation behaviour in two very different biogeochemical environments suggest that fluctuation analysis holds significant promise as a method to distinguishing biological from chemical redox transformations. The higher scaling exponents which only arise in the biological systems may provide a physical signature of biologically-driven redox processes.

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