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Speciation and Sequestration of Rhenium in Sulfidic and Polysulfidic Natural Waters

Trent P. Vorlicek, Ph.D.

I. Abstract

Global warming is expected to intensify the effects of coastal anoxia. Knowledge of the causes of geohistorical anoxic episodes may prove critical in developing strategies for the mitigation of or adaptation to the consequences of climate change upon the global aquatic environment. The geochemistry of Re provides the means to acquiring this knowledge. Within oxic waters, Re exists as geochemically-inert ReO_4^-. Under reducing conditions, Re is removed from the aqueous phase and deposited in sediments. Unfortunately, an incomplete understanding of Re geochemistry hampers exploitation of Re as a paleoredox indicator. Authors purport Re sequestration begins in suboxic environments; others produce evidence supporting removal under sulfidic conditions. Some suggest precipitation as ReS_2; others hint at scavenging by pyrite. The proposed research will begin clarifying such issues by positing a plausible pathway to Re fixation. Reductively labile thioperrhenates initiate the pathway:

$$Re^{VII}O_4^-{}_{(aq)} + nH_2S_{(aq)} \rightleftharpoons Re^{VII}O_{4-n}S_n^-{}_{(aq)} + nH_2O_{(l)} \qquad (n = 1\text{-}4)$$

Mineral oxides promote thioperrhenate formation, explaining why Re uptake occurs within the sediments vs. sulfidic water column of seasonally anoxic basins. S^0-donors induce $Re^{(VII)}$ reduction to $Re^{(V)}$-polysulfido species:

$$Re^{VII}S_4^-{}_{(aq)} + 5S_5^{2-}{}_{(aq)} \rightleftharpoons 5S_4^{2-}{}_{(aq)} + Re^{V}(S_4)(S_4)S^-{}_{(aq)}$$

Reduction of $Re^{(VII)}$ facilitates uptake by pyrite, yielding surface Fe-Re-S cubane clusters, which require reduced Re to overcome coulombic impediments. Laboratory experiments will **(a)** define Re speciation in sulfidic and polysulfidic environments, **(b)** quantify kinetic constants for

mineral oxide catalysis of thioperrhenate formation and define the chemistry of the catalytic process, and **(c)** identify preferentially pyrite-scavenged Re species and elucidate chemical controls on sequestration.

II. Relevance to Fundamental Research in the Petroleum Field

Black shales serve as source rocks for petroleum generation. These shales are highly enriched in organic matter and several redox-sensitive metals (e.g., V, U, Mo, Re) (Kara-Gulbay, 2007; Kara-Gulbay and Korkmaz, 2008; Akinlua and Smith, 2010). Trace metal signatures can yield valuable information about the paleoenvironmental conditions which favor source rock formation (Lipinski et al., 2003; Langrock and Stein, 2004). Re is especially attractive as a proxy for ancient paleoredox conditions. Its enrichment factor in oil-producing shales vs. average shales can be greater than 300 (Kara-Gulbay, 2007; Kara-Gulbay and Korkmaz, 2008). Further, Re-Os isotopes are useful for dating and sourcing oil deposits (Selby and Creaser, 2005; Xiugen et al., 2008).

III. Introduction

III.A. Rhenium Geochemistry

Interest in utilizing rhenium (Re) as a proxy for paleoredox conditions stems from its disparate behavior within oxic vs. suboxic and anoxic environments. In oxic waters, Re is present as the geochemically-inert perrhenate (ReO_4^-) anion. The passivity of this oxyanion is demonstrated by the conservative profile of Re within oxygen-rich seawater where Re displays a steady concentration of 40 pM (Anbar et al., 1992). Not surprisingly, ReO_4^- shows marginal affinity for various adsorbents (e.g., silica, ferromanganese oxide, hematite, alumina) from pH 2 to 10 (Yamashita et al., 2007; Guzman et al., 2009).

In contrast, Re sequestration initiates within suboxic and anoxic porewaters (Colodner et al., 1993; Morford et al., 2005, 2007; Chappaz, 2008). As a consequence, Re is highly enriched in suboxic and anoxic sedimentary environments (Colodner et al., 1993; Morford and Emerson, 1999; Nameroff et al., 2002; Morford et al., 2009; Brucker et al., 2011). In black shales, Re enrichment factors may be in excess of 300 (Kara-Gulbay and Korkmaz, 2008). This value is relatively remarkable and explains why Re has piqued interest as a paleoenvironmental indicator of geohistorical (Morford et al., 2001; Anbar et al., 2007; Brucker et al., 2011) and recent (Chappaz et al., 2008) redox conditions in spite of its marginal concentration vs. other prominent paleoredox proxy candidates like Mo (~0.1 μM; Collier, 1985). As potential deleterious impacts of global warming on aquatic environments (Middelburg and Levin, 2009; Ozaki et al., 2011) become manifest (Kopprio et al., 2010), geochemists will be called upon to define what geohistorical anoxic episodes (e.g., during the Phanerozoic Eon) can reveal about the potentialities of future anoxic events. Such information could prove critical toward developing strategies for the mitigation of or adaptation to the consequences of climate change.

Unfortunately, an incomplete understanding of Re geochemistry hampers its exploitation as a tool for reconstructing paleoredox conditions at the time of deposition. The biological or chemical mechanism responsible for Re sequestration and enrichment in sediments remains elusive and disputed. While there is general agreement that Re enrichment requires reducing conditions, the required severity of the reducing conditions is inconclusive. Morford et al. (1999, 2005) use sedimentary evidence to argue that Re accumulation begins under suboxic conditions. Sediments with oxygen penetration depths of <4 mm had redox sensitive metals removed in a depth order of Re<U<Mo (Morford et al., 2007). The order of removal depth for Re and Mo in conjunction with the Re/Mo ratio indicates whether deposition in sediments occurred under oxic,

suboxic, or anoxic conditions (Crusius et al., 1996). Some authors (Crusius et al., 1996; Nameroff et al., 2002) indicate that Re is enriched between microbial-mediated $Fe^{(III)}$ and SO_4^{2-} reduction. However, results of microcosm experiments led Maset et al. (2006) to imply that Re deposition requires SO_4^{2-} reduction. Based on field- (Dellwig et al., 2002; Chappaz et al., 2008) or laboratory- (Yamashita et al., 2007; Dolor et al., 2009) based experiments, several authors opine that sulfide must be present for Re removal.

Microbial experiments involving ReO_4^- in the presence of $Fe^{(III)}$- or SO_4^{2-}-reducing strains yielded no Re loss in one week, pointing away from a direct or short term indirect microbial mediated Re removal process (Dolor et al., 2009). However, some uptake of ^{187}Re occurs in glucose-amended sediments, but no loss is observed if the sediment is previously leached with H_2O_2, suggesting a possible microbial mediated pathway (Yamashita et al., 2007). Several authors (Dellwig et al., 2002; Sundby et al., 2004; Yamashita et al., 2007; Chappaz et al., 2008) conjecture that Re sequestration involves a slowly precipitated product. However, there is disagreement on the identity of the precipitated phase. Chappaz et al. (2008) uses thermodynamic and field data to argue that $ReS_{2(s)}$ is the sequestered form of Re. Leaching experiments with peats indicate that Re is present in the sulfide fraction or associated with pyrite surfaces (Dellwig et al., 2002). XANES data is used by Yamashita et al. (2007) to argue that Re is partially deposited as $ReO_{2(s)}$.

Crusius et al. (1996) use sediment trap data in the Black Sea to argue that Re enrichment only occurs at or below the sediment-water interface. However, Colodner et al. (1995) clearly show that Re removal processes are operating within the water column of the Black Sea. On the other hand, Chappaz et al. (2008) quantified Re concentrations in the lower water column (to 5 cm above interface) and porewaters (to 10 cm depth) of three seasonally anoxic freshwater lakes

(See bottom three rows of profiles in Fig. 2 of Chappaz et al., 2008.). All three lakes show either saturation or supersaturation with respect to $ReS_{2(s)}$ within the sediments and extending throughout the 5 cm of overlying water. However, Re removal only occurs at or below the sediment-water interface in all three lakes. Because a sulfidic water column inherently abhors mixing, evidence of Re loss ought to extend into the water column where precipitation is thermodynamically predicted to commence. While this result agrees with Crusius et al. (1996), it conflicts with Colodner et al. (1995). There must be either different controls on Re removal in perennially vs. temporally anoxic basins. Or, the chemical pathway to removal in temporally anoxic waters involves catalysts which are substantially present only within the sediments.

III.B. Potential Pathway to Re Sequestration

A possible pathway to Re fixation that has received scant attention (Tossel, 2005) is one in which the thioperrhenate anions partake. The stepwise sulfide substitution reactions involve preservation of $Re^{(VII)}$ and may be expressed as:

$$Re^{VII}O_4^-{}_{(aq)} + nH_2S_{(aq)} \rightleftharpoons Re^{VII}O_{4-n}S_n^-{}_{(aq)} + nH_2O_{(l)} \qquad (n = 1\text{-}4) \qquad (1)$$

Similar reactions for the thiomolybdates are believed to lie in the pathway to Mo fixation (Erickson and Helz, 2000). Information on the thioperrhenates is scarce. The inorganic chemistry of ReS_4^- has been reviewed (Rauchfuss, 2004). Using quantum mechanical models, Tossel (2005) has calculated stability constants for the sulfidation reactions and UV-Vis spectra of the thioperrhenates. However, neither kinetic nor equilibrium constants for these reactions have been quantified through experimental means. In Ph.D. thesis work, Dolor (2009) attempted to quantify equilibrium constants for the thioperrhenate formation reactions. Unfortunately, thioperrhenate spectra were difficult to interpret because the optical method required high Re

concentrations ($\Sigma Re = 10^{-3}$ M), leading to the formation of a colloidal intermediate (e.g., $Re_2S_{7(s)}$) which escaped filtration.

The thioperrhenates are much more reductively labile than ReO_4^-. The standard reduction potentials vs. normal hydrogen electrode for ReS_4^- and ReO_4^- are -1.18 V vs. -2.91 V (Tossel, 2005). Conversion of ReO_4^- to the thioperrhenates may facilitate Re fixation if the sequestration mechanism involves reduction as conjectured by various authors (Yamashita et al., 2007; Chappaz et al., 2008). Presently, there is no information available on the kinetics of thioperrrhenate reactions, other than they are sluggish and may take years to reach equilibrium with ReS_4^- (Dolor, 2009). No potential catalysts have been identified. Because of their high surface areas and hydrated surface properties, mineral oxides are known to influence various environmentally relevant reactions within porewaters of soils and sediments (Vorlicek and Helz, 2002; Kim et al., 2004; Lan et al., 2007). Mineral catalysts have been shown (Vorlicek and Helz, 2002) to greatly enhance the rate of thiomolybdate reactions. This finding helped explain why Mo fixation occurs primarily in the sediments vs. overlying sulfidic water column of seasonally or intermittently anoxic basins (Francois, 1988; Zheng et al., 2000; Adelson et al., 2001). Perhaps, thioperrhenate formation is also catalyzed by mineral oxides, helping explain why Re removal is limited to sediments in these basins.

Reaction with S^0 offers an environmentally available (Wang and Tessier, 2009) pathway to Re^{VII} reduction via ligand-induced reduction by polysulfide ligands. This reduction mechanism has been recognized in the chemistry of Mo^{VI} (Müller et al., 1978), V^V (Halbert et al., 1986), W^{VI} (Cohen and Stiefel, 1985), and Re^{VII} (Müller et al., 1986; Hobert et al., 2001). The reduction pathway has only begun to receive attention (Vorlicek et al., 2004; Wang et al., 2011) for its possible role in the geochemistry of redox-sensitive and thioanion-forming trace

metals. There are few field studies (Boulegue et al., 1982; Wang and Tessier, 2009) of S^0 influence on metal speciation. It is worth suggesting that S^0-donors may be ephemerally present within sub-oxic environments as S^{2-} diffuses into localized regimes and partially oxidizes.

In ligand-induced reduction of Re^{VII}, an S^0-donor (polysulfide anion, $S_{8(aq)}$, or organic di- or polysulfide) converts a pair of S^{2-} ligands in a thioperrhenate anion to a bidentate S_n^{2-} ligand (Coucouvanis, 1998). In the process, an electron pair is transferred from one S^{2-} ligand to the Re^{VII} center, reducing it to Re^{V}. For example, Müller et al. (1986) have shown that $Re^{VII}O_4^-$ is converted to $Re^{V}OS_8^-$ or $Re^{V}S_9^-$ upon heating in a polysulifidic solution. The Re^{V} species may also be represented as $Re^{V}(S_4)(S_4)O^-$ or $Re^{V}(S_4)(S_4)S^-$ to indicate the presence of two S_4^{2-} ligands. Given the reductive lability of the thioperrhenates (Tossel, 2005), a plausible chemical pathway to Re fixation may include formation of the thioperrhenates followed by reduction to Re^{V}-polysulfido anions. A possible reaction may be represented by:

$$Re^{VII}S_{4\,(aq)}^- + 5S_5^{2-}{}_{(aq)} \rightleftharpoons 5S_4^{2-}{}_{(aq)} + Re^{V}(S_4)(S_4)S^-_{(aq)} \qquad (2)$$

where S_5^{2-} and S_4^{2-} are representative polysulfides present in natural waters (Wang and Tessier, 2009).

Vorlicek et al. (2004) demonstrated that S^0 promotes the uptake of Mo by pyrite surfaces via formation of $Mo^{(IV)}$-polysulfido complexes. Because Mo uptake by pyrite has been shown to result in Fe-Mo-S surface cubane clusters (Bostick et al., 2003) and these clusters contain Mo^{III} and Mo^{IV}, the authors posited that reduction of the Mo^{VI} thiomolybdates to Mo^{IV}-polysulfido complexes facilitates sequestration by pyrite. Re, like V, W, and Mo, is known to form extremely stable Fe-$Re^{(III\ or\ IV)}$-S cubane cluster compounds (Ciurli et al., 1989; Ciurli et al., 1990; Ciurli and Holm, 1991). Re may experience similar chemistry to Mo upon encountering

pyrite surfaces. Leaching experiments with peats hint at possible Re-pyrite association (Dellwig et al., 2002).

III.C. Research Questions and Hypotheses

Critical questions regarding Re speciation and sequestration require attention.

1) What is the aqueous-phase speciation of Re in sulfidic waters?

2) Do S^0-donors influence the speciation of Re?

3) What role does Re speciation play in Re sequestration?

4) Why does Re sequestration occur primarily within the sediments of some seasonally anoxic basins but not in the overlying sulfidic water columns?

5) Is Re ultimately deposited as a precipitated product or scavenged species?

The proposed research will begin answering these questions by concentrating its focus on the following set of hypotheses:

Hypothesis 1: Within sulfidic waters, ReO_4^- initially reacts with sulfide to yield the reductively labile thioperrhenate anions.

Hypothesis 2: Within sulfidic sediment porewaters, the rate of thioperrhenate formation is enhanced via mineral surface catalysis.

Hypothesis 3: The reductively labile thioperrhenate anions undergo ligand-induced reduction by S^0-donors to yield reduced Re-polysulfido anions (e.g., $Re^V(S_4)(S_4)\,S^-$).

Hypothesis 4: Reduced Re-polysulfido anions are readily and preferentially sequestered by pyrite (FeS_2) surfaces, resulting in surface Fe-Re-S cubane clusters.

III.D. Supporting Objectives

Data obtained from the proposed research will be used to fulfill four overriding objectives:

Objective 1: Quantify equilibrium and kinetic constants for thioperrhenate and Re-polysulfido complex formation.

Objective 2: Quantify kinetic constants for surface-catalyzed thioperrhenate or Re-polysulfido formation reactions, and elucidate the chemistry governing the catalytic processes.

Objective 3: Integrate equilibrium and kinetic constants into a speciation model which can be used to predict Re speciation in perennially and seasonally anoxic water columns and sediments.

Objective 4: Quantify uptake of Re by pyrite surfaces when S^0-donors are present and absent in solution, and define the role Re speciation plays in facilitating sequestration by pyrite.

IV. Proposed Research

IV.A. Overview

The proposed research seeks to answer the research questions, test the hypotheses, and attain the objectives listed above by focusing on three experimental plans. Experiments will involve reacting ReO_4^- with sulfide or polysulfide in the absence and presence of mineral oxide or pyrite surfaces over a range of aqueous-phase conditions.

IV.B. Experimental Plan 1: Quantify kinetic and equilibrium constants for ReO_4^- reactions occurring within sulfidic or polysulfidic solutions.

Rationale and IC Preliminary Data- The experiments outlined here are designed to allow for quantification of kinetic and equilibrium constants for the thioperrhenate (ReO_3S^-, $ReO_2S_2^-$,

$ReOS_3^-$, ReS_4^-) and Re-polysulfido formation reactions represented by reactions (1) and (2). Preliminary evidence is also presented which demonstrates the utility of IC for monitoring Re speciation throughout the proposed research.

To demonstrate the usefulness of IC for quantifying the perrhenates and thioperrhenates, a series of ReO_4^- ($NaReO_4$) calibration solutions from 0.10 to 10 µM ReO_4^- were prepared in deionized H_2O. IC conditions were as follows: injection volume = 100 µL, flow rate = 1.2 mL/min, eluent = 50 mM KOH (isochratic), column = Dionex AS-16 (0.4 mm x 250 mm), detection = suppressed conductivity. Figure 1 displays the resulting chromatograms (left panel) and calibration curve (right panel). The figure indicates that ReO_4^- elutes at 21.2±0.1 minutes and response linearity can be achieved down to at least 0.10 µM Re. Up to 1000 µL injection loops are available if greater sensitivity is needed.

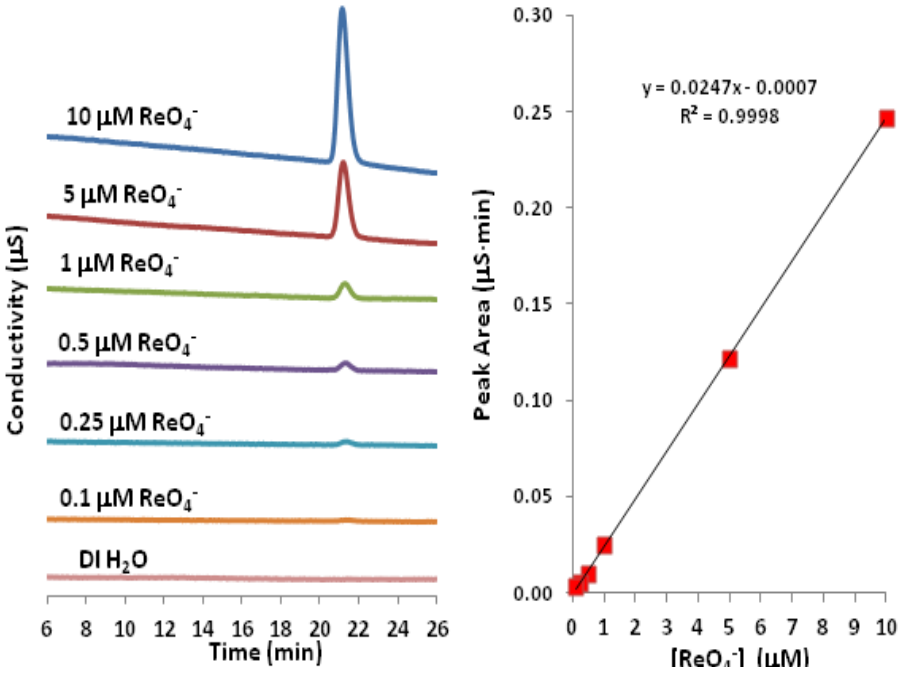

Figure 1: Series of chromatograms (left panel) for 100 µL injections of deionized water and 0.1 µM to 10 µM ReO_4^- solutions prepared in deionized water. The chromatograms indicate that ReO_4^- elutes with a retention time of 21.2 ± 0.1 min. The right panel displays the resulting calibration curve for ReO_4^- derived from the ReO_4^- peak areas of the chromatograms shown in the left panel. The IC data was obtained by MSUM undergraduate researchers, Claton Wagner (Chemistry BS ACS) and Megan Maloney (Biochemistry BS).

Analogous experiments with added elemental sulfur are designed to test whether Re-polysulfido complexes form in solution. While I hypothesize that the pathway to Re sequestration involves uptake of reduced Re-polysulfido species by pyrite surfaces, it is also possible that Re-polysulfido formation facilitates $Re^{IV}S_{2(s)}$ deposition, a phase posited by others (Chappaz et al., 2009). Such a reaction may be expressed as follows:

$$Re^{V}(S_4)(S_4)S^{-}_{(aq)} + 3e^{-} + 2H^{+}_{(aq)} + 5S_4^{2-}{}_{(aq)} \rightleftharpoons 5S_5^{2-}{}_{(aq)} + 2HS^{-}_{(aq)} + Re^{IV}S_{2(s)} \quad (3)$$

The design of these experiments allows for this possibility to be tested. For the polysulfide solutions, monitoring ΣRe after filtration will be imperative for determining the presence of a solid phase. If $Re^{IV}S_{2(s)}$ escapes filtration as a colloid, it will produce no direct signal on the IC since it is uncharged. However, its presence will be accounted for indirectly in the Re mass balance.

Figure 2 (following page) demonstrates the utility of IC for monitoring these reactions. The figure shows a series of chromatograms over the first 8 minutes (left panel) and final 22 minutes (right panel) after injection. Test solutions were buffered at pH = 9.3 using borate (80 mM ΣBorate) and initially contained 10 μM ReO_4^- with 10 mM ΣS^{2-}. Aliquots (10 mL) of this master solution were added to a series of centrifuge tubes with either no added elemental sulfur (top chromatogram in both panels) or 0.05 g of elemental sulfur (second chromatogram from top in both panels). The tubes were capped and remain stored in the glovebox; similar control solutions were also prepared. After 19.9 days of reaction, 100 μL of test and control solutions were injected into the IC, resulting in the chromatograms depicted in Figure 2. The polysulfidic solution remained saturated with elemental sulfur throughout the reaction period.

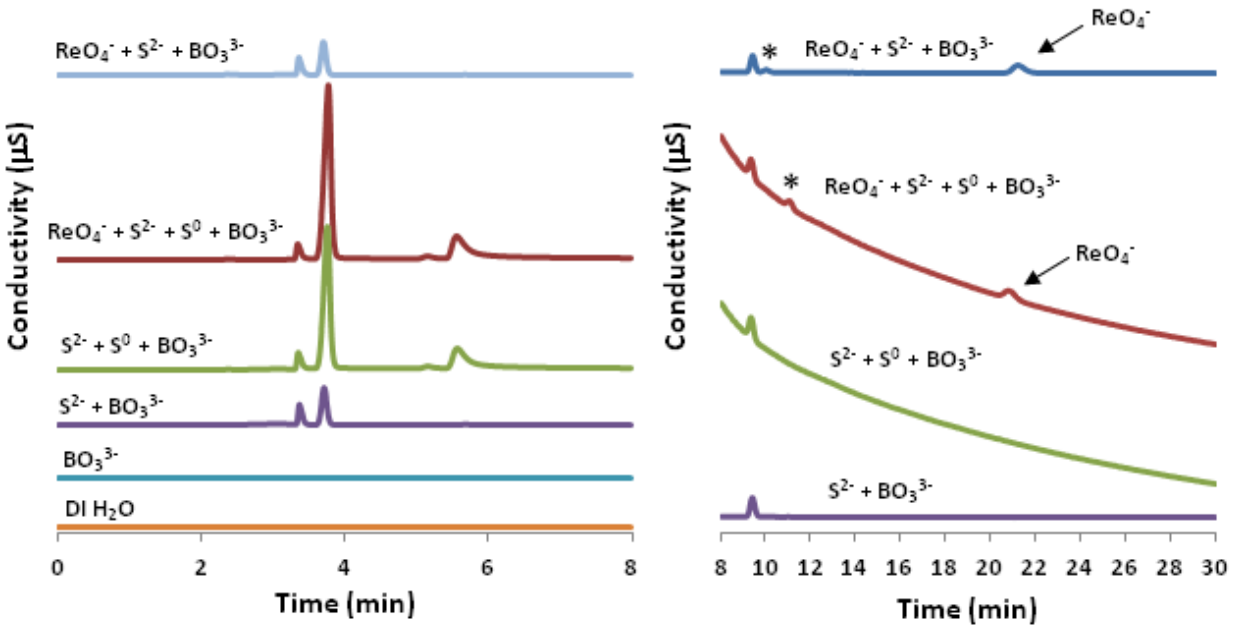

Figure 2: Chromatograms of ReO_4^- test solutions, control solutions under analogous conditions, and deionized water. The left and right panels show the first eight minutes or final 22 minutes of the chromatograms. Test solutions were allowed to react for 19.9 days; all solutions were filtered through 0.45 µm filters prior to IC analyses. Further information is provided in the text. Test solutions and IC data were prepared and obtained by MSUM undergraduate researcher, Laura Groskreutz (Chemistry BS ACS).

Test solution chromatograms (top two chromatograms) each show the characteristic ReO_4^- peak at ~21.2 minutes, which is well resolved from all other solution species. After 19.9 days, neither test solution shows any distinct peaks after the ReO_4^- peak (last 15 minutes not shown), which is where thioperrhenates would be expected to elute as suggested by IC work with thioarsenates using the same column and similar method (Elliott, 2010). However, each test solution shows an unassigned (relative to controls) and unique peak denoted by asterisks at ~10 and ~11 minutes. These peaks may be unique contaminants, oxidized sulfide species (e.g., $S_2O_3^{2-}$), both thioperrhenates, or a thioperrhenate and a Re-polysulfido anion.

ReO_4^- remaining in the test solutions was calculated from ReO_4^- peak areas in Fig. 2. These data indicate that <1% ReO_4^- was lost in the sulfidic test solution and ~7% ReO_4^- was lost in the polysulfidic test solution; ΣRe analysis was not performed. These marginal losses may be

due to experimental error, responsible for the unassigned peaks in Fig. 2, or result from the loss of a Re-S solid phase to the 0.45 μm filters. Regardless, the data point to a very slow conversion of ReO_4^- for the conditions tested. Several researchers (Yamashita et al., 2007; Dolor et al., 2009; Dolor, 2009) indicate ReO_4^- reactions under reducing conditions are sluggish.

Experimental Design- Test solutions will be prepared and stored in 15 mL plastic centrifuge tubes within a glovebox in a similar manner to preliminary experiments. Gloveboxes will be outfitted with lattice shelving to provide ample storage space for test solutions. Avoiding glass ampoules for storage is ideal. Preliminary results indicate negligible loss of ΣS^{2-} after storing a 1 mM ΣS^{2-} solution at pH 7 in a centrifuge tube for six weeks. Test solution conditions will be varied to form a matrix of compositions to ensure the integrity of kinetic and equilibrium constants. The pH will be varied using appropriate buffers from 6 to 10 to approximate the range of many natural waters. ΣS^{2-} will be varied from 0.1 to 10 mM. To date, $Na_2S{\cdot}9H_20$ has been the source of S^{2-} in test solutions. However, Fig. 2 shows three significant peaks for the S^{2-} control solution ($S^{2-} + BO_3^{3-}$), suggesting an oxidized sulfide species is present in the salt (e.g., $S_2O_3^{2-}$). As a result, HS^- stock solutions will be prepared by bubbling bottled H_2S through deoxygenated NaOH solutions. ΣRe will be varied from 1 to 10 μM. Ionic strength will range from no added background electrolyte to μ=0.7 M (as $NaNO_3$).

At recorded times (e.g., weekly), centrifuge tubes will be opened in the glovebox and pH measured. All solutions will be filtered through 0.45 μm syringe filters prior to further analysis. Polysulfide speciation and $S_{8(aq)}$ will be quantified (Vorlicek et al., 2004) using UV-Vis spectroscopy over a wavelength range of 275-500 nm. Any spectral influence from the thioperrhenates will be calculated from known extinction coefficients (Tossel, 2005). ΣS^{2-} will

be quantified by potentiometric titration with $HgCl_2$ using a Ag/Ag_2S electrode vs. double junction reference electrode. Because Re has high detection limits (~10^{-4} M) for AAS, ΣRe will need to be analyzed using ICP which is unavailable at MSUM. Aliquots of filtered samples will be frozen and saved for further ICP analyses at Minnesota Valley Testing Laboratories in New Ulm, MN. Alternatively, we will do reconnaissance experiments to determine if adding an oxidizing agent (e.g., NaOCl, BrCl, H_2O_2) to test samples results in quantitative conversion of ΣRe to ReO_4^-. If so, then IC can be used to quantify ΣRe. IC will be used to quantify ReO_4^-, thioperrhenates, and Mo-polysulfido species. These latter species will be quantified by difference between ΣRe and ReO_4^-. For more definitive identification of any unassigned IC peaks, the IC's fraction collector will be employed. Fractions at retention times of interest will be promptly injected into the MS portion of the LC-MS (i.e., bypass column) to obtain molecular weight information for the eluted species.

Kinetic constants will be calculated from initial rate information. Ideally, reactions will be monitored until equilibrium is reached. However, it is possible that complete equilibrium for some conditions may not be reached for years (Dolor, 2009). If this occurs, then reaction progress will be followed until least squares analyses provide apt fits to reaction data and suitable extrapolation to equilibrium conditions. Based on the identity of thioperrhenates and Re-polysulfido species present in test solutions, an equilibria and kinetic model describing the various reactions will be developed. Equilibrium constants will be quantified by least squares analyses using a suitable data fitting program such as TKSolver™. These constants will be used to predict Re speciation in natural waters.

IV.C. Experimental Plan 2: Quantify kinetic constants for ReO_4^- reactions occurring within sulfidic solutions in the absence vs. presence of mineral oxide solid phases.

Rationale- This experimental plan intends to quantify the influence of oxide surfaces on the rate of thioperrhenate formation reactions. Here, *oxide* refers to primarily clays (e.g., kaolinite, illite) and metal oxyhydroxides (e.g., $Al(OH)_3$, $Si(OH)_4$). This portion of the proposed research was conceived in response to data indicating that Re removal in seasonally anoxic lakes occurs at or below the sediment-water interface but not in the overlying sulfidic water column (Chappaz, 2009). It is hypothesized that mineral oxide surfaces catalyze thioperrhenate formation reactions, promoting reduction and uptake of Re within porewaters.

Experimental Design- While this set of experiments will be similar to those found in Vorlicek and Helz (2002), the proposed research does not seek to repeat that work in terms of Re. Moreover, the aim of this research will not be to survey the catalytic properties of an exhaustive list of oxide surfaces. Rather, the proposed research will focus on demonstrating the principals underlying kinetic enhancement of thioperrhenate formation via catalysis by select well-characterized synthetic oxide phases (e.g., alumina (Al_2O_3), silica (SiO_2), and, perhaps, anatase (TiO_2)) over a range of aqueous-phase conditions. This research will not involve more complex minerals like clays unless unique results with the synthetic phases invites further inquiry. I believe limiting the scope of this research is warranted since a thorough study has already been done for Mo.

These experiments will involve measuring the initial rates of reactions occurring in the presence and absence of synthetic δ-Al_20_3 (Aluminium Oxid C; Degussa Corp.) and SiO_2 (Aerosil 200; Degussa Corp.) phases. These phases are chosen because they are both present in clay structures and well characterized (Young, 1981; Goldberg et al., 1998). ReO_4^- has little affinity for mineral surfaces (Yamashita et al., 2007) which is ideal for surface catalysis because reaction products will not block active sites; it is reasonable to assume that the thioperrhenates

will display similar affinities. A master solution will be prepared under conditions analogous to those described in Experimental Plan 1. Aliquots of a portion of this solution will be added to a series of centrifuge tubes containing given masses of δ-Al_20_3 or SiO_2; the remaining portion will be added to empty centrifuge tubes. Initially, slurries will maintain suspension by using a rotating mixer. If rates are still relatively slow with catalysis, slurries will be stored and periodically shaken. Reaction progress will be monitored as noted and initial rate data gathered as a function of pH, μ, ΣS^{2-}, ΣRe, and aereal concentration of δ-Al_20_3 and SiO_2. The kinetic constants will be used to compare rates of thioperrhenate formation for hypothetical porewaters vs. an overlying sulfidic water column.

IV.D. Experimental Plan 3: Quantify uptake of Re species by pyrite (FeS_2) surfaces from sulfidic or polysulfidic solutions.

Rationale- This experimental plan aims to quantify the uptake of Re by pyrite surfaces as ReO_4^- transforms into the thioperrhenates or Re-polysulfido complexes identified and quantified under Experimental Plan 1. Thus, this research seeks to identify and quantify <u>specific</u> Re species preferentially sequestered by pyrite and elucidate the chemistry controlling scavenging.

Experimental Design- While the design of the proposed experiments will be similar to Vorlicek et al. (2004), the scope will be much more robust and yield valuable information about the sequestration mechanism of Re by pyrite. The previous study was limited to only one set of solution conditions. Further, the Mo work was for solutions with $\Sigma Mo = 10^{-3}$ M. Proposed test solutions will have 10^{-5} to 10^{-6} M ΣRe.

At various times during reaction progress, aliquots of sulfidic and polysulfidic test solutions described under Experimental Plan 1 will be exposed to natural pyrite (Ward's Natural

Science) in centrifuge tubes. After a set period of mixing, the slurries will be filtered and analyzed for ΣRe using methods described above. UV-Vis spectra of filtered solutions will be taken to determine if aqueous Fe-Re-S species are present. ΣFe will be monitored using AAS. Test solution aliquots not exposed to pyrite will be analyzed at the same time for the solution components listed under Experimental Plan 1. Pyrite scavenging experiments will not be done for every set of test solutions listed under Experimental Plan 1. Rather, the proposed research will focus its efforts on contrasting a given solution parameter while holding all other conditions constant (e.g., pH = 6 vs. pH = 9; ΣS^{2-} = 1 mM vs. ΣS^{2-} = 10 mM; ΣRe = 10^{-6} M vs. ΣRe = 10^{-5} M; $\mu = 10^{-3}$ M vs. μ = 0.7 M). These contrasting conditions should yield useful information about the chemistry controlling Re uptake.

IV.E. Statement of Availability to Pursue Proposed Research

I will almost certainly be on sabbatical during the entire 2012-2013 academic year (pending President's approval), completely releasing me from my regular teaching obligations so I can be wholly dedicated to pursuing research aims with undergraduates. In the proceeding academic years of the proposal period, I intend to apply for reassigned time to partially free me from teaching duties. The College of Science, Engineering, and Technology has a regular application process for obtaining reassigned time.

IV.F. Budget Justification

Beyond my own summer salary, funds are requested to cover the cost of paying two undergraduate students to perform research for forty hours per week over ten weeks during each summer of the project's duration. Small grants are available through MSUM's Undergraduate

Research Center to assist in purchasing some supplies and provide student academic-year or summer stipends.

In addition to the capital equipment (glovebox) discussed in the application, funds are requested for supplies such as: chemicals, glassware, pipettors and tips, glovebox and AAS gasses, bottled H_2S, IC supplies, ICP analyses, pH electrodes, magnetic stirrers, syringes and filters, centrifuge tubes for sample storage, and a small rotating mixer for suspending mineral catalysts. Additional funding ($1500 per year) is requested for travel to ACS or Goldschmidt conferences for two undergraduate researchers. MSUM's Undergraduate Research Center offers small student travel grants to cover costs in excess of the requested amount. Travel for Vorlicek will be covered using employer-provided development funds.

Proposal Narrative = 3978 words

V. References

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MINNESOTA STATE UNIVERSITY
MANKATO

October 18, 2011

Dear ACS-PRF Grants Committee:

I am writing this letter to confirm that I have agreed to provide the following Minnesota State University, Mankato funds in support of the research aims of the FY2012 grant proposal submitted by Dr. Trent Vorlicek (PI).

MSUM funds in the amount of $5,000 will be provided to cover half the cost of a double length benchtop glovebox with antechamber (LCBT-210 LC Technology Solutions) and vacuum pump.

Sincerely,

Dr. Vijendra Agarwal, Dean
College of Science, Engineering, and Technology

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