



Theoretical modeling of rhenium isotope fractionation, natural variations across a black shale weathering profile, and potential as a paleoredox proxy



Christian A. Miller^{a,b,*}, Bernhard Peucker-Ehrenbrink^a, Edwin A. Schauble^c

^a Dept. of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, 360 Woods Hole Road, Woods Hole, MA 02543, USA

^b Dept. of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

^c Dept. of Earth, Planetary, and Space Sciences, University of California–Los Angeles, 595 Charles Young Dr. E, Los Angeles, CA 90095, USA

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ABSTRACT

We present the first data documenting environmental variations in the isotope composition of Re, and the first theoretical models of equilibrium Re isotope fractionation factors. Variations of $\delta^{187}\text{Re}$ at modern surface temperatures are predicted to be ‰ level for redox ($\text{Re}^{\text{VII}} \rightleftharpoons \text{Re}^{\text{IV}}$) and perrenate thiolation reactions ($\text{Re}^{\text{VII}}\text{O}_4^- \rightleftharpoons \text{Re}^{\text{VII}}\text{O}_x\text{S}_{4-x}^- \rightleftharpoons \text{Re}^{\text{VII}}\text{S}_4^-$). Nuclear volume fractionations are calculated to be smaller than mass dependent effects. Values of $\delta^{187}\text{Re}$ from New Albany Shale samples presented in this work and in a previous study show a range of 0.8‰ over a stratigraphic interval of ~20 m. The magnitude of variation is consistent with theoretical predictions and may provide evidence for changing $\delta^{187}\text{Re}$ of seawater in the geologic past. A -0.3‰ change in $\delta^{187}\text{Re}$ across a 14 m horizontal black shale weathering profile is accompanied by a hundred-fold decrease in Re concentration and a 75% decrease in organic carbon associated with the transition from reducing to oxic weathering environment. We attribute decreasing $\delta^{187}\text{Re}$ to the loss of organically bound Re component ($\delta^{187}\text{Re} = -0.28\text{‰}$). The Re isotope composition of the complementary detrital silicate fraction varies from -0.59 to -1.5‰ , depending on the choice of silicate Re concentration.

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1. Introduction

Black shales show significant accumulations of organic carbon (C_{org}) that, in turn, promote diagenetic enrichment of a suite of “redox-sensitive” metals. If these metals are conservative in seawater, metal abundance and isotopic characteristics from a single black shale locale may be used to infer global oceanic redox conditions. Isotope studies of Mo, and more recently U have been employed in this way to identify global changes in oceanic oxidation state (e.g. Arnold et al., 2004; Brucker et al., 2009; Montoya-Pino et al., 2010), while elemental studies of Re, Mo and U are used to describe local depositional conditions (Crusius et al., 1996; Morford and Emerson, 1999; Tribovillard et al., 2012).

Like Mo and U, Re enrichment in modern and ancient organic-rich sediment is substantial (Koide et al., 1986; Crusius et al.,

1996), but it possesses other attributes in addition to this broad geochemical coherence. Sedimentary metal enrichment of Re (and U) occurs under both suboxic and sulfidic conditions, but under exclusively sulfidic conditions for Mo (Crusius et al., 1996; Morford and Emerson, 1999). In addition, the seawater residence time of Re (1.3×10^5 yr, Miller et al., 2011) is significantly shorter than that of either Mo or U (4.4×10^5 yr, and $3.2\text{--}5.6 \times 10^5$ yr respectively, Dunk et al., 2002; Miller et al., 2011). Also, though the oxic mobility of all three metals is very high, the ratio of dissolved riverine to crustal Re concentration is the highest of all metals (based on data from Mason and Moore, 1982; McLennan, 2001 and Miller et al., 2011), and its weathering is uncomplicated by sorption to Mn and Fe oxides (Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002; Pierson-Wickmann et al., 2002) as occurs for Mo and U.

The unambiguous enrichment of these metals under reducing conditions along with observed $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ fractionation between modern oxidized and reduced depositional environments (Siebert et al., 2003; Weyer et al., 2008; Montoya-Pino et al., 2010) and the existence of isotopic variation in commercially-prepared Re materials (Miller et al., 2009) suggest that $\delta^{187}\text{Re}$ analyses may be applied to studies of ancient and modern redox processes.

* Corresponding author. Current address: Department of Geology & Geophysics, School of Ocean and Earth Science and Technology, University of Hawai'i at Mānoa, 1680 East-West Road, POST Building, Room 606, Honolulu, HI 96822, USA. Tel.: +1 808 956 9607.

E-mail address: cmiller3@hawaii.edu (C.A. Miller).

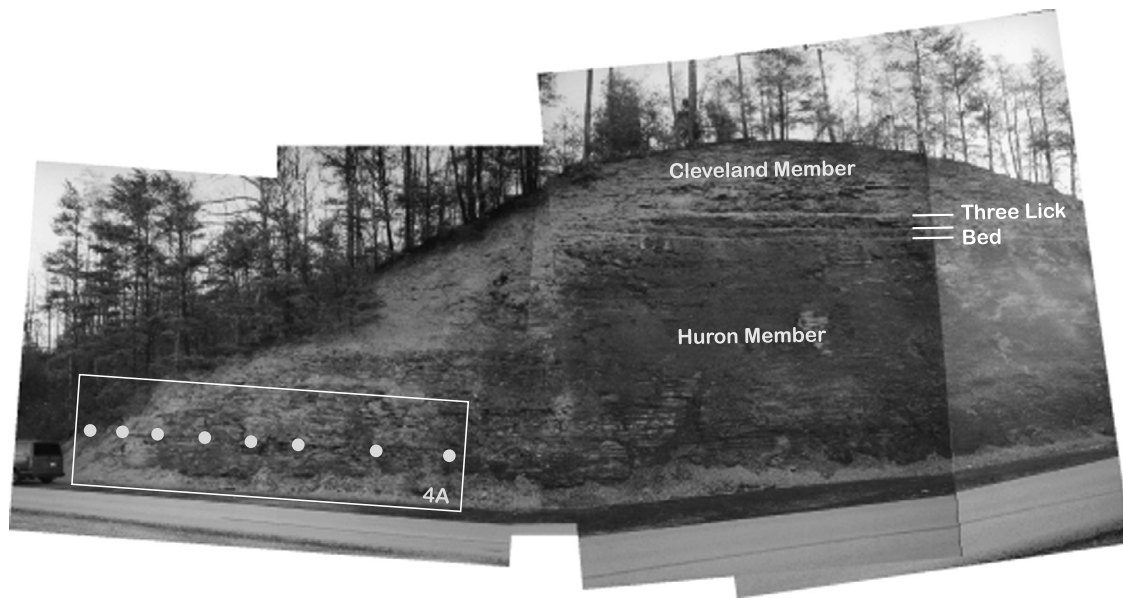


Fig. 1. Photomosaic of the weathering NAS outcrop, consisting of the top portion of the Huron Member, the three greenish-grey shale beds comprising the Three Lick Bed, and the bottom portion of the Cleveland Member. The locations of samples used in this study (see also Fig. 4A) are indicated at left.

The existence of redox-variable $\delta^{187}\text{Re}$ would be enhanced by the greater sensitivity of Re to reductive enrichment and its shorter seawater residence time.

The measurement and interpretation of Re isotope data is nonetheless complicated by a number of factors. Typical concentrations of Re in Earth surface reservoirs are 2–3 orders of magnitude smaller than those of Mo and U. The proportional mass difference between measured Re isotopes of 1.1% $\left(\frac{|184.953 \text{ amu} - 186.956 \text{ amu}|}{(184.953 \text{ amu} + 186.956 \text{ amu})/2} \times 100 \right)$ is smaller than that of both the less massive $\delta^{98}\text{Mo}$ and more massive $\delta^{238}\text{U}$ (3.1 and 1.3%, respectively). As a result, measured deviations due to mass fractionation will likely be smaller for Re than for Mo or U, even for per amu fractionation factors (α) that are identical.

Previous theoretical and experimental studies have observed mass-independent fractionation for very heavy elements such as Hg, Tl, and U ($Z = 80, 81,$ and 92 ; Bigeleisen, 1996; Nomura et al., 1996; Bergquist and Blum, 2007; Schauble, 2007, 2013; Abe et al., 2008; Fujii et al., 2009; Ghosh et al., 2013) arising from isotopic differences in nuclear volume or magnetic moment. A theoretical examination of Os ($Z = 76$; Knyazev and Myasov, 2001) predicted mass independent fractionation factors of 1.3‰ for $^{192}\text{Os}/^{188}\text{Os}$ ($\sim 0.32\text{‰ amu}^{-1}$) during redox fractionation ($\text{Os}^{\text{VI}} \rightleftharpoons \text{Os}^{\text{IV}}$). Because Re is of similar atomic number ($Z = 75$), we might expect mass independent fractionation to be of similar magnitude. Magnetic effects, which are kinetic phenomena observed most prominently between odd and even isotopes, are unlikely for Re which only has odd isotopes with the same nuclear spin ($5/2$). Nuclear volume fractionation enriches larger (usually heavier) isotopes in species where the electron density at the nucleus is smaller, due either to a lack of s -electrons or screening by p -, d -, or f -electrons. For Re, we might expect nuclear volume effects to manifest due to its redox chemistry. Oxidized Re^{VII} has a closed-shell electron structure ($[\text{Xe}] 4f^{14}$), while reduced Re^{IV} has additional $5d$ electrons ($[\text{Xe}] 4f^{14}5d^3$) which decrease the near nuclear electron density by screening s electrons. In such cases, nuclear volume fractionation is expected to oppose the mass dependent fractionation associated with redox change (e.g. U; Schauble, 2007). With only two isotopes, however, observed Re fractionation cannot be apportioned into mass dependent and mass independent contributions through use of three-isotope plots.

This study investigates natural Re isotope fractionation from two perspectives: by modeling expected Re stable isotope fractionation from first principles, and evaluating observed $\delta^{187}\text{Re}$ fractionation across a modern black shale weathering profile. As the first investigation of $\delta^{187}\text{Re}$ in natural samples, and an evaluation of $\delta^{187}\text{Re}$ across a redox gradient, this study also seeks to comment on the potential utility of $\delta^{187}\text{Re}$ as a paleoredox proxy.

2. Materials and methods

2.1. Sampling

Samples were obtained from an outcrop encompassing the top of the Huron Member, the Three Lick Bed, and the bottom of the Cleveland Member of the Devonian New Albany Shale (NAS) near Clay City, Kentucky, USA (see Fig. 1). Road construction in 1960 exposed a buff-colored weathering rind around a darker, less-weathered core. Strata are nearly horizontal allowing easy stratigraphic control while sampling across the weathering profile. Due to these features, numerous weathering studies of C_{org} and trace metals have been conducted at or near this site (Petsch et al., 2000; Jaffe et al., 2002; Tuttle and Breit, 2009; Tuttle et al., 2009). The upper part of the NAS is also known as the Ohio Shale at some locations, and United States Geological Survey Standard Reference Material SDO-1 was taken from an outcrop of the Huron Member 45 km northeast of Clay City (see Supplementary Material for further details).

The sampled horizon is located approximately 9 m below the Three Lick Bed. The weathering profile was sampled horizontally across a single stratigraphic horizon (Figs. 1, 4A), with the degree of weathering decreasing with increasing depth from the edge of the outcrop. The deepest samples (>10 m) contain fresh cm-sized pyrite crystals attesting to the lack of O_2 penetration.

2.2. Elemental analyses

Concentrations of C_{org} and Re were previously published in Jaffe et al. (2002), and analytical descriptions are found therein. Concentrations of Fe, Mo, and U were obtained from the Service d'Analyse des Roches et des Minéraux (SARM) du Centre National de la Recherche Scientifique (CNRS) in Vandoeuvre-lès-Nancy, France,

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