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

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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 perrhenate 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 fractionation 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 ($\delta^{187}\text{Re} = -0.28$ ‰). 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.

Key words: rhenium, isotopes, $\delta^{187}\text{Re}$, black shale, weathering, paleoredox

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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. 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; Abe et al., 2008; Fujii et al., 2009; Ghosh et al., 2013; Schauble, 2013) arising from isotopic differences in nuclear volume or magnetic moment. A theoretical examination of Os ($Z=76$; Knyazev and Myasoedov, 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 com-

ment 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-coloured 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) de la Centre Nationale de la Recherche Scientifique (CNRS) in Vandoeuvre-lès-Nancy, France, using ICP-AES (Fe) and ICP-MS (Mo, U). Uncertainties of Fe, Mo, and U concentrations are all <5% (2 s.d.).

Figure 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.

2.3. $\delta^{187}\text{Re}$ analyses

Sample powders were ashed for 12 hr at 450°C to oxidize organic matter, and then subjected to a series of strong acid leaches: concentrated HCl, inverse aqua regia, concentrated HNO₃. This leaching procedure liberated $\geq 90\%$ of sample Re in all but two cases (NAS14: 78%, NAS46: 84%, average of all samples is 95%). Chromatographic isolation of the leached Re (after Morgan et al., 1991) is quantitative (Miller et al., 2009), with bulk Re showing no fractionation after collection of 80% of the total. Rhenium is then taken up in 0.8 mol L⁻¹ HNO₃, doped with tungsten (W) from the National Institute of Standards and Technology (NIST) standard reference material (SRM) 3163 (available as a 1.2 mol L⁻¹ HNO₃ and 1.1 mol L⁻¹ HF solution). Analysis was done by multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) with a Thermo Fisher Scientific Neptune at the WHOI ICP-MS facility, using a quartz spray chamber and X-cones. Ion beam intensities of W and Re are measured using Faraday cups, and ¹⁸⁹Os is monitored using the axial secondary electron multiplier (SEM) to provide a correction for isobaric ¹⁸⁷Os. Instrumental

mass fractionation of measured $^{187}\text{Re}/^{185}\text{Re}$ is corrected with $^{186}\text{W}/^{184}\text{W}$ (0.92767, Völkening et al., 1991) according to an exponential law in combination with standard-bracketing. Data are converted to δ -notation,

$$\delta^{187}\text{Re} = \left(\frac{^{187}\text{Re}/^{185}\text{Re}_{\text{smpl}}}{^{187}\text{Re}/^{185}\text{Re}_{\text{std}}} - 1 \right) \times 1000$$

using National Bureau of Standards (NBS, now NIST) SRM 989 ($^{187}\text{Re}/^{185}\text{Re}_{\text{std}} = 1.7640 \pm 0.0011$, 95% CI; Gramlich et al., 1973, originally provided as Re metal). Reproducibility of standard solutions at the analyte levels used for this study (35 ng g⁻¹ W, 10 ng g⁻¹ Re) is $\pm 0.1\text{‰}$ (2 $\times$ s.d., Miller et al., 2009).

The Os isotopic compositions ($^{187}\text{Os}/^{188}\text{Os}$) of these samples were previously reported by Jaffe et al. (2002), allowing comparison of Os-corrected and -uncorrected $^{187}\text{Re}/^{185}\text{Re}$ values. The largest change imposed by ^{187}Os correction is 0.04‰, indicating that further Re purification via sparging or CrO₃-H₂SO₄+HBr micro-distillation is unnecessary (Miller et al., 2009).

2.4. Modeling equilibrium Re isotope fractionation

We estimated likely causes and magnitudes of $^{187}\text{Re}/^{185}\text{Re}$ fractionation at equilibrium with a combination of electronic structure modeling techniques. We investigated perrhenate ($\text{Re}^{\text{VII}}\text{O}_4^-$), the dominant species in the aqueous environment (Brookins, 1986), as well as thio-perrhenates ($\text{Re}^{\text{VII}}\text{O}_x\text{S}_{4-x}^-$) which may be intermediate in the reduction of Re^{VII} to Re^{IV} (Helz and Dolor, 2012).

We note here that, aside from sulfide minerals (e.g., Takahashi et al., 2007), the specific Re^{IV} species found in nature remains unknown. The Re^{IV} species we evaluate include $\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ and three variously-hydrated oxide and oxy-hydroxide molecules— $\text{Re}^{\text{IV}}\text{O}(\text{OH})_2(\text{H}_2\text{O})_3^0$, $\text{Re}^{\text{IV}}\text{O}(\text{OH})_2(\text{H}_2\text{O})_2^0$, $\text{Re}^{\text{IV}}\text{O}(\text{H}_2\text{O})_5^{2+}$. We include $\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ as it has published vibrational frequencies (as do perrhenate and the thio-perrhenates) allowing for comparison with our modeled values. However, $\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ tends to be stable only at high concentrations of HCl, and hydrolyzes at higher pH (after Busey et al., 1966). The various Re^{IV} oxide and oxy-hydroxide species do not have published frequency data, but they are included because it has been suggested that Re reduction can occur via hydroxide

intermediates (Chappaz et al., 2008) and by analogy to observed Tc^{IV} species (Breynaert et al., 2009).

Various studies have shown that Re (presumably as Re^{IV}) is bound to black shale organic materials (Selby and Creaser, 2005), in particular the high molecular-weight asphaltenes. The large sizes and unknown structures of these Re-organometallics prevented their inclusion in our modeling study. Likewise, the inclusion of less massive Re^{VII} -organometallics, such as thioperrhenate-maleic acid and/or thioperrhenate-fumaric acid adducts hypothesized by Helz and Adelson (2013), is prevented by our ignorance regarding the structures of these species.

Mass dependent fractionations were calculated using the standard thermodynamic method (Bigeleisen and Mayer, 1947) with estimates of molecular vibrational frequencies from hybrid density-functional methods such as B3LYP (Becke, 1993). We used the aug-cc-pVDZ-PP basis set and effective core potential for Re (Figgen et al., 2009), and the all-electron aug-cc-pVDZ basis set for all other atoms (Dunning, 1989; Woon and Dunning, 1993), though use of other basis sets yield similar results indicating that the choice of basis set was not a critical factor. The B3LYP/aug-cc-pVDZ-PP method appeared to somewhat underestimate frequencies for the $\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ complex, perhaps due to the larger negative charge; the accuracy of these estimates was improved by scaling the frequencies upwards by 11% (see Fig. 2, Table S1). Calculated frequencies for the other species showed little or no systematic offset relative to measurements (± 1 –2%), and no frequency scaling factors were applied. Though reconnaissance calculations were carried out with several software packages, the results from Gaussian03 (Frisch et al., 2004) were used for the isotope fractionation estimates reported here.

Nuclear volume driven fractionations were estimated for the same species using the method of Schauble (2007), based on relativistic Dirac-Hartree-Fock calculations with the Dirac08 software package (Visscher et al., 2008). Rhenium was modeled with the double-zeta quality basis set developed by Dyll (2004), while all other elements were modeled with the cc-pVDZ basis set (Dunning, 1989; Woon and Dunning, 1993); all basis sets were used in uncontracted form. As with mass-dependent vibrational frequency estimates, basis set choice did not appear to be a critical factor. We further simplified the calculations by using an approximate, classical treatment of the

small-component two-electron integrals for constructing Fock matrices (Visscher, 1997). Resulting $\text{Re}^{\text{VII}}\text{S}_4^- \rightleftharpoons \text{Re}^{\text{VII}}\text{O}_4^-$ isotope fractionation was within 0.005‰ of the fully relativistic estimate at 25°C. Root-mean-squared nuclear charge radii for ^{187}Re and ^{185}Re were taken from the compilation of Angeli (2004); other compilations yielded calculated nuclear volume fractionations within 0.02‰ of those determined with the Angeli (2004) radii at 25°C. Previous calculations with similar basis sets and parameters successfully reproduced measured isotope shifts in the optical spectra of heavy elements with a mean absolute error of about 20% (Schauble, 2007).

More details are available in the Supplementary Information.

3. Results

3.1. First principles modeling of Re isotope fractionation

Vibrational frequencies calculated for use in modeling mass dependent fractionation are presented in the supplementary material (Table S1, see also Fig. 2), as are calculated energies and ^{187}Re - ^{185}Re energy shifts used for modeling nuclear volume effects (Table S2). Calculated $^{187}\text{Re}/^{185}\text{Re}$ equilibrium isotope fractionation factors for mass dependent, nuclear volume and total (net) fractionation are presented in Table 1 (see also Fig. 3). Table 1 also shows fractionation factor estimates relative to $\text{Re}^{\text{VII}}\text{O}_4^-$ at average temperatures for Clay City, KY; these estimates were calculated using the polynomial fit factors seen in Table 2. Deviations of polynomial estimates from those determined from first-principles modeling are small, with a maximum of 0.02‰ occurring at 270 K for $\text{Re}^0 \rightleftharpoons \text{Re}^{\text{VII}}\text{O}_4^-$ and $\text{Re}^0 \rightleftharpoons \text{Re}^{\text{VII}}\text{O}_3\text{S}^-$; all other deviations are within $\sim 0.01\%$.

3.2. Elemental variability

The redox gradient between the largely unweathered core of the outcrop and the heavily weathered outcrop edge is observed as a 75% decrease in C_{org} (Table 3, Fig. 4), significant decreases in N and S (as well as the disappearance of cm-scale pyrite crystals; Jaffe et al., 2002), and an increase in the Fe content. Though Re, Mo, and U are considered geochemically coherent, in that they are soluble under oxidizing conditions and insoluble in reducing environments, they exhibit differing responses within the weathering profile. The response of Re to the onset of oxic weathering broadly

Figure 2: Comparison of measured and calculated vibrational frequencies. Note that calculated frequency data for $\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ have not been scaled up by 11% for this figure. References for measured frequency data are given in the footnotes to Table S1.

Table 1: Equilibrium $^{187}\text{Re}/^{185}\text{Re}$ fractionation factors relative to Re^0 vapor at 298.15 K (25°C) and relative to $\text{Re}^{\text{VII}}\text{O}_4^-$ at 286.05 K (12.9°C, the average annual temperature estimate for Clay City) presented as $10^3 \times \log_e(\alpha_{187-185})$. Estimates relative to Re^0 vapor at 25°C are direct model outputs, those relative to $\text{Re}^{\text{VII}}\text{O}_4^-$ at 12.9°C are calculated using polynomial fit factors (see Table 2).

Species	$10^3 \times \log_e(\alpha_{187-185})$ relative to Re^0 vapor, 25°C			$10^3 \times \log_e(\alpha_{187-185})$ relative to $\text{Re}^{\text{VII}}\text{O}_4^-$, 12.9°C		
	Mass dependent	Nuclear volume	Total	Mass dependent	Nuclear volume	Total
$\text{Re}^{\text{VII}}\text{O}_4^-$	2.88	-0.16	2.73	0.00	0.00	0.00
$\text{Re}^{\text{VII}}\text{O}_3\text{S}^-$	2.55	-0.13	2.42	-0.35	0.02	-0.33
$\text{Re}^{\text{VII}}\text{O}_2\text{S}_2^-$	2.23	-0.11	2.12	-0.69	0.03	-0.64
$\text{Re}^{\text{VII}}\text{OS}_3^-$	1.92	-0.07	1.85	-1.01	0.09	-0.92
$\text{Re}^{\text{VII}}\text{S}_4^-$	1.63	-0.01	1.62	-1.32	0.15	-1.17
$\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ ^a	1.02	0.29	1.31	-1.98	0.46	-1.52
$\text{Re}^{\text{IV}}\text{O}(\text{OH})_2(\text{H}_2\text{O})_3^0$	1.66	0.33	2.00	-1.30	0.52	-0.78
$\text{Re}^{\text{IV}}\text{O}(\text{OH})_2(\text{H}_2\text{O})_2^0$	1.74	0.34	2.07	-1.21	0.50	-0.70
$\text{Re}^{\text{IV}}\text{O}(\text{H}_2\text{O})_5^{2+}$	1.56	0.42	1.98	-1.41	0.60	-0.81

^a Fractionation estimates for $\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ are based on model frequencies that have been scaled up by 11%.

Table 2: Polynomial fits for the interpolation of fractionation factors for the various Re-containing species relative to Re^0 . Each fit is of the form: $10^3 \times \log_e(\alpha_{187-185}) = A/T + B/T^2 + C/T^4$, where A describes nuclear volume fractionation, B and C describe mass dependent fractionation, and T is the temperature in kelvins.

Species	A, K^{-1}	B, K^{-2}	C, K^{-4}
$\text{Re}^{\text{VII}}\text{O}_4^-$	-46.4	3.088×10^5	-4.638×10^9
$\text{Re}^{\text{VII}}\text{O}_3\text{S}^-$	-39.6	2.689×10^5	-3.712×10^9
$\text{Re}^{\text{VII}}\text{O}_2\text{S}_2^-$	-32.4	2.294×10^5	-2.773×10^9
$\text{Re}^{\text{VII}}\text{OS}_3^-$	-21.6	1.922×10^5	-1.861×10^9
$\text{Re}^{\text{VII}}\text{S}_4^-$	-2.6	1.558×10^5	-9.565×10^8
$\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ ^a	85.7	9.320×10^4	-2.348×10^8
$\text{Re}^{\text{IV}}\text{O}(\text{OH})_2(\text{H}_2\text{O})_3^0$	101.2	1.687×10^5	-1.883×10^9
$\text{Re}^{\text{IV}}\text{O}(\text{OH})_2(\text{H}_2\text{O})_2^0$	97.7	1.780×10^5	-2.023×10^9
$\text{Re}^{\text{IV}}\text{O}(\text{H}_2\text{O})_5^{2+}$	124.5	1.593×10^5	-1.820×10^9

^a Fit parameters for $\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ were obtained after scaling up model frequencies by 11%.

mimics that of C_{org} . The response of Mo is most similar to Fe as both show 50–100% increases in concentration in the most heavily weathered part of the outcrop. In contrast, U does not appear to show any clear geochemical trend, as the highest concentrations are found in both the unweathered core and weathered rind of the outcrop (Fig. 4).

Note that the raw elemental profiles seen in Fig. 4 are representative of elemental mobility due to the consistent concentrations of immobile elements, including major elements such as Al (Table 3), as well as trace elements such as Zr (not shown).

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3.3. $\delta^{187}\text{Re}$ variability

Variation in $\delta^{187}\text{Re}$ across the NAS weathering profile (shown in Fig. 5, Table 3) traces the extent of oxic weathering, with ^{187}Re enriched values in the less weathered portion of the profile, and ^{187}Re depletion in the more intensely weathered outcrop edge (Fig. 5). All $\delta^{187}\text{Re}$ values for the profile are less than 0‰ (−0.21 to −0.59‰). In contrast, data for three commercially available Re standard materials—Re ribbon from H.R. Cross Co., perrhenic acid (HReO_4), and the SDO-1 rock standard—all have $\delta^{187}\text{Re}$ values of 0‰ or greater (0 to 0.29‰; Miller et al., 2009); the total

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Table 3: Element concentration and $\delta^{187}\text{Re}$ data from the NAS weathering profile.

Sample	Length to edge of outcrop, m	$\text{C}_{\text{org}},^{\text{a}}$ weight %	Al, weight %	Fe, weight %	Mo, $\mu\text{g g}^{-1}$	$\text{Re},^{\text{a}}$ ng g^{-1}	U, $\mu\text{g g}^{-1}$	$\delta^{187}\text{Re},$ ‰
NAS0	0	1.8	8.4	4.9	92	0.89	24	-0.51
NAS3	0.91	1.5	7.6	5.7	126	0.85	30.	-0.59
NAS8	2.44	4.3	7.4	3.0	69	18	21	-0.32
NAS14	4.27	7.3	7.7	2.7	82	89	25	-0.25
NAS20	6.10	6.0	7.6	3.0	73	116	17	-0.24
NAS26	7.92	7.1	7.6	3.4	84	75	20.	-0.32
NAS36	10.97	7.8	7.6	3.3	83	81	19	-0.34
NAS46	14.02	6.8	7.9	3.2	74	80.	39	-0.22

^a Concentrations of C_{org} and Re were first reported in Jaffe et al. (2002).

Re isotopic variability seen in natural and industrial samples to date is therefore 0.9‰.

4. Discussion

4.1. Theoretical modeling of equilibrium Re isotope fractionation

Figure 3A–3C shows the expected mass dependent, nuclear volume, and total (net) equilibrium fractionation for all examined Re^{IV} and Re^{VII} species relative to Re^0 . The neutron-rich ^{187}Re tends to become more concentrated in the oxidized species (Fig. 3A). A comparison of Fig. 3A and Fig. 3B indicates that the expected fractionations due to nuclear volume are less pronounced than mass dependent effects. In general, the redox-related nuclear volume effects were smaller than the 0.32‰ amu^{-1} prediction for Os (Knyazev and Myasoedov, 2001), though the nuclear volume component of $\text{Re}^{\text{VII}}\text{O}_4^- \rightleftharpoons \text{Re}^{\text{IV}}\text{O}(\text{H}_2\text{O})_5^{2+}$ is similar (0.30‰ amu^{-1} , calculated from values in Table 1). The magnitude of both mass dependent and nuclear volume fractionation decreases with increasing temperature; this is accompanied by an increase in the relative importance of nuclear volume effects, which we would expect given that these scale with T^{-1} while mass dependent effects scale with T^{-2} .

Mass dependent fractionation favors the accumulation of heavier isotopes into “the chemical compound in which the element is bound more strongly” (Bigeleisen, 1965). In light of this, uniformly positive values of $\alpha_{187-185}$ for all species relative to unbonded Re^0 vapor are not surprising

Figure 3: Full caption on page 15

Figure 3 (continued): Full caption on page 15

Figure 3: Equilibrium $^{187}\text{Re}/^{185}\text{Re}$ fractionation factors, $10^3 \times \log_e(\alpha_{187-185})$, for various Re-containing species relative to Re^0 (A–C) and $\text{Re}^{\text{VII}}\text{O}_4^-$ (D–F) as a function of temperature.

(A) Mass dependent component relative to Re^0 ,

(B) Nuclear volume component relative to Re^0 ,

(C) Total (net) fractionation relative to Re^0 ,

(D) Mass dependent component relative to $\text{Re}^{\text{VII}}\text{O}_4^-$,

(E) Nuclear volume component relative to $\text{Re}^{\text{VII}}\text{O}_4^-$, and

(F) Total (net) fractionation relative to $\text{Re}^{\text{VII}}\text{O}_4^-$. Also shown is the mean annual temperature estimate for Clay City, Kentucky (based on data from NOAA’s National Weather Service for Lexington, Kentucky from <http://www.crh.noaa.gov/lmk/?n=clilex>). Ranges of $\delta^{187}\text{Re}$ (relative to SRM 989) from Miller et al. (2009, *) and this study (†) are shown at right.

(Fig. 3A). In general, more-oxidized Re^{VII} species are more ^{187}Re -enriched than those of the less-oxidized Re^{IV} . Within the Re^{VII} species, $\text{Re}^{\text{VII}}\text{O}_4^-$ is the most enriched, with progressive thiolation decreasing $\alpha_{187-185}$ by about 0.3‰ per S substitution at 25°C (Fig. 3A, Table 1). Within the Re^{IV} species, Re is more strongly bound in the hydrated species than in $\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$, which displays the smallest mass dependent fractionation, relative to Re^0 , of any compound considered.

Nuclear volume fractionation tends to “concentrate heavier nuclei in species where the electron density at the nucleus is small” (Schauble, 2007). Lower near-nuclear electron densities are favored by fewer s electrons, which have larger densities at the nucleus, or by having more p , d , and f electrons, which screen s electrons. That Re^{IV} species ($[\text{Xe}] 4f^{14}5d^36s^0$) are ^{187}Re -enriched relative to Re^0 ($[\text{Xe}] 4f^{14}5d^56s^2$) indicates that the loss of two $6s$ electrons decreases the near-nuclear electron density more than the loss of two $5d$ electrons raises it. That the Re^{VII} species ($[\text{Xe}] 4f^{14}5d^06s^0$) are ^{187}Re -depleted with respect to both Re^{IV} and Re^0 indicates the effects of further $5d$ electron loss. Also, nuclear volume fractionation between Re^0 and closed-shell Re^{VII} is not as pronounced as it is between Re^0 and Re^{IV} . Nuclear volume fractionation factors for $\text{Re}^0 \rightleftharpoons \text{Re}^{\text{IV}}$ are positive, while those for $\text{Re}^0 \rightleftharpoons \text{Re}^{\text{VII}}$ are negative (Fig. 3B, see also Table 2: polynomial fit factor A). As a result, nuclear volume fractionation “enhances” mass dependent fractionation for Re^{IV} , while “muting” mass dependent fractionation of Re^{VII} , relative to Re^0 .

The modest differences in nuclear volume fractionation within the Re^{VII} and Re^{IV} groupings are consistent with variations in the size “effective” $5d$ electron populations; that is to say, the effective $5d$ electron population sizes for Re^{VII} species are,

The sequence for the Re^{IV} species is,

Smaller effective $5d$ electron populations do less to screen s electrons, increasing the near-nuclear electron density, and resulting in isotopically lighter Re (Fig. 3B). Put another way, the Re bonding environment becomes more ionic with a smaller effective $5d$ electron population (please see the supplementary material for further discussion).

Because $\text{Re}^{\text{VII}}\text{O}_4^-$ is the dominant aqueous species at the Earth's surface (Brookins, 1986), the data seen in Fig. 3A–3C are re-expressed relative to $\text{Re}^{\text{VII}}\text{O}_4^-$ in Fig. 3D–3F. Note that—because Re^0 is not shown in Fig. 3D–3F, and because $\text{Re}^{\text{VII}}\text{O}_4^-$ is both the most-positively mass fractionated species and the most-negatively nuclear volume fractionated species—the expected range of fractionation relative to $\text{Re}^{\text{VII}}\text{O}_4^-$ is significantly smaller than it is relative to Re^0 (compare Fig. 3C and 3F). In any case, these results indicate that Re thiolation ($\text{Re}^{\text{VII}}\text{O}_4^- \rightleftharpoons \text{Re}^{\text{VII}}\text{O}_\text{X}\text{S}_{4-\text{X}}^-$) and redox ($\text{Re}^{\text{VII}} \rightleftharpoons \text{Re}^{\text{IV}}$) reactions, should exhibit observable Re equilibrium fractionation at low to moderate geological temperatures (≤ 1000 K).

Overall, fractionation favors high $^{187}\text{Re}/^{185}\text{Re}$ in $\text{Re}^{\text{VII}}\text{O}_4^-$ relative to all other species. Thiolation of $\text{Re}^{\text{VII}}\text{O}_4^-$ progressively lowers $\alpha_{187-185}$ with every S substitution at 25°C (see Table 1). The extent of redox fractionation at this temperature appears to depend on the type of reduced species considered; reduction of $\text{Re}^{\text{VII}}\text{O}_4^-$ to the hydrated oxide/oxy-hydroxide species ($\text{Re}^{\text{IV}}\text{O}(\text{OH})_2(\text{H}_2\text{O})_2^0$, $\text{Re}^{\text{IV}}\text{O}(\text{OH})_2(\text{H}_2\text{O})_3^0$, $\text{Re}^{\text{IV}}\text{O}(\text{H}_2\text{O})_5^{2+}$) results in a $\delta^{187}\text{Re}$ shift of about -0.75‰ , while fractionation associated with reduction to $\text{Re}^{\text{IV}}\text{Cl}_6^{2-}$ is about twice as large (-1.52‰ , see Figure 3F and Tables 1, 2).

4.2. Elemental and $\delta^{187}\text{Re}$ mobility across a modern redox profile

The oxidative weathering of the outcrop at Clay City is apparent not only visually (Fig. 1), but is also expressed geochemically through a systematic loss of C_{org} at the outcrop edge (Fig. 4B; %N and %S show similar behavior, see Jaffe et al. 2002). The weathering profile of Re is superficially similar to that of C_{org} in that it too shows a marked decrease at the outcrop edge. In addition, on the basis

282 of $^{187}\text{Re} - ^{187}\text{Os}$ systematics, the outcrop shows considerable gain and loss of Re from the original,
283 reconstructed Re concentration of 63 ng g^{-1} (see Jaffe et al., 2002, for a full discussion). The
284 weathered edge of the outcrop represents a Re concentration decrease of approximately two orders
285 of magnitude, while the unweathered interior sees up to a doubling of the original Re concentration.
286 The Re is added to the organic-rich portions of the outcrop after being mobilized by oxic weathering
287 of overlying strata (see Fig 1), and the redistribution of Re within the weathering profile is ongoing.

288 The other redox sensitive metals—Fe, Mo, and U—have patterns similar to one another across
289 the weathering profile (Fig. 4C, 4E, 4F), and none show the extreme weathering depletion seen for
290 Re and C_{org} . In contrast, they tend to be more enriched at the more heavily weathered outcrop
291 edge than in the unweathered core. According to a nearby study of another Huron Mbr. weathering
292 profile (approximately 8.25 km away: Tuttle and Breit, 2009; Tuttle et al., 2009), these are secondary
293 enrichments. Iron enrichment is due to the formation of $\text{FeO}(\text{OH})$, both amorphous and as goethite,
294 in the oxidized portions of the outcrop; likewise, Tuttle et al. (2009) consider Mo enrichment in
295 outcrop edge to be due to Mo sorption to Fe-oxides; while U has also been shown to cycle with
296 metal oxides (e.g. Weyer et al., 2008), Tuttle et al. (2009) view the accumulation of U in this region
297 as resulting from the affinity between U and modern organic matter. It should be noted that the
298 high concentration for U deep in the outcrop is not understood; the concentration of U in sample
299 NAS46 (14.02 m, $39 \text{ } \mu\text{g g}^{-1}$) is anomalously high in comparison to the rest of the unweathered
300 horizon (about $20 \text{ } \mu\text{g g}^{-1}$).

301 These features emphasize the differences in Re geochemical behavior from Mo or U. All three are
302 mobile under oxic weathering conditions, but only Re is insensitive to oxide or hydroxide formation,
303 or any other oxic weathering-related enrichment process.

304 The profile of $\delta^{187}\text{Re}$ (Fig. 5A), like those of Re and C_{org} concentrations, displays an obvious
305 and systematic weathering response. The coincidence of low $\delta^{187}\text{Re}$ and Re concentration with
306 decreased C_{org} indicate that the -0.3‰ change in $\delta^{187}\text{Re}$ is the result of oxic weathering. The
307 0.3‰ change is significantly smaller than might be expected on the basis of theoretical equilibrium
308 fractionation ($\text{Re}^{\text{VII}} \rightleftharpoons \text{Re}^{\text{IV}}$) for the species evaluated in this study. Also, the respective loss and
309 gain of Re seen in the weathered edge and unweathered core of the outcrop indicates that Re is

Figure 4: Sampling locations and compositional variation across the NAS weathering profile near Clay City, Kentucky, United States (see also Table 3). Data for Re and C_{org} (4B, 4D) were originally published in Jaffe et al. (2002). Uncertainties of all data are smaller than the symbol size.

310 currently an open system, and therefore not at equilibrium at the scale of the weathering profile.

311

Figure 5: See full caption on page 20

Figure 5: $\delta^{187}\text{Re}$ across the weathering profile as a two-component mixing process.

(A) $\delta^{187}\text{Re}$ data across the NAS weathering profile from near Clay City, Kentucky, United States, and the results of a two-component mixing model (solid line). The two component mixing model, describes either of two choices of silicate Re concentration presented below (5B, 5C).

(B) $\delta^{187}\text{Re}$ vs. the abundance of *org* Re as a proportion of total Re (*org* + *sil*), assuming a silicate Re concentration of 0.85 ng g^{-1} (NAS3). The *y*-intercept of a linear regression (dashed line) gives a $\delta^{187}\text{Re}_{\text{sil}}$ of -0.56‰ . The $\delta^{187}\text{Re}_{\text{org}}$ was presumed to be -0.28‰ (see text).

(C) The same plot as 5C, but with a silicate Re concentration of 0.2 ng g^{-1} (after Peucker-Ehrenbrink and Jahn, 2001). The regressed value of $\delta^{187}\text{Re}_{\text{sil}}$ is -1.5‰ .

4.3. Empirical Re isotope fractionation I: two-component mixing

Black shales by their nature are mixtures of mineral and organic components, and so will host different Re reservoirs. The systematic variation in Re concentration across the profile, as well as the recognized mobility of Re weathered from black shales (Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002; Pierson-Wickmann et al., 2002), suggests the profile may variably sample two isotopically distinct Re reservoirs. This is further supported by the occurrence of isotopically heavier and lighter Re in the C_{org} -rich and -poor portions of the outcrop (Fig. 5A, Table 3) and by previous observations of the predominant association of Re with black shale organic matter (e.g., Selby and Creaser, 2005). In this context, the shales contain Re in both an immobile, low abundance, lighter $\delta^{187}\text{Re}$ silicate-hosted reservoir, as well as a mobile, high abundance, heavier $\delta^{187}\text{Re}$ organic-hosted reservoir.

As previously noted, the original Re concentrations of 63 ng g^{-1} were reconstructed using ^{187}Re - ^{188}Os and $^{187}\text{Os}/^{188}\text{Os}$ data (Jaffe et al., 2002). The average $\delta^{187}\text{Re}$ for all samples with Re concentrations $>63 \text{ ng g}^{-1}$ is $-0.28 \pm 0.1\text{‰}$. Samples that have gained mobilized Re to moderate (e.g. NAS46, $80. \text{ ng g}^{-1}$) or large degrees (e.g. NAS20, 116 ng g^{-1}) are isotopically indistinguishable, indicating that -0.28‰ is a good estimate not only for the $\delta^{187}\text{Re}$ of the mobile, organically-bound reservoir, but also for the unweathered samples as a whole.

The systematic difference in $\delta^{187}\text{Re}$ seen in the heavily weathered portion of the outcrop reflects the influence of the lower abundance silicate-bound Re. Because even the most heavily weathered samples contain weight % quantities of C_{org} (Fig 4B ,Table 3), the Re concentration of the exclusively silicate reservoir is unknown. Estimates of Re concentrations in the continental crust

include 0.2, 0.4, and 2 ng g⁻¹ (Peucker-Ehrenbrink and Jahn, 2001; Esser and Turekian, 1993; Sun et al., 2003, respectively). The two most weathered samples, NAS0 and NAS3, have Re concentrations within this range (0.89, 0.85 ng g⁻¹) as well as mutually consistent values of $\delta^{187}\text{Re}$ (-0.51 , -0.59‰), and so may accurately describe the silicate Re reservoir despite their % level C_{org} concentrations. However, if silicate concentrations are better described by the 0.2 or 0.4 ng g⁻¹ estimates, these samples still contain significant proportions of organically-hosted Re.

The isotopic composition of Re across the weathering profile can be modeled with a sample-specific (*simpl*) model of the mixing of the organic (*org*) and silicate (*sil*) reservoirs:

$$\frac{{}^{187}\text{Re}}{{}^{185}\text{Re}}_{\text{simpl}} = \frac{\text{prop } Re_{\text{org}} \frac{\frac{{}^{187}\text{Re}_{\text{org}}}{{}^{185}\text{Re}_{\text{org}} + 1}}{\frac{{}^{187}\text{Re}_{\text{org}}}{{}^{185}\text{Re}_{\text{org}} + 1}} + (1 - \text{prop } Re_{\text{org}}) \frac{\frac{{}^{187}\text{Re}_{\text{sil}}}{{}^{185}\text{Re}_{\text{sil}} + 1}}{\frac{{}^{187}\text{Re}_{\text{sil}}}{{}^{185}\text{Re}_{\text{sil}} + 1}}}{\text{prop } Re_{\text{org}} \frac{1}{\frac{{}^{187}\text{Re}_{\text{org}}}{{}^{185}\text{Re}_{\text{org}} + 1}} + (1 - \text{prop } Re_{\text{org}}) \frac{1}{\frac{{}^{187}\text{Re}_{\text{sil}}}{{}^{185}\text{Re}_{\text{sil}} + 1}}}$$

where *prop Re_{org}* refers to the proportion of total Re found in the organic reservoir (*prop Re_{org}* + *prop Re_{sil}* = 1). If the difference between $\frac{{}^{187}\text{Re}_{\text{sil}}}{{}^{185}\text{Re}_{\text{sil}}}$ and $\frac{{}^{187}\text{Re}_{\text{org}}}{{}^{185}\text{Re}_{\text{org}}}$ is less than 0.105 ($|\delta^{187}\text{Re}_{\text{sil}} - \delta^{187}\text{Re}_{\text{org}}| < 60\text{‰}$), the results of this model are identical to those of the much simpler expression,

$$\delta^{187}\text{Re}_{\text{simpl}} = \text{prop } Re_{\text{org}} (\delta^{187}\text{Re}_{\text{org}}) + (1 - \text{prop } Re_{\text{org}}) (\delta^{187}\text{Re}_{\text{sil}})$$

which rearranges to a straight line equation in $\delta^{187}\text{Re}_{\text{simpl}}$ vs. *prop Re_{org}* space (see Fig. 5C–D).

$$\delta^{187}\text{Re}_{\text{simpl}} = \text{prop } Re_{\text{org}} (\delta^{187}\text{Re}_{\text{org}} - \delta^{187}\text{Re}_{\text{sil}}) + \delta^{187}\text{Re}_{\text{sil}}$$

The $\delta^{187}\text{Re}$ value of the silicate component is heavily dependent on the silicate Re concentration value chosen. If we assume that the Re silicate reservoir is accurately represented by NAS3 (0.85 ng g⁻¹), then the $\delta^{187}\text{Re}_{\text{sil}}$ value is -0.56‰ (Fig. 5C), indistinguishable from the NAS3 value of -0.59‰ . Choosing a silicate Re concentration of 0.2 ng g⁻¹ (Peucker-Ehrenbrink and Jahn, 2001), results in a $\delta^{187}\text{Re}_{\text{sil}}$ of -1.5‰ (Fig. 5D), while a concentration of 0.4 ng g⁻¹ (Esser and Turekian, 1993) gives a $\delta^{187}\text{Re}_{\text{sil}}$ of -0.87‰ (not shown). Adding to this uncertainty, it should be noted that the silicate reservoir was not fully accessed as Re from these samples was liberated through a

352 succession of strong acid leaches rather than by total dissolution.

353 The large difference between silicate and organic Re abundances drastically affects the *prop Re_{org}*
354 values for NAS0 and NAS3. A silicate concentration of 0.85 ng g⁻¹ results in organic Re propor-
355 tions of essentially 0 for NAS0 and NAS3; choice of 0.2 ng g⁻¹ means that roughly 75% of the
356 Re in these samples is organic. We do not consider the silicate estimate of 2 ng g⁻¹ proposed by
357 Sun et al. (2003) to be representative of the silicate fraction in the NAS, given that it would result
358 in negative values of *prop Re_{org}* for NAS0 and NAS3. There is no basis for choosing a particular
359 silicate Re concentration on the basis of “goodness of fit” as the coefficient of determination ($R^2 =$
360 0.94) does not vary with silicate Re content. Therefore, the results of the two-component mixing
361 model (Fig. 5A) describes the choice of silicate Re presented in either of Fig. 5B or 5C.

362 Clearly, two-component mixing can accurately describe the observed variation in $\delta^{187}\text{Re}$. The
363 large disparities between the Re content of the *sil* and *org* reservoirs effectively result in a step
364 function as *Re_{org}* overwhelms the combined Re reservoir in all but the two most weathered samples.
365 Assuming that silicate Re is 0.85 ng g⁻¹ likewise assumes that loss of organic Re is complete in the
366 most weathered samples, and that the isotopic difference between organic and silicate reservoirs is
367 a modest 0.3‰. Assuming a silicate concentration of 0.2 ng g⁻¹, implies that samples NAS0 and
368 NAS3 have only begun their isotopic evolution toward the much more $\delta^{187}\text{Re}$ depleted silicate end-
369 member. Though an uncertain silicate Re concentration does not allow us to explicitly constrain
370 $\delta^{187}\text{Re}$ for the silicate component, we can nonetheless state that the weathering profile indicates
371 the existence of two isotopically distinct contemporaneous Re sources.

372 In addition, the $\delta^{187}\text{Re}$ value of -0.28‰ for both the mobile component and bulk unweathered
373 shale is $\sim 0.5\text{‰}$ lower than that of the NAS-correlative USGS Devonian Ohio Shale standard, SDO-
374 1 (0.21‰ Miller et al., 2009). Both are from the Huron Member of the Ohio shale and were
375 collected about 45 km apart (see Fig. S1). A consideration of the available stratigraphic data (see
376 Supplementary Information) indicates the NAS weathering profile is located 20–22 m above the
377 SDO-1 sampling horizon. This corresponds to about 40% of the total thickness of Upper Devonian
378 rocks at these locations. If we assume a constant accumulation rate for this Epoch, this corresponds
379 to a separation of between 3 and 12 Myr (see Supplementary Information). Given these estimates

and the comparatively short residence time of Re in modern seawater ($\tau_{\text{Re}}: 1.3 \times 10^5$ yr, Miller et al., 2011), the observed -0.5‰ change in $\delta^{187}\text{Re}$ that occurred between the deposition of SDO-1 and the NAS weathering profile would reflect realistic variations in the isotopic composition of Devonian seawater.

That the $\delta^{187}\text{Re}$ of black shales is identical to that of contemporaneous seawater is assumed by analogy to Mo. For example, both have similar levels of enrichment in euxinic sediments and their similar levels of depletion in the deep waters of the modern Black Sea (e.g., Colodner et al., 1995; Crusius et al., 1996). This assumption would need to be tested. Secular change in seawater isotopic composition is also a feature of the $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ isotope systems (e.g., Siebert et al., 2003; Weyer et al., 2008), and the change observed for $\delta^{187}\text{Re}$ is similar in magnitude to Jurassic and Cretaceous changes in $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ (Pearce et al., 2008 and Montoya-Pino et al., 2010, respectively). Because $\text{Re}^{\text{VII}}\text{O}_4^-$ is ^{187}Re -enriched when compared to any of the Re^{IV} species considered, we might be tempted to ascribe the 0.5‰ decrease seen between deposition of SDO-1 and the NAS weathering profile to a decrease in the export of Re^{IV} from seawater as a consequence of diminishing anoxic or euxinic depositional area. However, this would be premature given our ignorance regarding $\delta^{187}\text{Re}$ fractionation between modern seawater and sedimentary reservoirs. In any case, these considerations illustrate the potentially informative aspects of the $\delta^{187}\text{Re}$ system in the study of paleoredox, especially in combination with $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ systems which, though less temporally sensitive due to their longer seawater residence times, also incorporate information for oxic sinks.

4.4. Empirical Re isotope fractionation II: progressive (Rayleigh) fractionation

Though two-component mixing can explain the observed data, there is an alternative, or perhaps additional possibility. An examination of Fig. 3F shows a positive fractionation for the oxidation of a Re^{IV} reservoir to $\text{Re}^{\text{VII}}\text{O}_4^-$. Subsequent loss of mobile $\text{Re}^{\text{VII}}\text{O}_4^-$ would then deplete the remaining immobile Re^{IV} pool of ^{187}Re . The progressive fractionation of a reservoir is most commonly described with the Rayleigh model, and the continuous oxidation and loss of Re across the weathering profile might then be modeled as a Rayleigh distillation process,

$$\frac{{}^{187}\text{Re}}{{}^{185}\text{Re}}_{\text{simpl}} = \frac{{}^{187}\text{Re}}{{}^{185}\text{Re}}_{\text{init}} \times f_{\text{simpl}}^{\left(1/\alpha_{187-185} - 1\right)}$$

where *simpl* and *init* refer to the observed and calculated initial reservoirs, while f_{simpl} is the fraction of the initial Re reservoir remaining. The decrease in $\delta^{187}\text{Re}$ with more intense weathering of the outcrop is consistent with this model.

The four most weathered samples show unambiguous Re loss relative to the initial concentration of 63 ng g⁻¹ (Table 3). Applying a Rayleigh model to these samples yields a $10^3 \times \log_e(\alpha_{187-185}^{\text{IV} \rightleftharpoons \text{VII}})$ value of -0.08‰. This is much smaller than any of the theoretical values obtained for fractionation between any of the Re^{IV} species considered and Re^{VII}O₄⁻ (-0.70‰ to -1.53‰, see Table 1). The only Re^{IV} ⇌ Re^{VII} pairs for which the Rayleigh model is consistent are Re^{IV}O(OH)₂(H₂O)₂⁰ ⇌ Re^{VII}O₂S₂⁻ and Re^{IV}O(OH)₂(H₂O)₃⁰ ⇌ Re^{VII}O₂S₂⁻ ($10^3 \times \log_e(\alpha_{187-185}^{\text{IV} \rightleftharpoons \text{VII}})$ = -0.06‰ and -0.14‰, respectively), but a study of Re^{VII}O₄⁻ thiolation failed to detect Re^{VII}O₂S₂⁻ (Helz and Dolor, 2012).

The lack of agreement between estimated and observed fractionation factors would seem preclude progressive/Rayleigh fractionation as the cause of $\delta^{187}\text{Re}$ variation across the weathering outcrop. However, as we do not yet know the precise Re^{VII} ⇌ Re^{IV} mechanism, we are unable to rule it out. We should also note that, for a number of reasons, it is not entirely appropriate to treat our data as an example of Rayleigh fractionation.

The NAS weathering profile also exhibits unambiguous Re gain in the deeper sections of the outcrop (Jaffe et al., 2002), yet all of these samples display consistent values of $\delta^{187}\text{Re}$ (-0.28 ± 0.1‰). This low Re isotope variability for high Re concentration samples does not seem a likely result of variable enrichment of Re mobilized (and presumably fractionated) from elsewhere in the outcrop. Rayleigh distillation also assumes a well-mixed residual reservoir; though this weathering profile was chosen because it provides a consistent lithology across different degrees of weathering, the weathering strata cannot be considered well-mixed.

Because the weathering profile does not meet all criteria of the Rayleigh model, and due to our ignorance of the precise redox mechanism, we do not think it is productive to interpret the NAS weathering profile data in this context. We cannot explicitly rule out progressive fractionation as

the cause of the $\delta^{187}\text{Re}$ variability, but think this would be better evaluated in a more controlled setting, such as a laboratory study.

5. Conclusions

First principles modeling of equilibrium mass dependent and nuclear volume effects among a variety of Re^{VII} and Re^{IV} species predicts observable variations in $\delta^{187}\text{Re}$ at low to moderate geological temperatures (≤ 1000 K), with ‰-level variations expected for net fractionation at modern surface temperatures. Nuclear volume effects are expected to be smaller than mass-dependent ones, about 15–20% for fractionation relative to Re^0 vapor, but increasing to 25–50% when evaluated relative to $\text{Re}^{\text{VII}}\text{O}_4^-$ (the most abundant Re species in the modern surface environment: Brookins, 1986). In addition, because $\text{Re}^{\text{VII}}\text{O}_4^-$ shows the most positive mass-dependent effects and the most negative nuclear volume effects, net fractionation for all other species is “muted” relative to $\text{Re}^{\text{VII}}\text{O}_4^-$.

The isotopic composition of Re is shown to vary by 0.3‰ across a 14 m New Albany Shale (NAS) horizontal weathering profile. The combination of the fractionation seen here, and documented in an earlier study (Miller et al., 2009) increases the observed $\delta^{187}\text{Re}$ range to 0.9‰ in line with the theoretical predictions. The variation of “unweathered” $\delta^{187}\text{Re}$ observed within the NAS across a stratigraphic interval of 20 m is 0.5‰ (−0.28‰ to +0.21‰). Because the source of Re to black shales is ultimately seawater, this change potentially represents a similar change in the seawater Re isotopic composition. Changing $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ in black shale sequences are interpreted as recording changes in global redox; with its predicted redox fractionation, insensitivity to oxic sinks, and comparatively rapid modern seawater residence time, Re has the potential to make significant contributions to our understanding of global paleoredox.

The cause of fractionation observed across the NAS weathering profile is ambiguous. Though the isotopically lighter Re seen in the most weathered samples is consistent with Re^{IV} oxidation to and subsequent loss of Re^{VII} , a variety of factors, including the presence of Re gain in the unweathered core and the small degree of observed fractionation indicate that the profile is not well described by progressive (e.g. Rayleigh) fractionation, though we cannot definitively rule it out. We believe the $\delta^{187}\text{Re}$ variation is better described by two-component mixing, with each sample

being composed of varying proportions of a low abundance, silicate-hosted, immobile phase, and a high abundance, organically-hosted mobile phase. While consistent values of $\delta^{187}\text{Re}$ allow us to constrain the isotopic composition of the organically-hosted reservoir (-0.28‰), subtracting this proportion to evaluate the silicate-hosted phase is heavily dependent on the value assumed for the Re concentration in the silicates. Assuming this is well-approximated by the Re concentrations of the most weathered samples yields a value of -0.56‰ ; using lower estimates of crustal Re decreases the $\delta^{187}\text{Re}$ of this end-member to -0.87‰ to -1.5‰ (using estimates from Esser and Turekian, 1993, and Peucker-Ehrenbrink and Jahn, 2001). In any case, the weathering outcrop provides evidence for contemporaneous deposition of isotopically distinct Re reservoirs in the geologic past.

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