

# Validating the rhenium proxy for rock organic carbon oxidation using weathering profiles

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1	Validating the rhenium proxy for rock organic carbon oxidation using
2	weathering profiles
3	Katherine E. Grant <sup>1,2*</sup> , Mathieu Dellinger <sup>2,3</sup> , Alexander J. Dickson <sup>4</sup> , Mateja Ogric <sup>2</sup> , Kate Horan <sup>2</sup> ,
4	Steve Petsch <sup>5</sup> , Robert G. Hilton <sup>6*</sup>
5	1. Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, CA
6	94550, USA
7	2. Department of Geography, Department of Earth Sciences, Durham University, Durham, DH1 3LE, UK
8	3. Environnements Dynamiques et Territoires de la Montagne (EDYTEM), CNRS – Université Savoie Mont-
9	Blanc, Le Bourget du Lac, 73370, France
10	4. Centre of Climate, Ocean and Atmosphere, Department of Earth Sciences, Royal Holloway University of
11	London, Egham, Surrey, TW20 0EX, UK
12	5. Department of Earth, Geographic, and Climate Sciences, University of Massachusetts, Amherst, MA
13	01003, USA
14	6. Department of Earth Sciences, University of Oxford, South Parks Rd, Oxford, OX1 3AN, UK
15	
16	*corresponding authors; grant39@llnl.gov; robert.hilton@earth.ox.ac.uk
17	
18	Abstract
19	Chemical weathering over geological timescales acts as a source or sink of atmospheric carbon
20	dioxide (CO <sub>2</sub> ), while influencing long-term redox cycling and atmospheric oxygen (O <sub>2</sub> ) at
21	Earth's surface. There is a growing recognition that the oxidative weathering of rock organic
22	carbon ( $OC_{petro}$ ) can release more $CO_2$ than is locally drawn down by silicate weathering, and
23	may vary due to changes in erosion and climate. The element rhenium (Re) has emerged as a
24	proxy to track the oxidative weathering of $OC_{petro}$ , yet uncertainties in its application remain
25	namely that we lack a systematic assessment of the comparative mobility of Re and $OC_{petro}$

39	1. Introduction:
38	global-scale rates of this important source of CO <sub>2</sub> in the geochemical carbon cycle.
37	OC <sub>petro</sub> oxidation and allow future work to further improve our knowledge of regional and
36	protected from weathering. Overall, our measurements provide validation for the Re proxy of
35	derives from silicate or sulfide phases, while some OC <sub>petro</sub> may be physically or chemically
34	expectations that, typically, between $\sim 0-20\%$ of the Re liberated by sedimentary rock weathering
33	(Marcellus Shale), the average ratio was lower at $0.58 \pm 0.11$ . The excess loss of Re matches
32	$OC_{petro}$ to Re loss was 0.84 ± 0.15, with 8 out of 9 sites having a ratio >0.74. At one site
31	loss of any other major element. Across the weathering profiles, the average molar ratio of
30	and sulfide (S) weathering. Across the dataset, Re loss is correlated with OC <sub>petro</sub> loss but not with
29	Re and OC <sub>petro</sub> loss alongside major elements that reflect silicate (Na, Mg), carbonate (Ca, Mg)
28	>10%. At nine sites we use titanium to account for volume changes during weathering and assess
27	rock weathering at 12 global sites, spanning a range of initial $OC_{petro}$ values from ~0.2% to
26	during sedimentary rock weathering. Here we measure Re and $OC_{petro}$ loss across gradients in

40 When sedimentary rocks are brought to Earth's surface during exhumation and erosion 41 (Blair et al., 2003; Hilton et al., 2011), organic matter that is millions of years old re-enters the 42 contemporary carbon cycle (Copard et al., 2007; Petsch, 2014; Petsch et al., 2000; Wildman et 43 al., 2004). The oxidative weathering of this rock-derived organic carbon (petrogenic OC; OC<sub>petro</sub>) 44 can release carbon dioxide (CO<sub>2</sub>) and consume oxygen (O<sub>2</sub>) (Petsch, 2014; Roylands et al., 2024; 45 Soulet et al., 2021) at globally significant rates (Zondervan et al., 2023). In addition, the importance of physical erosion in driving weathering fluxes (Bolton et al., 2006; Hilton et al., 46 47 2014) raises the question as to whether oxidative weathering has changed alongside global 48 denudation (Syvitski et al., 2005) through the Cenozoic (Salles et al., 2023). To move forward,

49 we require measurements of oxidative weathering across scales, which will allow us to build and 50 test quantitative models that explore its role in setting long-term CO<sub>2</sub> and O<sub>2</sub> concentrations 51 (Berner, 2003; Zondervan et al., 2023) and, assess how weathering and erosion combine to force 52 net exchanges of carbon between the lithosphere and atmosphere (Hilton and West, 2020). 53 Rhenium (Re) is a proxy that can track and quantify oxidative weathering of rock organic 54 carbon. Re and organic matter are coupled during shallow marine diagenesis as marine sediment 55 porewaters become anoxic (Colodner et al., 1993; Crusius and Thomson, 2000) and Re is immobilized. A close association of Re and OC<sub>petro</sub> in sedimentary rocks has been recognized 56 57 (Selby and Creaser, 2003). The first studies of Re mobility during weathering revealed a coupled 58 loss of Re and OC<sub>petro</sub> in a black shale weathering profile (Jaffe et al., 2002; Peucker-Ehrenbrink 59 and Hannigan, 2000). Upon oxidation, Re is soluble as perrhenate (ReO<sub>4</sub><sup>-</sup>) and is thought to be 60 carried away from the reaction site by water (Colodner et al., 1993), while the carbon may be released as CO<sub>2</sub> (Keller and Bacon, 1998; Soulet et al., 2018) or mobilized as dissolved organic 61 62 carbon (Schillawski and Petsch, 2008). Following the work of Dalai et al., (2002), a growing 63 number of studies have used the dissolved Re flux (or oxidized Re flux) from a landscape to 64 estimate oxidative weathering of OC<sub>petro</sub> (Ghazi et al., 2022; Hilton et al., 2014; Hilton et al., 65 2021; Horan et al., 2019; Horan et al., 2017). The oxidative weathering flux (or yield) of OC<sub>petro</sub>,  $J_{OCpetro-ox}$  (tC yr<sup>-1</sup>), is usually calculated from the measured dissolved rhenium flux ( $J_{Re}$ ) (t yr<sup>-1</sup>) 66 67 (Dalai et al., 2002; Dellinger et al., 2023; Hilton et al., 2014), using:

68 
$$J_{OCpetro-ox} = J_{Re} \times \left(\frac{[OC_{petro}]}{[Re]}\right)_i \times f_c \times (1 - f_{graphite})$$
 (1)

69 where  $([OC_{petro}]/[Re])_i$  is the initial concentration ratio in the rocks undergoing weathering. The 70 term  $f_C$  is the fraction of the dissolved Re flux derived from  $OC_{petro}$ , with the remainder 71 mobilized by weathering other phases, e.g. sulfide and silicate minerals (Horan et al., 2019). The final term  $f_{\text{graphite}}$  recognizes a fraction of the OC<sub>petro</sub> pool which may not be susceptible to oxidation, for instance in high grade metamorphic rocks where graphite is present (Galy et al., 2008; Horan et al., 2017). In addition, some landscapes with low weathering rates and local historic fossil fuel burning power plants or other industries may have contributions of Re to river waters (Ogrič et al., 2023).

77 To validate the Re proxy for OC<sub>petro</sub> oxidation and reduce the uncertainty in its application (Zondervan et al., 2023), we need to quantify coupled loss of Re and OC<sub>petro</sub> over a 78 79 range of possible weathering environments. Although Re measurements have become more 80 common (Sheen et al., 2018), especially in river environments (Dellinger et al., 2021; Hilton et 81 al., 2014; Horan et al., 2017; Ogrič et al., 2023), we still lack comprehensive tests of Re loss 82 from the solid phase residue of weathering (Jaffe et al., 2002; Ogrič et al., 2023); especially in 83 weathering profiles ranging in OC content, sulfur content and reactive Fe content (Petsch et al., 84 2000). Measuring the residual weathered material can give site-specific insights into what 85 products are release during weathering. The Re proxy can be applied to river fluxes (Equation 1), 86 but can also be calculated from solid samples if landscape weathering profiles are available. In terms of the residual phases of weathering (e.g. soils) that can be found in the landscape, OC<sub>petro</sub> 87 88 oxidation can be constrained as:

89 
$$J_{OCpetro-ox} = -D \times ([OC_{petro}]_{w*} - [OC_{petro}]_{i*})$$
 (2)  
90  $J_{Re} = -D \times ([Re]_{w*} - [Re]_{i*})$  (3)

where D is the total denudation rate (t yr<sup>-1</sup>), the subscript w refers to the concentration in the products of weathering in the landscape compared to the initial, *i*, and \* refers to a correction for concentration changes associated with volume changes with weathering as both increases in volume due to plant and organic matter deposition and mass loss associated with chemical

95	weathering and volumetric strain need to be accounted for (Brimhall and Dietrich, 1987;
96	Chadwick et al., 1990; Hayes et al., 2019). From this, Equation 1 can be re-written as:
97	$\frac{([oc_{petro}]_w - [oc_{petro}]_i)}{[oc_{petro}]_i} = \frac{([Re]_w - [Re]_i)}{[Re]_i} \times f_c \times (1 - f_{graphite}) $ (4)
98	which demonstrates how, if the Re proxy was operating to track OC <sub>petro</sub> , weathering products
99	should show coupled loss of OC <sub>petro</sub> and Re, moderated by the factors $f_{\rm C}$ and $f_{\rm graphite}$ .
100	Here we address how well Re can trace $OC_{petro}$ during rock weathering through new
101	analysis of previously collected and freshly sampled weathering profiles across 9 sites and
102	combine these data with previously published studies to create a compiled data set of 104
103	measurements. These include samples from weathered and unweathered black shales ( $OC > 1$
104	wt. %) and organic rich mudstones which we term here "grey shales" (OC < 1 wt.%) which are
105	globally relevant to Re and OC <sub>petro</sub> weathering fluxes (Sheen et al., 2018; Zondervan et al.,
106	2023). Re mobility is assessed alongside $OC_{petro}$ , using radiocarbon ( <sup>14</sup> C) where appropriate, and
107	major and trace elements to track silicate, carbonate, and sulfide mineral weathering. We use the
108	index element titanium (Ti) at the 9 sites to account for pedogenic volume changes (Kurtz et al.,
109	2000) and calculate a "loss ratio" to understand the coupled loss of $OC_{petro}$ and Re across
110	different systems and evaluate the use of the Re proxy.

#### 112 2. Materials and Methods:

113

Table 2. List of tectonic and climate information for the sampling sites.

		Tectonic		
Location	Rock type	Setting	Relief	Climate <sup>1</sup>
Waiapoa	gray shale	active	High	Temperate
Waipu	gray shale	active	High	Temperate
Marcellus	black shale	inactive	modest	humid continental
New Albany (Clay				
city)	black shale	inactive	modest	humid continental

Woodford Shale	black shale	inactive	modest	humid tropical
Green River	black shale	inactive	modest	Steppe
Monterey	black shale	active	High	Mediterranean Sub-tropical
Taiwan	grey shale	active	High	Rainforest
East River	grey shale	inactive	High	Steppe

- <sup>1</sup>Based on zones reported in Beck et al., 2023
- 115
- 116 **2.1 Weathering profiles**

117 New measurements were made on 40 individual samples which included a set of six black shale 118 weathering profiles (n = 33) (OC<sub>petro</sub> > 1%) collected from across the continental USA, and two 119 grey shale weathering profiles (n=7) (OC<sub>petro</sub> < 1%) collected from New Zealand. Black shale 120 samples were processed to analyze Re and major elements from profiles characterized previously 121 for OC<sub>petro</sub>, and S loss (Petsch, 2014; Petsch et al., 2000). The samples include the six sites 122 published in Petsch et al. (2000) and additionally reviewed in Petsch (2014). Briefly, at each site 123 we have 4-6 samples ranging from highly weathered to un-weathered from collected from road 124 cuts. To reduce possibility for interbed variability, collected samples were carefully chosen to 125 sample single sedimentary beds or horizons (Table 1).

126 The six collection sites are listed with their geologic age and measured %OC content in 127 the un-weathered samples (Petsch et al., 2000), they range across different erosional settings 128 from teconically inactive to active, while covering three different climatic zones. The New 129 Albany Shale (Clay City; NACC) and New Albany Shale (Deatsville; NADV) are of late 130 Devonian Age, and have un-weathered OC contents ranging between 9–12% OC. The NACC 131 samples were collected from Clay City, Powell Co., Kentucky, USA and the NADV samples 132 were collected from Deatsville, Nelson Co., Kentucky, USA. The Woodford shale (WF) is also Devonian in age, with a variable 15–25% OC in the un-weathered samples. These were collected 133

from Arbuckle Mtns., Murray Co., Oklahoma, USA. The Marcellus shale (ME) is mid-Devonian
age and samples collected contain 8–10% OC in the un-weathered shale. These samples are from
Warren, Herkimer Co., New York, USA. The Monterey shale (MO) is Miocene age and
collected from Gaviota Beach, Santa Barbara Co., California, USA. The OC contents range from
8–20% in the un-weathered samples. The Green River shale (GR) is from the Eocene and was
collected from Nine Mile Canyon, Duchesne Co., Utah, USA; unweathered samples contain 15–
18% OC.

141 The mid to late Devonian shales (NACC, NADV, WF, and ME) were all deposited in 142 oxygen-deficient, highly productive epeiric seas on the craton of eastern North America (Petsch 143 et al., 2000). The New Albany and ME shales contain abundant clay and detrital quartz, whereas 144 the WF is more silica rich. These organic sediments are mainly composed of marine 145 phytoplankton with minor contributions from bacteria and terrestrial plants. These rocks have 146 abundant pyrite formation and limited OM sulfurization. The GR, an Eocene formation, is a 147 lacustrine formation formed by the rise of the Rocky Mountains and is dominated by carbonate-148 rich marl. There is low sulfate and detrital iron which limited OM sulfurization and pyrite 149 formation. The Miocene MO formation was deposited in a restricted marine basin off the 150 Californian coast. It is composed of siliceous sediments with marine carbonates and some detrital 151 material derived from the Coastal Range mountains. These organic matter rich rocks are low in 152 pyrite and had high OM sulfurization leading to large sulfur rich organic macromolecules. The 153 OM is mainly marine phytoplankton and bacteria with some terrestrial plant material. There are 154 three main types of OM from this study (I, II, and II-S), where GR is Type I, NACC, NADV, 155 WF, and ME are Type II, and MO is Type II-S. All of these rocks, except for ME, are thermally

immature and are expected to have a lower degree of graphitization than thermally matureshales.

158 Two sites in New Zealand that were sampled represent lower OC<sub>petro</sub> contents more 159 typical of the majority of continental surface rocks (Zondervan et al., 2023). These are from the 160 Waipaoa (WPO) catchment, collected in April 2018 and the Waiapu (WPU) catchment collected 161 in September 2014. Both weathering profiles were collected from road cuts, with samples of 162 weathered material near the modern vegetation and soil interface, and less weathered material 163 with depth in the profile. In this part of New Zealand, the Raukumara Ranges (Kuehl et al., 164 2016) experience ongoing tectonic uplift and high rates of denudation which expose a sequence 165 of deformed but weakly metamorphosed Cretaceous and Tertiary sedimentary rocks, dominated 166 by mudstones (Mazengarb and I.G.Speden, 2000). The WPO profile is located on the mid 167 Miocene Tolaga Group, and is comprised of grey, slightly calcareous mudstones. The WPU 168 profile formed on the same geological unit but is located to the northern part of the Raukumara 169 peninsular, where mudstones with minor carbonate content are interbedded with fine sandstones. 170 The Early Cretaceous mudstones of the Mokoiwi Formation (Ruatoria Group) which outcrop to 171 the north of this location have been the focus of a field-based study of CO<sub>2</sub> production during 172 mudstone weathering (Roylands et al., 2022) and have OC<sub>petro</sub> contents of ~0.7–0.8 %.

173

#### 174 **2.2 Published data**

Three profiles with previously published rhenium concentration and OC data are used in this study. In those works, OC<sub>petro</sub> concentration was determined using radiocarbon activity and a two end member mixing model to account for biospheric contribution to the OC (Zhang et al, 2024).
We include samples from the Upper Devonian Ohio Shale (Jaffe et al., 2002), the East River

179	Bradley Meadow site (Hilton et al., 2021), and samples from the Central Range in Taiwan
180	(Hilton et al., 2014; Hilton et al., 2010). The Ohio Shale is the same shale as the previously
181	described NACC black shale. It was sampled by Petsch and others from the same roadcut from
182	Clay City, Kentucky in 2009, but from a distinct sedimentary horizon. Re and $OC_{petro}$
183	concentrations were previously reported in Jaffe et al. (2002), and Re isotopic composition was
184	reported in (Miller et al., 2015). The East River Bradley Meadow site is instrumented within the
185	Lawrence Berkely National Laboratory's Watershed Function Scientific Focus Area (SFA)
186	(Winnick et al., 2017) and is located in the upper East River catchment of the Colorado Rocky
187	Mountains. The soil-subsurface profile was collected in 2019 and is a subalpine meadow located
188	at 2,987 m elevation. [Re], TOC and F <sup>14</sup> C data were first presented in Hilton et al. (2021). Paired
189	[Re] and OC <sub>petro</sub> loss was also calculated in solid samples from the Central Range Taiwan, where
190	weathered materials from soils (Hemingway et al., 2018) were compared to less weathered
191	OC <sub>petro</sub> in riverbed materials (Hilton et al., 2014). The Taiwan case provides a higher
192	metamorphic grade case study than most of the other sites. All samples utilized in this study are
193	presented in Table 1 and 2.

- 195 **2.3 Geochemical methods**
- 196 Carbon isotopic measurements

197 The majority of samples used in this study had previously reported organic carbon

198 concentrations, organic carbon isotope composition (stable isotopes, radiocarbon), and OC<sub>petro</sub>

199 concentrations. The Waipaoa and Waiapu profiles were analyzed and reported here for the first

200 time. The black shale samples used in this study were previously measured for OC concentration

201 ([OC],%), stable isotope composition ( $\delta^{13}$ C; ‰),<sup>14</sup>C (F<sup>14</sup>C, "fraction modern") and pyrite sulfur

202	([S],%) determined by H <sub>2</sub> S liberation with acidic CrCl <sub>2</sub> and reported in Petsch et al. (2001b) and
203	Petsch et al. (2000). For a subset of the grey shale samples, Taiwan and East River, we use
204	previously reported carbon isotopic measurements and OC <sub>petro</sub> concentrations (Hilton et al.,
205	2014; Hilton et al., 2021). The Waiapu grey shale samples were measured for [OC], $\delta^{13}$ C, and
206	<sup>14</sup> C after a 0.2 N HCl leaching protocol (Galy et al., 2007) to remove carbonates following Horan
207	et al., (2017). Aliquots of dried sample were loaded into pre-combusted tin capsules for EA-
208	IRMS measurement at Durham University. Samples were measured on a Costech elemental
209	analyzer coupled to a Thermo Fisher Scientific V Advantage Isotope Ratio Mass spectrometer
210	and normalized to the composition of international standards (reported relative to Vienna Pee
211	Dee Belemnite with a precision of 0.2‰). The Waiapu WPU grey shale profile samples were
212	analyzed for the radiocarbon activity (reported as Fraction Modern, $F^{14}$ C) at the University of
213	California, Irvine Keck Carbon Cycle Facility following closed tubed combustion and
214	graphitization (Horan et al., 2017). The Waipaoa WPO grey shale was processed using the HCl
215	fumigation method to remove carbonates (Komada, et al., 2008), while the radiocarbon activity
216	(reported as F <sup>14</sup> C) was measured o at ETH-Zurich at the Laboratory of Ion Beam Physics using
217	the coupled EA-Mini Radiocarbon Dating System (MICADS) with CO2 as the source of the ion
218	beam. (McIntyre et al., 2017). Each radiocarbon faculty uses standard background corrections
219	and reports data according to Stuiver and Polach (1977). F <sup>14</sup> C measurements were used to
220	constrain a two-endmember mixing model to calculate an $OC_{petro}$ concentration for the Waipaoa
221	and Waiapu profiles, with a $F^{14}$ C value for OC <sub>petro</sub> of 0, and the biospheric end member having a
222	$F^{14}C = 1.0 \pm 0.1$ which reflects the steep, shallow organic soils in these setting.

223 Sample handling and digestion

224 For the new Re data reported here, the black shale samples and WPO profile were ground 225 to a fine powder in an agate planetary rotary mill and then digested with modified methods 226 reported by Dellinger et al. (2020). Due to a concurrent aim to obtain enough Re mass for 227 isotopic measurements (not reported here), larger masses for the black shale samples were used 228 than are strictly necessary for [Re] measurements. Briefly, sample aliquots (~500 mg) were 229 loaded into Savilex Teflon beakers and digested with 2:1 16 M HNO3: 10 M HCl aqua regia 230 solution for 24 hours. Samples were dried down at 80 °C and digested with ~1-3 ml 29 M HF to 231 remove silica content, then slowly dried again at 80 °C before being redigested at 120 °C in aqua 232 regia to remove precipitated fluorides. This process was repeated ~3 times to ensure complete 233 digestion.

234 For the black shales, after an initial, extended digestion, the high refractory OC content of 235 the black shales lead to a black solid residue. A set of 30 ml BaekDu<sup>TM</sup> Digestion Vessels from 236 ODLAB were used to rapidly digest the organic matter content of these samples, with the 237 principal benefit of these vessels being a continued, repeated reflux of the sample through 238 deliberate and focused formation of an acid reflux that slightly pressurized and concentrated the 239 digestion residue. The sample was weighed into the bottom of the vessel with 3ml 16 M HNO<sub>3</sub> 240 then the interior cap was placed on the beaker and the exterior cap was filled with 2ml 16 M 241 HNO<sub>3</sub>, to ensure constant, sustained reflux. The reactor vessels were then heated on a hotplate 242 overnight (~12–16 hrs) at 200 °C. The entire sample (liquid and solid) was then transferred to a 243 Savillex Teflon beaker and silicates were removed through the HF digestion procedure described 244 above. These reactor vessels cut the entire digestion time to  $\sim 24-36$  hours from the previous 2-4 245 weeks. Digested samples were redissolved in 1 M HCl and a sample aliquot which we ensured 246 was <1% of total [Re] was taken for trace metal concentration analysis.

To purify for the black shale and WPO profile sample for [Re] measurement, the sample, with 1% total volume for total elemental analysis, was loaded onto a preconditioned polypropylene column with 1 ml AG1-X8 (200–400ml) resin according to methods described in Dellinger et al. (2020). The sample was washed with 10 ml 1 M HNO<sub>3</sub>, 15ml 0.5 HNO<sub>3</sub>, 1.5ml 4M HNO<sub>3</sub>, and then Re was eluted in 4 M HNO<sub>3</sub> and dried down. Samples were refluxed with 16 M HNO<sub>3</sub> at 150°C to remove any column bleed and diluted to an appropriate range to measure [Re].

The WPU profile was digested using similar methods as described above, but was analyzed using isotope dilution ICP-MS and purified using a solvent extraction. In summary,  $\sim 0.05$  g of sediment sample was doped with a known amount of <sup>185</sup>Re solution and digested in a 6:3 concentrated HF-HNO<sub>3</sub> mix (9 mL) for 24 hours at 120 °C, evaporated, then digested again in a 2:1 mix of concentrated HNO<sub>3</sub>-HCl (3 mL) for 24 h at 120 °C. The Re was isolated from the matrix using a NaOH-acetone solvent extraction (Cumming et al., 2013; Horan et al., 2019).

#### 261 Major elements and Trace elements

Major and trace elements were analyzed on an ICP-OES at Durham University after dilution to appropriate concentration ranges. A set of 6 to 7 multi-element calibration standards with concentrations ranging from 0.1 to 60 ppm were used. USGS shale rock standards MAG-1 (n=2 digestions and measurements), SDO-1 (n=1) and SBC-1 (n=2) were measured to assess the precision and accuracy of the measurements. Data agree with USGS certified values to within <5% for Al<sub>2</sub>O<sub>3</sub>, <7% for Fe<sub>2</sub>O<sub>3</sub>, <8% for CaO, <9% for MgO, <10% for TiO<sub>2</sub>, and <20% for Na<sub>2</sub>O, K<sub>2</sub>O and MnO.

269 *Rhenium measurements* 

270	All Re measurements, apart from those on the WPU profile, were made by multi-
271	collector inductively coupled plasma mass spectrometry (MC-ICP-MS; ThermoFisher Scientific
272	NeptunePlus without jet interface) at the Arthur Holmes Isotope Geology Laboratory, Dept.
273	Earth Sciences, University of Durham. Following separation of Re, samples were re-dissolved in
274	0.5 M HNO <sub>3</sub> and a small aliquot ( $\sim$ 2% of the sample mass) was taken to measure Re
275	concentration by MC-ICP-MS. External calibration curves were determined via sample dilution
276	(Dellinger et al., 2020).
277	The WPU profile was analyzed from purified Re aliquots in 0.8 M HNO <sub>3</sub> using a Thermo
278	Scientific X-Series Q-ICP-MS to analyze the modified Re isotope composition (following <sup>185</sup> Re
279	spike addition) and corrected for mass fractionation and blank contributions (Horan et al., 2019).
280	Concentrations were calculated by isotope dilution using the measured <sup>185</sup> Re/ <sup>187</sup> Re ratio. The
281	sample precision and accuracy of these methods and those used in the literature previously
282	(Dellinger et al., 2021; Hilton et al., 2014; Jaffe et al., 2002) are not vastly different, and we do
283	not expect any systematic biases between the specific analysis protocols used.
284	

285 **2.4 Metric of loss** 

To accurately quantify the loss of an element of interest, in this case, Re or OC<sub>petro</sub>,
normalization to an immobile, 'index', element is a common practice (Brimhall and Dietrich,
1987; Kurtz et al., 2000). This eliminates the need to understand the volume loss of the profile,
to accurately quantify the mass loss (Chadwick et al., 1990; Hayes et al., 2019).

290 
$$\Delta X_{Ti} = \frac{([X]_n/[Ti]_n - [X]_i/[Ti]_i)}{[X]_i/[Ti]_i}$$
(5)

Where X is the mobile element of interest, [Ti] is the titanium concentration, and *n* refers to a sample above the deepest or least weathered in the profile, and *i* identifies the deepest sample.

This loss quantity can be considered a "pseudo" tau value, as it is not trying to explicitly say what the parent is, but rather quantifying a relative loss compared to the least weathered sample (Anderson et al., 2002). Note, in our sample set we do not have the major elements for the deepest Woodford sample, instead we use the next deepest sample to normalize these calculations.

**3. Results:** 

299 All raw sample data are found in the Supplementary Information (SI Table 1) and a complied 300 list of new measurements are in Table 1. First, we examined individual weathering profiles as 301 done previously in Jaffe et al. (2002) and Dalai et al. (2002), to examine the relationship between 302 Re geochemistry and OC<sub>petro</sub> loss at the site scale. For example, in the New Albany Clay City 303 black shale weathering profile we find: i) an apparent coupled loss of OC<sub>petro</sub> and Re with depth; 304 and ii) a deeper pyrite weathering front, suggesting sulfur depletion is spatially decoupled from 305 Re depletion (Figure 1). In this example, the unweathered samples had OC<sub>petro</sub> concentrations of 306  $\sim$ 7 to 8% and [Re]  $\sim$  100 ng/g. In the weathered samples, OC<sub>petro</sub> drops to 1.8% and [Re] drops to 307 1.52 ng/g, while sulfur is fully removed from the profile except for the most unweathered 308 sample. Similar patterns are observed in other new black shale and grey shale data and have been 309 observed in other weathering profiles (Hilton et al., 2021; Zhang et al., 2024).



Figure 1: Example of rhenium and rock organic carbon ( $OC_{petro}$ ) loss during weathering. A weathering profile from New Albany Clay City showing changes in  $OC_{petro}$ , pyrite S and rhenium concentration with depth in profile.

311 Other trace and major elements for each of the newly measured black shales are given in 312 the SI Table 1. Concentrations of Ti are used to calculate the loss metric of [Re], [OC<sub>petro</sub>], and a 313 subset of mobile elements of interest such as Na, Ca, and S as described above ( $\Delta X_{Ti}$ ). The loss 314 of Re does not correlate with any major element linked to carbonate weathering or silicate 315 weathering (Figure 2A and B), and is not coupled with sulfide oxidation and iron cycling (Figure 316 2C and D). In more detail, we found that normalized Re loss ( $\Delta$ [Re]<sub>Ti</sub>) was not significantly 317 correlated (Pearson correlation) with calcium loss (r = -0.10, p = 0.59), sodium loss (r = 0.09, p =0.61), sulfur loss (r= -0.02, p=0.93); or iron loss (r =0.17, p=0.40). 318



Figure 2: Relative changes in rhenium concentration in the studied weathering profiles, reported as a loss coefficient relative to the deepest sample and normalized to titanium concentrations. Rhenium loss plotted with: A: calcium loss (r = -0.10, p = 0.59); B: sodium loss (r = 0.09, p = 0.61); C: sulfur loss (r = -0.02, p = 0.93); and D: iron loss (r = 0.17, p = 0.40).

Across the weathering profiles, we found a significant correlation between  $OC_{petro}$  loss and Re loss (r = 0.66, p < 0.05). The average ratio of  $OC_{petro}$  and Re loss was  $0.84 \pm 0.15$ , with 8 out of 9 sites having a ratio >0.74. At one site (Marcellus Shale), the average ratio was lower at  $0.58 \pm 0.11$  (Table 3), possibly due to the different thermal maturity of this shale (Dickson et al., 2020).

Table 3. List of shale weathering profiles and their respective average  $\Delta[OC_{petro}]_{Ti}/\Delta[Re]_{Ti}$  loss 

Location	Rock type	$\Delta [OC_{petro}]_{Ti}/\Delta [Re]_{Ti}$
Waiapoa	gray shale	$0.94 \pm 0.05$
Waipu	gray shale	$0.78 \pm 0.14$
Marcellus	black shale	$0.58 \pm 0.12$
New Albany (Clay city)	black shale	$0.81 {\pm}~ 0.15$
Woodford Shale	black shale	$0.74 \pm 0.36$
Green River	black shale	$0.88 {\pm}~ 0.18$
Monterey	black shale	$0.79 {\pm}~ 0.18$
Taiwan	grey shale	$0.95 {\pm}~0.09$
East River	grey shale	$1.11 \pm 0.00$
All sites	n.a.	$0.84 {\pm}~ 0.15$

ratio across measured samples, reported with the standard deviation.

327	For the seven black shale weathering profiles, with an initial OC <sub>petro</sub> content of 6.11–
328	22.55 wt%, we assume the total OC in the shale is $OC_{petro}$ . The weathered black shales range in
329	OC content between 0.98–5.01 %. [Re] ranged from 31 ng/g to 671 ng/g in the un-weathered
330	shale, and ranged from 0.38 ng/g to 278 ng/g in the weathered shales.
331	From the grey shale profiles from New Zealand, Taiwan, and the East River, $OC_{petro}$
332	contents were expectedly much lower than in the black shales, as expected, with the least
333	weathered samples having concentrations which range from 0.17 to 0.76%. Weathered materials
334	have OC <sub>petro</sub> contents of 0.04–0.38%. The [Re] of these grey shales is similarly low, ranging
335	from 0.03–2.10 ng/g in the weathered samples and from 0.31–4.31 ng/g in the less weathered
336	materials. These are more similar to the continental crustal value of $< 1$ ng/g (Peucker-
337	Ehrenbrink and Jahn, 2001) than the concentrated Re values in the black shales.
338	



Figure 3: Relative changes in sulfur (S) and iron (Fe) in the studied weathering profiles. Differences between the concentrations of the deepest sample reported as a loss coefficient normalized to titanium concentrations, where negative values indicate relative loss and positive values indicate relative gain, for: A: rock organic carbon concentration  $(OC_{petro})$  vs sulfur; B: rock organic carbon concentration  $(OC_{petro})$  vs iron.

340 Finally, we compared the OC<sub>petro</sub> loss ( $\Delta$ [OC<sub>petro</sub>]<sub>Ti</sub>) to both the sulfur loss ( $\Delta$ [S]<sub>Ti</sub>) and iron

341 loss ( $\Delta$ [Fe]<sub>Ti</sub>) across the measured profiles. We find that ( $\Delta$ [OC<sub>petro</sub>]<sub>Ti</sub>) does not correlate with

342 ( $\Delta$ [S]<sub>Ti</sub>), using a Pearson correlation (r =0.32, p= 0.16) or  $\Delta$ [Fe]<sub>Ti</sub>) (r = 0.05, p =0.81). Sulfur and

- iron in these samples are likely coming from the initial oxidation of sulfides and then
- 344 incorporated into secondary minerals and biogeochemical cycling. These results show OC<sub>petro</sub>
- 345 loss is decoupled from both sulfur and iron loss.
- 346 **4. Discussion:**

347 A number of studies have used isolated weathering profiles (e.g. Figure 1) to show that Re

348 loss during weathering is coupled to OC<sub>petro</sub> loss (Jaffe et al., 2002; Zhang et al., 2024), a key

- 349 foundation in the use of the Re-proxy for OC<sub>petro</sub> oxidation (Dalai et al., 2002). Here, we provide
- a systematic assessment of Re mobility, using immobile elements to robustly quantify element

losses across ranges in sedimentary rock types,  $OC_{petro}$  contents, and weathering intensities. We show that despite differences in climate, denudation rate, and tectonic setting,  $OC_{petro}$  loss and Re loss are linked in weathering profiles. This result confirms the appropriate use of the Re proxy in eq.1 for  $OC_{petro}$  oxidation studies.

355

### 4.1. Decoupling of Re loss from carbonate, silicate and sulfide weathering

356 Rhenium concentrations vary significantly between the different outcrops studied here (Table

357 1). This may reflect different hosts of Re in the solid phase, which are known to include OC<sub>petro</sub>

358 (Selby and Creaser, 2003), silicate minerals (Burton et al., 2002) and sulfides (Colodner et al.,

359 1993; Dalai et al., 2002; Ross and Bustin, 2009). Carbonates are not thought to be a major host

of Re (Miller et al., 2011), although diagenetic processes may redistribute Re and this has not

361 been well studied (Helz, 2022). Generally, in silicate minerals, Re is thought to be relatively low

362 concentration, as crustal abundances are on average of ~0.93 ng g<sup>-1</sup> and 0.2-2 ng g<sup>-1</sup> in oceanic

and continental crust, respectively (Peucker-Ehrenbrink and Jahn, 2001).

364 Silicate weathering is generally measured through the flux of Na, Ca, Mg phases in river

365 waters and weathered products, as the major rock types are composed of these base cations

366 (Gaillardet et al., 1999). Carbonate weathering is tracked by the major elements Ca and Mg

367 (Beaulieu et al., 2011; Spence and Telmer, 2005). Across the weathering profiles studied here,

368 we find a correlation between Mg loss and Na loss (Pearson r = 0.45, p= 0.0071) and Mg loss

and Ca loss (r= 0.29 value and p = 0.12, not significant). These patterns are broadly consistent

370 with silicate and carbonate weathering processes operating across the sampling locations.

371 Variability in these loss ratios will reflect the variability in the mineralogy of silicate and

372 carbonate minerals, and the detailed reaction kinetics operating as a function of water residence

time and physical weathering processes (Brantley et al., 2013; Brantley et al., 2017; Gu et al.,
2020), but is not the focus of the study here.

375 When we compare Re loss ( $\Delta Re_{Ti}$ ) to the tracers of silicate and carbonate weathering, we do 376 not find any significant correlations (Figure 2). First, this suggests that across the profiles, 377 silicate and carbonate minerals are not the dominant hosts of Re. This fits with findings from 378 sequential extractions of Mackenzie River sediments, a mix of sedimentary rock grains, where 379 only 3–7% of Re could be linked to a silicate-mineral host, and only <6% in a potential 380 carbonate hosted pool (Dellinger et al., 2021). Similar sequential extractions results were 381 reported in Zhang et al. (2024). Miller et al. (2015), also suggested silicates and carbonate are a 382 minor host of Re using Re isotope mass balance. Second, it suggests that the bulk loss of Re is 383 not being meaningfully driven by silicate or carbonate mineral weathering.

384 Sulfides have been proposed as a potential host of Re in sedimentary rocks and an 385 important source of Re in global rivers, based on a broad and scattered relationship between 386 dissolved Re and SO<sub>4</sub><sup>2-</sup> concentrations (Miller et al., 2011). However, this has been disputed by 387 dissolved ion mixing analyses in the Mackenzie River and Rio Madre de Dios (Dellinger et al., 388 2023; Horan et al., 2019), which point toward sulfide minerals only being a dominant host of Re 389 in a handful of small catchments. Hydrological behavior of Re in alpine streams also appears to 390 be decoupled from the production and export of  $SO_4^{2-}$ , a weathering product of sulfide oxidation 391 (Hilton et al., 2021; Winnick et al., 2017). Indeed, in support of these river-based studies, we 392 find that individual weathering profiles show a decoupling of S loss and Re loss (Figure 1) 393 similar to the first assessment of Re loss across a black shale weathering profile (Jaffe et al., 394 2002). Overall, across the black and grey shales studied here, we find no meaningful relationship 395 between S loss (i.e. sulfide oxidation) and Re loss (Figure 2C). While this does not preclude

- 396 sulfides as an important Re host in some locations, it suggests that Re loss and delivery to the
- 397 hydrosphere and river waters is not closely coupled to sulfide oxidation.
- 398

#### **4.2.** Coupled loss of Re and OC<sub>petro</sub> across weathering profiles

- 400 We find a systematic loss of Re and OC<sub>petro</sub> across the black and grey shale weathering profiles
- 401 (Figure 3) and the  $\Delta Re_{Ti}$  and  $\Delta [OC_{petro}]_{Ti}$  values are statistically significant (r =0.66, p < 0.05).
- 402 About 17 samples lie within  $\pm 10\%$  of congruent, 1:1 Re and OC<sub>petro</sub> loss during weathering. This
- 403 occurs in samples with variable Re and OC<sub>petro</sub> concentrations, initial Re to OC<sub>petro</sub> ratios in rocks
- 404 (Table 3), relative losses of Re and S (Figure 2C,D), and variations in Fe cycling (Figure 4).
- 405 Additionally, our sample set ranges in weathering intensity, climatic and geomorphic settings,
- 406 different physical rock properties, and different geochemical characteristics of OC<sub>petro</sub>. The first
- 407 order conclusion from these findings is that Re provides a robust proxy for OC<sub>petro</sub> oxidation.



Figure 4:  $OC_{petro}$  and Re loss in the weathering profiles, accounting for volume changes using Ti normalization. A 1:1 loss ratio is shown as a black line. Dashed lines indicate a 1:1 loss to within  $\pm 10\%$ . The shaded grey domain is the predicted region (Equation 4) based on the combination of: i) presence of Re hosted in sulfide and silicate phases alongside  $OC_{petro}$ , and ii) incomplete weathering of  $OC_{petro}$ .

409	In more detail, we find that the average ratio of $\Delta[OC_{petro}]_{Ti}$ to $\Delta Re_{Ti}$ is 0.84± 0.15, and
410	several sites have values < 1. There are three reasons why Re loss may be proportionally more
411	than OC <sub>petro</sub> loss which have been discussed in the literature (Horan et al., 2019). First, while Re
412	loss is not clearly linked to carbonate, silicate, and sulfide weathering patterns (Figure 2), these
413	phases could host >10% of the Re within some rock types. The contributions of Re from organic
414	matter vs carbonate, silicate and sulfide phases could vary based on depositional setting, and
415	geochemistry of the initial sedimentation environment and the continued diagenesis of the
416	sediments (Sheen et al., 2018) and inorganic weathering of Re can proceed without OC

417 oxidation. Second, Re is a highly mobile, soluble element (Colodner et al., 1993) in oxic 418 environments whose association with organic matter in rocks is still not well understood (Selby 419 and Creaser, 2003). It is possible that Re may be mobilized during water-rock interactions while 420 some OC<sub>petro</sub> is not lost. Finally, OC<sub>petro</sub> may include physically protected organic matter (Gu and 421 Brantley, 2022) or thermally mature OC<sub>petro</sub>, including graphite, which is more resistant to 422 OC<sub>petro</sub> oxidation and that may or may not host Re (Toma et al., 2022). The presence of more 423 recalcitrant OC could lead to a residue of unweathered, Re-poor OC<sub>petro</sub> accumulating in soils 424 and weathered rocks.

425 There is relatively little known about the detailed chemical association of Re and OC<sub>petro</sub>. 426 We know that during reduction in surface marine sediments where OC accumulates, ReO<sub>4</sub><sup>-</sup> is 427 immobilized (Colodner et al., 1993; Crusius and Thomson, 2000). Inorganic thermodynamic 428 considerations predict that rhenium may be precipitated as ReS<sub>2</sub> (Chappaz et al., 2008; 429 Yamashita et al., 2007), or form thioperrhenate (ReOxS4-x-) or Re(VII)-sulfide precipitates 430 (Helz and Dolor, 2012; Vorlicek et al., 2015). A co-precipitation of iron-based phases has also 431 been invoked in sulfidic waters (Helz, 2022; Helz and Dolor, 2012). However, correlations 432 between OC and Re in sedimentary rocks, chemical extractions of Re from shales (Selby and 433 Creaser, 2003) support a dominant role of an organic matter host, also indirectly supported by 434 the observed coupled loss of Re and OC (Figure 3).

435 Regardless of the details of the organic matter host for Re, it is plausible that there are a 436 range of  $OC_{petro}$ -S-Re bonding environments that form in many sedimentary rocks. These could 437 have different weathering rates based on their inherent or apparent reactivity. For instance, the 438 majority Re could be hosted in a "fast weathering"  $OC_{petro}$  structure that is linked to an early 439 diagenetic process of reduction in marine sediments. In contrast, Re-poor organic matter

440 delivered from terrestrial ecosystems may be mineral-bound (Repasch et al., 2021), and this may 441 weather at a different rate. The weathering profile with the lowest  $\Delta [OC_{petro}]_{Ti}$  to  $\Delta Re_{Ti}$  ratio is 442 the Marcellus shale which is known to be more thermally mature than the other black shales in 443 this study. In summary, it is unlikely that all OC<sub>petro</sub> is homogenous, meaning OC<sub>petro</sub> and 444 associated Fe and S phases could weather incongruently, which may have variable Re 445 concentrations depending on depositional environment, mixing, and subsequent diagenesis. 446 An addition consideration is that the OC<sub>petro</sub> and Re might have different bioavailability, 447 which could lead to a discrepancy in the measured loss ratio. The bioavailability of Re in 448 terrestrial or marine systems is not well understood, with very few studies measuring Re in plant 449 or microbial tissues (Ghazi et al., 2024). While Re has no known role in biology and is not an 450 essential trace element for biological function in either the terrestrial or marine systems, some 451 uptake has been observed in corals of the gulf coast (Prouty et al., 2014), but has not been widely 452 measured in other plant tissues. However, OC<sub>petro</sub> may be utilized by microbial life, as carbon 453 sources are important for microbial and plant life. Petsch et al. (2001) found uptake of <sup>14</sup>C free 454 organic matter into the microbial cell walls of living biomass, while Hemingway et al. (2018) 455 measured OC<sub>petro</sub> oxidation in Taiwan of up to 60%, meaning that a large portion of OC could be 456 mineralized and potentially utilized for microbial metabolism. This potentially could lead to a 457 discrepancy in the 1:1 Re/OC<sub>petro</sub> if OC<sub>petro</sub> is preferentially removed from the system, while Re 458 is conservative.

In most profiles, we find Re loss relative to the least weathered sample. However, there are a few samples which show elevated Re concentrations and an apparent Re enrichment. Based on our current understanding of the Re system, there are two explanations for these elevated Re concentrations. The first is an anthropogenic input of Re. The sampled road cuts are not entirely

463 isolated from wet or dry atmospheric deposition, either onto the surface of the outcrop, or from 464 the surface soil down via critical zone processes such as root invasion, water percolation, and 465 freeze/thaw cycles. In the northeast USA, where the NACC and NADV samples were collected, 466 Ogrič et al. (2023) found elevated anthropogenic Re input to the upper few centimeters of soils 467 in the Shale Hills CZO likely due to coal burning and local industry. In that small catchment, the 468 majority of the dissolved Re in streams was derived from anthropogenic inputs rather than 469 weathering (Ogric et al., 2023). It is thus reasonable that some atmospheric deposition of Re 470 could have occurred at some sites. The Re to OC<sub>petro</sub> ratio of this material is not well constrained, 471 but may differ from that in bulk sedimentary rocks. Another possibility discussed by Jaffe et al. 472 (2002), is that Re could be transported vertically through the soil. These profiles are above 473 ground and are likely influenced by organic acids and precipitation transported through the 474 soil/regolith system. Soils undergo microscale redox processes, so under certain conditions, there 475 could be Re mobilization and movement in the subsurface, but not complete loss to the river 476 system. This could cause elevated [Re] based on the critical zone properties. 477

478 Despite these caveats, we find the range of  $\Delta$ [OC<sub>petro</sub>]<sub>Ti</sub> to  $\Delta$ Re<sub>Ti</sub> values that have been used in



Figure 5: Ratio of titanium normalized loss relative to the deepest sample in each profile (Figure 4), with box showing the interquartile range, line showing the median, square showing the mean, and whiskers showing the 2SE bounds. The sites are sub-grouped for profiles with <1% OC<sub>petro</sub> (WPO, WPU, ER, TW), GR (Green River), ME (Marcellus Shale), MO (Monterey Shale) and a subgroup of the New Albany and Woodford Shales (NACC, NADV, WF).

479 studies using dissolved Re proxy to calculate OC<sub>petro</sub> oxidation are robust. These are shown by 480 the shaded part of Figure 4, using typical ranges of  $f_{\rm C} + f_{\rm graphite}$  values (assumed to be ~0-30%) 481 (Equation 1). The fact that all the weathered materials sit within this domain provides further 482 support for the proxy. We find that the absolute ratio of Re loss to OC<sub>petro</sub> loss (without Ti normalization) is rather consistent for grey shales, with a value of  $2.7 \pm 1.6 \times 10^{-7} \text{ g s}^{-1}$  (SI Table 483 484 1). This is similar to values used in a recent global analysis of river Re fluxes and application of 485 the Re proxy (Zondervan et al., 2023), suggesting no systematic bias in these fluxes. However, 486 the absolute ratio of Re and OC<sub>petro</sub> loss (without Ti normalization) does differ across the profiles

487	studied here in the black shales (SI Table 1) ranging from $1.16 \ge 10^{-8} \text{ g s}^{-1}$ to $5.56 \ge 10^{-6} \text{ g s}^{-1}$
488	with the average being $1.2 \pm 1.6 \times 10^{-6} \text{ g s}^{-1}$ (SI Table 1) about an order of magnitude more than
489	the grey shales, showing how important it can be at a small catchment-scale to try and constrain
490	the behavior of Re and $OC_{petro}$ in the weathering zone using an index element normalization.
491	Finally, we note that by studying the weathering residues, we cannot conclude the fate of
492	the lost OC <sub>petro</sub> (Petsch, 2014). While Re is likely to be oxidized to the soluble ion ReO <sub>4</sub> -, OC <sub>petro</sub>
493	could be oxidized to CO <sub>2</sub> , as measured in exposed mudstones of New Zealand (Roylands et al.,
494	2022) and marls of the French pre-Alps (Soulet et al., 2021), along with deep sedimentary tills
495	(Keller and Bacon, 1998) and mudstones in the Eel River catchment (Tune et al., 2020).
496	Alternatively, the microbial-processing of OC <sub>petro</sub> (Matlakowska and Sklodowska, 2011;
497	Wlodarczyk et al., 2018) could lead to biomass build up in the weathered rocks that may be <sup>14</sup> C-
498	depleted (Hemingway et al., 2018; Petsch et al., 2001a) and/or be leached as dissolved organic
499	matter away from the weathering site (Schillawski and Petsch, 2008). This microbial biomass or
500	dissolved organic matter may then be bioavailable for heterotrophic consumption (Schillawski
501	and Petsch, 2008). Therefore, while the study here concludes the loss of Re is a robust proxy for
502	OC <sub>petro</sub> loss during weathering, and likely CO <sub>2</sub> production, a coupled approach which seeks to
503	track carbon species at a variety of scales alongside trace metal and Re mobility will provide
504	further insight to how OC <sub>petro</sub> weathering impacts the geochemical carbon cycle.

506 5. Conclusions

To appropriately quantify OC<sub>petro</sub> weathering fluxes, the Re proxy must be validated. This study
clearly shows that across a range of weathering rates, scales, denudation rates, geochemical
content, the Re proxy for OC<sub>petro</sub> oxidation is robust. OC<sub>petro</sub> weathering contributes to an equal

510	flux that is drawn down by silicate weathering, thus it is an important, but understudied part of
511	the global carbon cycle. We find a broad correlation between $OC_{petro}$ and Re across our samples,
512	with no correlation between Re and products of sulfide, carbonate, or silicate weathering. While
513	we cannot rule out some influence in the Re flux from these other sources, our finding suggest
514	that $OC_{petro}$ is the dominate host of Re. We find the average value of 0.84 ±0.15 for the loss ratio
515	of $OC_{petro}$ and $Re (\Delta[OCpetro]_{Ti}/\Delta[Re]_{Ti})$ across gray and black shales of different chemistries
516	and we urge this value to be used in systems as an estimate of the $(1 - (f_c + f_{graphite}))$ term in the
517	calculation of OCpetro oxidation from dissolved Re flux (Equation 1). The [Re] proxy for
518	calculating $OC_{petro}$ fluxes across environments is valid and can be used to constrain $OC_{petro}$ input
519	to modern environments.
520	
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