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4

5 LOW RATES OF Rock organic carbon oxidation and ANTHROPOGENIC CYCLING OF rhenium IN A  
6 SLOWLY DENUDING LANDSCAPE

7

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### 43 **AUTHOR CONTRIBUTIONS**

44 *Conceptualization:* MO, MD, RGH

45 *Funding Acquisition:* RGH, SLB

46 *Methodology:* MO, MD, RGH, KEG, VG, XG

47 *Investigation:* MO, XG

48 *Resources:* SLB, XG

49 *Supervision:* RGH, MD, SLB

50 *Writing – initial draft:* MO

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52

53

### 54 **DATA AVAILABILITY STATEMENT**

55 All data used for the production of this manuscript can be found in Table 1 and  
56 Table 2 within the main text.

57

58

59 Abstract

60 The oxidation of petrogenic organic carbon (OC<sub>petro</sub>) is a source of carbon dioxide to the atmosphere  
61 over geological timescales. The rates of OC<sub>petro</sub> oxidation in locations that experience low rates of  
62 denudation remain poorly constrained, despite these landscapes dominating Earth's continental  
63 surface area. Here, we track OC<sub>petro</sub> oxidation using radiocarbon and the trace element rhenium (Re)  
64 in the deep weathering profiles, soils and stream waters of the Susquehanna Shale Hills Critical Zone  
65 Observatory (PA, USA). In a ridge-top borehole, radiocarbon measurements reveal the presence of a  
66 broad OC<sub>petro</sub> weathering front, with a first order assessment of ~40% loss occurring over ~6 m.  
67 However, the low OC<sub>petro</sub> concentration (<0.05 wt.%) and inputs of radiocarbon throughout the  
68 deepest parts of the profile complicate the assessment of OC<sub>petro</sub> loss. The OC<sub>petro</sub> weathering front  
69 coincides with a zone of Re depletion (~90% loss), and we estimate that >80% of Re in the rock is  
70 associated with OC<sub>petro</sub>, based on Re/Na and Re/S ratios. Using estimates of long-term denudation

71 rates, the observed  $OC_{\text{petro}}$  loss and the Re proxy are equivalent to a low  $OC_{\text{petro}}$  oxidation yield of  
72  $<1.7 \times 10^{-2} \text{ tC km}^{-2} \text{ yr}^{-1}$ . This is consistent with the low  $OC_{\text{petro}}$  concentrations and low denudation rates  
73 at this location. In addition, we find the surface cycle of Re is decoupled from that of deep  
74 weathering, with an enrichment of Re in surface soils and elevated Re concentrations in stream  
75 water, precipitation, and shallow groundwater. A mass balance model shows that this can be  
76 explained by a historical anthropogenic contribution of Re through atmospheric deposition. We  
77 estimate that the topsoil Re pool could take decades to centuries to deplete and call for a renewed  
78 focus on anthropogenic perturbation of the surface Re cycle in low denudation rate settings.

79

80 **Keywords:** *chemical weathering, rock organic carbon, oxidation, rhenium, low denudation,*  
81 *anthropogenic impacts.*

82

### 83 Introduction

84 The transfer of carbon between biogeochemical reservoirs is one of the main drivers of climate  
85 change over geological timescales (Berner and Canfield, 1989; Derry and France-Lanord, 1996). Over  
86 long time periods, carbon dioxide ( $CO_2$ ) emissions through volcanism, carbonate weathering by  
87 sulfuric acid, and oxidation of rock-derived organic carbon (petrogenic,  $OC_{\text{petro}}$ ) are countered by  $CO_2$   
88 sequestration through silicate weathering, carbonate formation, and burial of biospheric organic  
89 carbon ( $OC_{\text{bio}}$ ) (Hilton and West, 2020). The  $CO_2$  emissions from  $OC_{\text{petro}}$  oxidation (Petsch, 2014; Gu  
90 and Brantley, 2022) and carbonate weathering by sulfuric acid (Torres et al., 2017; Burke et al., 2018)  
91 may be of similar magnitude to the release of  $CO_2$  from volcanic degassing ( $79 \pm 9 \text{ MtC yr}^{-1}$ , Plank and  
92 Manning, 2019), yet the global rates of  $OC_{\text{petro}}$  oxidation remain poorly constrained (Petsch, 2014).

93 The oxidative weathering of  $OC_{\text{petro}}$  has been assessed in river catchments using the trace element  
94 rhenium (Re) (Dalai et al., 2002; Hilton et al., 2014, 2021; Horan et al., 2017, 2019). Rhenium is  
95 enriched in sediments deposited in reducing conditions, and preserved in sedimentary rocks  
96 (Morford et al., 2012), especially in organic carbon-rich black shales (Colodner et al., 1993), due to a  
97 close association of Re with organic matter in rocks (Selby and Creaser, 2003). Coupled loss of Re  
98 and  $OC_{\text{petro}}$  has been observed during oxidative weathering (Jaffe et al., 2002; Hilton et al., 2014),  
99 with the mobilization of Re in the dissolved load over the large pH range (5.5 to 9.5) and in  
100 oxygenated waters ( $E_h > 0 \text{ V}$ ), typical of most river waters (Colodner et al., 1993). As such, dissolved  
101 Re flux has been used as a proxy to estimate catchment-wide  $OC_{\text{petro}}$  oxidation rates in highly erosive  
102 catchments of the Himalaya (Dalai et al., 2002), Taiwan (Hilton et al., 2014) and New Zealand (Horan  
103 et al., 2017) and in moderate erosive setting of the Mackenzie River basin (Horan et al. 2019), the  
104 European Alps (Hilton et al., 2021) and Pacific Northwest of the USA (Ghazi et al., 2022).

105 Applying the Re proxy to settings with moderate to high erosion rates has been important for  
106 establishing the role of  $OC_{\text{petro}}$  supply in driving weathering fluxes (Hilton et al., 2014; Horan et al.,  
107 2017; Ghazi et al., 2022). However, there are reasons why lower erosion rate settings deserve focus.  
108 First, low denudation rates ( $<0.5 \text{ mm yr}^{-1}$ ) are common over the majority of Earth's continents, and  
109 these settings contribute to  $\sim 60\%$  of global chemical denudation (Larsen et al., 2014). Second, low  
110 erosion rates can lead to the development of thick weathering profiles, helping to reveal reaction  
111 fronts of  $OC_{\text{petro}}$  and sulfide oxidation (Petsch et al., 2000; Wildman, 2004; Brantley et al., 2013a; Gu  
112 and Brantley, 2022) and track the mobility of Re during weathering (Jaffe et al., 2002). Finally,  
113 settings with lower chemical denudation could be more sensitive to Re inputs from anthropogenic  
114 sources (Miller et al., 2011; Rahaman et al., 2012), helping us understand the modern-day

115 perturbation of the Re cycle (Sen and Peucker-Ehrenbrink, 2012). This is because Re is enriched in  
116 fossil fuels (Bertine and Goldberg, 1971; Selby et al., 2007), volatile at temperatures >270 °C  
117 (Colodner et al., 1995), and can be deposited from ash fallout after coal combustion. Anthropogenic  
118 Re inputs have been invoked to explain high dissolved Re concentrations in large European rivers  
119 (Danube, Rhine), the Yangtze and the Mississippi rivers (Miller et al., 2011) alongside lake and  
120 marine records from North America (Chappaz et al., 2008; Prouty et al., 2014).

121 In this study we explore  $OC_{\text{petro}}$  weathering and the trace element Re in deep shale weathering  
122 profiles (~30 m) in an OC-poor and low denudation rate setting to provide estimates of long-term  
123  $OC_{\text{petro}}$  oxidation rates. Having done so, we provide new constraints on anthropogenic Re  
124 perturbation in the near surface environment on a catchment scale.

## 125 Methodology and methods

126 The study is set in the Shale Hills catchment of the Susquehanna Shale Hills Critical Zone Observatory  
127 (SSH-CZO). There, a low denudation rate results in deep weathering profiles (Jin et al., 2010; Brantley  
128 et al., 2013; Sullivan et al., 2016; Gu et al., 2020a). We quantify  $OC_{\text{petro}}$  weathering using a  
129 combination of new radiocarbon and Re measurements, with previously published S and major  
130 element concentration data (Brantley et al., 2013; Sullivan et al., 2016), applied to samples from  
131 subsurface boreholes, surface soils, rainwater and stream water.

## 132 Study site

133 Shale Hills is a small (0.08 km<sup>2</sup>), first order catchment located in the Appalachia of central  
134 Pennsylvania (Figure 1a). The catchment is almost exclusively underlain by Rose Hill Formation of  
135 Silurian age, with low total organic carbon (TOC) concentrations of <0.05 wt.% (Jin et al., 2014).  
136 Shale beds that are interlayered with more limestone- and sand-rich units have been observed  
137 towards the catchment outlet (Jin et al., 2010; Sullivan et al., 2016). The site has gentle slopes, forest  
138 cover and very low long-term denudation rates of 0.010 – 0.025 mm yr<sup>-1</sup> based on measurements on  
139 meteoric beryllium-10 (<sup>10</sup>Be; West et al., 2013) and uranium isotope disequilibrium (Ma et al., 2010).

140 The climate is humid-continental, with a mean annual temperature of 10 °C and mean annual  
141 precipitation of 1070 mm (Jin et al., 2010; NADP, 2020).

142

143 From the early 1800s, the Shale Hills catchment and wider region was logged for charcoal production  
144 to support the local iron industry (Herndon et al., 2011; Kraepiel et al., 2015). Today, iron ore  
145 smelting and the majority of steel production in the vicinity of Shale Hills has largely stopped.  
146 However, several studies report Mn and Pb enrichments in Shale Hills soils derived from coal burning  
147 and iron smelting inputs (Herndon and Brantley, 2011; Herndon et al., 2011; Ma et al., 2014). This  
148 anthropogenic activity has resulted in acidic (pH ~5.4) and SO<sub>4</sub><sup>2-</sup> enriched local precipitation (Jin et  
149 al., 2011). A steadily increasing trend in the rain water pH is observed since the early 2000s (NADP,  
150 2020).

151 Extensive prior research at the SSH-CZO provides insights on carbonate and silicate weathering (Jin  
152 et al., 2010, 2011, 2014; Shaughnessy et al., 2020), oxidative weathering of pyrite (Brantley et al.,  
153 2013), water-rock interactions (Herndon et al., 2015a; Sullivan et al., 2016), porosity generation and  
154 chemical weathering (Gu et al., 2020a, 2020b), and accumulation of metals in top soils (Herndon and  
155 Brantley, 2011; Herndon et al., 2011; Ma et al., 2014; Kraepiel et al., 2015). In terms of physical rock  
156 degradation, four weathering layers on the Rose Hill shale have been identified: i) soil (hand-  
157 augerable material), ii) highly fractured saprock, iii) less fractured saprock and iv) the largely

158 unaltered protolith (Brantley et al., 2013; Jin et al., 2014; Sullivan et al., 2016; Gu et al., 2020a). The  
159 term saprock describes fractured bedrock that can reach close to the catchment surface. Previous  
160 work attempted a first order estimate of  $OC_{\text{petro}}$  oxidation, assuming a complete loss of OC from  
161 deep samples to the surface (Jin et al., 2014). The authors noted considerable uncertainty due to the  
162 low OC concentrations and inputs of carbon from the biosphere.

## 163 Materials

164 Samples were selected from boreholes to assess deeply weathered materials nearer the surface and  
165 less weathered samples at depth, using published sulfur concentrations (Brantley et al., 2013;  
166 Sullivan et al., 2016; Gu et al., 2020a) to guide where oxidative weathering fronts were located. We  
167 focused on two boreholes located in the valley ('CZMW2' and 'CZMW10'; Figure 1b). Borehole  
168 CMZW2 (sample number; n=11) covers depths between 0.5 m and 16.0 m and documents  
169 prominent weathering fronts (Brantley et al., 2013). Deeper samples (7.6 m to 34.9 m) from  
170 borehole CZMW10 (n=5) were selected, because they show a wider zone of alteration below the  
171 valley (Gu et al., 2020a). The boreholes CZMW2 and CZMW10 were drilled less than 5 m distance  
172 from one another, and are considered here as a continuous profile. A third borehole CZMW8,  
173 located on the South ridge of the catchment (Figure 1b), has a deeper weathering front, and 8  
174 samples were selected from 0.2 m to 30.6 m depth. Finally, to examine Re in soils, 4 samples from  
175 the upper 50 cm deep soil profile previously collected on the south ridge of the catchment (Figure  
176 1b) by Herndon et al. (2011) were selected.

177 Details of soil and borehole sample and data collection methods are provided in previous work  
178 (Herndon et al., 2011; Brantley et al., 2013; Sullivan et al., 2016). In summary, the solid samples were  
179 air dried, crushed and analyzed for major elements by inductively coupled plasma atomic emission  
180 spectroscopy (ICP-AES) and total sulfur (S) by LECO Sulfur Coulometer and LECO Carbon Sulfur  
181 Analyzer at Pennsylvania State University. Concentration data have been previously published for  
182 boreholes in Brantley et al. (2013), Sullivan et al. (2016) and Gu et al. (2020a).

183 In this study, 11 stream water samples from the catchment outlet gauging station were collected  
184 between June 2018 and June 2019. In August 2018, groundwater samples were collected from wells  
185 CZMW2, CMZW8, CZMW6, and wells number 9, 11, and 12 (Figure 1b). Water samples were  
186 collected in clean Nalgene bottles, pre-rinsed with the sample water and immediately filtered  
187 through 0.22  $\mu\text{m}$  Millipore filters and transferred into acid-cleaned Nalgene bottles (Hilton et al.,  
188 2014; Horan et al., 2017). All samples used for trace elements and major cations analyses were  
189 acidified to  $\text{pH} \sim 2$  with  $\text{HNO}_3$ . An un-acidified aliquot was collected in bottles pre-cleaned with  
190 demineralized water and filtered stream water for anion analysis, and stored at  $4^\circ\text{C}$  in the dark.  
191 Archived precipitation samples (n=4) collected and stored by similar methods from 2013 (July and  
192 October) and 2014 (February and October) were analyzed.

## 193 Geochemical analysis

194 Geochemical analysis of the solid samples from the boreholes included measurements of total  
195 organic carbon concentration (TOC), stable OC isotope ratios (reported as  $\delta^{13}\text{C}_{\text{oc}}$  relative to VPDB),  
196 radiocarbon measurements ( $^{14}\text{C}$ ) of OC, and Re concentrations. Water samples (stream water,  
197 groundwater, precipitation) collected for this study were measured for major ion concentrations and  
198 trace element Re.

199 For TOC and  $\delta^{13}\text{C}_{\text{oc}}$  measurements, carbonate was removed by weighing  $\sim 40$  mg of a dry sample into  
200 a pre-combusted ( $450^\circ\text{C}$  for 4 hours) silver capsule and adding 2 drops of 1M HCl, followed by drying  
201 of the sample in an oven at  $60^\circ\text{C}$ . To ensure the complete removal of carbonates, each sample was

202 rinsed with 1M HCl three times. The samples were measured on a Sercon ANCA-EA system linked to  
203 a Sercon 2022 isotope ratio mass spectrometer (Elementex, Stable Isotope Analytical Laboratory,  
204 Cornwall, UK). Corrections for the procedure and instrumental blanks were applied. The method was  
205 validated by measuring the soil standard material NCS-DC73319 for TOC concentration and two  
206 international certified synthetic standards, IAEA 600 (caffeine) and IAEA CH3 (cellulose), for  $\delta^{13}\text{C}_{\text{OC}}$   
207 values. The standard materials were treated in the same way as the samples. The precision for  $\delta^{13}\text{C}_{\text{OC}}$   
208 values was 0.20 ‰ and 0.15 ‰ for IAEA 600 (n=6) and IAEA CH3 (n=6), respectively.

209 Radiocarbon measurements were made on nine rock samples from the CZMW8 ridgetop borehole.  
210 Crushed samples were acid leached (1M HCl) in pre-combusted glassware to remove carbonate  
211 minerals. Samples were centrifuged, rinsed with deionized water, and dried in a 60 °C oven at  
212 Durham University, Department of Geography. De-carbonated samples were sent to the National  
213 Ocean Sciences Acceleration Mass Spectrometry Facility (NOSAMS) at Woods Hole Oceanographic  
214 Institution (WHOI) for  $^{14}\text{C}$  analysis. A sample aliquot was combusted with CuO and Ag at 850 °C in an  
215 evacuated quartz tube.  $\text{CO}_2$  was graphitized and measured for radiocarbon following standard  
216 procedures via Accelerated Mass Spectroscopy (AMS; McNichol et al., 1994). An aliquot of the  $\text{CO}_2$   
217 was used to measure  $\delta^{13}\text{C}_{\text{OC}}$  using a VG Prism dual-inlet IRMS. All measurements were corrected for  
218 a total procedural blank (combusted quartz sand put through the whole process) according to  
219 conventional radiocarbon reporting standards and reported as Fraction modern ( $\text{F}^{14}\text{C}$ ) as per Stuiver  
220 and Polach (1977).

221 Rhenium concentrations in the borehole solids were measured following complete acid digestion  
222 ( $\text{HF}+\text{HNO}_3$ , followed by aqua regia) and anion exchange column chemistry as per methods of  
223 Dellinger et al. (2020). The Re solutions were measured on a Thermo Scientific Neptune Plus at  
224 Durham University, Department of Earth Sciences. Standard reference materials were digested in  
225 each batch to validate the method; a marine sediment (MAG-1), basalt (BHVO-2, BCR-2), and  
226 serpentinite (UB-N), which returned values for this study in close agreement; <15% with previously  
227 published data (Meisel and Moser, 2004; Jochum et al., 2016) and <10% with long-term in-house  
228 reproducibility (Dellinger et al., 2020).

229 Major ions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) in water samples were determined by ion chromatography  
230 (Dionex ICS 3000, Durham University, Department of Geography), validated by a certified river water  
231 reference standard material (Sangamon-03). The difference between our measurements and  
232 certified reference material values for all major elements was <5% (n=3). The analytical precision  
233 determined by running replicates on selected samples was <3% (n=5) for all reported major ions.

234 Concentrations of dissolved Re were determined by a direct calibration method (Horan, 2018) on  
235 Agilent Technologies 7900 inductively coupled plasma mass spectrometer (ICP-MS) at Durham  
236 University, Department of Geography. The detection limit defined as 3 standard deviations of the  
237 replicate measurements of a blank solution was 0.01 ppt for Re. Repeated measurements of the  
238 river water standard sample SLRS-5 for Re are  $64.6\pm 6.1$  ppt ( $\pm 1\text{SD}$ , n=6) and 10- and 100-times  
239 dilutions are  $6.2\pm 0.7$  ppt ( $\pm 1\text{SD}$ , n=6) and  $0.63\pm 0.1$  ppt ( $\pm 1\text{SD}$ , n=6), respectively. These are in  
240 agreement with the long-term in house reproducibility, that is SLRS-5= $63.0\pm 3.5$  ppt ( $\pm 1\text{SD}$ , n=24),  
241 SLRS-5 $\times 10=6.2\pm 0.3$  ppt ( $\pm 1\text{SD}$ , n=21), and SLRS-5 $\times 100=0.61\pm 0.10$  ppt ( $\pm 1\text{SD}$ , n=35), and with Re  
242 concentrations for SLRS-5 reported in literature:  $66\pm 12$  ppt (Yeghicheyan et al., 2013).

243 Calculation of mass transfer coefficient ( $\tau$ )

244 In the borehole sediments, a mass transfer coefficient ( $\tau$ ) was calculated to characterize the mobility  
245 of S, TOC, and Re during weathering. The coefficient  $\tau$  describes a gain or loss of an element relative

$$\tau_{i,s} = \frac{C_{j,s} C_{i,p}}{C_{j,p} C_{i,s}} - 1 \quad (1)$$

246 to the parent material by applying Equation 1 (Brimhall and Dietrich, 1987; Anderson et al., 2002).

247 Where C is the concentration of the mobile element (j) or immobile element (i) in the protolith (p) or  
248 soil/saprock (s). The approach assumes that composition of the protolith is relatively homogeneous,  
249 with mean composition and variability that can be defined, and that the species (i) is immobile  
250 through the weathering profile. A negative  $\tau$  value describes a relative depletion of an element  
251 compared to the immobile element in the parent material. We use Zr as the immobile element  
252 following the approach of Kraepiel et al. (2015).

## 253 Results

254 Here, a summary of previous results is provided before outlining new measurements of TOC,  $\delta^{13}\text{C}_{\text{OC}}$ ,  
255  $^{14}\text{C}$  and Re concentrations (Figure 2). Mobility during oxidative weathering is assessed with mass  
256 transfer coefficients for S, TOC and Re (Figure 3). New measurements of major ion and Re  
257 concentrations in stream water, groundwater and precipitation are given to constrain Re cycling in  
258 the near surface environment.

### 259 Published sulfur concentrations in borehole materials

260 The depletion of S in the borehole samples provides insight on oxidative weathering of pyrite at  
261 Shale Hills because almost all sulfur in the parent rock is present in pyrite (Brantley et al., 2013;  
262 Sullivan et al., 2016; Gu et al., 2020a). In the valley (CZMW2, CZMW10), the S concentrations are low  
263 from the surface through the weathered saprock to depths of  $\sim 6.5$  m, with a mean S of  $0.005 \pm 0.002$   
264 wt.% ( $n=17$ ,  $\pm 1\text{SD}$ ; Brantley et al., 2013; Gu et al., 2020a). A wide ( $\sim 15$  m) pyrite depletion zone, with  
265 continuous increase in S concentration is observed between  $\sim 6.5$  m and  $\sim 21.4$  m, with a mean  
266 S of  $0.08 \pm 0.03$  wt.% ( $n=26$ ,  $\pm 1\text{SD}$ ). The highest S concentrations are measured below  $\sim 21.4$  m, with a  
267 mean S of  $0.15 \pm 0.04$  wt.% ( $n=17$ ,  $\pm 1\text{SD}$ ) in the protolith. On the ridge, the weathered saprock  
268 extends deeper, to  $\sim 15.4$  m and has mean S of  $0.02 \pm 0.03$  wt.% ( $n=10$ ,  $\pm 1\text{SD}$ ; Sullivan et al., 2016).  
269 Beneath the S-depleted layers, a sharp increase in S concentrations from below detection limit  
270 ( $\sim 0.002$ ) to 0.14 wt.% is observed between 15.4 m and 16.4 m depth. This increase is consistent with  
271 decrease of saprock porosity and fracture density (Sullivan et al., 2016; Gu et al., 2020a).

### 272 TOC, $\delta^{13}\text{C}_{\text{OC}}$ and $^{14}\text{C}$ in borehole materials

273 The TOC concentrations are highest in the surface soil, with 0.14 wt.% and 0.32 wt.% measured in  
274 the valley (down to  $\sim 1$  m; CZMW2). Lower TOC concentrations were found in the upper part of the  
275 weathered saprock (down to  $\sim 6.5$  m, i.e. above the pyrite depletion zone; CZMW2), with TOC values  
276 of 0.06 wt.% and 0.07 wt.%. At a depth of  $\sim 8.4$  m the TOC concentrations are the lowest at 0.03 wt.%  
277 and they stay low until  $\sim 16$  m depth, with a mean value of  $0.04 \pm 0.01$  wt.% ( $n=6$ ,  $\pm 1\text{SD}$ , CZMW2). On  
278 the ridge, the TOC concentrations are also the highest in the surface soil at 0.41 wt.% (down to  
279  $\sim 0.3$  m; CZMW8). The TOC concentrations drop in the weathered saprock ( $\sim 0.9$  to  $\sim 12.4$  m) to span a  
280 range of values between 0.09 wt.% (the top most sample at 0.9 m) to 0.05 wt.% at  $\sim 12.4$  m. At  
281  $\sim 15.4$  m depth the lowest TOC concentration is measured at 0.03 wt.%, which gradually increases in  
282 the protolith to a value of 0.06 wt.% at 30.5 m depth (CZMW8). The TOC values are similar to those



283 reported by Jin et al. (2010, 2014) sampled in borehole DC1, located on the North ridge of the Shale  
284 Hills catchment (Figure 1b).

285 The stable carbon isotopic composition of the organic carbon ( $\delta^{13}\text{C}_{\text{OC}}$ ) varies by up to  $\sim 2$  ‰, but does  
286 not show any systematic variation between the soil, saprock and protolith samples, in both  
287 boreholes CZMW2 ( $-26.3$  ‰ to  $-24.4$  ‰) and CZMW8 ( $-27.0$  ‰ to  $-26.2$  ‰). These values are similar  
288 to  $\delta^{13}\text{C}_{\text{OC}}$  values of soils ( $-25.8$  ‰ to  $-25.3$  ‰) and protolith samples ( $-27.1$  ‰ to  $-25.9$  ‰) previously  
289 published for Shale Hills in Jin et al. (2014).

290 The radiocarbon activity, reported as Fraction modern ( $F^{14}\text{C}$ ), in the CZMW8 ridgetop borehole varies  
291 between  $0.91 \pm 0.005$  near the surface, to  $0.24 \pm 0.003$  in the saprock, at  $\sim 15.4$  m depth. The high  $F^{14}\text{C}$   
292 measured in the top soil is consistent with organic matter dominated by the modern biosphere,  
293 resulting in a  $F^{14}\text{C}$  value close to 1 (Trumbore, 2009). Within the saprock, lower  $F^{14}\text{C}$  values are  
294 consistent with some input of  $\text{OC}_{\text{petro}}$  from the Silurian Rose Hill formation that was deposited  $\sim 443$   
295 to 416 million years ago ( $F^{14}\text{C}$  value=0). However, the presence of  $^{14}\text{C}$ , with  $F^{14}\text{C}$  between  $0.26 \pm 0.003$   
296 and  $0.32 \pm 0.003$  in the deep profile, suggests potential aging of biospheric OC and/or another source  
297 of  $^{14}\text{C}$ -enriched C in the deepest samples, as discussed in Section 4.1.

298 Re concentration in borehole materials and surface soils

299 The protolith samples (below  $\sim 21.4$  m) under the valley (CZMW2 and CZMW10) have the highest Re  
300 concentrations, ranging between 0.10 ppb and 0.42 ppb. These are similar to Re concentrations for  
301 the protolith under the ridge (below  $\sim 15.4$  m in CZMW8) of 0.11 ppb to 0.23 ppb. The Re  
302 concentrations in the Shale Hills protolith are more than 100-times lower than those measured in  
303 black shale weathering profiles from the US (Jaffe et al. 2002) and Nepal (Pierson-Wickmann et al.,  
304 2002), but similar to those from river bed material in the western Southern Alps of New Zealand  
305 (mean Re =  $0.12 \pm 0.02$  ppb), which is also derived from an OC-poor (TOC  $\sim 0.13\%$ ) rock (Horan et al.,  
306 2017).

307 In the valley, Re is depleted in the weathered saprock from  $\sim 0.9$  m to  $\sim 6.5$  m to between 0.02 ppb  
308 and 0.03 ppb. Similar Re concentrations are measured in saprock under the ridge. The pattern of Re  
309 depletion is spatially consistent with the S depletion (Brantley et al., 2013; Sullivan et al., 2016; Gu et  
310 al., 2020b) and is consistent with weathering profiles developed on black shales (Jaffe et al., 2002;  
311 Pierson-Wickmann et al., 2002). A slight increase in Re concentration towards the surface soil is  
312 measured in both boreholes to  $\sim 0.06$  ppb. In the ridgetop soil profile (Figure 2f), the highest Re  
313 concentration of 0.12 ppb is measured in the top soil (2.5 cm), which decreases to 0.01 ppb at 42.5  
314 cm depth.

315

316

317

318 Mass transfer coefficient

319 To assess the loss or gain of elements, the composition of the parent material must be  
320 characterized. At SSH-CZO, this is not straightforward, due to potential heterogeneity of the parent  
321 material over the deep weathering zone (Brantley et al., 2013b; Gu et al., 2020b) and appearance of  
322 deep fractures that sometimes show localized zones of weathering depletion (Gu et al., 2020a).  
323 Previous studies have used an average over several samples to characterize the parent material, and  
324 the standard deviation to assess potential variability on tau values (Brantley et al., 2013; Sullivan et

325 al., 2016; Gu et al., 2020b). Due to the limited number of Re and  $^{14}\text{C}$  measurements in the protolith  
326 (Figure 2b and e), we here use the deepest sample and assume that the variability in the protolith  
327 for those elements is similar to that measured for S (relative standard deviation).

328 The calculated tau values for S (Figure 3a and d), reveal nearly complete loss of S from the top 6.5 m  
329 under the valley ( $\tau_{\text{Zr,S}}=-0.95\pm 0.08$ ) and from the top 15.4 m under the ridge ( $\tau_{\text{Zr,S}}=-0.89\pm 0.19$ ),  
330 agreeing with previous results (Brantley et al., 2013; Sullivan et al., 2016; Gu et al., 2020a). The tau  
331 values for Re are less negative than S, but still show substantial depletion in the valley ( $\tau_{\text{Zr,Re}}=-0.84$   
332 to  $-0.93$ ; Figure 3f) and under the ridge ( $\tau_{\text{Zr,Re}}=-0.77$  to  $-0.92$ ; Figure 3c). Due to a lower number of  
333 samples analyzed for Re, the comparison between S and Re is not straightforward. Nonetheless,  
334 depletion of Re and S is coherent at 15.4 m and 6.5 m depth under the ridge and valley, respectively  
335 (Figure 3).

336 There is TOC accumulation in the top meter of the profile under the valley ( $\tau_{\text{Zr,TOC}}=+5.9$  and  $+2.0$ ;  
337 Figure 3e) and the ridge ( $\tau_{\text{Zr,TOC}}=+3.6$ ; Figure 3b). For the ridge profile, TOC shows a decrease in tau  
338 between 21.4 and 15.4 m, with a minimum value of  $\tau_{\text{Zr,TOC}}=-0.55$  (Figure 3b), tracking Re loss. A less  
339 pronounced depletion zone is observed in the borehole under the valley, with the deepest sample  
340 being the most depleted showing a  $\tau_{\text{Zr,TOC}}$  of  $-0.41$ .

341

#### 342 Stream water chemistry

343 The stream water is dominated by  $\text{Ca}^{2+}$ , with a mean value of  $205\pm 83 \mu\text{mol l}^{-1}$  (all stream waters:  
344  $n=11$ ,  $\pm 1\text{SD}$ , unless otherwise stated).  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  concentrations are lower, with a mean  
345 value of  $88\pm 21 \mu\text{mol l}^{-1}$ ,  $28\pm 5.6 \mu\text{mol l}^{-1}$  and  $80\pm 6.6 \mu\text{mol l}^{-1}$ , respectively. These measurements are  
346 consistent with data collected at SSH-CZO between 2006 and 2011 (Herndon et al., 2015a). Dissolved  
347 Re concentrations show less variation than the major ions, with values between 3.8 to  $5.5 \text{ pmol l}^{-1}$ ,  
348 and a mean of  $4.3\pm 0.6 \text{ pmol l}^{-1}$ , which is towards the lower end of published Re values for river water  
349 (Miller et al., 2011). During the sampling period (2018-2019), average daily water discharge was  
350  $2.27 \text{ l s}^{-1}$ , which is slightly higher than the long term mean (2008-2015) of  $1.07 \text{ l s}^{-1}$  (Shi and Xiao,  
351 2019).

#### 352 Groundwater and precipitation chemistry

353 In agreement with previous work (Jin et al., 2014), groundwater is more concentrated in  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  
354 and  $\text{Mg}^{2+}$  ions compared to stream water (Table 2). In contrast, the mean  $\text{SO}_4^{2-}$  concentration in  
355 groundwater of  $76\pm 30 \mu\text{mol l}^{-1}$ , is similar to values measured in the stream. Rhenium concentrations  
356 in groundwater samples show a larger range, from  $1.3 \text{ pmol l}^{-1}$  to  $10.0 \text{ pmol l}^{-1}$ . The highest Re  
357 concentrations were measured in two wells located along the stream channel:  $6.3 \text{ pmol l}^{-1}$  and  
358  $10.0 \text{ pmol l}^{-1}$  for CZMW2 and Well 11 (Figure 1b). In these wells, water table was close to the land  
359 surface, indicating a groundwater contact with surface soils.

360 The Re concentration in precipitation ranged between  $0.43 \text{ pmol l}^{-1}$  and  $2.95 \text{ pmol l}^{-1}$ , with a mean  
361 value of  $1.27 \pm 1.14 \text{ pmol l}^{-1}$  ( $n=4$ ;  $\pm 1\text{SD}$ ) close to those measured in stream water. This is in contrast  
362 to very low dissolved Re concentrations of  $<0.2 \text{ pmol l}^{-1}$  in rain from New Zealand (Horan et al.,  
363 2017), the European Alps (Hilton et al., 2021) and the coastal range California (Ghazi et al., 2022),  
364 but is similar to the values reported for rainwater from Falmouth, Massachusetts, on the East coast  
365 of the US, which reach  $5.9 \text{ pmol l}^{-1}$  (Miller et al., 2011). Discussion

366 The borehole materials from Shale Hills display notable Re loss, with a depletion front which broadly  
367 coincides with that of pyrite (S) loss. Assessing the location of the  $OC_{\text{petro}}$  reaction front using only  
368 %TOC is challenging, with clear evidence for modern OC inputs in the near surface samples. Here we  
369 use radiocarbon and attempt to quantify  $OC_{\text{petro}}$  content with an aim to determine the long-term Re  
370 and  $OC_{\text{petro}}$  oxidation rates. Finally, we discuss the enrichment of Re in the near surface soils, stream  
371 water and precipitation, in the context of anthropogenic inputs of Re in a low denudation setting.

#### 372 Evidence for $OC_{\text{petro}}$ loss during weathering

373 The borehole profiles of TOC and  $\tau_{Zr,TOC}$  contain information on  $OC_{\text{petro}}$  loss, and show a depletion of  
374 TOC coincident with the Re and S reaction fronts (Figure 3). However, the TOC concentration in the  
375 Rose Hill shale is low (Table 1, Jin et al., 2014), and C inputs from organic matter of the modern  
376 biosphere or other non-petrogenic sources need to be assessed carefully. The  $\delta^{13}C_{OC}$  values are not  
377 helpful to distinguish source, showing no systematic variation between the soil, saprock, and  
378 protolith (Figure 2d).

379 Instead, we use the radiocarbon activity ( $F^{14}C$ ) of the bulk organic matter in the ridgetop borehole  
380 (CZMW8) (Figure 2e). However, we find no fully  $^{14}C$ -depleted sample, contrasting with other  
381 sedimentary rock weathering profiles where OC content of the rock is >1% (Petsch, 2014; Hilton et  
382 al., 2021). This requires a source of OC at depth that contains radiocarbon. The most  $^{14}C$ -enriched  
383 source in the catchment is recent organic matter formed by photosynthesis ( $F^{14}C \sim 1$ ). The sample at  
384 0.23 m depth, with a  $F^{14}C=0.91$ , could be mostly explained by input from modern  $OC_{\text{bio}}$ . To explain  
385 the input of  $^{14}C$  over the deep weathering profile studied here, we discuss three possibilities: i) aging  
386 of plant derived particulate matter, ii) supply and aging of dissolved OC (DOC), and/or iii)  
387 chemotrophic fixation of DIC at depth.

388 The aging of plant-derived organic matter in mineral soil horizons lowers  $F^{14}C$  (e.g.,  $F^{14}C$  value of 0.7  
389 corresponds to 2,865 radiocarbon years). This could fully explain the surface most sample ( $F^{14}C=0.91$ )  
390 and partly explain the  $^{14}C$ -depletion of the sample at 0.88 m depth ( $F^{14}C=0.47$ ). Large particles of OC  
391 from the biosphere may be transported deeper into the profile during drilling process. However,  
392 other pathways, such as percolating dissolved OC (DOC) downwards from the surface via flow  
393 pathways through the saprock (Marin-Spiotta et al., 2011), or colloidal transport of OC (Yan et al.,  
394 2018; Kim et al., 2018) are also possible. A final mechanism to deliver  $^{14}C$ -rich OC to depth could be  
395 via the dissolved inorganic carbon (DIC) pool via chemotrophic production of organic matter. The DIC  
396 pool may have  $F^{14}C$  between 0.5 and 1.0 reflecting acid hydrolysis of carbonate and silicate minerals  
397 from a mixture of atmospheric  $CO_2$  and carbonate mineral weathering (Jin et al., 2014). This could be  
398 incorporated into microbial biomass under water-saturated conditions (i.e. low  $O_2$ ) via  $SO_4^{2-}$   
399 reduction (Schwab et al., 2019). Distinguishing these pathways is not possible here, but remains an  
400 important avenue for future research if these processes can store significant amounts of recent  
401 carbon at depth in weathered rocks.

402 To quantify  $OC_{\text{petro}}$  using  $^{14}C$  we consider all of these possible pathways for  $^{14}C$  addition. We assume  
403 that the bulk OC pool is a mixture between  $OC_{\text{petro}}$  ( $F^{14}C=0$ ) and an  $^{14}C$ -enriched pool (Blair et al.,  
404 2003; Galy et al., 2008; Hemingway et al., 2018). In the near surface, we assume that the  $F^{14}C$  values  
405 of the enriched pool vary between 1.1 (potential bomb  $^{14}C$  inputs) to 0.9 (potential aged particulate  
406 or DOC). Deeper in the profile, we consider C with  $F^{14}C$  values between 0.9 (potential aged DOC) to  
407 0.5 (chemotrophic C input from DIC). As per Hilton et al. (2021) this range is used for each sample  
408 with a Monte Carlo simulation (1,000-times per sample) to return modelled  $OC_{\text{petro}}$  concentration  
409 values, reported as the 50% (median),  $+2\sigma$  and  $-2\sigma$ , together including 95% of the predicted  $OC_{\text{petro}}$   
410 values (Table 1, Figure 4a).

411 The least well constrained  $OC_{\text{petro}}$  contents are from the most surface sample, with modelled values  
412 between 0.057% and 0.001%. These correspond to a  $\tau_{Zr,OC_{\text{petro}}}$  value varying between +0.46 and -0.97  
413 (Figure 4b). The uncertainty comes from the modest  $^{14}\text{C}$ -depletion, which could be entirely explained  
414 by biospheric OC aging (i.e., negligible  $OC_{\text{petro}}$  inputs), and because the  $OC_{\text{petro}}$  contents are low  
415 compared to the %TOC values (Figure 2c). It is likely that the approach here over-estimates  $OC_{\text{petro}}$  in  
416 the upper most sample. With increasing depth  $OC_{\text{petro}}$  concentration is better constrained. Between  
417 21.5 m and 15.4 m there is a decrease in modelled  $OC_{\text{petro}}$ , from 0.04% to 0.02% (Figure 4a). The  
418 corresponding  $\tau_{Zr,OC_{\text{petro}}}$  decreases from +0.22 to -0.36 (Figure 4b).

419 Despite the very low  $OC_{\text{petro}}$  contents of the protolith at Shale Hills, the challenges of applying  $^{14}\text{C}$  as  
420 a proxy for  $OC_{\text{petro}}$  input and limited number of samples, there is evidence for an  $OC_{\text{petro}}$  reaction  
421 front. Admittedly, there may be variability in the  $OC_{\text{petro}}$  content of the bedrock, but this variation  
422 would have to be coincident with the depths at which S and Re are depleted. Future work could  
423 unpack OC inputs and C cycle processes using the ramped pyrolysis oxidation (RPO) coupled to  
424 radiocarbon technique, to isolate OC with different thermal reactivity (Hemingway et al., 2017;  
425 Grant et al., 2019). Here, we turn to the loss of Re as an alternative approach to constrain oxidative  
426 weathering processes and fluxes at Shale Hills.

427

#### 428 Source of Re in borehole sediments

429 The application of Re as a proxy for  $OC_{\text{petro}}$  oxidation rates is built on an assumption that  $OC_{\text{petro}}$   
430 represents a major source of Re in the weathered lithology (Dalai et al., 2002; Hilton et al., 2014).  
431 Here, we use the ratio of Re to Na and S to quantify the role of sulfide- and silicate-derived Re (as  
432 per Horan et al., 2019 and Hilton et al., 2021). In general, Re concentrations of silicate and sulfide  
433 minerals are low, resulting in low Re/Na ratios for silicates, and low Re/S ratios for sulfides (Peucker-  
434 Ehrenbrink and Hannigan, 2000; Dalai et al., 2002; Miller et al., 2011). In contrast, Re enrichment  
435 associated with OC can increase Re/Na and Re/S ratios (Das et al., 2012). Horan et al. (2019)  
436 proposes a Re/S ratio of  $6.0 \times 10^{-4}$  pmol/ $\mu\text{mol}$ ; however, recent work showed that Re/S ratio can be  
437 as low as  $9.1 \times 10^{-5}$  in a sedimentary, shale environment (Ogrič, 2021). The end-member composition  
438 for silicates (Re/Na) is between  $2.4 \times 10^{-4}$  and  $2.2 \times 10^{-3}$  pmol/ $\mu\text{mol}$  (Dalai et al., 2002).

439 The three-component mixing domain suggests that in the deeper samples, Re is largely associated  
440 with  $OC_{\text{petro}}$  (Figure 5), having a range of relative inputs between 77% and 93%, and a mean value of  
441  $83 \pm 6\%$  ( $\pm 1\text{SD}$   $n=13$ ). Moving towards the surface, an increase in Re/S and decrease in Re/Na ratios  
442 are seen in weathered samples (Figure 5). The increase in Re/S ratio though weathering implies  
443 preferential loss of S relative to Re. The decrease in Re/Na ratio suggests that Re associated with  
444  $OC_{\text{petro}}$  is lost during weathering, consistent with evidence for  $OC_{\text{petro}}$  loss (Figure 4). These  
445 observations suggest that, despite the low %TOC of the rocks, the majority of Re is associated with  
446  $OC_{\text{petro}}$  at depth, and that Re loss results in a residual that becomes more dominated by silicate-  
447 derived Re. Rhenium isotope measurements from a black shale weathering profile were explained  
448 invoking similar behavior (Miller et al., 2015).

449

#### 450 Loss of Re, S and $OC_{\text{petro}}$ through weathering

451 To provide further insights on the mobility of Re, S and  $OC_{\text{petro}}$  during weathering we discuss the  
452 mass transfer profiles in the ridgetop borehole (CZMW8) (Figure 3, Figure 4). While direct  
453 comparison is challenging because of a lower number of samples analyzed for Re and  $OC_{\text{petro}}$

454 compared to S, we observe a broadly coincidental loss of S, OC<sub>petro</sub> and Re at 15.4 m. The pyrite  
 455 oxidation (S loss) front is sharp, with an abrupt change in  $\tau_{Zr,S}$  from -0.99 to +0.20 over a vertical  
 456 distance of ~1 m (Figure 3a). The depletion of OC<sub>petro</sub> across the weathering front appears more  
 457 gradual (Figure 4b), albeit with lower sample resolution, with  $\tau_{Zr,OC_{petro}}$  values from -0.36 to +0.22  
 458 over a longer vertical distance of ~6 m. The number of samples for Re at this depth make the  
 459 comparison harder, but the Re loss profile shows a gradual increase over ~6 m from -0.93 to -0.53  
 460 (Figure 3c), similar to the OC<sub>petro</sub> profile.

461 A decoupling of S loss from OC<sub>petro</sub> loss has been reported in other shale weathering profiles (Jaffe et  
 462 al., 2002; Gu and Brantley, 2022), with the S oxidation front being deeper than the coupled Re and  
 463 OC<sub>petro</sub> oxidation. The deeper S front than OC<sub>petro</sub> oxidation front presumably reflects the faster  
 464 reaction kinetics of pyrite (Petsch et al., 2000; Gu and Brantley, 2022). However, this assumes that  
 465 O<sub>2</sub> in air and water has access to phases in the subsurface. This may not be the case at Shale Hills,  
 466 where the generation of porosity and permeability is inherently linked to chemical weathering  
 467 processes themselves (Gu et al., 2020a, 2020b). At SSH-CZO, previous work has suggested the  
 468 oxidation of pyrite minerals plays a crucial role in subsequent oxidative weathering and acid  
 469 hydrolysis reactions (Brantley et al., 2013; Gu et al., 2020a). This is because pyrite oxidation  
 470 produces sulfuric acid, an acid that can dissolve both carbonates and clay minerals, resulting in  
 471 increased pore space in the weathered matrix (Gu et al., 2020b). After pyrite is completely  
 472 exhausted from the saprock, oxygen can more effectively enter through the new porosity, reacting  
 473 with the remaining rock matrix (Jin et al., 2010; Brantley et al., 2013; Gu et al., 2020a). This may  
 474 explain the link between the depths of S, OC<sub>petro</sub> and Re depletion.

475 The observed lower degree of OC<sub>petro</sub> loss compared to the Re and S loss in the surface samples could  
 476 come about by incomplete OC<sub>petro</sub> oxidation. The slight metamorphic alteration of the Rose Hill shale  
 477 (Gu et al., 2020b) could have thermally matured the organic matter in the rock, making the OC in the  
 478 rock more resistant to weathering (Petsch, 2014). Alternatively, association of OC<sub>petro</sub> or its  
 479 weathered products with clay minerals may protect them from further oxidation (Hemingway et al.,  
 480 2019; Gu and Brantley, 2022).

481 Long-term OC<sub>petro</sub> oxidation rates

482 Depletion profiles of Re (Figure 3c) and OC<sub>petro</sub> (Figure 4b) in the borehole samples can be used to  
 483 quantify OC<sub>petro</sub> oxidation rate that occurred over the timescales of the weathering profile formation,  
 484 and by inference, estimate the release of CO<sub>2</sub> from sedimentary rock weathering. We find evidence  
 485 for OC<sub>petro</sub> loss at a weathering front, which could correspond to a CO<sub>2</sub> release over the timescales of

$$J_{OC_{petro}} = \omega \times \frac{([OC_{petro}]_p - [OC_{petro}]_s)}{100} \times \rho_p \quad (2)$$

486 weathering front formation, quantified by:

487 where  $\omega$  is denudation rate (10-25 m Myr<sup>-1</sup>; West et al., 2013), [OC<sub>petro</sub>]<sub>p</sub> is the concentration below  
 488 the reaction front (0.04±2σ%) and [OC<sub>petro</sub>]<sub>s</sub> is the concentration above the weathering front  
 489 (0.02±2σ%). Density of the protolith samples ( $\rho_p$ ) is 2.7 g cm<sup>-3</sup> (Gu et al., 2020b). Using these values,  
 490 the OC<sub>petro</sub> weathering at Shale Hills is estimated between 2.0×10<sup>-3</sup> and 1.7×10<sup>-2</sup> tC km<sup>-2</sup> yr<sup>-1</sup>, the  
 491 range reflecting the uncertainty on the quantification of OC<sub>petro</sub> (Section 4.1) and denudation rate at  
 492 this site.

493 The trace element Re has been more precisely determined in these OC-poor samples. To apply the

$$J_{OC_{\text{petro}}-Re} = \omega \times \frac{([Re]_p - [Re]_s)}{[Re/OC]_{\text{petro}}} \times F_{Re-OC} \times \rho_P \quad (3)$$

494 Re proxy to track  $OC_{\text{petro}}$  oxidation rates ( $J_{OC_{\text{petro}}-Re}$ ), the following Equation 3 is used:

495 where  $F_{Re-OC}$  is the fraction of Re derived from  $OC_{\text{petro}}=83\pm6\%$  (Figure 5). The  $[Re/OC]_{\text{petro}}$  and  $[Re]_p$  are  
496 the ratio and Re concentration below the weathering front,  $4.3\times 10^{-7} \text{ g g}^{-1}$  and 0.11 ppb, respectively  
497 and  $[Re]_s$  is the Re concentration above the front (0.02 ppb). The long-term  $OC_{\text{petro}}$  emissions at Shale  
498 Hills determined by the Re proxy are estimated between  $4.4\times 10^{-3}$  and  $1.3\times 10^{-2} \text{ tC km}^{-2} \text{ yr}^{-1}$ , reflecting  
499 uncertainty on the denudation rate estimates and the  $[Re/OC]_{\text{petro}}$  ratios of the protolith samples. In  
500 the protolith samples from the CZMW8 borehole,  $[Re/OC]_{\text{petro}}$  varies between  $3.1\times 10^{-7} \text{ g g}^{-1}$  and  
501  $8.1\times 10^{-7} \text{ g g}^{-1}$ . Globally, this ratio can vary in a range between  $10^{-7} \text{ g g}^{-1}$  and  $10^{-8} \text{ g g}^{-1}$  across different  
502 sedimentary environments (Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002; Ross and  
503 Bustin, 2009; Sheen et al., 2018).

504 A previous estimate of  $CO_2$  release from  $OC_{\text{petro}}$  oxidation at Shale Hills by Jin et al. (2014) assumed  
505 that all TOC in the bedrock was depleted by weathering during soil production ( $20 \text{ mM yr}^{-1}$ , Ma et  
506 al., 2010). The corresponding  $CO_2$  release rate was  $1.5\times 10^{-2} \text{ tC km}^{-2} \text{ yr}^{-1}$  (Jin et al., 2014), which is  
507 broadly similar, given uncertainties, to our maximum estimates presented above, using  $OC_{\text{petro}}$  loss  
508 ( $1.7\times 10^{-2} \text{ tC km}^{-2} \text{ yr}^{-1}$ ) and the Re proxy ( $1.3\times 10^{-2} \text{ tC km}^{-2} \text{ yr}^{-1}$ ).

509 The  $OC_{\text{petro}}$  oxidation rate at Shale Hills is expected to be low for two reasons: i) the shale is  $OC_{\text{petro}}$ -  
510 depleted; and ii) denudation rates are extremely low. Numerical models of  $OC_{\text{petro}}$  oxidation,  
511 constrained by the reactivity of coal from abiotic laboratory incubations (Chang and Berner, 1999),  
512 suggest that  $OC_{\text{petro}}$  oxidation is limited by supply of fresh, un-oxidized material (Bolton et al., 2006).  
513 Dissolved Re fluxes from catchments in Taiwan and New Zealand confirm this, showing increases in  
514 erosion are linked to increases in  $OC_{\text{petro}}$  weathering (Hilton et al., 2014; Horan et al., 2017).  $OC_{\text{petro}}$   
515 oxidation at Shale Hills is 2 to 3 orders of magnitude lower than  $OC_{\text{petro}}$  oxidation rates based on the  
516 dissolved Re proxy in high erosive catchments of the Himalaya (Dalai et al., 2002), Taiwan (Hilton et  
517 al., 2014), New Zealand (Horan et al., 2017), and the Mackenzie river system (Horan et al., 2019)  
518 (Figure 6).

519 The SSH-CZO  $OC_{\text{petro}}$  oxidation estimate reaffirms that supply of  $OC_{\text{petro}}$  to the weathering zone is a  
520 key driver of  $OC_{\text{petro}}$  oxidation on a global scale (Figure 6). The observed variability in Figure 6 may be  
521 associated with variable  $OC_{\text{petro}}$  concentrations and weathering intensity ( $\chi$ ), which can vary between  
522 different settings (Hilton and West, 2020). The weathering of  $OC_{\text{petro}}$  may be locally limited by  
523 temperature (Soulet et al., 2021), oxygen supply (Bolton et al., 2006), microbial activity (Hemingway  
524 et al., 2018), and/or the particle size of  $OC_{\text{petro}}$  (Gu and Brantley, 2022). These processes could be  
525 tracked with time-series data for reaction products in the weathering zone and may be most  
526 important in erosive settings where sediment supply to the near surface environment is high.

527

528

529 A decoupling of stream water Re from deep weathering

530 Stream water Re concentrations are high at SSH-CZO (Table 2), despite the very deep Re weathering  
531 front and relatively low Re concentrations of the protolith (Figure 3). Previous work has suggested  
532 that dissolved Re could be influenced by anthropogenic perturbation of the Re cycle (Miller et al.,  
533 2011; Rahaman et al., 2012). Here we explore its role at Shale Hills, where denudation rates and  
534 OC<sub>petro</sub> contents are low. We take advantage of our precise characterization of Re content in  
535 bedrock, soils and water to build a dissolved-particulate mass budget to quantify the Re contribution  
536 from weathering vs. anthropogenic inputs in the present day.

537 To assess the surface cycling of Re in this catchment, the present-day Re flux in stream water leaving  
538 the catchment ( $Re_{stream}$ ,  $\text{pmol m}^{-2} \text{yr}^{-1}$ ) is estimated using the discharge-weighted average (Equation

$$Re_{stream} = \frac{\overline{Re} \times \overline{Q}_t}{\overline{Q}_a} \times \overline{Q}_a \quad (4)$$

539 4):

540 where  $Re$  ( $\text{pmol l}^{-1}$ ) is Re concentration measured in stream water over the sampling period,  $Q_t$  ( $\text{l s}^{-1}$ )  
541 is the instantaneous discharge measure at the time of sample collection (Table 2), and  $\overline{Q}_a$  is the  
542 mean annual stream discharge. Using the long term mean annual discharge (2008-2015) as  $\overline{Q}_a$  ( $1.07$   
543  $\text{l s}^{-1}$ ) gives dissolved Re flux estimate of  $2.1 \times 10^3 \text{ pmol m}^{-2} \text{yr}^{-1}$ . The  $\overline{Q}_a$  over our sampling period  
544 (2018-2019) was higher at  $2.27 \text{ l s}^{-1}$ , meaning the annual Re flux from June 2018 to June 2019 may  
545 have been closer to  $4.4 \times 10^3 \text{ pmol m}^{-2} \text{yr}^{-1}$ .

546 We can compare this flux to an estimate of how much Re is produced by weathering of the protolith

$$Re_{CW} = (\overline{[Re]}_p - \overline{[Re]}_s) \times \rho_p \times \omega \quad (5)$$

547 ( $Re_{CW}$ ;  $\text{pmol m}^{-2} \text{yr}^{-1}$ ), using Equation 5.

548 Here the mean Re concentration in the protolith ( $\overline{[Re]}_p$ ) and the saprock ( $\overline{[Re]}_s$ ) are used. Other  
549 terms are defined in Equation 3. The expected release of Re due to weathering of the protolith  
550 ( $Re_{CW}$ ) is between  $0.02$  and  $0.05 \times 10^3 \text{ pmol m}^{-2} \text{yr}^{-1}$ , the range reflecting variability in the denudation  
551 rate estimates. This is  $<3\%$  of the dissolved Re flux from the stream, suggesting a negligible  
552 contribution of dissolved Re from chemical weathering.

553 To explore this stark decoupling of weathering inputs and dissolved exports, we turn to the  
554 precipitation and surface soil samples. The area surrounding the Shale Hills is known for coal burning  
555 activities, with a number of historical iron furnaces, fueled by local Pennsylvania coal (Herndon et al.,  
556 2011; Kraepiel et al., 2015). Furthermore, contemporary coal power plants are located upwind of the  
557 catchment (Lima et al., 2005; Ma et al., 2014). During coal combustion ( $500\text{--}700 \text{ }^\circ\text{C}$ ), Re may be  
558 volatilized and released to the atmosphere as  $\text{Re}_2\text{O}_7$  (Colodner et al., 1995). It can then be deposited  
559 on the surrounding landscapes through either wet or dry deposition (Novo et al., 2015). The  
560 abundance of Re in coal fly ash, a by-product of coal burning, may be high, as suggested by high Re  
561 concentration ( $5.2 \text{ ppb}$ ) measured in a Coal Fly Ash standard reference material 1633a (product of  
562 Pennsylvania and West Virginia coals) for this study.

563 The present-day atmospheric Re flux ( $Re_{Atm}$ ) can be estimated by multiplying the average Re  
564 concentration of precipitation samples ( $1.28 \pm 0.99 \text{ pmol l}^{-1}$ ) with the mean annual precipitation for

565 Shale Hills, of  $1070 \text{ mm yr}^{-1}$  (Jin et al., 2014). A present-day atmospheric deposition of Re at Shale  
566 Hills is  $1.4 \pm 1.1 \times 10^3 \text{ pmol m}^{-2} \text{ yr}^{-1}$  (Figure 7). By itself, the modern Re input from precipitation is  
567 almost 20-times the chemical weathering supply of Re. Precipitation inputs can account for ~60% of  
568 the long term (2008-2015) Re flux estimate in this small catchment.

569 Additional insight comes from shallow groundwater samples, which have elevated Re concentrations  
570 (Table 2), suggesting inputs from surface soils, where rainfall events may leach previously deposited  
571 Re. These observations suggest that past deposition of Re on the landscape may have been higher,  
572 as recently observed for atmospheric deposition of sulfate at the study site (Shaughnessy et al.,  
573 2020). At the Shale Hills catchment, the surface soils appear to act as a temporary Re reservoir  
574 enriched in anthropogenic Re, suggesting that the present-day Re cycle in the dissolved load has  
575 been perturbed by recent human activities.

576 Rhenium deposited in the catchment through wet or dry atmospheric deposition, might be retained  
577 in the soil through either a pH-dependent control on the Re mobility, and/or as a solid particle form  
578 which subsequently undergoes weathering and oxidation. In terms of the pH control, the perrhenate  
579 ion,  $\text{ReO}_4^-$ , can be mobilized at low pH of forest soils at the SSH-CZO (pH  $4.0 \pm 0.1$  on the ridge and  
580  $4.7 \pm 0.2$  in the valley; Jin et al., 2011; Herndon et al., 2015b). A laboratory based study by Kim et al.  
581 (2004) showed that more than 40% of  $\text{ReO}_4^-$  could be reabsorbed onto organic molecules at pH ~4.  
582 Continuous acidic precipitation, with pH 4.2 – 4.4 monitored since the 1980s (NADP, 2020), but may  
583 have started as early as the 1800s (Herndon et al., 2011; Kraepiel et al., 2015) may cause absorption  
584 of Re into the forest soils at SSH-CZO. With the increasing precipitation pH over recent years  
585 (pH ~5.6; NADP Program Office, 2020), the reabsorbed Re could be leached into the surface waters,  
586 explaining the high Re concentrations in stream waters. While this mechanism is viable, we cannot  
587 rule out the role of Re-enriched particles deposited on the catchment, which subsequently release  
588 Re as they weather.

589 A deposition of Re on the catchment is consistent with the enrichment of Re concentration towards  
590 the top-most soil layer in a 50 cm deep soil profile (Figure 2f). Accumulation of several other metals  
591 in the top soil is also seen at the SSH-CZO, e.g. Mo and Mn (Herndon et al., 2011; Kraepiel et al.,  
592 2015), Pb (Ma et al., 2014) and Hg (Richardson et al., 2018). To further explore the behavior of Re in  
593 the surface soils we plot Re, Mo and Mn concentrations normalized to Al (Figure 7 b-d). Aluminum is  
594 not impacted by atmospheric deposition (Kraepiel et al., 2015) and is immobile in the soil profile  
595 (Kim et al., 2018). All three elemental ratios are elevated in the upper 5 cm of the soil profile, which  
596 would imply present-day inferred inputs from anthropogenic activities, i.e., coal burning, gasoline  
597 combustion, and/or steel plants (Herndon et al., 2011). Down to 25 cm depth, Re/Al and Mn/Al  
598 ratios decrease by a factor of ~4 and Mo/Al for a factor of ~1.5. Below 25 cm depth, Mn/Al and  
599 Mo/Al remain constant, but Re/Al ratio further decreases. These differences probably reflect the  
600 biogeochemical processes impacting the elements. For example, oxidized Mo is soluble ( $\text{MnO}_4^{2-}$ ) and  
601 mobile, like Re. However, previous studies have suggested adsorption of Mo to oxyhydroxides  
602 and/or organic compounds in soils at ~pH 4 (King et al., 2018). In contrast, Mn is thought to be  
603 largely involved in bio-cycling (Herndon and Brantley, 2011; Herndon et al., 2015b) resulting in long  
604 residence times in the soil (Kraepiel et al., 2015). The precise nature of Re adsorption in soils could  
605 be explored in future studies using the Re isotopic system (Miller et al., 2015; Dellinger et al., 2020,  
606 2021).

607 To explore the legacy of anthropogenic deposition of Re to the catchment soils we here provide an  
608 estimate of the time needed to deplete the accumulated Re in surface soils (turnover time). First,  
609 the total Re mass in soil per unit land surface area ( $\text{pmol m}^{-2}$ ) is summarized over depth intervals  
610 ( $\Delta d$ ) as shown in Equation 6:



$$m_{Re,soil} = \sum \Delta d \times \rho_{soil} \times [Re]_{soil} \quad (6)$$

611 Where  $[Re]_{soil}$  is Re concentration in soil at certain depth (Table 1) and  $\rho_{soil}$  is the soil density at  
 612 different intervals as reported in Lin et al. (2006). The total Re mass in the upper 50 cm of a soil  
 613 profile is  $1.1 \times 10^5$  pmol  $m^{-2}$ . To explain the measured dissolved Re flux, soil leaching  
 614 ( $Re_{leach,soil} = Re_{stream} - Re_{atm} - Re_{cw}$ ) would have to contribute  $0.7 \times 10^3$  pmol  $m^{-2} yr^{-1}$  (Figure 7a) to the long  
 615 term (2008-2015) dissolved Re flux. With this constraint, we can estimate the turnover time,

$$T_{Re} = \frac{m_{Re,soil}}{Re_{leach,soil}} \quad (7)$$

616 assuming this leaching of Re is constant over time and acts to deplete the surface soil reservoir:

617 This returns an estimate of  $T_{Re}$  of 160 years. This is a notable timeframe over which dissolved Re  
 618 concentrations could be elevated.

619 This study shows that in locations where denudation rates are low and atmospheric metal  
 620 deposition rates are high, the surface Re cycling is significantly perturbed by anthropogenic  
 621 impacts. While our study covers a small catchment, these findings echo global assessments  
 622 suggesting that the current cycling and usage of Re associated with human activities is equivalent to  
 623 a Re flux of  $0.15 \pm 0.01$  Gg  $yr^{-1}$ , which is three times larger than the natural Re flux  $0.05 \pm 0.03$  Gg  $yr^{-1}$   
 624 (Sen and Peucker-Ehrenbrink, 2012). Our study calls for future work to better constrain modern and  
 625 historic Re inputs to the surface of catchments, and highlights that the dissolved Re proxy for  $OC_{petro}$   
 626 oxidation (Dalai et al., 2002; Hilton et al., 2014) may result in overestimation in low denudation  
 627 settings.

628

629

## 630 Conclusions

631 This study combines measurements of radiocarbon in the organic carbon reservoir and trace  
 632 element Re to examine oxidative weathering of  $OC_{petro}$  in a setting experiencing low denudation. In  
 633 deep weathering profiles from the Susquehanna Shale Hills Critical Zone Observatory, we find  
 634 evidence for  $OC_{petro}$  depletion across a broad,  $\sim 6$  m wide weathering front in a borehole from the  
 635 ridge (CZMW8), with a tau ( $\tau_{Zr,OC_{petro}}$ ) value of around -0.4. However, the measurements of  
 636 radiocarbon require a deep input of  $^{14}C$ , which makes quantifying  $OC_{petro}$  loss challenging. We turn to  
 637 the trace element Re, and use Re/Na and Re/S ratios to estimate that  $\sim 80\%$  of Re is derived from  
 638  $OC_{petro}$  in this setting. The depletion profile of Re occurs over a broad reaction front (similar to  $OC_{petro}$   
 639 front), with  $\tau_{Zr,Re}$  between -0.77 and -0.93. In contrast, the pyrite weathering front (S loss) in the  
 640 ridgetop borehole appears narrower ( $\sim 1$  m) at a similar depth of 15.4 m and the S is almost fully  
 641 depleted ( $\tau_{Zr,S} = -0.99$ ). We use the  $OC_{petro}$  depletion and the Re loss profiles to quantify long-term  
 642  $OC_{petro}$  oxidation rates, which are low ( $< 1.7 \times 10^{-2}$  tC  $km^{-2} yr^{-1}$ ), but consistent with low denudation  
 643 rates ( $0.01 - 0.025$  mm  $yr^{-1}$ ), confirming the important role of mineral supply and erosion rate on  
 644  $OC_{petro}$  oxidation.

645 We find a pronounced contrast between the deep weathering and surface cycle of Re in this  
 646 catchment. The low oxidative weathering rates supply only small amounts of Re ( $< 0.05 \times 10^3$  pmol  $m^{-2}$

647 yr<sup>-1</sup>), and the saprock is Re depleted. In contrast, the long term annual dissolved Re export from the  
648 catchment is estimated at  $2.1 \times 10^3$  pmol m<sup>-2</sup> yr<sup>-1</sup>, with precipitation, shallow groundwater, and  
649 surface soils all showing elevated Re concentrations. An anthropogenic Re input due to historical  
650 steel production and coal burning activities can explain these patterns. Rhenium may have  
651 accumulated in the surface soil and is now being slowly leached to the stream waters. At the current  
652 mobilization rate, the reservoir of anthropogenic Re in the surface soil could take centuries to  
653 deplete. This study highlights that anthropogenic inputs of Re can be a large component of the Re  
654 budget in settings with low denudation rates. It calls for renewed focus on the recent perturbation  
655 of the Re cycle and how this element could help elucidate the legacy of pollution impacts in  
656 catchment soils.

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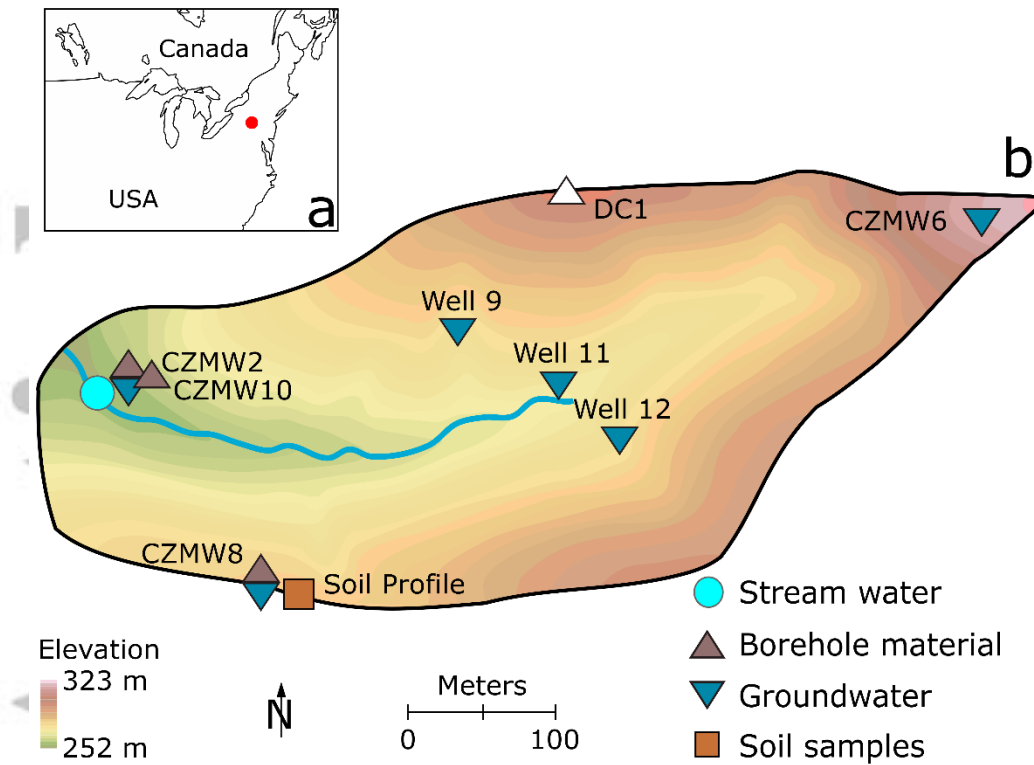
**TABLE 1** Published sulfur, zirconium and titanium concentrations alongside new measurements of total organic carbon (TOC), stable carbon isotope of organic carbon ( $\delta^{13}\text{C}_{\text{OC}}$ ), radiocarbon activity ( $F^{14}\text{C}$ ), and rhenium (Re) in the studied borehole profiles and the topsoil profile. Classification of material type is based on previous work by Sullivan et al., 2016 (1), Brantley et al., 2013 (2) Gu et al, 2020a (3) and Herndon et al., 2011 (4). Radiocarbon activities of the biospheric OC input used in the two end-member mixing model applied for determination of  $\text{OC}_{\text{petro}}$  concentrations are discussed in section 4.1 ( $F^{14}\text{C} = 1.1 - 0.9$  for samples labelled \* and  $F^{14}\text{C} = 0.9 - 0.5$  for samples labelled \*\*).

Borehole	Sample ID	Depth (m)	Material type	$\delta^{13}\text{C}$ ‰	TOC (%)	$F^{14}\text{C}$	$\text{OC}_{\text{petro}}$ (%)	$\text{OC}_{\text{petro}} + 2\sigma$	$\text{OC}_{\text{petro}} - 2\sigma$	Re (ppb)	S (%)	Zr (ppb)	Ti (%)	S, Ti (%), Zr (ppb) and material type ref.
CZMW8	SSH0001SI	-0.27	Soil	-26.2	0.37	$0.91 \pm 0.005$	0.03*	0.057	0.001	0.05	0.006	186	0.62	1
	SSH0001SJ	-0.88	Saprock	-26.4	0.09	$0.47 \pm 0.003$	0.03**	0.037	0.007	0.03	0.007	158	0.59	1
	SSH0001SL	-5.94	Saprock	-27.0	0.06	$0.30 \pm 0.003$	0.03**	0.032	0.020	0.02	0.001	163	0.62	1
	SSH0001T5	-12.04	Saprock	-26.7	0.05	$0.31 \pm 0.003$	0.02**	0.029	0.018	-	0.005	152	0.59	1
	SSH0001TH	-15.36	Saprock	-26.4	0.03	$0.24 \pm 0.003$	0.02**	0.021	0.015	0.02	0.002	141	0.59	1
	SSH0001TP	-16.40	Protolith	-26.9	0.04	$0.27 \pm 0.003$	0.02**	0.023	0.016	-	0.142	145	0.63	1
	SSH0001TX	-18.75	Protolith	-26.7	0.05	$0.28 \pm 0.003$	0.03**	0.032	0.021	0.14	0.122	149	0.58	1
	SSH0001O7	-21.49	Protolith	-26.8	0.07	$0.26 \pm 0.003$	0.04**	0.041	0.028	0.11	0.100	142	0.61	1
Parent	SSH0001V4	-30.36	Protolith	-26.8	0.06	$0.32 \pm 0.003$	0.03**	0.034	0.020	0.23	0.172	138	0.61	1
CZMW2	SSH000SWY	-0.46	Soil	-25.9	0.32	-	-	-	-	0.06	0.006	225	0.55	2
	SSH000SX0	-1.07	Soil	-26.0	0.14	-	-	-	-	0.04	0.006	230	0.58	2
	SSH0001KN	-2.29	Saprock	-25.1	0.07	-	-	-	-	0.03	0.007	175	0.53	2
	SSH000SX5	-3.81	Saprock	-26.2	0.06	-	-	-	-	0.03	0.006	245	0.58	2
	SSH000SX6	-6.55	Saprock	-26.2	0.06	-	-	-	-	0.02	0.007	185	0.47	2
	SSH000SX8	-8.38	Saprock	-25.2	0.03	-	-	-	-	0.12	0.091	160	0.58	2
	SSH000SX9	-9.91	Protolith	-25.8	0.04	-	-	-	-	0.15	0.098	165	0.58	2
	SSH000SXA	-11.43	Protolith	-26.1	0.05	-	-	-	-	0.13	0.114	140	0.58	2
	SSH000SXB	-12.96	Protolith	-24.4	0.05	-	-	-	-	0.17	0.110	175	0.57	2
	SSH000SXC	-14.48	Protolith	-25.5	0.05	-	-	-	-	0.12	0.082	165	0.59	2
	SSH000SXD	-16.01	Protolith	-26.3	0.04	-	-	-	-	0.24	0.089	315	0.64	2
CZMW10	SSH0003DG	-7.62	Saprock	-	-	-	-	-	-	0.14	0.126	166	0.59	3
	SSH0003DV	-20.27	Protolith	-	-	-	-	-	-	0.10	0.063	156	0.56	3
	SSH0003EO	-24.23	Protolith	-	-	-	-	-	-	0.37	0.140	239	0.53	3
	Parent	SSH0003EC	-34.90	Protolith	-	-	-	-	-	0.42	0.168	185	0.62	3
Soil profile	SSH00000R	0-5	Soil							0.12		250	-	4

	SSH00000R	10-15	Soil							0.05		275	-	4
	SSH00000R	20-30	Soil							0.06		210	-	4
	SSH00000R	40-50	Soil							0.01		170	-	4

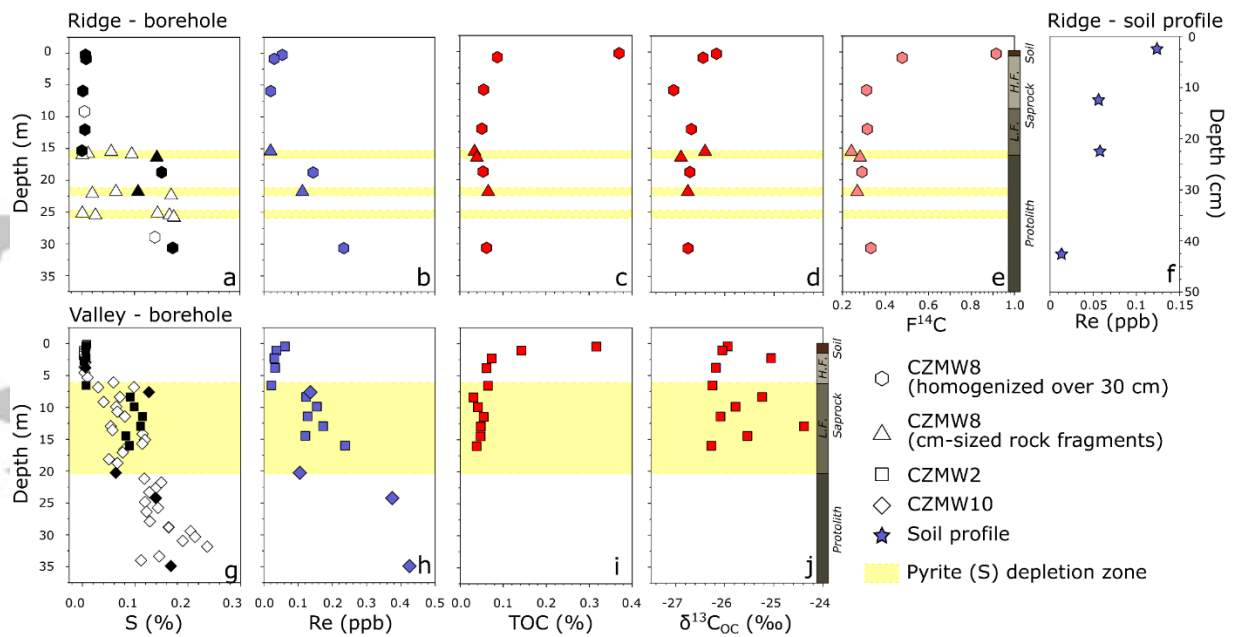
**TABLE 2.** Dissolved load chemistry on stream water, groundwater and precipitation samples. Major ions on the precipitation samples are from NADP Program Office (2020) database obtained in the same week as the samples analyzed for Re.

Sample Name	Sampling Date	Sample type	Location	Instantaneous discharge $\text{l s}^{-1}$	Cl <sup>-</sup> $\mu\text{mol}$	SO <sub>4</sub> <sup>2-</sup> $\mu\text{mol}$	Na <sup>+</sup> $\mu\text{mol}$	K <sup>+</sup> $\mu\text{mol}$	Mg <sup>2+</sup> $\mu\text{mol}$	Ca <sup>2+</sup> $\mu\text{mol}$	Re $\mu\text{mol}$
SH18-04	19/08/2018	Stream water	Gauging station	0.3	21	77	30	28	101	242	5.16
SH 20-06-18	20/06/2018	Stream water	Gauging station	20.4	23	83	40	29	131	332	4.09
SH 03-08-18	03/08/2018	Stream water	Gauging station	1.2	16	65	20	26	53	57	5.51
S19-1	06/02/2019	Stream water	Gauging station	2.8	20	76	25	25	69	101	4.17
S19-2	27/02/2019	Stream water	Gauging station	1.5	17	83	25	22	79	146	3.81
S19-3	13/03/2019	Stream water	Gauging station	4.2	18	86	23	20	74	292	4.67
S19-4	31/03/2019	Stream water	Gauging station	0.6	18	89	29	22	97	243	4.11
S19-5	17/04/2019	Stream water	Gauging station	3.1	16	81	23	23	73	149	3.76
S19-6	01/05/2019	Stream water	Gauging station	0.6	19	87	33	25	104	256	4.22
S19-7	23/05/2019	Stream water	Gauging station	1.0	18	81	28	25	94	218	3.99
S19-8	03/06/2019	Stream water	Gauging station	1.0	18	80	28	25	91	212	3.91
SH18-02	19/08/2018	Groundwater	Well nr. 11	-	28	80	40	29	86	69	10.00
SH18-05	19/08/2018	Groundwater	CZMW2	-	29	132	296	17	214	1028	6.26
SH18-10	20/08/2018	Groundwater	Well nr. 09	-	25	78	43	35	99	97	4.93
SH18-12	20/08/2018	Groundwater	Well nr. 12	-	37	47	162	37	504	330	1.27
SH18-11	20/08/2018	Groundwater	CZMW8	-	20	64	31	25	49	39	3.55
SH18-13	20/08/2018	Groundwater	CZMW6	-	23	54	29	36	270	257	4.51
Rain 10/07/13	07/10/2013	Rain	-	-	1.3	4.5	0.9	2.6	0.7	1.1	0.43
Rain 2014/10/23	23/10/2014	Rain	-	-	1.0	19.2	0.2	0.2	0.5	1.9	2.95
Rain 7/1/13	01/07/2013	Rain	-	-	1.0	7.8	0.3	0.3	0.4	1.6	1.02
Snow 02/07/14	07/02/2014	Snow	-	-	2.1	3.9	0.7	0.2	0.2	0.7	0.70

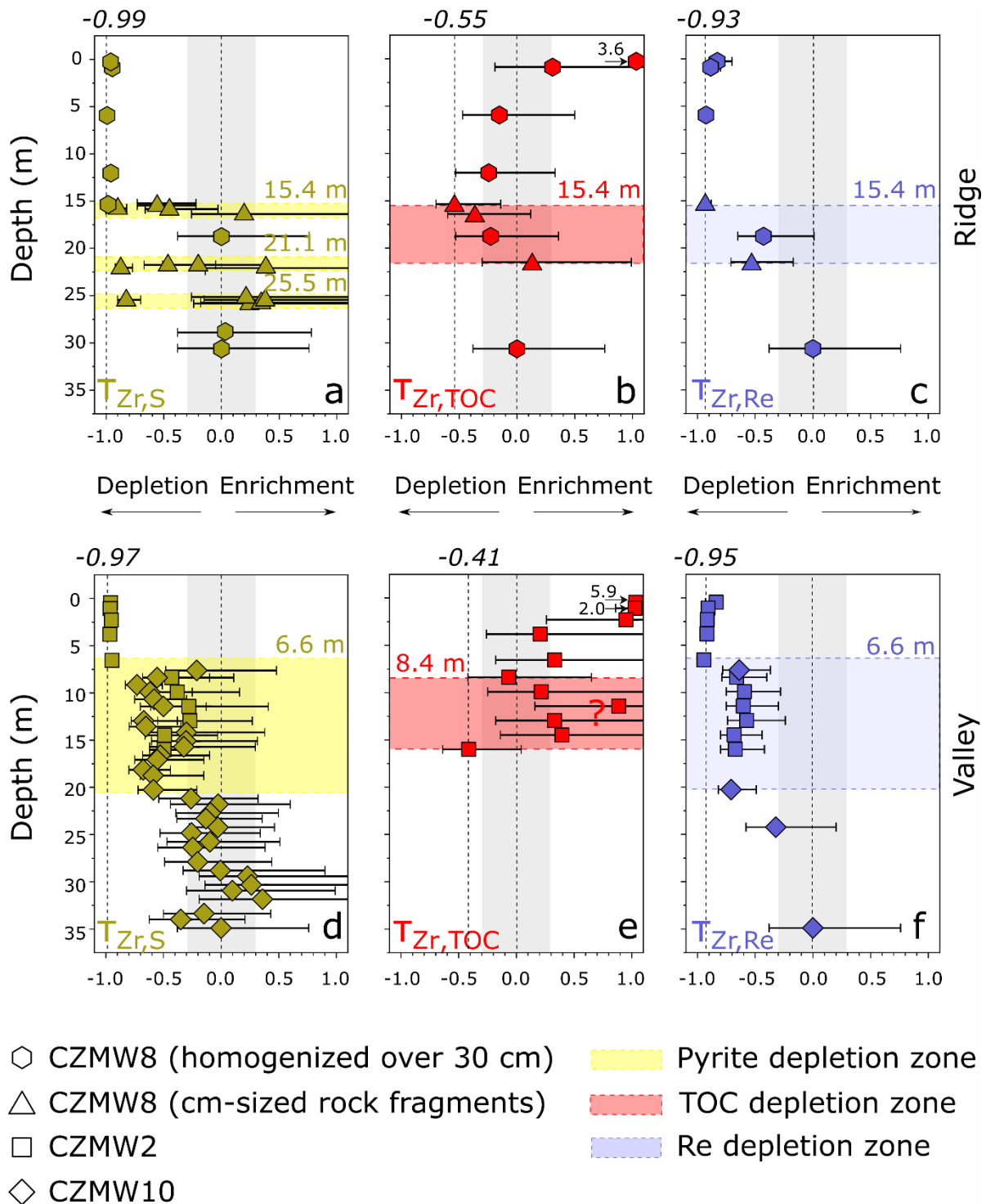


**FIGURE 1** (a) The Susquehanna Shale Hills Critical Zone Observatory in central Pennsylvania. (b) The first order Shale Hills catchment and samples analyzed in this study: recovered borehole material (brown triangles) as cuttings (CZMW2, CZMW10) or core (CZMW8); a soil profile (brown square), groundwater samples (blue triangles), and time series stream water samples (June 2018 - June 2019; blue circles). Previously published results from DC1 borehole (white triangle; Jin et al., 2014) are used to help interpretation of the results.

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**FIGURE 2** Geochemical profiles for boreholes CZMW8 (southern ridge) and CZMW2, CZMW10 (valley). (a) Previously published measurements of sulfur (S) concentrations from boreholes CZMW2 and CZMW10 in Brantley et al. (2013) and Gu et al. (2020a) and from the borehole CZMW8 in Sullivan et al. (2016) and Gu et al. (2020a). Samples were selected (black symbols in figures (a) and (g) and analyzed for rhenium (b) and (h), total organic carbon (c) and (i), stable carbon isotope of organic carbon (d) and (j), and radiocarbon (Fraction modern, e). From the borehole CZMW8 two types of samples were collected: bulk core material homogenized over 30 cm depth (hexagons) and cm-sized rock fragments (triangles). Bar to the right side of plots (e) and (j) show approx. depths of changes in structure due to chemical and physical degradation of the protolith (Sullivan et al., 2016). H.F. stands for highly fractured saprock and L.F. stands for less fractured saprock. The yellow shading on all plots show depth intervals where pyrite depletion was detected (Brantley et al., 2013; Sullivan et al., 2016; Gu et al., 2020a). The uppermost white band for each borehole represents the bulk oxidation zone because almost no pyrite remains unoxidized at shallower depths (lower yellow bands are fracture sets as described by (Gu et al., 2020a). Figure (f) shows Re concentrations from a soil profile sampled next to CZMW8.

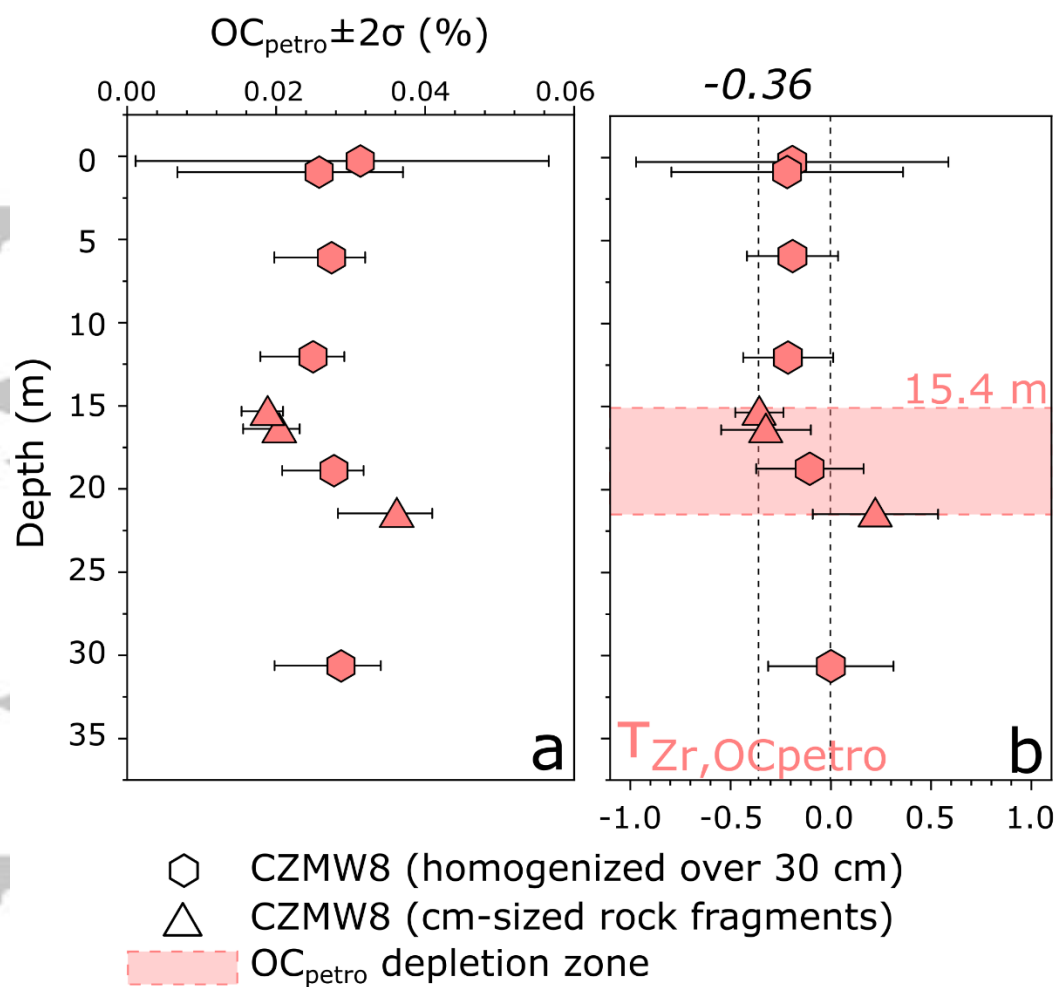


**FIGURE 3** Mass transfer coefficient profiles for boreholes CZMW8 (southern ridge) and CZMW2, CZMW10 (valley). Parent composition was determined from the concentration measured on the deepest protolith sample in the CZMW8 and CZMW10. Zirconium (Zr) was used as an immobile element. The error bars show variation of the parent material for S (33%) and Zr (18%). For TOC and Re it is assumed that the variability in the parent material is similar to the S (~30%). Shaded grey zone represents one SD of uncertainty due to variable parent composition within the catchment (a)  $\tau_{Zr,S}$  profile from the ridge (CZMW8). Data and interpretation is from Gu et al. (2020a). (b)  $\tau_{Zr,TOC}$

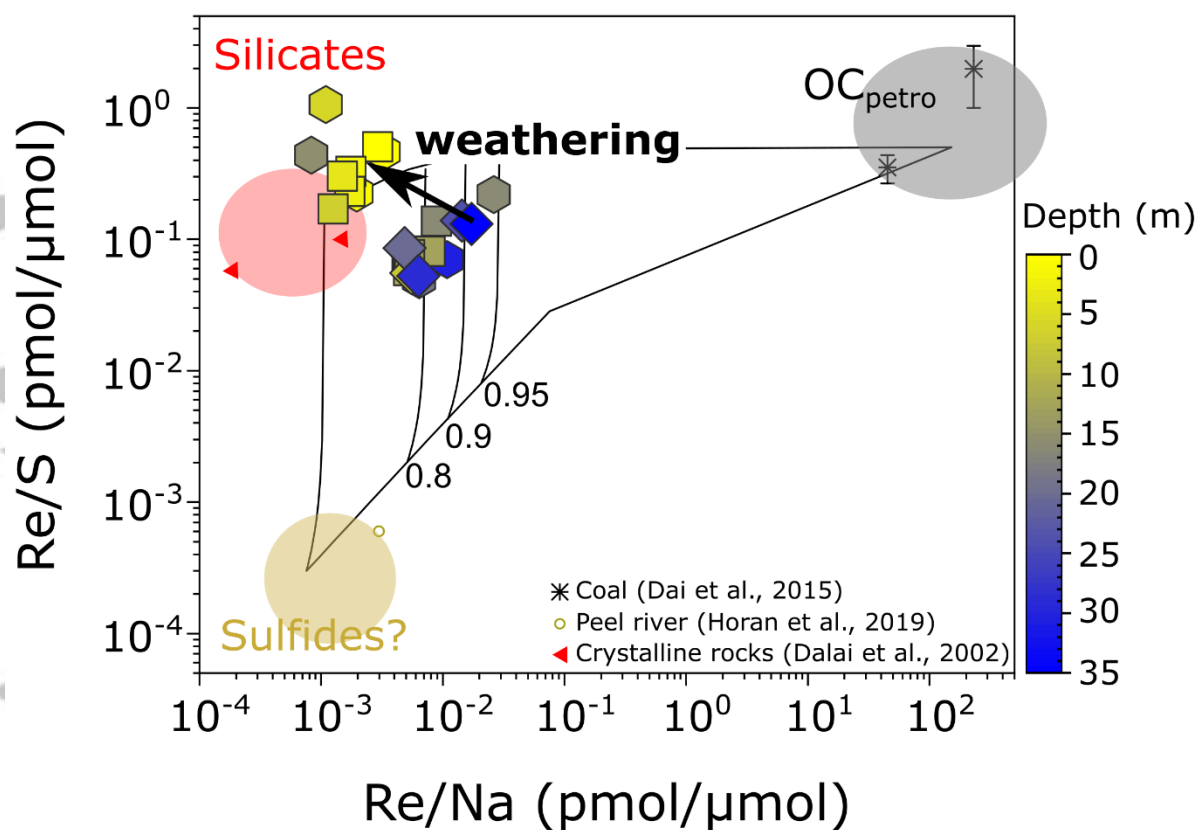
profile from the ridge (CZMW8). (c)  $\tau_{Zr,Re}$  profile from the ridge (CZMW8). (d)  $\tau_{Zr,S}$  profile from the valley (CZMW2, CZMW10). Data and interpretation is from (Brantley et al., 2013; Gu et al., 2020a). (e)  $\tau_{Zr,TOC}$  profile from the valley. (f)  $\tau_{Zr,Re}$  profile from the valley.

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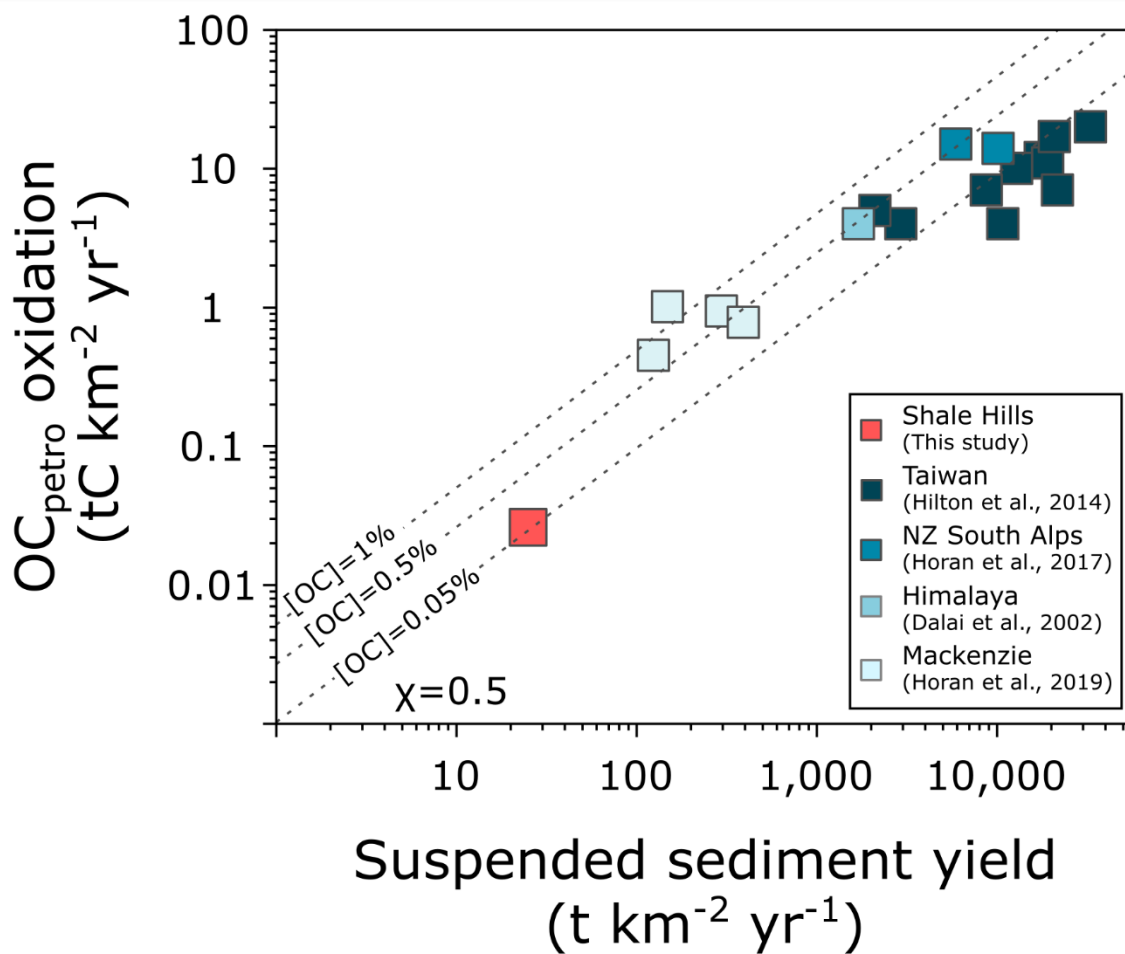


**FIGURE 4** (a) Modelled rock organic carbon concentrations ( $OC_{\text{petro}}$ ) determined from radiocarbon measurements on the samples from the ridge borehole (CZMW8). (b) Mass transfer coefficients plotted versus depth to track mobility of  $OC_{\text{petro}}$ . Parent composition was determined from the concentration measured on the deepest protolith sample in CZMW8. Zirconium (Zr) was used as an immobile element.



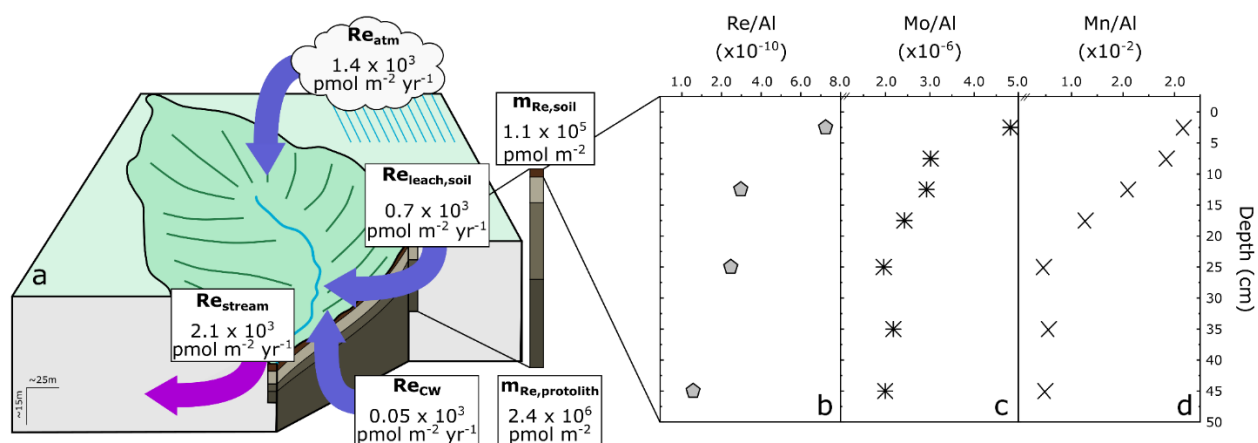
**FIGURE 5** Source of rhenium at the study site using Re/Na versus Re/S ratio from the three boreholes studied here: CZMW2 (valley, squares), CZMW10 (valley, diamonds), CZMW8 (ridge, hexagons). The shaded areas represent the likely end-member composition, based on limited data available in the literature (Dalai et al., 2002; Horan et al., 2019).

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**FIGURE 6** Global compilation of the control of erosion on  $OC_{\text{petro}}$  oxidation rates ( $tC \text{ km}^{-2} \text{ yr}^{-1}$ ) determined with the Re proxy. The suspended sediment yield is a proxy for erosion rate. For Shale Hills, the suspended sediment yield is estimated from the long-term denudation rate estimates (Ma et al., 2011). The stippled lines represent expected weathering rates for various initial organic carbon contents (as shown) and a weathering intensity ( $\chi$ ) of 50%.

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**FIGURE 7** Reservoirs ( $\text{pmol m}^{-2}$ ) and fluxes ( $\text{pmol m}^{-2} \text{ yr}^{-1}$ ) of rhenium (Re) at the Shale Hills catchment.

The blue arrows represent Re input to the catchment through different geochemical processes. The purple arrow represents Re output from the catchment. Abbreviations:  $Re_{atm}$  = Re derived through present day atmospheric deposition;  $Re_{cw}$  = Re derived through chemical weathering of the protolith;  $Re_{leach,soil}$  = Re leaching through surface soils;  $Re_{stream}$  = Re export from the catchment via stream discharge;  $m_{Re,soil}$  = Re stock in the top 0.5 m of the surface soils;  $m_{Re,protolith}$  = Re stock over 11 m of the protolith.

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