

## Mobility of rhenium, platinum group elements and organic carbon during black shale weathering

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### Abstract

This study investigates the effects of black shale weathering on the Re–Os isotope system, platinum group element concentrations and the degradation of organic matter. Samples from a weathering profile in Late Devonian (~365 Myr) Ohio Shale show a pronounced decrease (~77%) in organic carbon ( $C_{\text{org}}$ ) near the present soil surface, relative to the interior portion of the outcrop. A similar trend is observed for total N (~67% loss). Conversely, organic phosphorus ( $P_{\text{org}}$ ) concentrations increase by ~59% near the soil surface. The decrease in  $C_{\text{org}}$  is accompanied by a pronounced decrease in Re (~99%) and, to a lesser extent, Os (~39%). Palladium and Pt do not appear to be significantly mobile. The effects of Re and Os mobility on the Re–Os isotope system are significant: none of the samples plots on a 365 Myr isochron. Rather, the samples define a trend with a slope corresponding to an age of ~18 Myr with an initial  $^{187}\text{Os}/^{188}\text{Os}$  of ~6.1. This indicates recent disturbance of the Re–Os system. Isotope mass balance calculations imply that the labile fraction of Os is significantly more radiogenic ( $^{187}\text{Os}/^{188}\text{Os}$  of ~7.8) than the average of the unweathered samples ( $^{187}\text{Os}/^{188}\text{Os}$  of ~6.4). Based on data from this study, the molar ratio of labile Re to  $C_{\text{org}}$  in Ohio Shale is estimated at  $7 \times 10^{-8}$ . We estimate the present-day riverine, black shale-derived Re flux to seawater using literature data on Re burial in anoxic marine sediments, and assuming steady-state between Re release during black shale weathering and Re burial in anoxic marine sediments. Then, the labile Re/ $C_{\text{org}}$  observed in this study implies that ~0.5 Tmol of  $C_{\text{org}}$  is released annually from weathering of black shales, a trace lithology in the continental crust. This flux corresponds to ~12% of the estimated annual  $\text{CO}_2$  flux from oxidative weathering of sedimentary rocks. The labile molar Re/Os of ~270 indicates that black shale weathering releases ~130 mol Os per year, which accounts for ~7% of the riverine Os input to seawater. The data from this study support the notion that the crustal cycles of labile  $C_{\text{org}}$ , Re and Os are tightly coupled. Gray shales, which are less  $C_{\text{org}}$ -, Re- and Os-rich, but much more abundant in the continental crust than black shales, are likely to be even more important continental sources of Re and Os to seawater. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The  $^{187}\text{Os}/^{188}\text{Os}$  of seawater has increased by  $\sim 260\%$  since the Cretaceous–Tertiary boundary [1–3]. This and the corresponding increase in the marine  $^{87}\text{Sr}/^{86}\text{Sr}$  have been interpreted to reflect increased silicate weathering [1,2,4,5] during the Cenozoic, resulting in long-term net consumption of atmospheric  $\text{CO}_2$ . Ravizza et al. [6] and Peucker-Ehrenbrink and Ravizza [3] recently suggested an alternative mechanism for the observed increase in the marine  $^{187}\text{Os}/^{188}\text{Os}$  during much of the Cenozoic. They argue that weathering of sediments rich in organic matter (OM) at a constant rate will lead to increasing  $^{187}\text{Os}/^{188}\text{Os}$ , because such sediments are characterized by high  $^{187}\text{Re}/^{188}\text{Os}$  ( $\sim 800$ ). If correct this implies that the trend towards more radiogenic marine  $^{187}\text{Os}/^{188}\text{Os}$  during much of the Cenozoic does not need to reflect a change in the weathering flux of Os from OM-rich sediments. However, since this mechanism was proposed, new data suggest that the majority of OM-rich sediments are characterized by an average  $^{187}\text{Re}/^{188}\text{Os}$  of  $\sim 300$ . This indicates that only  $\sim 1/3$  of the observed increase in the marine  $^{187}\text{Os}/^{188}\text{Os}$  can be accounted for by steady-state erosion of OM-rich sediments. In addition, the inferred secular increase in erosion rates during the Neogene implies a corresponding increase in weathering of OM-rich sediments, because it is unlikely that a trace lithology in the continental crust does not respond to a global increase in continental erosion. Although increased weathering of OM-rich sediments is also consistent with the marine  $^{187}\text{Os}/^{188}\text{Os}$  record, the magnitude of this increase in weathering rate can be smaller than that required by models of the  $^{187}\text{Os}/^{188}\text{Os}$  record that do not take into account radiogenic ingrowth within the OM-rich sediment reservoir. Improving our understanding of the coupling between the surficial cycles of Re, Os and  $\text{C}_{\text{org}}$  in OM-rich sediments may help to better constrain temporal changes in global weathering fluxes. Such constraints have important implications for the interpretation of the  $\delta^{13}\text{C}$  record of bulk marine carbonate, the related burial flux of marine OM, and

the net flux of  $\text{O}_2$  and  $\text{CO}_2$  to or from the sedimentary  $\text{C}_{\text{org}}$  subcycle [7].

Previous weathering studies have shown that OM-rich sediments lose most of their  $\text{C}_{\text{org}}$  upon exposure to oxidizing surface conditions [8–14]. In this study, we investigate the mobility of Re, Os and complementary platinum group elements (PGE) during weathering of OM-rich sediments taken from a weathering profile exposed in Upper Devonian ( $\sim 365$  Myr) Ohio Shale in Kentucky, USA. A similar study, conducted by Peucker-Ehrenbrink and Hannigan [11], compares unweathered samples from drill cores with their weathered, time-correlative equivalents from nearby ( $< 1$  km) outcrops in Upper Ordovician Utica Shale from Quebec, Canada. Although utmost care was taken in that study to ensure that weathered–unweathered pairs were collected from the same bed (i.e. time-correlative), the possibility remains that some of the observed chemical variability reflects temporal and spatial variability at the time of deposition, rather than the effects of weathering. This prompted us to reevaluate the effects of black shale weathering on the mobility of Re–Os and complementary PGE. Combined, these two studies yield a clearer view of how degradation of OM during weathering of black shales affects the Re–Os isotope system and the mobility of Re and PGE.

## 2. Samples

A road cut ( $37^\circ 52.167' \text{N}$ ,  $83^\circ 56.767' \text{W}$ ) near Clay City (Powell County, KY, USA) exposes a weathering profile in Upper Devonian ( $\sim 365$  Myr) Ohio Shale (Fig. 1; see also [12–15], termed ‘New Albany Shale’ in [13–15]). The Ohio Shale was deposited in a highly productive, oxygen deficient, epicontinental marine environment to the west of the eastern part of the North American craton. The majority of the OM is derived from marine phytoplankton (kerogen type II), with minor contributions from bacteria and terrestrial plants [13]. Sulfate reduction during early diagenesis led to formation of abundant pyrite and sulfurization of OM [13]. Ohio Shale in Powell

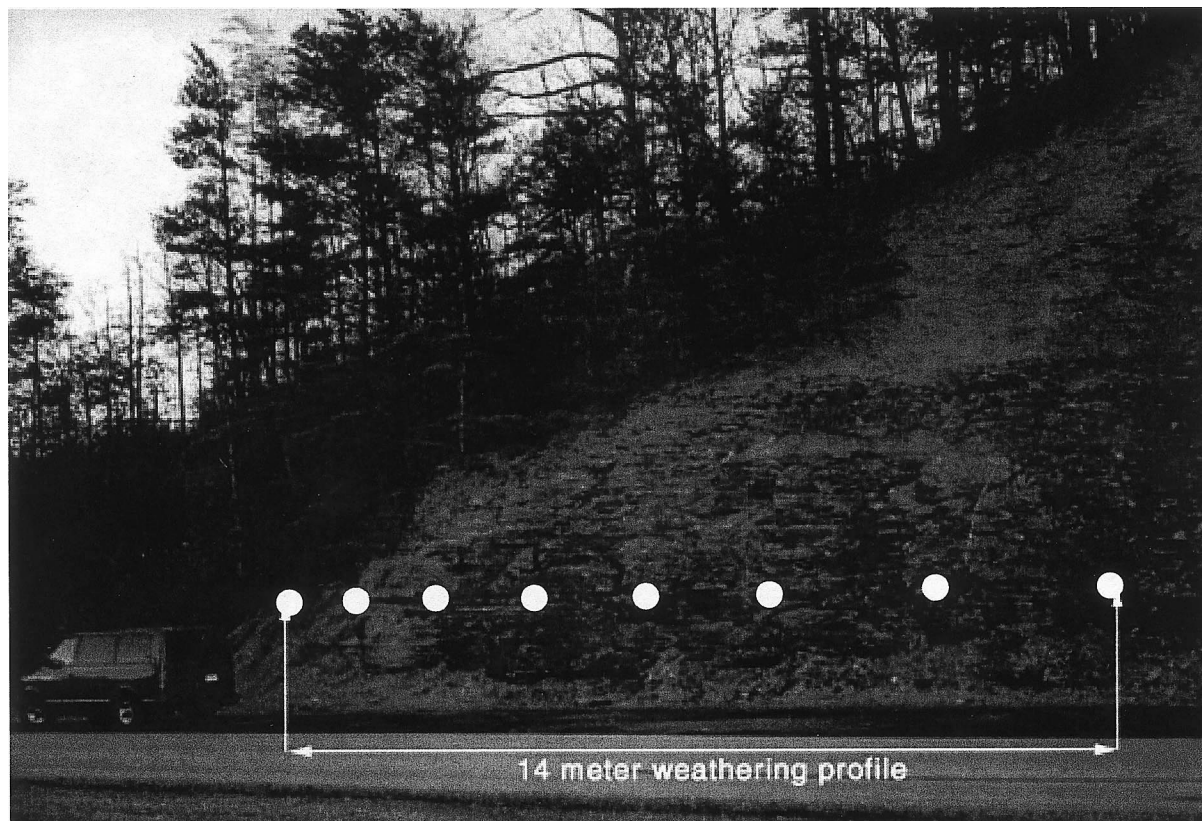


Fig. 1. Ohio Shale weathering profile exposed near Clay City, KY, USA. Sample locations are marked (white circles), starting from the soil horizon (left, 0 m) to the interior of the outcrop (right, 14 m). Note the 2–4 m thick, light colored, intensely weathered zone underneath the present soil horizon.

County is characterized by very low vitrinity reflectance ( $R_o = 0.53$ ), indicative of thermally immature shales [16]. Creaser et al. [17] have shown that hydrocarbon overmature organic-rich shales from the Devonian–Mississippian Exshaw Formation in the Western Canada Sedimentary Basin plot on the same Re–Os isochron as immature shales from the same formation. This indicates that thermal maturation of OM-rich sediments has little effect on the Re–Os isotope system.

In January 2000, we collected eight samples from a single,  $\sim 10$  cm thick horizontal bed of the Huron Member of the Ohio Shale, starting from the present soil horizon (0 m) to 14 m into the interior of the outcrop (Fig. 1). We attempted to minimize the effects of weathering and contamination of the outcrop surface during the 40 yr

since the road cut was blasted by digging  $\sim 10$  cm into the outcrop before removing samples. The samples were collected as close to a single,  $\sim 10$  cm thick stratigraphic horizon as possible, in order to maintain homogeneity in the original chemistry of the sediments and to minimize chemical fluctuations due to lateral depositional variation. We estimate that variations in the vertical positioning of samples relative to the targeted stratigraphic horizon are less than 2 cm. Minimizing such variations is important in order to minimize variations in the initial shale chemistry. Samples near the present soil surface (0–3 m) are light brown and friable. Further into the weathering profile ( $> 3$  m) the samples become much darker brown to black in color and harder to break. Samples from 6–14 m contain abundant

pyrite and appear fresh. Previous work on this weathering profile [13–15] revealed significant decrease in  $C_{\text{org}}$  and pyrite S as well as progressive relative loss of aliphatic carbon and a relative gain in aromatic carbon in the direction of the present soil horizon.

The location of the Clay City outcrop is south of the southernmost extent of the late Cenozoic ice sheets. The  $\sim 2\text{--}4$  m thick, fully oxidized weathering zone may thus be significantly older than post-glacial.

### 3. Analytical procedures

The samples were dried at  $60^\circ\text{C}$  until their weight was constant ( $<1\%$  change). Subsequently, the samples were crushed into pea-sized chunks with a Teflon rod and powdered in an Al-ceramic shatter box. All analytical data are reported on a dry sediment basis.

Total carbon and total nitrogen were analyzed on 5–10 mg sample splits using a PE 2400 CHN Elemental Analyzer at WHOI. Inorganic carbon (carbonate carbon) was measured on a Coulometrics  $\text{CO}_2$  Coulometer using 5–10 mg sample splits. Total and inorganic phosphorous were determined with the Aspila method [18] on 5–10 mg powdered samples. Phosphorus was analyzed in quadruplicate using the phosphomolybdate blue method [19], and samples with concentration variations exceeding 5% were reanalyzed. Organic carbon ( $C_{\text{org}}$ ) and organic phosphorous ( $P_{\text{org}}$ ) were determined by difference. The negligible inorganic carbon concentrations made uncertainties in the calculation of  $C_{\text{org}}$  contents by difference very small.

For Os and PGE analysis, we followed the procedure developed by Ravizza and Pyle [20]. Between 5 and 10 g powdered samples were spiked with a solution enriched in  $^{99}\text{Ru}$ ,  $^{105}\text{Pd}$ ,  $^{190}\text{Os}$ ,  $^{191}\text{Ir}$ , and  $^{198}\text{Pt}$ , then mixed with a borax–nickel–sulfur flux. This mixture was fused for 120 min at  $1020^\circ\text{C}$  into a nickel–sulfide bead containing the metals of interest. This bead was dissolved in 6.2 N HCl, and the solution was passed through a  $0.45\ \mu\text{m}$  cellulose filter, capturing the insoluble PGE-containing particles onto the filter paper.

This paper was dissolved in hot, concentrated, ultrapure  $\text{HNO}_3$  to dissolve the PGE. The sparging method [21] was then used to determine the  $^{187}\text{Os}/^{188}\text{Os}$  and Os concentration with a Finnigan Element inductively coupled plasma-mass spectrometer (ICP-MS). Analysis of PGE was subsequently performed on the liquid residue after sparging using the ICP-MS with conventional liquid uptake. All samples were analyzed in duplicate for  $^{187}\text{Os}/^{188}\text{Os}$  and PGE concentrations. Unless otherwise noted, average values are reported that have been corrected for loss of OM during weathering. To simplify this correction we assume that the labile OM has an idealized chemical composition of  $\text{CH}_2\text{O}$  (i.e. 40 wt%  $C_{\text{org}}$ ). The choice of OM composition is not critical as all corrections affect the measured values by less than 20%.

Rhenium was analyzed by first ashing approximately 1 g of sample at  $400^\circ\text{C}$  for 12 h in a muffle furnace without active air flow to oxidize the OM and to facilitate dissolution with mineral acids. Experiments by Singh et al. [22] show that this pretreatment does not volatilize Re. About 100 mg of ashed sample was then placed into microwave bombs together with a  $^{185}\text{Re}$  spike solution and a mixture of concentrated HF, HCl, and  $\text{HNO}_3$  acids. Subsequently, the solution was dried down and redissolved in concentrated ultrapure  $\text{HNO}_3$ . Rhenium was separated using anion exchange columns and analyzed by ICP-MS [23].

In order to investigate the effects of ashing on the Os concentration of black shales, 2 g of sample from 11 m and 14 m was ashed at  $400^\circ\text{C}$  for 12 h. These samples were analyzed in duplicate to determine the loss of Os due to volatilization of  $\text{OsO}_4$ . These samples were prepared for ICP-MS analysis in the same fashion as the unashed samples.

## 4. Results and discussion

### 4.1. OM

Concentrations of  $C_{\text{org}}$ , total N, and  $P_{\text{org}}$  were measured to determine the influence weathering has on  $C_{\text{org}}/\text{N}/P_{\text{org}}$  ratios (Figs. 2 and 3). Fig. 2b,c shows  $C_{\text{org}}$  and total N concentrations over

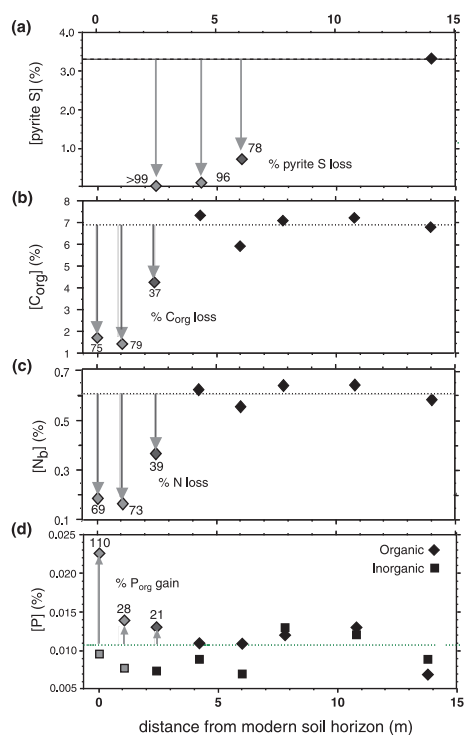


Fig. 2. Pyrite sulfur (a; data from [13] were measured on different samples from the same stratigraphic horizon. Distances were converted from those perpendicular to the outcrop surface to those parallel to the bedding plan), organic carbon (b), bulk nitrogen (c) and inorganic (squares) and organic (diamonds) phosphorus (d) concentrations, corrected for weight loss due to loss of OM near the surface. Apparently unweathered samples are shown in black, moderately weathered samples in dark gray, and intensely weathered samples in light gray. Stippled lines approximate initial concentrations before weathering. The calculated relative loss near the weathering surface is given for each element.

the profile. Surface samples (0 and 0.9 m) show a significant decrease ( $\sim 77\%$   $C_{\text{org}}$ ,  $\sim 71\%$  N) in concentration relative to samples deeper into the profile ( $> 4.2$  m). Concentrations of  $P_{\text{org}}$  along the profile (Fig. 2d) show that the weathered samples have higher  $P_{\text{org}}$  concentrations ( $\sim 59\%$  gain) than the rest of the profile. This may be a result of external  $P_{\text{org}}$  input (rain, aerosols, etc.) or reflect redistribution of  $P_{\text{org}}$  from anoxic portions of the profile to the oxidative weathering front. Organic phosphorus is mobile under acidic anoxic conditions and may be redeposited in the oxic portion

of the profile in association with Fe-oxyhydroxides (K. Ruttenger, personal communication, 2001). The latter explanation is supported by the observed  $\sim 50\%$  increase in total Fe concentration near the surface of the profile (Table 1). Alternatively, the increase in  $P_{\text{org}}$  towards the surface may reflect bioaccumulation of phosphate by soil microbiota. Petsch et al. [15] report a  $> 10$ -fold increase in phospholipid fatty acid concentrations towards the weathering surface at the Clay City outcrop.

Each nutrient profile ( $C_{\text{org}}$ , total N,  $P_{\text{org}}$ ) shows near constant values beyond  $\sim 4$  m, indicating that surficial weathering has affected  $C_{\text{org}}$ , total N, and  $P_{\text{org}}$  concentrations only in the outermost  $\sim 4$  m. Profiles for pyrite S (Fig. 2a) indicate that it is much more susceptible to weathering than  $C_{\text{org}}$ . However, samples from 6–14 m still contain abundant pyrite S, indicating that oxidative weathering has little effect on shales deeper into the profile. All calculations of element mobility are based on the assumption that these samples represent virtually unweathered shales. We will show later that apparently unweathered samples have been affected by remobilization of Re. We will use Re–Os isotope systematics to calculate primary Re concentrations to correct for this remobilization process. The calculated primary Re concentrations are slightly lower than those measured in samples from 6–14 m, and calculated Re mobility is based on these corrected concentration values.

Ohio Shale is highly enriched in  $C_{\text{org}}$  relative to N and  $P_{\text{org}}$  (Fig. 3), when compared to fresh marine OM. High  $C_{\text{org}}/N/P_{\text{org}}$  ratios of  $\sim 1630/125/1$  are not uncommon for black shales, which can boast values as high as  $\sim 5000/170/1$  [24]. Preferential release of  $P_{\text{org}}$  and N during early diagenesis results in elevated  $C_{\text{org}}/N$  and  $C_{\text{org}}/P_{\text{org}}$  (e.g. [24–26]). As  $C_{\text{org}}$  concentrations in OM-rich sediments are generally positively correlated with Re and Os concentrations (e.g. [27–29]), unweathered OM-rich sediments have high Re and Os concentrations relative to average continental crust. The fate of Re and Os during weathering of OM-rich sediments may therefore significantly impact the mobile inventory of these elements in the continental crust.

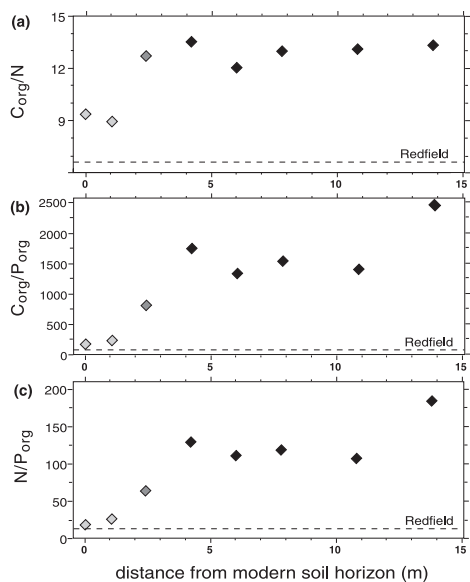


Fig. 3. Organic carbon/bulk nitrogen (a), organic carbon/organic phosphorus (b), and bulk nitrogen/organic phosphorus (c) values for the weathering profile. Redfield ratios are marked with stippled lines.

#### 4.2. Rhenium and osmium

Rhenium concentrations decrease by  $\sim 99\%$  within 2.4 m of the present soil surface (Fig. 4a, note logarithmic scale on ordinate), whereas the interior of the profile is characterized by high ( $\sim 88$  ng/g) and fairly constant Re concentrations. Rhenium concentrations are positively correlated with  $C_{\text{org}}$  concentrations over the profile ( $r^2 = 0.78$ ), supporting the hypothesis that Re is closely associated with  $C_{\text{org}}$ .

In contrast to Re, Os concentrations do not correlate well with  $C_{\text{org}}$  content (Fig. 4b, cf. [30]). Although the lowest Os concentration (357 pg/g) is observed in the present soil horizon, its second highest concentration (622 pg/g) corresponds to the lowest  $C_{\text{org}}$  concentration of 1.46 wt% at 0.9 m. Furthermore, the second lowest concentration (487 pg/g) occurs at 14 m, a significant drop in concentration relative to the remainder of the seemingly unweathered samples. Duplicate Os analyses of all samples show that Os concentrations deviate by less than 3% from the average, which indicates that the scatter is not caused by analytical problems. As the low Os

concentration at 14 m does not coincide with low Re or  $C_{\text{org}}$  concentrations, processes other than oxidative weathering may influence the mobility of Os in the apparently unweathered portion of the outcrop. The  $\sim 39\%$  decrease in Os concentration near the soil surface is the only fluctuation in Os concentration that can be confidently attributed to surficial weathering. These data may therefore indicate that Os is less mobile during weathering than Re. Alternatively, mobilization of Os may be partly masked by adsorption of Os onto Fe-oxyhydroxides near the weathering surface (note elevated Fe concentrations, Table 1), leading to samples that are less depleted in Os than Re. Pierson-Wickmann et al. [31] have shown that Fe-oxyhydroxide coatings on altered black shales have high Os, but low Re concentrations. Adsorption of Os, but not Re, onto Fe-oxyhydroxides as an explanation for the observed Os and Re profiles is consistent with significant enrichments of Os, but little Re, in oxic metalliferous marine sediments [32].

Results from the ashing experiments, designed to oxidize OM, show up to  $\sim 85\%$  loss in Os. This experiment suggests that the majority of the Os in these samples is associated with OM. Natural loss of Os ( $\sim 39\%$ ) during black shale weathering is significantly smaller despite near quantitative loss of  $C_{\text{org}}$ . This discrepancy is likely caused by the very different removal mechanisms of Os by ashing (loss of volatile  $\text{OsO}_4$ ) compared with natural weathering (partial loss of dissolved Os). Under natural conditions, adsorption of Os onto Fe-oxyhydroxides near the weathered surface may scavenge a significant portion of the Os that was originally associated with OM. The  $\sim 15\%$  decrease in  $^{187}\text{Os}/^{188}\text{Os}$  upon ashing is similar to the observed decrease in  $^{187}\text{Os}/^{188}\text{Os}$  ( $\sim 11\%$ ) as a result of weathering near the surface, proposing that radiogenic  $^{187}\text{Os}$  is more easily volatilized during ashing of OM and more easily lost during weathering than common Os.

#### 4.3. PGE

In contrast to previous results for black shales from the Utica Shale Formation in Quebec, Canada [11], Pd and Pt concentrations do not vary

Table 1  
Geochemical data for a weathering profile in Late Devonian Ohio Shale near Clay City, KY, USA

Sample no.	Distance (m)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	C <sub>org</sub> (wt%)	N (wt%)	P <sub>org</sub> (wt%)	P <sub>inorg</sub> (wt%)	Os (pg/g)	Ir (pg/g)	Pt (ng/g)	Pd (ng/g)	Re (ng/g)	<sup>187</sup> Os/ <sup>188</sup> Os (± 2σ)	<sup>187</sup> Re/ <sup>188</sup> Os
244	0.0	6.10	1.75	0.19	0.023	0.010	356	76	1.27	2.46		5.762 ± 0.021	18.3
252	0.0										0.89		
276	0.0						358	40	1.16	2.72		5.698 ± 0.073	18.1
245	0.91	7.06	1.46	0.17	0.014	0.008	627	50	1.84	2.54		6.434 ± 0.018	10.3
253	0.91										0.85		
277	0.91						615	41	1.79	2.65		6.434 ± 0.011	10.5
246	2.44	4.07	4.29	0.37	0.013	0.007	600	29	3.30			6.090 ± 0.113	237
254	2.44										17.7		
278	2.44						593	27	1.65	2.64		6.240 ± 0.030	242
247	4.27	3.81	7.3	0.6	0.11	0.009	592	15	1.84	2.34		6.528 ± 0.026	1335
255	4.27										89.4		
279	4.27						596	19	1.71	2.19		6.502 ± 0.109	1324
248	6.10	4.23	5.95	0.55	0.011	0.007	583	62	1.77	2.64		6.409 ± 0.017	1738
256	6.10										115.6		
280	6.10						552	17	1.62	2.09		6.390 ± 0.017	1834
249	7.92	4.79	7.13	0.64	0.012	0.013	649	33	1.63	2.76		6.386 ± 0.051	1006
257	7.92										74.5		
281	7.92						659	25	1.69	2.08		6.381 ± 0.046	998
285	7.92										75.1		
250	10.97	4.69	7.80	0.64	0.013	0.012	626	58	1.83			6.376 ± 0.028	1132
258	10.97										81.1		
282	10.97						624	24	1.62	2.00	81.0	6.303 ± 0.026	1131
272	10.97ash						66	19	1.54			5.814 ± 0.243	
274	10.97ash						78	61	2.22	2.41		5.327 ± 0.753	
251	14.02	4.53	6.75	0.58	0.007	0.009	482	20	1.40			6.959 ± 0.034	1477
259	14.02										78.0		
283	14.02						493	21	1.40	1.80		6.824 ± 0.026	1429
284	14.02										81.0		
273	14.02ash						70	27	1.31			5.970 ± 0.081	
275	14.02ash						113	73	1.97	1.87		5.871 ± 0.071	

Distance was measured from the weathering surface parallel to the nearly horizontal bedding plane into the outcrop. Different sample numbers for the same distance represent duplicate analyses of different splits of the same powder. Fe<sub>2</sub>O<sub>3</sub> was analyzed by ICP-MS at the Centre de Recherches Pétrographiques et Géochimiques (CNRS) in Nancy, France, with a relative uncertainty of ~1%. <sup>187</sup>Re/<sup>188</sup>Os were calculated for replicate Os isotope analyses using the Re concentration determined on a different sample split. Blank corrections are <10% for all elements. Values for the WHOI Os standard measured to monitor accuracy and precision of the sparging method [21] are: 0.17514 ± 1.05% (1 S.D., *n* = 5) for 80 pg total Os, 0.17453 ± 0.88% (1 S.D., *n* = 10) for 80–400 pg total Os and 0.17404 ± 0.21% (1 S.D., *n* = 9) for 1.23 ng total Os. These values are within uncertainty of the long-term average of 0.17410 ± 0.14% for the same standard using N-TIMS (NIMA-B). All concentrations are reported on a dry sediment basis, and were corrected for changes in mass caused by organic carbon loss (see text).

systematically along the profile and do not appear to be affected by weathering (Table 1). Surprisingly, duplicate Pd and Pt analyses of some, but not all, samples reproduce poorly. The high absolute Pd and Pt concentrations make it unlikely that these variations are caused by analytical problems such as blank corrections. As variations in Pd concentrations are not necessarily correlated with variations in Pt concentrations, Pd and Pt

are likely hosted in more than one phase. Palladium, Ir, and Pt show minimal trends relative to C<sub>org</sub> loss along the profile, with correlation coefficients of  $r^2 = 0.55$ ,  $r^2 = 0.05$ , and  $r^2 = 0.54$ , respectively. Iridium concentrations in all samples are comparable to average upper crustal values [33] that reflect lack of Ir enrichment in OM-rich sediments. Iridium concentrations in different splits of the same sample can vary by as much as

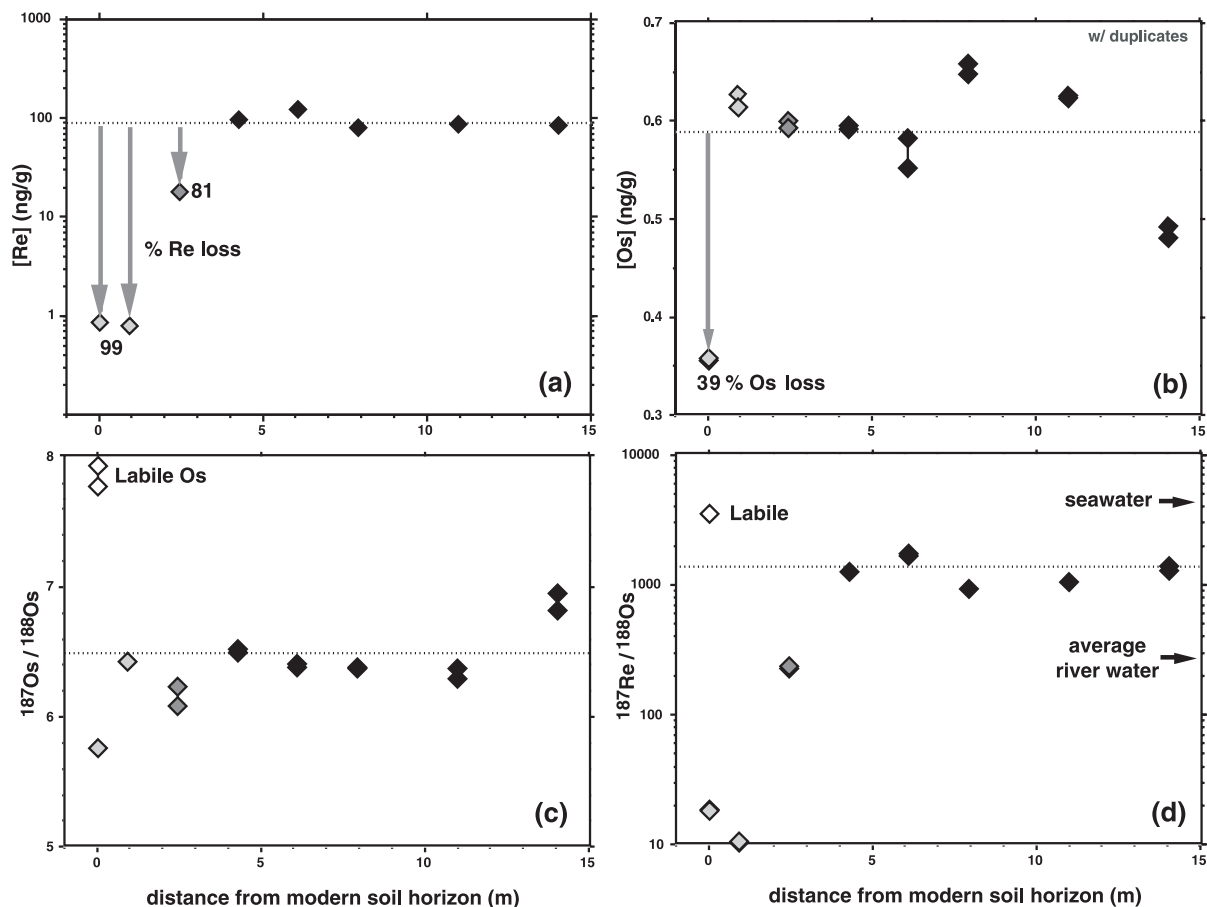


Fig. 4. Rhenium (a) and Os (b) concentrations as well as  $^{187}\text{Os}/^{188}\text{Os}$  (c) and  $^{187}\text{Re}/^{188}\text{Os}$  (d) values for the weathering profile. Concentrations are corrected for weight loss due to OM loss near the weathering surface. Stippled lines mark average composition of apparently unweathered samples. The labile component (open diamonds) has been calculated based on the difference between initial Re and Os concentrations and isotope ratios and the residual concentrations and isotope ratios after weathering. Note that the labile  $^{187}\text{Os}/^{188}\text{Os}$  is more radiogenic than all bulk samples. The labile component has a significantly higher  $^{187}\text{Re}/^{188}\text{Os}$  than average present-day river water (arrow), similar to that of present-day seawater (arrow).

a factor of 3.6 (sample at 6.1 m, sample #248, #280, Table 1), indicative of non-homogenous distribution of a trace phase (nugget effect). Consequently, the data do not provide clear evidence for Ir mobilization. It should be noted that Ir loss during black shale weathering, inferred in a previous study [11], is very small and possibly insignificant.

The Utica Shale study [11] compares outcrop samples with samples from a drilled core several hundred meters away. Spatial and temporal variation may have played a larger role in the chemical variation of the Utica Shale samples than

originally recognized [11]. In contrast, the present study investigates the chemistry of samples over a 14 m long profile and may thus more accurately reflect the effects of surficial weathering by substantially limiting the effects of depositional variability. Results from both studies are consistent in that they show significant losses in Re and, to a lesser degree, Os in the most weathered samples (Fig. 5).

#### 4.4. $^{187}\text{Re}$ – $^{187}\text{Os}$ systematics

Ratios of  $^{187}\text{Os}/^{188}\text{Os}$  for all samples, except the



soil sample ( $^{187}\text{Os}/^{188}\text{Os}$  of  $\sim 5.7$ ), average 6.447 with a standard deviation (S.D.) of  $\sim 3.5\%$ , indicating that the samples are isotopically quite homogenous throughout the profile (Fig. 4c). Uniform  $^{187}\text{Os}/^{188}\text{Os}$  stands in marked contrast to the extremely variable  $^{187}\text{Re}/^{188}\text{Os}$  (Fig. 4d). The Re–Os isochron diagram (Fig. 6) suggests recent open-system behavior. The  $^{187}\text{Os}/^{188}\text{Os}$  of Late Devonian seawater, and thus the initial  $^{187}\text{Os}/^{188}\text{Os}$  of the Ohio Shale, is unknown. However, the marine  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{187}\text{Os}/^{188}\text{Os}$  records correlate reasonably well during the Cenozoic (e.g. [1–3]). We therefore use the Late Devonian seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.708 [34,35] as a proxy for the marine  $^{187}\text{Os}/^{188}\text{Os}$ , and argue that Late Devonian seawater  $^{187}\text{Os}/^{188}\text{Os}$  may have been fairly radiogenic ( $\sim 0.7$ ). None of the samples plots along a 365 Myr isochron (approximate depositional age of the samples [12–15]), independent of the choice of permissible initial  $^{187}\text{Os}/^{188}\text{Os}$ . Rather, a linear least square fit of all data corresponds to an age of  $\sim 18$  Myr, with an initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $\sim 6.1$ .

There are two potential explanations for this observation. First, as noted by Ravizza et al. [28] for OM-rich sediments from the Black Sea, mixing lines with negative slopes at the time of deposition can develop positive slopes due to radioactive ingrowth of  $^{187}\text{Os}$  over time, thereby yielding an age that is significantly younger than the depositional age (see figure 10 in [28]). A

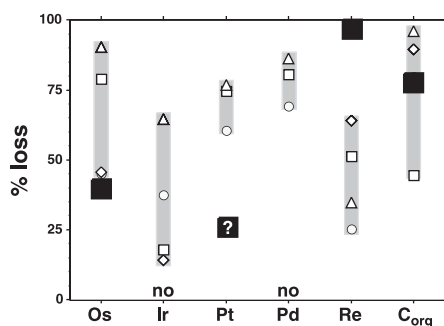


Fig. 5. Comparison of the relative losses of Os, Ir, Pt, Pd, Re and  $C_{\text{org}}$  between this study (black squares) and a previous study [11] of the Utica Shale (gray fields with symbols for the four time-correlative weathered–unweathered sample pairs). Note that absolute Ir mobility in the Utica Shale is very small because Ir concentrations are as low as average upper crust (22 pg/g; [33]).

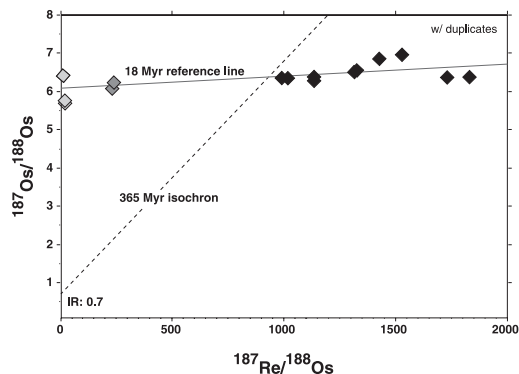


Fig. 6. Rhenium–osmium isochron diagram for the Ohio Shale. The samples (shown with duplicates) plot along a 18 Myr reference line. A 365 Myr isochron is shown for comparison.

reference line with a slope corresponding to an age of  $\sim 18$  Myr could thus be consistent with closed-system behavior for sediments deposited 365 Myr. However, this would require the samples to have plotted along a mixing line with a steep negative slope and an initial  $^{187}\text{Os}/^{188}\text{Os}$  of  $\sim 6.1$ . The only viable radiogenic end member for this scenario is weathered black shales with a  $^{187}\text{Os}/^{188}\text{Os}$  of  $\sim 6.1$ , and very low  $^{187}\text{Re}/^{188}\text{Os}$ , similar to the weathered samples from the Ohio Shale profile. We reject this explanation for the observed correlation because it is highly unlikely that weathered black shales (i.e. a trace lithology in the continental crust) dominated the input of detrital Os into the Ohio Shale depositional environment.

Our preferred interpretation of the Re–Os isochron diagram assumes recent open-system behavior, consistent with chemical trends observed along the weathering profile. As the shales are of Late Devonian age, and seawater  $^{187}\text{Os}/^{188}\text{Os}$  has probably never significantly exceeded the present-day riverine  $^{187}\text{Os}/^{188}\text{Os}$  of  $\sim 1.4$ , the disturbance of the Re–Os system must have occurred recently. Samples that plot to the left of the intersect between the 365 Myr isochron and the 18 Myr reference line must have recently experienced up to 99% Re loss or at least four-fold Os addition (Fig. 7). Concentration data for Re and Os strongly favor the former. In contrast, samples plotting to the right of the intersect between the

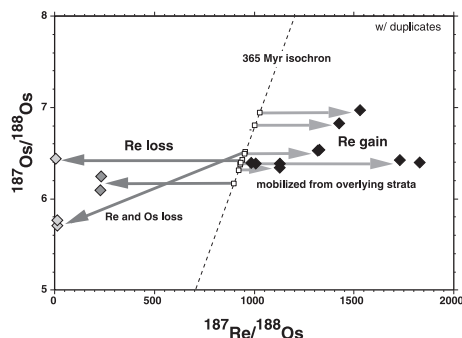


Fig. 7. Open-system scenario for the observed Re–Os isochron relationships. See text for discussion.

two lines must have experienced up to two-fold increase in Re concentration or a 50% loss of Os. As these are exclusively samples with high  $C_{org}$  concentrations, loss of Os appears an unlikely explanation. Addition of Re, however, could be caused by weathering of the shale beds that overlie our profile. Some of the Re mobilized from overlying, weathered strata could have moved downward through cracks in the subsurface and, temporarily, be redeposited under anoxic conditions in the unweathered horizons below (Fig. 8). The observed large spread in  $^{187}\text{Re}/^{188}\text{Os}$  could thus be a consequence of Re redistribution during weathering, evolving from the rather uniform  $^{187}\text{Re}/^{188}\text{Os}$  of  $\sim 800$  at the time of deposition (open squares on the 365 Myr isochron) that is typical for black shales [3,6]. This explanation is consistent with the fact that none of the apparently unweathered samples plots on a 365 Myr isochron. This confirms our suspicion that the chemistry of apparently unweathered samples from the center of the outcrop is not entirely unaltered. Preliminary results from an ongoing U–Th disequilibrium study reveal large disequilibria in  $^{234}\text{U}$ – $^{238}\text{U}$  and  $^{230}\text{Th}$ – $^{238}\text{U}$ , supporting this conclusion [36]. Element mobility is facilitated by pH as low as 1.8, measured in surface runoff from the road cut after rainfall in May 2001. Despite the observed Re mobility, average primary Re concentrations (small diamonds in Fig. 7) can be reconstructed using Re–Os isotope systematics. Average primary Re concentrations are estimated at  $\sim 63$  ng/g by projecting samples that lie to the right of the intersect between the 18 Myr reference

line and the 365 Myr isochron back onto the 365 Myr isochron. The results indicate that samples from the interior of the outcrop have recently gained 8–91% of their original Re concentrations (large diamonds in Fig. 8). It is important to point out that this added Re is stored only temporarily. At some point in time the oxidative weathering front will reach the underlying Boyle Dolomite, thereby eliminating underlying anoxic strata that can act as temporary sinks of Re mobilized during oxidative black shale weathering. Viewed globally and assuming steady-state, temporary redeposition of mobile Re in anoxic strata underlying oxic weathering zones does not affect our conclusion that oxidative black shale weathering is an important source of mobile Re. Based on this steady-state assumption we argue that primary Re concentrations computed above can be used to calculate Re losses during oxidative black shale weathering. This conclusion is supported by data from other studies indicating that runoff from black shales is characterized by high dissolved Re concentrations relative to average global river water (e.g. [37,38]). Dalai et al. [38], for example, report Re concentrations in mine waters percolating through phosphorite–black shale–carbonate sequences of up to 86.9 pM, about 40-fold

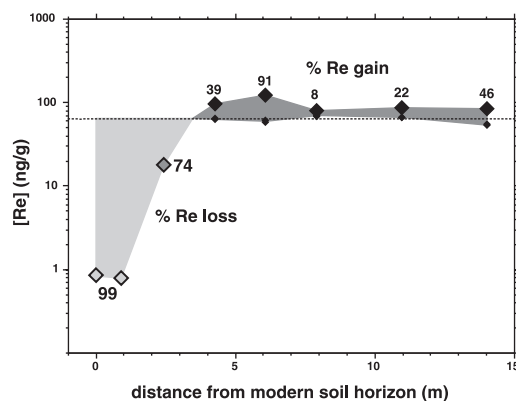


Fig. 8. Rhenium redistribution along the weathering profile. Average original Re concentration (63 ng/g), approximated by the stippled line, is lower than the average Re concentration of apparently unweathered samples (88 ng/g, see Fig. 4d). The original Re concentrations for apparently unweathered samples are shown as small diamonds. Present-day concentrations are shown as large diamonds. Relative gains and losses are given.

higher than the global average dissolved Re concentration in rivers [37].

It is worthwhile to point out that the pattern of Re redistribution within the outcrop is very similar to the pattern of Re redistribution in burn-down layers of marine organic-rich turbidites on the Madeira Abyssal Plain [39,40]. Such burn-down layers are, in many aspects, marine analogues of continental weathering profiles in OM-rich sediments. Interestingly, redistribution patterns for Re in marine burn-down layers are very similar to those for U. If the behavior of U during subaerial alteration of OM-rich sediments mimics that of Re, differential mobility of U and Th may permit the determination of weathering rates in OM-rich sediments by means of U-series disequilibrium techniques [36].

The noticeable drop in the  $^{187}\text{Os}/^{188}\text{Os}$  at the surface may result from preferential mobility of the  $^{187}\text{Os}$  isotope (Fig. 4c) relative to the other Os isotopes. Isotope mass balance calculations indicate that the mobile fraction of Os is significantly more radiogenic ( $^{187}\text{Os}/^{188}\text{Os}$  of  $\sim 7.8$ ) than the average ( $^{187}\text{Os}/^{188}\text{Os}$  of  $\sim 6.4$ ) of the unweathered samples. Therefore, significantly more radiogenic Os is being removed from the system during weathering. As radiogenic  $^{187}\text{Os}$  occupies sites formerly occupied by  $^{187}\text{Re}$ , and Re is the most mobile element analyzed in this study, loss of  $^{187}\text{Os}$  may mimic loss of Re more closely than the other Os isotopes. Weathering of OM-rich sediments may thus be an important surficial process fractionating  $^{187}\text{Os}$  from other Os isotopes. Whether  $^{186}\text{Os}$  is affected by similar preferential release, caused by  $\alpha$ -recoil during  $^{190}\text{Pt}$  decay, is unknown and remains to be investigated.

Based on a comparison of Os mobility in soils developed on glacial moraines of granitoid composition [41] with Os mobility during black shale weathering ([11] and this study), weathering of one black shale volume unit mobilizes two to three orders of magnitude more Os than weathering of one granitoid rock volume unit. If Re and radiogenic  $^{187}\text{Os}$  are lost predominantly in dissolved form, black shale weathering is an important source of radiogenic Os in seawater. It should be noted, however, that the calculated  $^{187}\text{Re}/^{188}\text{Os}$  of the mobile fraction ( $\sim 3700$ ) is sig-

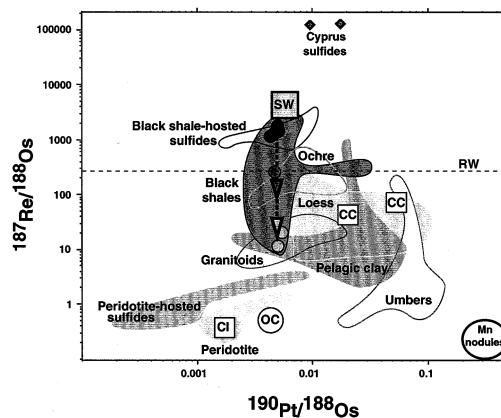


Fig. 9.  $^{187}\text{Re}/^{188}\text{Os}$  versus  $^{190}\text{Pt}/^{188}\text{Os}$  of Ohio Shale in comparison to other geochemical reservoirs such as continental crust (CC), CI chondrite (CI), outer core (OC), seawater (SW), average river water (RW is shown as a stippled line because the average Pt concentration of average river water is not known), various sediment types, loess, granitoid rocks and soils as well as Mn nodules (see [3] for references to original data). Apparently unweathered Ohio Shale is shown as black circles, moderately weathered shale as gray circle and intensely weathered shale as light gray circles. The arrow indicates the effect of weathering on the solid residue after weathering. Note that the labile fraction has a  $^{187}\text{Re}/^{188}\text{Os}$  that is very different than average, present-day river water, but  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{190}\text{Pt}/^{188}\text{Os}$  values are similar to modern seawater.

nificantly higher than the average global riverine  $^{187}\text{Re}/^{188}\text{Os}$  ( $\sim 265$ , [3]) and very similar to the  $^{187}\text{Re}/^{188}\text{Os}$  of seawater (4270, [3]). This indicates that runoff with lower  $^{187}\text{Re}/^{188}\text{Os}$ , possibly from much more abundant gray shales, dominates the global input of Re and Os to seawater (Fig. 9 and [42]). Weathering of very common gray shales has the potential of significantly affecting the global riverine Re and Os flux.

## 5. Implications for the global rhenium, osmium and organic carbon cycles

OM-rich sediments are considered the most important sink for dissolved Re in seawater [28,37,39,43]. Colodner et al. [37] estimate that about 43% (i.e.  $\sim 36000$  mol) of the present annual riverine Re input is sequestered by anoxic marine sediments. Crusius et al. [39] and Morford

and Emerson [43] consider suboxic sediments (i.e. oxygen penetration depths of  $< 1$  cm) to be even more important Re sinks, as they cover an area of the seafloor an order of magnitude larger ( $\sim 4\%$ ) than that of anoxic sediments ( $\sim 0.3\%$ ). This poses a problem for the global Re budget, because the sedimentary sinks alone (not considering the small hydrothermal sink) appear to be larger than the riverine source of Re estimated by Colodner et al. [37]. This may be caused by an underestimation of the global riverine Re flux or by neglecting potentially significant estuarine sources of Re [37]. Despite this apparent imbalance, we attempt to link the global cycles of Re to that of  $C_{\text{org}}$  and Os in an attempt to estimate the importance of black shale weathering on the atmospheric  $\text{CO}_2$  inventory and the riverine flux of Os.

As discussed above, our data indicate loss of  $\sim 62$  ng/g Re and  $\sim 5.5$  wt%  $C_{\text{org}}$  during weathering, equivalent to a molar ratio of labile  $\text{Re}/C_{\text{org}}$  of  $\sim 7 \times 10^{-8}$ . Data from the Utica Shale [11], for comparison, imply an average loss of  $\sim 1.9$  ng/g Re and  $\sim 4.5$  wt%  $C_{\text{org}}$  during weathering, which is equivalent to a molar ratio of labile  $\text{Re}/C_{\text{org}}$  of  $\sim 3 \times 10^{-9}$ . These numbers represent the ratio of Re to  $\text{CO}_2$  release only if loss of Re is as efficient as oxidation of  $C_{\text{org}}$  to  $\text{CO}_2$ . As indicated by high concentrations of dissolved  $C_{\text{org}}$  in rivers draining OM-rich sediments today, this is most likely not the case, and some decoupling of Re loss from  $C_{\text{org}}$  oxidation is to be expected. As we cannot yet quantify the importance of incomplete oxidation of  $C_{\text{org}}$ , the above numbers should be considered rough estimates only.

Critical for our calculation is a reasonable estimate of the fraction of the riverine Re flux that is derived from black shale weathering. This is a difficult task because the crustal abundance of black shales undergoing weathering is unknown. We therefore use the estimate for the burial flux of Re into anoxic marine sediments as a proxy for the release of Re from weathering black shales on the continents, assuming that the global Re cycle is presently at steady-state with respect to cycling of anoxic sediments. Then, sequestration of Re into anoxic marine sediments and release of Re through black shale weathering are in equilibrium, and the estimate of  $\sim 36\,000$  mol/yr Re burial

into anoxic marine sediments [37] can serve as a proxy for the release of Re during black shale weathering.

With these assumptions, the Ohio Shale data imply an annual release of 0.5 Tmol  $\text{CO}_2$  (Tmol =  $10^{12}$  mol), whereas the Utica Shale data require an annual  $\text{CO}_2$  release of 13 Tmol. Interestingly, using the same assumptions about the global Re flux as above, the mean labile  $\text{Re}/C_{\text{org}}$  value for burn-down layers in marine turbidites with 0.5–2 wt%  $C_{\text{org}}$  [39,40] corresponds to a release of  $\sim 0.4$  Tmol  $\text{CO}_2/\text{yr}$ . This may indicate that the lower estimate (i.e. the Ohio Shale estimate) is more representative of  $\text{CO}_2$  release during weathering of OM-rich sediments. The magnitude of this  $\text{CO}_2$  source is small compared to the estimated annual cycling of  $C_{\text{org}}$  between oxidized and reduced carbon pools ( $\sim 10$  Tmol; [44]). It is also significantly lower than estimates of  $\text{CO}_2$  evolved annually from oxidative weathering of sedimentary rocks ( $\sim 4$  Tmol; [45]). We argue that this discrepancy indicates that the majority of sedimentary rocks have significantly lower labile  $\text{Re}/C_{\text{org}}$  values than the sediments from this study. This is consistent with the observation that reducing conditions are required for substantial Re enrichments [37,39,43]. Globally, sediments with  $C_{\text{org}}$  contents  $> 5$  wt% and Re concentrations of  $> 60$  ng/g Re, such as the Ohio Shale, constitute a very small fraction of the sedimentary OM pool, which is characterized by average  $C_{\text{org}}$  concentrations of  $\sim 0.6$  wt% [46]. The fact that sediments with  $> 5$  wt%  $C_{\text{org}}$  – a trace lithology in the continental crust – can contribute  $\sim 10\%$  of the  $\text{CO}_2$  released annually from oxidative weathering of ancient sedimentary rocks indicates that they contribute a disproportionate fraction of the labile crustal reservoirs of  $C_{\text{org}}$  and Re.

As black shale weathering constitutes a  $\text{CO}_2$  source, it is informative to compare its magnitude with  $\text{CO}_2$  consumption caused by silicate weathering. For instance, the annual release of  $\sim 0.5$  Tmol  $\text{CO}_2$  from black shale weathering is nearly three times as large as the  $\text{CO}_2$  uptake by silicate weathering that France-Lanord and Derry [47] estimated for the entire Ganges-Brahmaputra drainage basin in the Himalaya during the Neogene (0.17 Tmol/yr). According to their estimates,

this drainage basin, covering  $\sim 1.2\%$  of the world's land surface area, accounts for about 2.6% of the present global  $\text{CO}_2$  uptake by silicate weathering [48]. According to our estimate, black shale weathering counterbalances  $\sim 8\%$  of the global atmospheric  $\text{CO}_2$  consumption caused by silicate weathering.

The data also enable us to estimate the relative contribution of labile, black shale-derived Os to the global riverine Os flux. The labile molar Re/Os values in the Ohio Shale profile and the Utica Shale, calculated based on the differences between initial and residual Re and Os concentrations in the weathered shales, are  $\sim 270$  and  $\sim 4\text{--}60$ , respectively. If the annual riverine Re input from black shale weathering is 36 000 mol, the labile Re/Os corresponds to an annual input of  $\sim 130$  mol (Ohio Shale) and between 630 and 8570 mol (Utica Shale) Os from black shale weathering. These Os inputs correspond to  $\sim 6\%$  (Ohio Shale) and between  $\sim 30\%$  and  $\gg 100\%$  (Utica Shale) of the annual riverine input of Os to seawater ( $\sim 1800$  mol/yr; [3,49]). These relative contributions are significantly higher than the relative abundance of black shales in the crust, indicating that weathering of black shales contributes disproportionately to the riverine Os budget. However, the most conservative flux estimate (130 mol/yr) is only a small contribution ( $\sim 6\%$ ) to the present-day global riverine Os flux to the ocean, which is consistent with isotope mass balance constraints indicating that very radiogenic black shales cannot be the main source of Os to seawater. More abundant 'gray shales' with moderate  $C_{\text{org}}$ , Re and Os enrichments relative to average upper crust are likely to be more important riverine sources of Re and Os to seawater. Unfortunately, little is known about the average  $C_{\text{org}}$ , Re and Os inventories of gray shales, and the effects of weathering of such rocks have not been investigated with respect to the mobility of Re and Os. Weathering of such lithologies will be the focus of a future study. Despite these deficits in our understanding of the surficial cycles of Re and Os, the results from this study support earlier inferences [8,29] that the crustal cycles of labile  $C_{\text{org}}$ , Re and Os are tightly coupled.

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## References

- [1] W.J. Pegram, S. Krishnaswami, G. Ravizza, K.K. Turekian, The record of seawater  $^{187}\text{Os}/^{186}\text{Os}$  variation through the Cenozoic, *Earth Planet. Sci. Lett.* 113 (1992) 569–576.
- [2] B. Peucker-Ehrenbrink, G. Ravizza, A.W. Hofmann, The marine  $^{187}\text{Os}/^{186}\text{Os}$  record of the past 80 million years, *Earth Planet. Sci. Lett.* 130 (1995) 155–167.
- [3] B. Peucker-Ehrenbrink, G. Ravizza, The marine osmium isotope record, *Terra Nova* 12 (2000) 205–219.
- [4] G. Ravizza, Variations of  $^{187}\text{Os}/^{186}\text{Os}$  ratio of sea water over the past 28 million years as inferred from metalliferous carbonates, *Earth Planet. Sci. Lett.* 118 (1993) 335–348.
- [5] K.K. Turekian, W.J. Pegram, Osmium isotope record in a Cenozoic deep-sea core: its relation to global tectonics and climate, in: W.F. Ruddiman (Ed.), *Tectonic Uplift and Climate Change*, Plenum Press, New York, 1997, pp. 383–397.
- [6] G. Ravizza, B. Peucker-Ehrenbrink, C.B. Tuit, Osmium isotopes as tracers of organic matter weathering, *EOS Trans. Am. Geophys. Union* 79 (1998) 427.
- [7] L.A. Derry, C. France-Lanord, Neogene growth of the sedimentary organic carbon reservoir, *Paleoceanography* 11 (1996) 267–275.

- [8] D. Leythaeuser, Effects of weathering on organic matter in shales, *Geochim. Cosmochim. Acta* 37 (1973) 113–120.
- [9] J.L. Clayton, P.J. Swetland, Subaerial weathering of sedimentary organic matter, *Geochim. Cosmochim. Acta* 42 (1978) 304–312.
- [10] R. Littke, U. Klussmann, B. Kroos, D. Leythaeuser, Quantification of loss of calcite, pyrite, and organic matter due to weathering of Toarcian black shales and effects on kerogen and bitumen characteristics, *Geochim. Cosmochim. Acta* 55 (1991) 3369–3378.
- [11] B. Peucker-Ehrenbrink, R. Hannigan, Effects of black shale weathering on the mobility of rhenium and platinum group elements, *Geology* 28 (2000) 475–478.
- [12] R.C. Keplerle, J.B. Roen, Chattanooga and Ohio shales of the southern Appalachian basin, in: T.G. Roberts (Ed.), *GSA Cincinnati '81 Field Trip Guidebooks, Volume II: Economic geology, structure*, Am. Geol. Inst., Falls Church, VA, 1981, 259ff.
- [13] S.T. Petsch, R.A. Berner, T.I. Eglinton, A field study of the chemical weathering of ancient sedimentary organic matter, *Org. Geochem.* 31 (2000) 475–487.
- [14] S.T. Petsch, R.J. Smernik, T.I. Eglinton, J.M. Oades, A solid state  $^{13}\text{C}$  NMR study of kerogen degradation during black shale weathering, *Geochim. Cosmochim. Acta* 65 (2001) 1867–1882.
- [15] S.T. Petsch, T.I. Eglinton, K.J. Edwards,  $^{14}\text{C}$ -dead living biomass evidence for microbial assimilation of ancient organic carbon during shale weathering, *Science* 292 (2001) 1127–1131.
- [16] S. Rimmer, D.J. Cantrell, P.J. Gooding, Rock-Eval pyrolysis and vitrinite reflectance trends in the Cleveland Shale Member of the Ohio Shale, eastern Kentucky, *Org. Geochem.* 20 (1993) 735–745.
- [17] R.A. Creaser, P. Sannigrahi, T. Chacko, Re–Os isotope systematics of hydrocarbon maturation in organic-rich sediments, *EOS Trans. Am. Geophys. Union* 81 (2000) 427.
- [18] K.I. Aspila, H. Agemian, A.S.Y. Chau, A semiautomatic method for the determination of inorganic and total phosphate in sediments, *Analyst* 101 (1976) 187–197.
- [19] F. Koreleff, Determination of nutrients, in: K. Grasshoff, M. Ehrhardt, K. Remling (Eds.), *Methods of Seawater Analysis*, 2nd edn., Verlag-Chemie, Weinheim, 1976, pp. 117–156.
- [20] G. Ravizza, D. Pyle, PGE and Os isotopic analyses of single sample aliquots with NiS fire assay preconcentration, *Chem. Geol.* 141 (1997) 251–268.
- [21] D. Hassler, B. Peucker-Ehrenbrink, G. Ravizza, Rapid determination of Os isotopic composition by sparging  $\text{OsO}_4$  into a magnetic-sector ICP-MS, *Chem. Geol.* 166 (2000) 1–14.
- [22] S.K. Singh, J.R. Trivedi, S. Krishnaswami, Re–Os isotope systematics in black shales from the Lesser Himalaya: Their chronology and role in the  $^{187}\text{Os}/^{188}\text{Os}$  evolution of seawater, *Geochim. Cosmochim. Acta* 63 (1999) 2381–2392.
- [23] E. Hauri, S.R. Hart, Re–Os isotope systematics of HIMU and EMII oceanic island basalts from the South Pacific Ocean, *Earth Planet. Sci. Lett.* 114 (1993) 353–371.
- [24] A.E. Murphy, B.B. Sageman, D.J. Hollander, Eutrophication by decoupling of the marine biogeochemical cycles of C, N, and P: A mechanism for the Late Devonian mass extinction, *Geology* 28 (2000) 427–430.
- [25] E.D. Ingall, P. Van Cappellen, Relation between sedimentation rate and burial of organic phosphorus and organic carbon in marine sediments, *Geochim. Cosmochim. Acta* 54 (1990) 373–386.
- [26] A.E. Murphy, B.B. Sageman, D.J. Hollander, T.W. Lyons, C.E. Brett, Black shale deposition and faunal overturn in the Devonian Appalachian basin: Clastic starvation, seasonal water-column mixing, and efficient bio-limiting nutrient recycling, *Paleoceanography* 25 (2000) 280–291.
- [27] G. Ravizza, K.K. Turekian, Application of the  $^{187}\text{Re}$ – $^{187}\text{Os}$  system to black shale geochronometry, *Geochim. Cosmochim. Acta* 53 (1989) 3257–3262.
- [28] G. Ravizza, K.K. Turekian, B.J. Hay, The geochemistry of rhenium and osmium in recent sediments from the Black Sea, *Geochim. Cosmochim. Acta* 55 (1991) 3741–3752.
- [29] G. Ravizza, B.K. Esser, A possible link between the seawater osmium isotope record and weathering of ancient sedimentary organic matter, *Chem. Geol.* 107 (1993) 255–258.
- [30] A.S. Cohen, A.L. Coe, J.M. Bartlett, C.J. Hawkesworth, Precise Re–Os ages of organic-rich mudrocks and the Os isotope composition of Jurassic seawater, *Earth Planet. Sci. Lett.* 167 (1999) 159–173.
- [31] A.-C. Pierson-Wickmann, L. Reisberg, C. France-Lanord, Behavior of Re and Os during low temperature alteration: results from Himalayan soils, *Geochim. Cosmochim. Acta* (2002) in press.
- [32] G. Ravizza, C.E. Martin, C.R. German, G. Thompson, Os isotopes as tracers in seafloor hydrothermal systems: Metalliferous deposits from the TAG hydrothermal area, 26°N Mid-Atlantic Ridge, *Earth Planet. Sci. Lett.* 138 (1996) 105–119.
- [33] B. Peucker-Ehrenbrink, B.-M. Jahn, Rhenium–osmium isotope systematics and platinum group element concentrations: Loess and the upper continental crust, *Geochim. Geophys. Geosyst.* 2 (2001) Paper number 2001GC000172.
- [34] W.H. Burke, R.E. Denison, E.A. Hetherington, R.B. Koepnick, N.F. Nelson, J.B. Otto, Variation of seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  throughout Phanerozoic time, *Geology* 10 (1982) 516–519.
- [35] R.E. Denison, R.B. Koepnick, W.H. Burke, E.A. Hetherington, A. Fletcher, Construction of the Silurian and Devonian seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  curve, *Chem. Geol.* 140 (1997) 109–121.
- [36] B. Peucker-Ehrenbrink, K.W.W. Sims, L.A. Jaffe, S. Petsch, N. Shimizu, Dating weathering of organic-rich shales with U-series disequilibrium techniques, in: *Eleventh Annual V.M. Goldschmidt Conference, Abstract*

- #3781, LPI Contribution no. 1088, Lunar Planet. Inst., Houston, TX, 2001 (CD-ROM).
- [37] D. Colodner, J. Sachs, G. Ravizza, K. Turekian, J. Edmond, E. Boyle, The geochemical cycle of rhenium: A reconnaissance, *Earth Planet. Sci. Lett.* 117 (1993) 205–221.
- [38] T.K. Dalai, S.K. Dings, J.R. Trivedi, S. Krishnaswami, Dissolved rhenium in the Yamuna river system and the Ganga in the Himalaya: Role of black shale weathering on the budgets of Re, Os and U in rivers and CO<sub>2</sub> in the atmosphere, *Geochim. Cosmochim. Acta* 66 (2002) 29–43.
- [39] J. Crusius, S. Calvert, T. Pedersen, D. Sage, Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition, *Earth Planet. Sci. Lett.* 145 (1996) 65–78.
- [40] J. Crusius, J. Thomson, Comparative behavior of authigenic Re, U, and Mo during reoxidation and subsequent long-term burial in marine sediments, *Geochim. Cosmochim. Acta* 64 (1999) 2233–2242.
- [41] B. Peucker-Ehrenbrink, J.D. Blum, Re–Os isotope systematics and weathering of Precambrian crustal rocks: Implications for the marine osmium isotope record, *Geochim. Cosmochim. Acta* 62 (1998) 3193–3203.
- [42] B. Peucker-Ehrenbrink, G. Ravizza, The global significance of organic-rich sediments for the crustal TOC, Re, and Os cycles, *EOS Trans. Am. Geophys. Union* 82 (2001) F1307.
- [43] J.L. Morford, S. Emerson, The geochemistry of redox sensitive trace metals in sediments, *Geochim. Cosmochim. Acta* 63 (1999) 1735–1750.
- [44] L.R. Kump, S.L. Brantley, M.A. Arthur, Chemical weathering, atmospheric CO<sub>2</sub>, and climate, *Annu. Rev. Earth Planet. Sci.* 28 (2000) 611–667.
- [45] R.A. Berner, Models for carbon and sulfur cycles and atmospheric oxygen: Application to Paleozoic history, *Am. J. Sci.* 287 (1987) 177–196.
- [46] H.D. Holland, *The Chemistry of the Atmosphere and Oceans*, Wiley, New York, 1978, 351 pp.
- [47] C. France-Lanord, L.A. Derry, Organic carbon burial forcing of the carbon cycle from Himalayan erosion, *Nature* 390 (1997) 65–67.
- [48] A.C. Lasaga, R.A. Berner, R.M. Garrels, An improved model of atmospheric carbon dioxide, in: E.T. Sundquist, W.S. Broecker (Eds.), *The Carbon Cycle and Atmospheric CO<sub>2</sub>: Natural Variations, Archean to Present*, *Geophys. Monogr.* 32, Am. Geophys. Union, Washington, DC, 1985, pp. 397–410.
- [49] S.P. Levasseur, J.-L. Birck, C.J. Allegre, The osmium riverine flux and the oceanic mass balance of osmium, *Earth Planet. Sci. Lett.* 174 (1999) 7–23.