

Basin Restriction or Oceanic Anoxic Event During the Upper Kellwasser Event in the Appalachian Basin: Insights From mm-scale Analysis of the Point Gratiot Bed

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Research Article

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Abstract

The Upper Kellwasser Event, a Late Devonian extinction event associated with widespread marine anoxia, is recorded in the Appalachian Basin by the Point Gratiot Bed (PGB), a decimeter-scale black shale in western New York State. Molybdenum (Mo) enrichment in the PGB is highest near the base of the bed and declines upsection, even as total organic carbon, pyrite abundance, and pyrite framboid diameter all indicate intensifying anoxia, a paradox explainable by basin restriction or by a global oceanic anoxic event. Here I present a millimeter-scale (~ 1.2 mm) energy-dispersive XRF dataset through a continuously cored section of the PGB along Eighteenmile Creek, Eden, New York, designed to test these models directly against the position of discrete bioturbated and gray mudstone intervals recording brief episodes of bottom-water ventilation. Six clastic regimes were defined from Al profiles; the Mo/Al decline is independent of this framework, ruling out a sedimentological or dilution-driven control. If basin restriction controlled Mo depletion, ventilation events should have reconnected bottom water to a comparatively Mo-replete reservoir, producing at least transient Mo recovery. No such recovery occurs: Mo in the sediment immediately overlying each bioturbated or gray mudstone interval shows no consistent increase relative to the sediment below it, and the bed-scale decline continues uninterrupted regardless of local redox oscillation. Uranium and vanadium, in contrast, show no depth-dependent trend, ruling out a whole-rock preservation or provenance artifact. These results indicate that a global oceanic anoxic event, rather than basin restriction, exerted primary control on Mo depletion in the PGB.

INTRODUCTION

The Phanerozoic rock record preserves five intervals of major biotic crisis (Raup & Sepkoski, 1982; Sepkoski, 1996), one of which falls late in the Frasnian Stage of the Upper Devonian, when two closely spaced pulses of extinction, the Lower and Upper Kellwasser events, decimated shallow marine ecosystems worldwide (Buggisch, 1972; McGhee, 1982; Copper, 1986, 1998; Schindler, 1990; Bond et al., 2004). Roughly half of marine genera were lost, with brachiopods, conodonts, corals, stromatoporoids, and trilobites suffering disproportionately (McGhee, 1996; Sepkoski, 1996). What ultimately triggered the Kellwasser crises remains contested. Proposed mechanisms include accelerated weathering tied to the expansion of vascular land-plant root systems (Algeo et al., 1995; Algeo & Scheckler, 1998; Whalen et al., 2015), climate change, and bolide impact (Copper, 1986; Chen et al., 2005; Xu et al., 2012;). More recently, mercury anomalies now documented across multiple continents at both the Frasnian-Famennian and Devonian-Carboniferous boundaries, together with refined radiometric dating of contemporaneous Large Igneous Provinces, have lent growing support to volcanism as a plausible trigger for one or both events (Racki et al., 2018; Racki and Pisarzowska, 2026). Whatever the ultimate cause, the globally widespread deposition of organic-rich limestone and shale during the Kellwasser events points to widespread marine oxygen depletion, though the extent, duration, and dynamics of that anoxia remain actively debated (Joachimski & Buggisch, 1993; Algeo et al., 1995; Bratton et al., 1999; Joachimski et al., 2001; Tribouillard et al., 2004; Boyer et al., 2014; Carmichael et al., 2014).

In the Appalachian Basin, the Upper Kellwasser Event (UKE) is recorded in western New York State by the Point Gratiot Bed (PGB), a decimeter-scale black shale near the top of the Hanover Shale Formation whose upper contact marks the Frasnian-Famennian boundary (Over, 1997, 2002; Over et al., 2013; Harrigan et al., 2021). Chemostratigraphic profiles through the PGB reveal a persistent and, at first glance, counterintuitive pattern: molybdenum (Mo) and, to a lesser extent, uranium (U) are enriched near the base of the bed but decline upsection, often to background shale values, even as independent indicators of bottom-water oxygen depletion, total organic carbon content, pyrite abundance, and mean pyrite framboid diameter, point toward intensifying rather than waning anoxia (Blood et al., in press_a). This same diagnostic fingerprint, elevated basal Mo declining upsection, low and largely invariant U, and a corresponding decrease in Mo/TOC, has since been used to identify the PGB roughly 70 km west southwest of the New York outcrop belt in subsurface core from Erie County, Pennsylvania (Blood, in press_b), and, most recently, in subsurface cores from eastern Ohio approaching the Findlay-Algonquin/Cincinnati Arch complex (Blood and Danielsen, in prep). That the same paradoxical trend recurs from the New York outcrop belt through subsurface Pennsylvania and into Ohio, across a substantial portion of the basin's western margin, argues against a purely local or idiosyncratic explanation and instead points to a mechanism, or combination of mechanisms, operating at basin scale.

Two explanatory models can account for a bed-scale decline in Mo enrichment despite intensifying anoxia. Under basin restriction, limited exchange with the open ocean progressively draws down a finite local reservoir of Mo as it is sequestered into accumulating sediment, the so-called basin reservoir effect (Algeo & Lyons, 2006; Tribouillard et al., 2008; Algeo & Tribouillard, 2009). Under an oceanic anoxic event (OAE), the same declining trend instead reflects depletion of the global seawater Mo reservoir as widespread anoxia sequesters trace metals into organic-rich sediments in the global ocean, a mechanism proposed for the Late Devonian by Algeo (2004) and more commonly invoked for Mesozoic anoxic events (Hetzl et al., 2009; Goldberg et al., 2016; Them et al., 2022). These models are not mutually exclusive, and the basin-to-basin gradient documented across the Illinois, Appalachian, Oklahoma basins, and Ouachita Trough, is consistent with both operating together, a global drawdown as the dominant control with local restriction modulating its magnitude at more isolated basins (Blood, 2026). Critically, however, neither the bed-scale trend nor comparisons among localities can discriminate between the two mechanisms on their own: both predict the same net decline in Mo from the base to the top of the PGB, integrated over the centimeter-scale and coarser sampling resolution of prior studies (Sageman et al., 2003; Lash, 2017; Blood et al., in press).

Distinguishing between these models requires resolving whether Mo tracks local, fine-scale redox conditions or is decoupled from them, a question that can only be addressed at a stratigraphic resolution finer than the sedimentary structures that record those local conditions. The PGB at several localities contains discrete bioturbated horizons, intervals of bottom-water oxygenation energetic enough to support burrowing infauna and, at least locally, to disrupt water-column stratification (Haddad et al., 2018). If Mo depletion in the PGB reflects basin restriction, then each such oxygenation event should have reconnected the local water mass to a comparatively Mo-replete exterior reservoir, and Mo

concentrations should recover, at least transiently, in sediment deposited immediately after bioturbation. If, instead, Mo depletion reflects a global anoxic event, local oxygenation cannot replenish a reservoir that is itself depleted, and Mo concentrations should remain low above bioturbated intervals regardless of local redox conditions. This is a directly falsifiable prediction, and testing it requires sampling at a resolution comparable to the millimeter- to centimeter-scale thickness of individual bioturbated horizons themselves, well below the resolution of previous geochemical studies of the PGB.

I present here a roughly millimeter-scale geochemical and sedimentological dataset through a complete, continuously cored section of the PGB collected along the south branch of Eighteenmile Creek, Eden, New York, designed as a direct test of this prediction. Energy-dispersive XRF analysis at approximately 1.2 mm resolution (across 222 mm of core), paired with bed-by-bed lithologic and ichnofabric logging, allows trace-element trends to be compared directly against the position, rather than merely the presence, of bioturbated horizons and other sedimentary structures within the bed. This data sheds light on the spatial relationship between Mo depletion and local redox indicators and their implication for the relative roles of basin restriction and global anoxia during the Upper Kellwasser Event in the Appalachian Basin.

GEOLOGICAL AND STRATIGRAPHIC SETTING

Tectonic and Paleogeographic Setting

During deposition of the upper Frasnian and lower Famennian, sediment accumulated in the northeast–southwest trending Appalachian Basin, a foreland basin situated at approximately 27° south paleolatitude (Scotese & McKerrow, 1990; Blakey, 2013). The basin was flanked to the east by the Acadian Highlands and to the west by the Findlay–Algonquin Arch complex, a broad structural high of Taconic ancestry that separated the Appalachian Basin from the contemporaneous Michigan and Illinois basins through much of the Middle and Late Paleozoic (Fig. 1; Scotese & McKerrow, 1990; Rast & Skehan, 1993; Ettensohn, 1992; Bose & Bartholomew, 2012; Blakey, 2013; Gooding & Ettensohn, 2019).

In western New York State, Upper Devonian strata represent the distal, basinward portion of a westward-thinning clastic wedge shed from the Catskill Delta complex to the southeast (Broadhead et al., 1982; Ettensohn, 1985; de Witt et al., 1993). These distal deposits consist of interbedded black, organic-rich, and gray, organic-lean mudstone, with subordinate siltstone and limestone, arranged in meter- to decameter-scale cycles. Each black shale interval records the onset of a drowning phase of the foreland basin, driven by some combination of flexurally induced subsidence associated with Acadian thrust loading to the east and eustatic sea-level rise (Ettensohn, 1985, 1987).

The Hanover Shale and the Point Gratiot Bed

This study targets the uppermost Hanover Shale Formation of the Java Group near its contact with the overlying Dunkirk Shale Formation of the Canadaway Group (Fig. 2). The Hanover Shale overlies the organic-rich black shale of the Pipe Creek Formation, a deep-water transgressive facies that is the local equivalent of the Lower Kellwasser Event (Johnson et al., 1985; Over, 1997; Lash, 2017). Across the western portion of the outcrop belt the Hanover Shale is roughly 30–35 m thick and dominated by organic-poor, bioturbated gray mudstone, interrupted by siltstone beds and by cyclic bundles of thin black shale that have been attributed to relative sea-level rise driven by orbital forcing, eustasy, tectonism, or some combination of the three (Lash, 2017; Bush et al., 2017).

Near the top of the Hanover Shale is the Point Gratiot Bed (Fig. 2), a conspicuous decimeter-scale black shale that records the Upper Kellwasser Event; the top of the bed marks the Frasnian–Famennian boundary, dated by Harrigan et al. (2021) to 372.15 ± 0.46 Ma (Over, 1997, 2002; Over et al., 2013). The PGB is traceable along roughly 90 km of lakeshore and creek exposures spanning from Java Village, New York, in the east to its type section at Point Gratiot, Dunkirk, New York, in the west, and it thickens systematically eastward — from 17 cm at Point Gratiot to approximately 70 cm at Java Village (Blood et al., 2025, in press). The basal contact of the bed is sharp and, at many localities, is preceded a few centimeters below by a thin (1–2 cm) black shale overlying gray mudstone rich in pyrite nodules and tubes. The upper contact is likewise sharp and is commonly marked by gray, mudstone-filled *Chondrites*, *Planolites* and *Thalassinoides*-type burrows.

The PGB is overlain by the Beaver Meadow Member (Fig. 2), the uppermost lithological unit of the Hanover Shale, formally named and described by Blood et al. (2025). The member is an eastward-thickening wedge of gray mudstone containing numerous thin, centimeter-scale black shale beds comprising both organic-rich hyperpycnites and transgressive black shales associated with continued marine flooding, along with nodular carbonate horizons and occasional siltstone beds. The Beaver Meadow Member is in turn unconformably overlain by the Dunkirk Shale Formation, with the contact commonly marked by a lag of reworked detrital pyrite, wood debris, fish bone, and conodonts (Baird & Brett, 1985, 1986a, b; Baird & Lash, 1990; Baird & Brett, 1991). The Dunkirk Shale itself comprises laminated, organic-rich, silty black shale with minor gray mudstone, siltstone beds, and carbonate concretion horizons.

MATERIALS AND METHODS

A hand sample of the entire Point Gratiot Bed was collected along the south branch of Eighteenmile Creek in Eden, New York at the coordinates: 42.625605, -78.838159. A vertical 2.54 cm diameter core was cut through the bed using a Pomeroy EZ Core D261-C Drill equipped with a heavy-duty, stainless steel, diamond core bit, and cooled with water.

The core was split in half using a DeWalt 10-inch (25.4 cm), 15-amp wet sliding table tile saw with a diamond blade. One half core face was polished using a HI-TECH Diamond All-U-Need 8-inch (20.3 cm) flat lap machine in a stepwise fashion with 180, 325, 600, and 1200 grit discs at 3400 rpm.

A spot on the stratigraphic base of the other half of the core was analyzed using a NITON XL3t GOLDD+ handheld energy dispersive X-ray fluorescence (EDXRF) spectrometer equipped with a silicon drift detector running for approximately 150 seconds. After analysis, the next 1 mm thickness was marked on the core. The lap machine and 180 grit disc were used to sand off that thickness and the analysis was repeated on the fresh bedding surface. An inability to precisely grind away a mm resulted in an average of about 1.2 mm of thickness between surfaces. Analyses proceeded upsection for the entire 222 mm thickness of the PGB resulting in 186 analyses. Elements are provided as concentrations, and element/Aluminum (Al).

Linear (Pearson) correlation was used to evaluate trends in Al and Al-normalized ratios and Mo, U, and V concentrations with depth. Differences between base and top intervals were evaluated using a two-sample t-test. Given depth-ordered, autocorrelated sampling, p-values are interpreted as relative signal strength rather than exact probabilities. Coefficients of variation ($CV = SD/mean \times 100$) are reported to compare relative variability among elements and regimes. Values reported below XRF detection limit were treated as missing.

RESULTS

Description of the Point Gratiot Bed

The PGB in this core measured approximately 222 mm (Fig. 3). The basal 3.6 mm comprises gray mudstone and occasional black shale-filled burrows. This is overlain by 6 mm of massive to burrowed silty black shale, which is in turn overlain by 2.4 mm of gray mudstone. The overlying 20.4 mm comprises massive silty black shale. The base of the overlying black shale is marked by a thin detrital pyrite lag, which is overlain by intervals of burrowed and massive black shale. 8.4 mm of gray mudstone overlie this interval. This is the highest occurrence of gray mudstone in the PGB. The overlying 64.8 mm of silty black shale contains minor visibly bioturbated intervals. This interval of black shale is interrupted by 33.6 mm of wavy to occasionally crossbedded siltstone and black shale of which approximately 6 mm of section, 4.8 mm below the top of the siltstone is bioturbated. The remaining 75.6 mm is characterized as silty black shale with no visible bioturbation, and occasional nodulus and beds of visible pyrite.

Clastic Elemental Profiles Through the Point Gratiot Bed

Six clastic regimes (CR1-6) were defined using the Al profile through the PGB (Fig. 4). Aluminum in CR1 (0.0-32.4 mm) ranges from 9.09% to 11.74% without a statistically significant net trend (linear regression, $r = 0.22$, $p = 0.25$), though values trend weakly higher toward the top of the interval. The maximum Al value (11.74%) occurs near the base, at 3.6 mm; the minimum (9.09%) occurs at the very base, 0.0 mm. Mean Si/Al (2.90 ± 0.26), Ti/Al (0.056 ± 0.003), and Zr/Al (23.4 ± 2.3).

CR2 (33.6–48.0 mm) begins at 33.6 mm and is capped by a gray mudstone bed identified independently in the core (Fig. 4). Aluminum rises through the interval from a basal value of 10.45% at 33.6 mm to a maximum of 12.33% at 45.6 mm, near the top of the gray mudstone; the rising trend is not statistically significant at this interval's limited sample size ($r = 0.44$, $p = 0.13$, $n = 13$). CR2 carries the lowest mean Si/Al (2.80 ± 0.16), Ti/Al (0.053 ± 0.003), and Zr/Al (22.5 ± 1.6) of any regime in the section. The interval ends with a sharp reversal: Al falls from 11.80% at 48.0 mm (the top of the gray mudstone) to 9.00% at 49.2 mm, a step change that marks the base of CR3 rather than a continuation of the CR2 trend.

CR3 (49.2–75.6 mm) begins with the abrupt drop in Al noted above, then recovers to a local maximum of 12.14% at 54.0 mm before declining to the interval's minimum of 9.94% at 74.4 mm, near its top (Fig. 4). The decline across CR3 is statistically significant ($r = -0.43$, $p = 0.039$) and is the clearest Al decline of any regime besides CR4. Mean Si/Al (2.90 ± 0.19), Ti/Al (0.055 ± 0.003), and Zr/Al (23.7 ± 1.8) are similar to CR1, indicating that despite the trend reversal at its base and the internal decline, CR3's grain-size ratios sit at the same background level as the other non-siltstone regimes.

CR4 (76.8–112.8 mm) begins at the single highest Al value measured in the entire 222 mm section (12.83% at 76.8 mm) and declines significantly and monotonically upsection to a minimum of 9.65% at 108.0 mm ($r = -0.54$, $p = 0.0019$) and is the most robust Al trend of any regime studied. Mean Si/Al (2.81 ± 0.17), Ti/Al (0.054 ± 0.004), and Zr/Al (23.4 ± 2.9) remain within the background range established in CR1 and CR3.

CR5 (114.0–146.4 mm) corresponds to the siltstone interval and is the most compositionally distinctive regime in the profile (Fig. 4). Mean Al (9.54%) is the lowest of any regime and by far the most variable (coefficient of variation $\approx 17\%$, versus 5–7% elsewhere). Al reaches a maximum of 12.17% near the base (115.2 mm) and a pronounced minimum of 4.98% at 120.0 mm, a single markedly Al-depleted, coarse-grained sample with no significant net trend across the interval ($r = 0.19$, $p = 0.34$). CR5 records the most extreme Al-normalized ratio values in the dataset: mean Si/Al is 3.72 ± 1.29 (versus 2.8–2.9 in every other regime), reaching 9.22 at its highest; Zr/Al averages 21.4 ± 5.0 , the lowest regime mean despite the widest range (16.5–41.6); and Ti/Al is also elevated (0.059 ± 0.009 , versus 0.053–0.056 elsewhere).

CR6 (147.6–222.0 mm) is the uppermost and most compositionally stable interval in the section: mean Al (10.63%) has the second-lowest coefficient of variation of any regime ($\sim 6.5\%$), and there is no significant net trend ($r = -0.17$, $p = 0.18$). The Al maximum (11.91%) occurs at 184.8 mm, roughly mid-interval, and the minimum (9.07%) at 200.4 mm. Mean Si/Al (2.88 ± 0.17), Ti/Al (0.055 ± 0.004), and Zr/Al (23.3 ± 2.3) sit at the same background levels found in CR1, CR3, and CR4.

DISCUSSION

At the south branch of Eighteenmile Creek, the PGB can be divided into three lithologic units (Fig. 3). The lower unit is a finely laminated to massive black shale containing several thin gray mudstone interbeds and bioturbated intervals. This is overlain by a middle siltstone unit that is wavy- to cross-bedded and

bioturbated near its top. The upper unit comprises finely laminated to massive black shale, with mm-scale pyrite laminae that increase in abundance upsection.

These three units correspond closely to the clastic regimes (CR1–CR6) defined by the Al-based geochemical profiles: the lower black shale spans CR1–CR4 and is the most heterogeneous interval in the bed, the siltstone corresponds to CR5, and the upper black shale corresponds to CR6, which shows comparatively little internal variation. Excluding CR2 – which comprises the gray mudstone interval itself – CR1, CR3, CR4, and CR6 share similar background element ratios, defining a largely uniform pattern of black mud accumulation through most of PGB deposition (Fig. 4).

The gray mudstone interbeds, thin (~ 2 mm) intervals within CR1, and the thicker interval that dominates CR2 (Fig. 2), indicate episodes of enhanced bottom water ventilation and argue against persistently anoxic conditions throughout PGB deposition. This is supported by gray, mud-filled *Planolites*- and *Chondrites*-type burrows present in the black shale directly underlying each gray mudstone interval, as well as near the top of the siltstone.

It is noteworthy that bioturbated and gray mudstone intervals are most common in the lower black shale, where Mo/Al is also highest (Fig. 5). From a maximum around 22.8 mm, Mo/Al decreases essentially continuously to the top of the bed, tracking a parallel decline in the occurrence of bioturbation. The stratigraphically highest gray mudstone interval occurs within CR2 at 48.0 mm, and the last bioturbated horizon occurs within the CR5 siltstone at 141.6 mm. These patterns are consistent with Haddad et al. (2018), who documented ichnofabric indices fluctuating between 1 and 3 through the PGB at distal localities, including Eighteenmile Creek, indicating episodically dysoxic to intermittently oxygenated bottom water rather than persistent anoxia. Haddad et al. (2018) attribute the large (> 1 cm), *Thalassinoides*-dominated burrows capping the PGB at each locality to a separate, rapid return to fully oxygenated bottom water following PGB deposition.

Both bioturbation and gray mudstone occurrence decline upsection through the PGB, and the upper black shale (CR6) is essentially devoid of bioturbation until this capping *Thalassinoides* horizon. Taken alone, this decline is consistent with the increasing intensity and persistence of anoxia documented at the centimeter scale by Blood et al. (in press), who found that TOC, pyrite abundance, and framboid size distributions all point toward increasingly reducing conditions from basal portion to the top of the PGB. This trend, however, runs counter to the behavior of Mo, which should become more strongly enriched, not less, as bottom water anoxia intensifies (Algeo & Tribovillard, 2009). Declining Mo enrichment despite intensifying anoxia constitutes the central paradox of the PGB (Blood et al., in press), and it is one that a purely local, redox-driven explanation cannot resolve. Blood et al. (in press) proposed that Mo supply to bottom water was instead throttled by one of two mechanisms: restriction of the basin from open-ocean water masses, or a global oceanic anoxic event that depleted the seawater Mo reservoir itself.

Under a basin restriction model, reduced exchange between the epeiric sea and the open ocean limits resupply of dissolved Mo to bottom water, producing authigenic Mo enrichments well below open-

marine values even under persistently euxinic conditions, the "basin reservoir effect" (Algeo & Lyons, 2006). This behavior is documented in strongly restricted modern systems such as the Black Sea (Algeo & Tribovillard, 2009) and has been inferred for semi-restricted intervals of the Devonian-Carboniferous North American Seaway, including comparable upward-declining Mo-TOC profiles in the Cleveland Shale Member of the Ohio Shale (Algeo et al., 2007). Basin restriction is a plausible mechanism for the Appalachian Basin more broadly, given that hydrographic connectivity varied considerably through Middle and Late Devonian time, from semi-restricted conditions during Marcellus Shale deposition (Lash & Blood, 2014) to comparatively open conditions during Genesee Shale deposition (Blood et al., 2017). For the PGB specifically, however, independent sedimentological evidence complicates a restriction-only interpretation: PGB deposition coincided with early marine transgression (Baird & Brett, 1991; Over, 2002; Devleeschouwer et al., 2002), and Lash (2017) interpreted correlative Hanover Shale strata at Walnut Creek as having accumulated under unrestricted marine conditions.

Alternatively, the Mo decline may reflect genuine depletion of the global seawater Mo reservoir during a widespread oceanic anoxic event. Algeo (2004) showed that sufficiently large-scale expansion of anoxic/euxinic seafloor can draw down the marine Mo inventory itself, modeling reductions to 30–50% of modern seawater concentrations during Late Devonian anoxic events; a comparable pattern of rising TOC alongside declining Mo and U was documented in the Cleveland Shale by Algeo and Maynard (2008), who interpreted it as a recurring feature of Late Devonian anoxic events rather than a purely local restriction signal. Under this model, Mo enrichment in the PGB is limited not by restricted resupply from an otherwise Mo-replete ocean, but by a genuinely Mo-depleted water column reaching the Appalachian Basin from the open ocean – consistent with the broader recognition of ocean anoxia as a driver of the Kellwasser events across multiple basins and depositional settings (Joachimski et al., 2001; Bond & Wignall, 2005; Boyer et al., 2014). Bioturbated intervals within the PGB offer a within-basin test of the relative contribution of each model.

The presence of burrows within black shale, gray mudstone, and bioturbated siltstone all indicates that anoxia was not persistent, and that oxygenated conditions returned to the seafloor for at least brief periods of time during deposition of the PGB (Haddad et al., 2018). Renewed bottom-water oxygenation of this kind requires, at minimum, a temporary breakdown of the density stratification that otherwise isolates anoxic or euxinic bottom water from the water column above, whether driven by storm-induced turbulence, seasonal overturn, or a shift in current regime. It is sustained stratification, rather than anoxia itself, that allows a local water mass to become progressively depleted in dissolved trace metals without resupply (Algeo & Maynard, 2008; Liu & Algeo, 2021), so any event capable of eroding that stratification necessarily reconnects local bottom water to an exterior reservoir. Whether that reconnection actually restores Mo concentrations depends on whether the exterior reservoir is itself Mo-replete: basins with short water-mass renewal times, such as the modern Cariaco Basin, show comparatively limited trace-metal depletion because resupply outpaces authigenic drawdown, whereas basins with renewal times on the order of centuries to millennia, such as the Black Sea and Framvaren Fjord, show pronounced depletion because resupply cannot keep pace (Algeo & Maynard, 2008). Therefore, gray mudstone and bioturbated intervals provide the opportunity to assess the resupply of trace metals, specifically Mo, to

bottom waters after seafloor ventilation events, and to test the relative role of basin restriction versus a global oceanic anoxic event. If basin restriction were the primary cause of Mo depletion in bottom waters, a recovery of Mo to pre-bioturbation levels at a minimum would be expected. Given the evidence for increasing anoxia upsection (Blood et al., in press), one might even expect elevated Mo in post-bioturbation compared to pre-bioturbation black shale. Under an oceanic anoxic event, however, the exterior water mass reconnecting with the seafloor during a ventilation event would itself be Mo-depleted, and no resupply would occur when stratified water layers mix. Molybdenum concentrations would instead continue to decrease in post-bioturbation intervals relative to pre-bioturbation intervals.

Across the PGB, Mo does not recover to, or exceed, pre-bioturbation values in the sediment immediately overlying each bioturbated interval. Point-to-point comparisons between the last pre-bioturbation sample and the first post-bioturbation sample yield both modest increases and decreases in Mo across different bioturbated intervals, with no consistent direction of change (Fig. 5). This absence of a systematic increase is itself informative: genuine resupply of Mo to bottom water should produce a consistent post-bioturbation increase across intervals, not the mixed pattern observed here. The overall trend remains one of decreasing Mo upsection, with no evidence of consistent recovery toward previous black shale maxima, despite evidence of increasing anoxia (Blood et al., in press). This decline, beginning around 22.8 mm, continues uninterrupted across all background clastic regimes: CR1, CR3, CR4, CR6 (Fig. 4). Because background sedimentation is broadly consistent across these regimes, continued Mo depletion cannot be attributed to changes in sediment supply or grain size.

Uranium and vanadium provide additional context for the Mo trend (Fig. 5), though each carries a different degree of caution. Uranium concentrations measured by ED-XRF should be treated cautiously as a quantitative enrichment record. Qualitatively, however, U (2.6–9.8 ppm) shows no significant relationship with depth ($r = -0.02$, $p = 0.81$) and no significant difference between the base and top of the bed (CR1: 6.2 ± 1.4 ppm; CR6: 6.4 ± 0.9 ppm; two-sample t-test, $t = -0.66$, $p = 0.51$), in marked contrast to the strong, statistically robust decline documented in the black shale-only Mo trend ($r = -0.94$, $p < 0.001$, $n = 125$). Because the same analytical method clearly resolves a Mo signal of that strength, the absence of a comparable trend in U cannot be attributed simply to instrumental noise obscuring a decline of similar magnitude.

Vanadium, which is not subject to the same analytical limitation, shows a comparably weak relationship with depth (73–167 ppm; $r = 0.003$, $p = 0.97$) and remains close to average shale values throughout (Fig. 5; mean 139 ppm vs. ~130 ppm; Wedepohl, 1971, 1991), with the lowest coefficient of variation of the three elements (V: 11%; U: 19%; Mo: 83%). A two-sample t-test does indicate a modest but statistically significant increase from the base to the top of the bed (CR1: 137.8 ± 10.8 ppm; CR6: 143.2 ± 12.7 ppm; $t = -2.07$, $p = 0.043$), consistent with the weak upsection increase in V/Al already noted across clastic regimes. This shift is minor in absolute terms, however, and V correlates far more strongly with Al ($r = 0.60$, $p < 0.0001$) than with depth, consistent with a substantial detrital, rather than authigenic seawater-derived, source for V in the PGB.

Neither element discriminates between the basin restriction and oceanic anoxic event models on its own – both act primarily on the dissolved Mo pool, and U and V are not expected to respond identically to either. What their behavior does rule out is a third possibility: that the Mo trend reflects a broader loss of trace-metal preservation potential or a shift in detrital sediment supply through the bed, rather than a genuine redox/hydrographic signal specific to Mo. Together, these observations indicate that an oceanic anoxic event, rather than basin restriction, exerted primary control on Mo depletion within the PGB.

CONCLUSIONS

Millimeter-scale (~ 1.2 mm) EDXRF analysis through a continuously cored section of the Point Gratiot Bed from the south branch of Eighteenmile Creek resolves individual bioturbated and gray mudstone intervals as discrete ventilation events, at a resolution below that of previous geochemical studies of the bed. Six clastic regimes (CR1–CR6), defined independently from Al, Si, Ti, and Zr profiles, show no relationship to the Mo/Al decline through the bed; background sedimentation is broadly consistent across CR1, CR3, CR4, and CR6, ruling out grain-size or provenance control on the Mo signal. Molybdenum does not recover to, or exceed, pre-bioturbation values in sediment immediately overlying bioturbated or gray mudstone intervals, despite the reconnection of bottom water to an exterior reservoir implied by each ventilation event, a result inconsistent with basin restriction as the primary control on Mo depletion, which predicts at least transient resupply following such events. Uranium and vanadium, in turn, show no depth-dependent trend through the bed and remain close to background or average-shale values throughout, in contrast to the strong, statistically significant decline in Mo over the same interval, indicating that the Mo trend reflects a mechanism specific to Mo cycling in bottom and pore waters rather than a generalized loss of trace-metal preservation potential or a shift in detrital sediment supply.

Together, these results favor a global oceanic anoxic event, rather than basin restriction, as the primary control on Mo depletion in the PGB. The millimeter-scale, bioturbation-based approach applied here provides a direct, falsifiable means of evaluating basin restriction against global anoxia within a single stratigraphic section, a test not available at the coarser resolution of prior studies. Applying this same approach at additional Appalachian Basin localities, and at localities outside the basin's hydrographic influence, would establish how broadly the results holds across the basin and beyond.

Declarations

Competing interests

I declare that I have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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The EDXRF dataset generated and analyzed during the current study is available from the author upon reasonable request.

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Figures

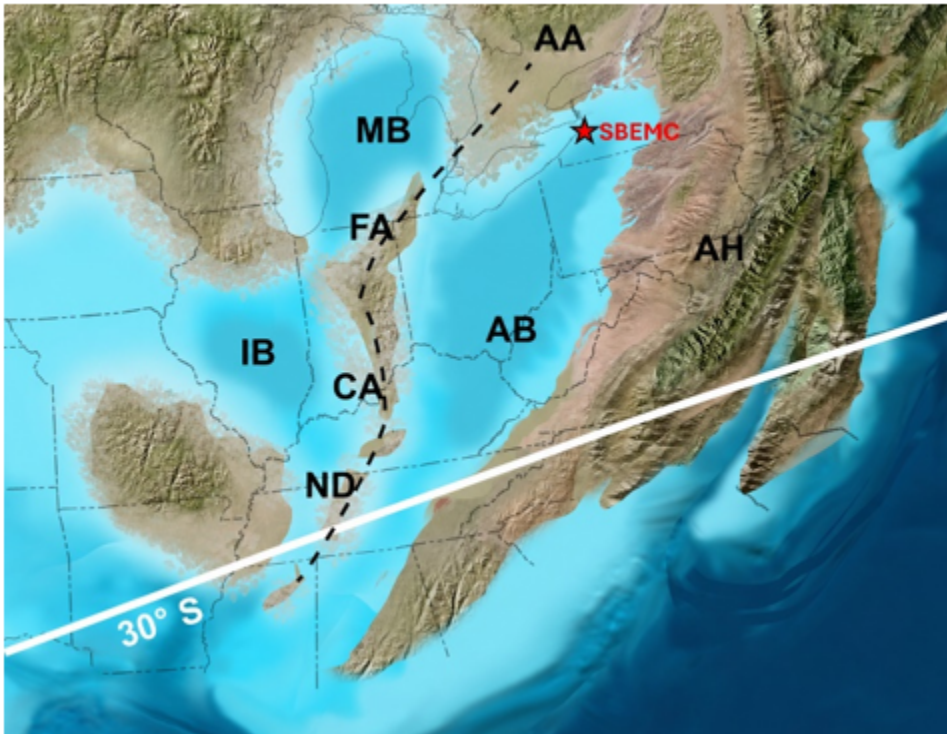


Figure 1

Paleogeographic reconstruction of the Appalachian Basin. Red star indicates the south branch of Eighteenmile Creek (SBEMC) study locality. The Algonquin and Findlay arches are denoted by a black dotted line. AA = Algonquin Arch; AB = Appalachian Basin; AH = Acadian Highlands; CA = Cincinnati Arch; FA = Findlay Arch; IB = Illinois Basin; MB = Michigan Basin; ND = Nashville Dome. Base map used with permission ©2023 Colorado Plateau Geosystems Inc

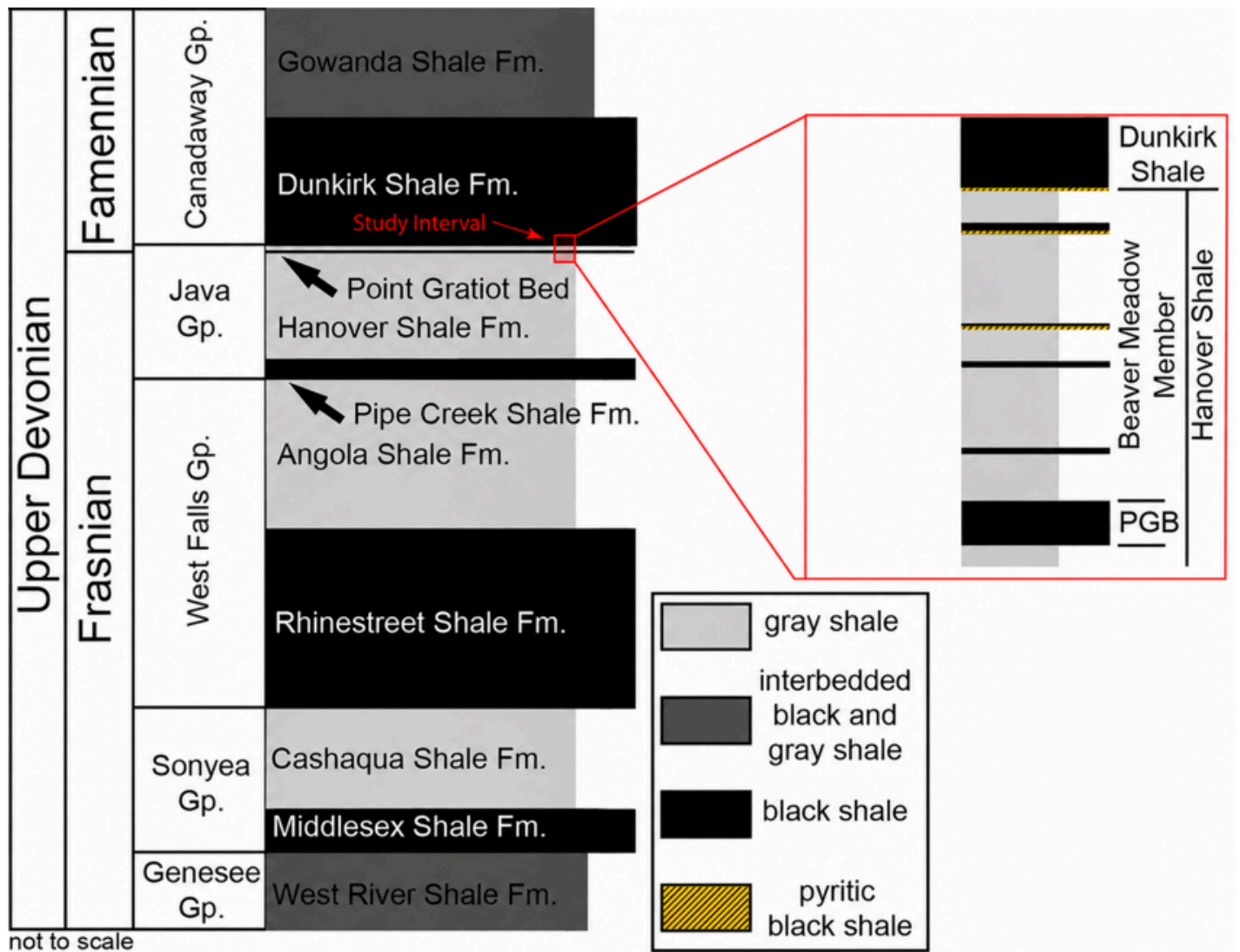


Figure 2

Generalized stratigraphic column depicting the shale-dominated Upper Devonian strata of western New York State. The red box denotes the study interval encompassing the Point Gratiot Bed and adjacent strata of the Beaver Meadow Member of the Hanover Formation and basal Dunkirk Formation; red connecting lines link the study interval to the expanded stratigraphic column at right. Patterns and shading denote gray shale, interbedded black and gray shale, black shale, and pyritic black shale as indicated in the legend; Gp. = Group; Fm. = Formation

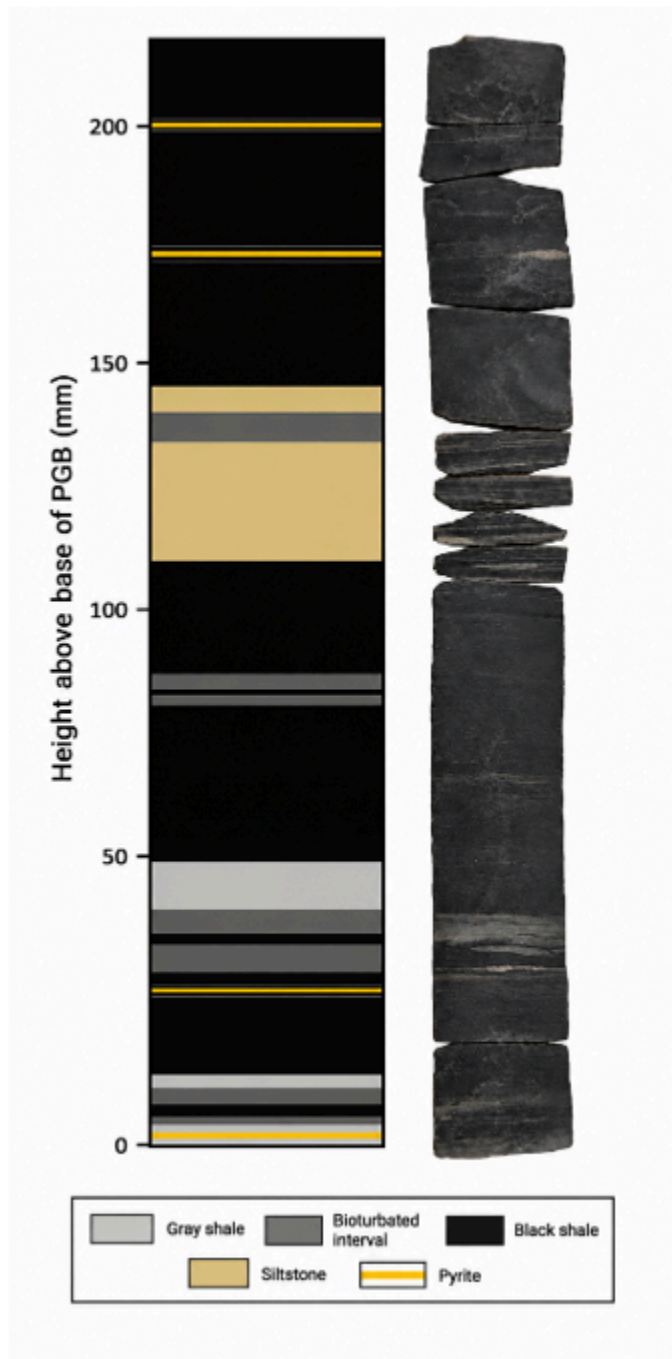


Figure 3

Lithologic column alongside an image of the polished half-core of the Point Gratiot Bed at the south branch of Eighteenmile Creek, Eden, New York. In the lithologic column, gray mudstone intervals are shown in light gray, bioturbated intervals in dark gray with a burrow-pattern symbol, and black shale in black. Siltstone intervals are shown in tan with a stippled pattern, and pyritic horizons are denoted by thin black-and-yellow diagonally patterned lines.

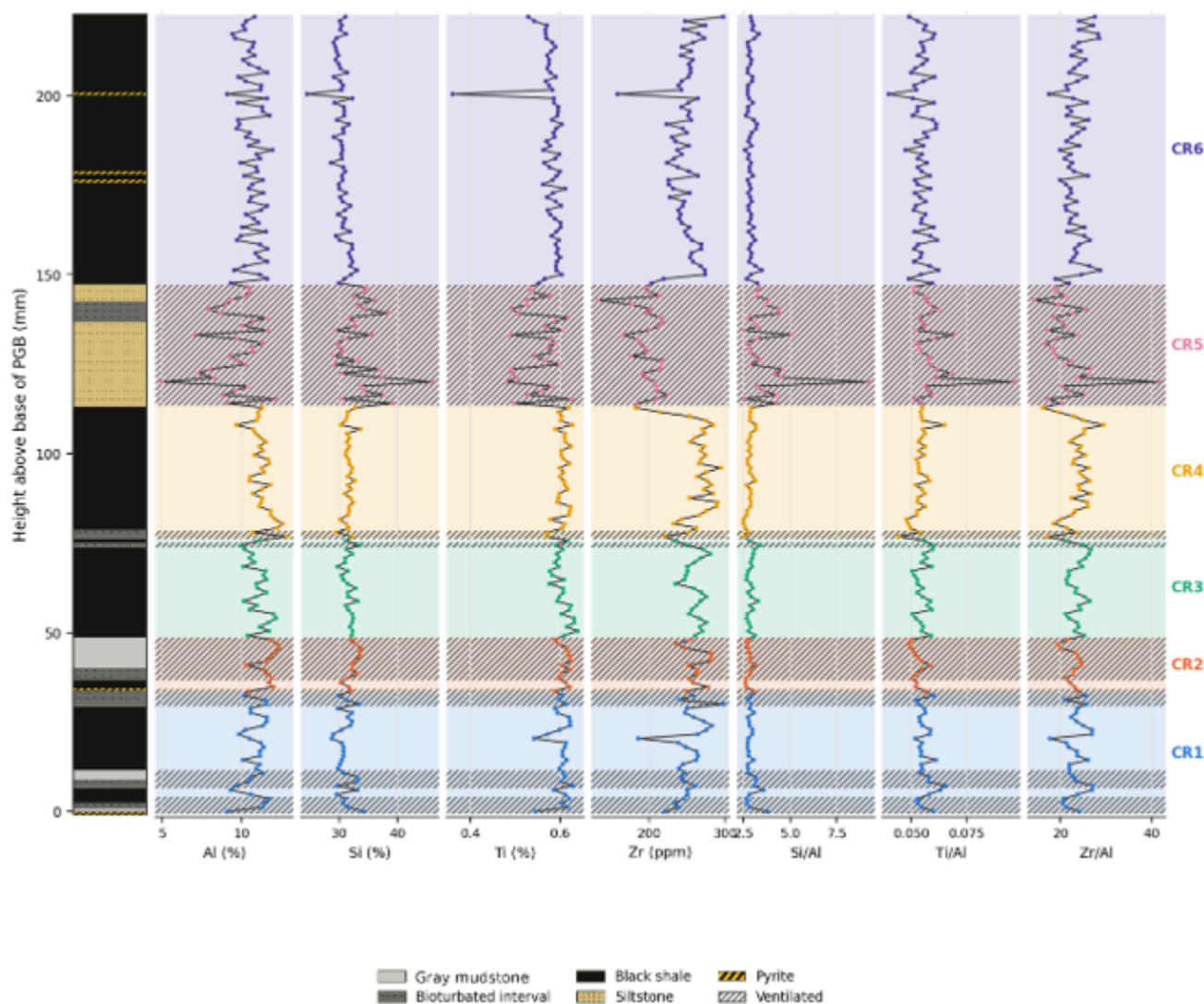


Figure 4

Lithologic column and clastic elemental profiles through the Point Gratiot Bed at the south branch of Eighteenmile Creek, Eden, New York, including aluminum (Al, wt.%), silicon/aluminum (Si/Al), titanium/aluminum (Ti/Al), and zirconium/aluminum (Zr/Al). In the lithologic column, gray mudstone is shown in light gray, bioturbated intervals in dark gray with a burrow pattern, black shale in black, siltstone in tan with a stippled pattern, and pyritic horizons by black-and-yellow diagonal stripes. Bioturbated and gray mudstone intervals are hatched across the elemental profiles to denote their interpretation as ventilation events. The Al profile forms the basis for the six clastic regimes (CR1–CR6) defined in this study, shown as shaded bands common to all elemental profiles. CR1, CR3, CR4, and CR6 represent consistent background delivery of the detrital elements Al, Si, Ti, and Zr; CR2 is dominated by gray mudstone; and CR5 corresponds to the siltstone interval. Height above the base of the PGB (0 mm) is shown on the vertical axis

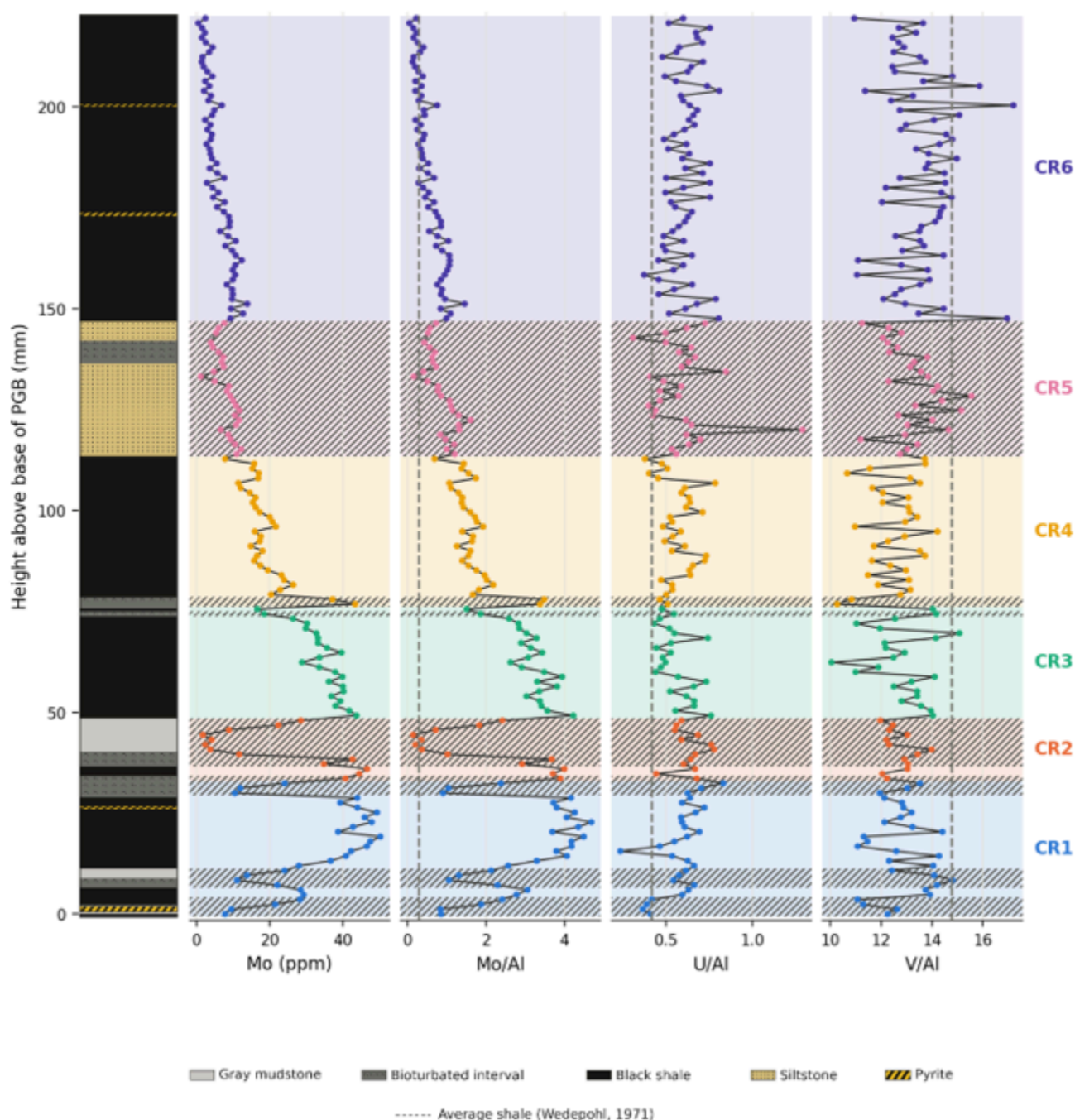


Figure 5

Lithologic column and redox-sensitive trace element profiles through the Point Gratiot Bed at the south branch of Eighteenmile Creek, Eden, New York, including molybdenum (Mo) molybdenum/aluminum (Mo/Al), uranium/aluminum (U/Al), and vanadium/aluminum (V/Al). In the lithologic column, gray mudstone is shown in light gray, bioturbated intervals in dark gray with a burrow pattern, black shale in black, siltstone in tan with a stippled pattern, and pyritic horizons by black-and-yellow diagonal stripes. Clastic regimes (CR1-CR6) are labeled on the right side of the plot. The decline in Mo/Al is continuous across these boundaries. Bioturbated and gray mudstone intervals are hatched across the elemental

profiles to denote their interpretation as ventilation events. Mo/Al does not increase following any of these intervals. U/Al shows slight enrichment to average shale values and no relationship with depth. V/Al is slightly depleted relative to average shale and shows a modest increase with depth. Height above the base of the PGB (0 mm) is shown on the vertical axis. Average shale values are from Wedepohl (1971)