



Mercury abundance and isotopic composition indicate subaerial volcanism prior to the end-Archean “whiff” of oxygen

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Earth’s early atmosphere witnessed multiple transient episodes of oxygenation before the Great Oxidation Event 2.4 billion years ago (Ga) [e.g., A. D. Anbar et al., *Science* 317, 1903–1906 (2007); M. C. Koehler, R. Buick, M. E. Barley, *Precambrian Res.* 320, 281–290 (2019)], but the triggers for these short-lived events are so far unknown. Here, we use mercury (Hg) abundance and stable isotope composition to investigate atmospheric evolution and its driving mechanisms across the well-studied “whiff” of O₂ recorded in the ~2.5-Ga Mt. McRae Shale from the Pilbara Craton in Western Australia [A. D. Anbar et al., *Science* 317, 1903–1906 (2007)]. Our data from the oxygenated interval show strong Hg enrichment paired with slightly negative $\Delta^{199}\text{Hg}$ and near-zero $\Delta^{200}\text{Hg}$, suggestive of increased oxidative weathering. In contrast, slightly older beds, which were evidently deposited under an anoxic atmosphere in ferruginous waters [C. T. Reinhard, R. Raiswell, C. Scott, A. D. Anbar, T. W. Lyons, *Science* 326, 713–716 (2009)], show Hg enrichment coupled with positive $\Delta^{199}\text{Hg}$ and slightly negative $\Delta^{200}\text{Hg}$ values. This pattern is consistent with photochemical reactions associated with subaerial volcanism under intense UV radiation. Our results therefore suggest that the whiff of O₂ was preceded by subaerial volcanism. The transient interval of O₂ accumulation may thus have been triggered by diminished volcanic O₂ sinks, followed by enhanced nutrient supply to the ocean from weathering of volcanic rocks causing increased biological productivity.

but cause–effect relationships between these events are so far unclear.

Here, we set out to more precisely track the relationship between volcanism and whiffs of O₂ using mercury (Hg) geochemistry. Throughout Earth’s history, volcanism has been the principal source of Hg to the environment. Therefore, elevated Hg concentrations in sediments have been proposed to indicate large subaerial volcanic eruptions (16). The emitted Hg(0) is highly volatile and can be transported globally during its relatively long present-day atmospheric residence time of up to ~2 y (17). Photo-oxidation of volcanically emitted gaseous Hg(0) creates highly reactive and water-soluble Hg(II), which is deposited in rainfall. Adsorption to organic matter or sulfide minerals can transfer this dissolved Hg into sediments (18). Since common modern Hg sources such as erosion of humic soils, forest fires, and coal combustion were absent before the evolution of land plants, Hg sources in the Archean were shallow submarine or subaerial volcanism, or oxidative weathering of Hg-bearing sulfide minerals on land (19, 20). The residence time of gaseous Hg(0) in the Archean atmosphere may have been longer in the absence of oxidants, or shorter in the presence of more intense photochemistry, but in any case, it is likely that an

Archean | mercury isotopes | atmospheric oxygenation

The stepwise oxygenation of Earth’s surface constituted a fundamental transformation of our planet’s atmosphere. The mechanisms driving this transition are still debated. The most studied part of this transformation is the first permanent rise in atmospheric O₂, which occurred ~2.45 billion years ago (Ga), termed the “Great Oxidation Event” (GOE) (1, 2). However, geochemical records (3–7) point to biological O₂ production in localized environments as much as 500 My before the GOE. These transient “whiffs” of O₂, which are archived in pyritic, organic-rich mudstones that are commonly ascribed to high biological productivity and organic carbon burial in Archean “oxygen oases” (8), raise questions about what may have stimulated the early production of O₂ and buffered its atmospheric concentration.

Volcanism can play a central role in modulating both sources and sinks of O₂. For instance, the production of O₂ could be stimulated by the emplacement of large igneous provinces (LIPs) because weathering of fresh basaltic crust liberates the essential macronutrient phosphorus (P) (9), which is thought to ultimately modulate primary productivity over geologic time scales (10). The consumption of O₂ is also affected by volcanism because reaction with volcanic gases provides a long-term sink for atmospheric O₂ (e.g., ref. 11), which might have diminished in strength over time (12, 13). Indeed, periods of Neoproterozoic subaerial volcanism roughly coincide with the hypothesized O₂ whiffs and accompanying euxinic (sulfide-rich) events (14, 15),

Significance

Earth’s atmosphere became oxygenated around 2.4 billion years ago, and this event was preceded by at least one short-lived “whiff” of free O₂ gas nearly 100 million years earlier. The cause of this whiff has so far been difficult to identify. Here, we present mercury concentrations and isotope ratios across the whiff interval and find evidence for significant subaerial volcanism immediately preceding oxygenation. We propose that subaerial weathering of fresh volcanic rocks acted as a fertilizer that stimulated biological productivity and O₂ production in the surface ocean. Our results indicate another strong linkage between planetary magmatic processes and the evolution of Earth’s atmosphere.

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atmospheric Hg cycle, driven by volcanic emissions, existed in the Archean.

The stable isotopic composition of Hg has been increasingly used to illuminate the movement of Hg through the environment. Hg isotopes can undergo mass-dependent fractionation (MDF) ($\delta^{202}\text{Hg}$), mass-independent fractionation of the odd isotopes (odd-MIF) ($\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$), and mass-independent fractionation of the even isotopes (even-MIF) ($\Delta^{200}\text{Hg}$ and $\Delta^{204}\text{Hg}$). For brevity, the magnitude of odd-MIF is reported here as $\Delta^{199}\text{Hg}$, and even-MIF as $\Delta^{200}\text{Hg}$. While Hg-MDF is associated with most biotic and abiotic pathways of the Hg cycle, Hg even-MIF is limited to photochemical transformations of Hg in the tropopause or stratosphere, while Hg odd-MIF is limited to photochemical transformations in the troposphere and in surface waters (18, 21–23). In the Archean, in the absence of an ozone shield, the intensity and spatial distribution of UV-driven photochemistry may have been different from today, but previous work has shown that strong MIF effects associated with atmospheric Hg cycling were present at that time (24), and therefore Hg-MIF can help distinguish between subaerial and submarine volcanism as well as provide insights into atmospheric composition.

LIP events during the Phanerozoic appear to have released enormous amounts of Hg into the surface environment, creating significant Hg enrichments and isotopic excursions in the stratigraphic record that have been used in numerous studies to identify links between LIPs, ocean redox changes, and biotic turnover (reviewed in ref. 16). Perhaps the best example is a shift of up to 0.2‰ in $\Delta^{199}\text{Hg}$ across the end-Permian mass extinction event, reflecting the emplacement of the Siberian Traps (25). These findings open up the tantalizing possibility of investigating similar linkages between volcanism and biogeochemical perturbations in the Neoproterozoic. Here, we present Hg isotope data across the well-studied ~2.5-Ga Mt. McRae Shale, which records the best-documented O_2 oxygenation episode prior to the GOE (3, 7, 26). We present data across the anoxic-oxic transition and consider their potential to constrain the driver(s) of the observed O_2 whiff.

Geological Setting

Our samples came from drill core ABDP-9 drilled in Caliwingina Creek at 21°59'29.5"S, 117°25'13.6"E (SI Appendix, Fig. S1), drill hole azimuth 186°, dip 89°. The Mount McRae Shale was deposited along the southern margin of the Pilbara craton (27) in a deep subtidal environment by hemipelagic sedimentation (28). It is about 100 m thick and is underlain by the Mt. Sylvania Formation and capped by the Dales Gorge Member of the Brockman Iron Formation. Anbar et al. (3) obtained an age of $2,501.1 \pm 8.2$ million years from Re/Os geochronology for the drill core ABDP-9; subsequent reanalysis by Kendall et al. (29) yielded two less precise but more methodologically sound dates of $2,495 \pm 14$ Ma for the 145- to 148-m interval and $2,495 \pm 20$ Ma for the 128- to 129-m interval. Rasmussen et al. (30) obtained a date of $2,504 \pm 5$ million years from U/Pb geochronometry of zircons in tuff from elsewhere in the Mt. McRae Shale, but the precise stratigraphic location within the formation was not reported. Rocks underlying the Mt. McRae Shale in the area of ABDP-9 have only been metamorphosed to prehnite-pumpellyite facies (31–33). Deformation has been limited to very gentle open folding and sparse formation of ~1-cm chlorite veins oriented parallel to bedding (34). Potential metasomatic effects on primary geochemical proxies distal to veins have previously been discounted; they are unlikely to have been significant, given the consistency between multiple redox indicators across the whiff interval (29, 34).

The Mt. McRae Shale in ABDP-9 extends from 105 to 190 m. The uppermost 20 m are characterized by interbedded calcitic carbonates and gray/black shale with pyrite sparsely present, gradually passing down into black shale with increasing pyrite. Pyrite nodules occur in great abundance from 131 m to 134 m, underlain by a 15-m-thick section of black shale with frequent pyrite laminae and nodules. Below this section, pyrite content drops as the dominant lithology passes into laminated sideritic and ankeritic carbonates with black shale interbeds. Beneath 173-m depth, pyritic black shale becomes dominant again, with carbonate/marl interbeds occurring until the base of the Mt. McRae Shale. The core was sampled at ~2-m intervals for high stratigraphic resolution. Sampling deliberately avoided pyrite

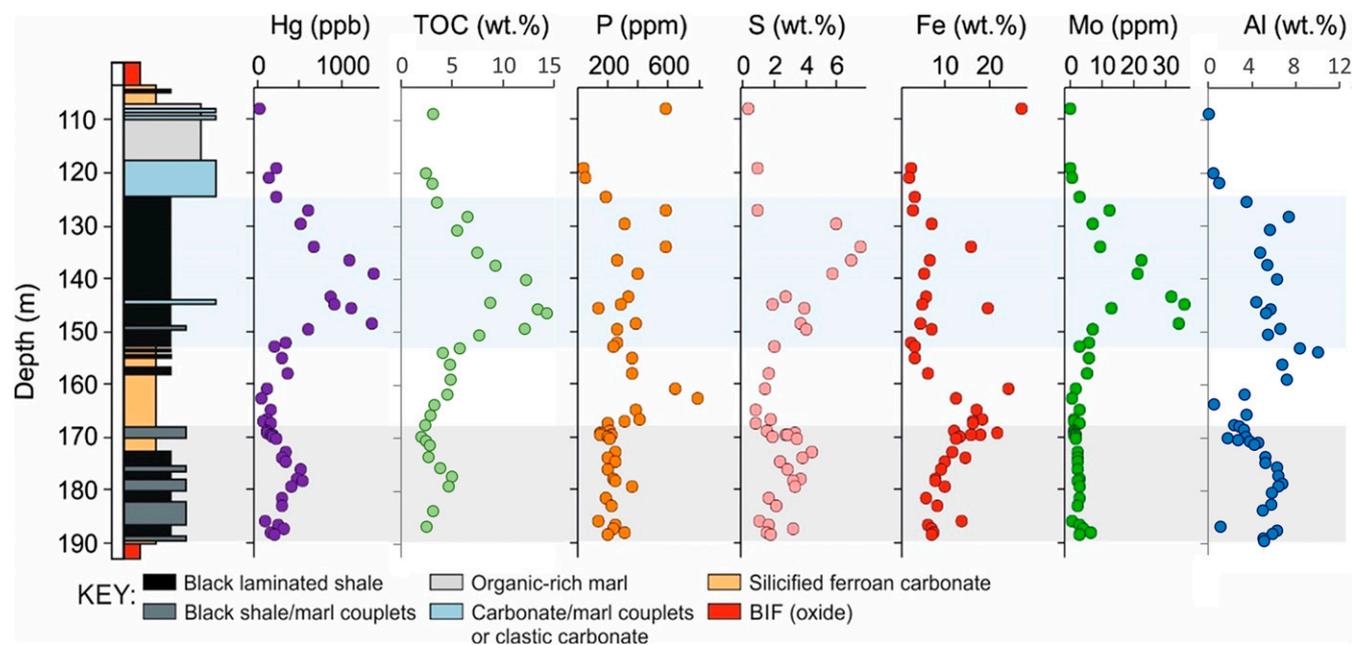


Fig. 1. Lithology and chemostratigraphy of the Mt. McRae Shale. TOC, P, S, and metal data were taken from the literature (3, 6). The gray and blue shaded areas mark the lower and upper shale horizons, respectively, showing Hg enrichments and isotopic excursions.

nodules and laminae to avoid secondary concentrations of Hg in remobilized sulfide minerals. Sampling also avoided proximity to chlorite veins to minimize any potential metasomatic effects.

Results

High-resolution Hg chemostratigraphy (Figs. 1 and 2) reveals two distinct excursions in Hg concentrations in regions dominated by organic-rich, pyritic black shale, with maxima of 491 ng/g at 179.05 m and 1,593 ng/g at 141.47-m stratigraphic depth. We examined these two intervals from 190 to 168 m and from 153 to 125 m at high stratigraphic resolution (approximately two samples per meter). When normalized to traditional sequestration proxies (total organic carbon [TOC], total sulfur [TS], Al, Fe, and Mo), Hg/TOC (in nanograms/gram/weight percent) shows a notable increase in the lower interval with a local maximum of 122.1 at 173.5 m and 118.8 at 137.31 m. Hg/Fe and Hg/Mo show enrichments in the lower interval rising to 68.9 (ng/g/wt%) and 199.2 (ng/g/ $\mu\text{g/g}$), respectively, between 177 and 179 m, while Hg/TS and Hg/Al do not change appreciably (*SI Appendix, Fig. S2*). In the upper interval, Hg/Mo remains at the base level while Hg/TS, Hg/Fe, and Hg/Al show enrichment and fluctuations. Phosphorus remains constant in the lower interval averaging $\sim 226 \mu\text{g/g}$, then sharply spikes between 170 m and 160 m with a maximum of $790 \mu\text{g/g}$, and is then followed by fluctuating values averaging $337.5 \mu\text{g/g}$ in the upper interval.

$\delta^{202}\text{Hg}$ exhibits a slight decreasing trend up section, ranging from -0.71‰ to -1.5‰ and averaging -0.94‰ across the core. In the lower interval, $\Delta^{199}\text{Hg}$ steadily decreases up-section from a local maximum of $+0.198\text{‰}$ to $+0.06\text{‰}$, averaging $+0.138\text{‰}$. In the upper interval, $\Delta^{199}\text{Hg}$ decreases to negative values, with a local minimum of -0.047‰ at 147.3 m, then shows a slight increase to $+0.019\text{‰}$ at 132.13 m, with an average value of -0.02‰ . In contrast, $\Delta^{200}\text{Hg}$ displays an opposite pattern to $\Delta^{199}\text{Hg}$, negative in the lower interval (average -0.05‰ with a local minimum of -0.071‰ at 178.61 m) and then increasing up-section and fluctuating around a mean of $+0.007\text{‰}$ in the upper interval.

Discussion

The Upper Mt. McRae Shale: Evidence of Oxidative Weathering. Several geochemical proxies in the organic-rich shale section from ~ 125 m to ~ 153 m have previously been interpreted as evidence of transient oxygenation of shallow waters above a euxinic wedge, linked to a pulse of oxidative continental weathering and elevated primary productivity along continental margins (3, 26, 34–36). The Mt. McRae Shale would thus preserve a local, basinal expression of this event. We found strong Hg enrichment in this interval, coincident with excursions in TOC and redox-sensitive Mo and Re. Hg has a high affinity for organic matter, which is thought to be the main control on Hg sequestration into sedimentary rocks over geologic time scales (16). The linear relationship

between Hg and TOC in this upper interval (Fig. 3) indicates that Hg removal was controlled by this well-known process. While the high TOC levels are explicable by heightened productivity linked to the whiff, the concurrent enrichment of Hg relative to TOC requires that the Hg reservoir in seawater also increased, suggesting enhanced Hg input from other sources.

We note that Hg/Mo remained constant, and these two elements were strongly correlated (*SI Appendix, Figs. S2 and S3*). As Mo is preferentially sequestered into sediments in a sulfidic water column, this correlation may indicate that Hg sequestration was facilitated by the expansion of euxinic conditions during this interval (35). However, given that sulfur was generally not an abundant constituent of Archean seawater (37) and the expansion of sulfidic conditions is therefore temporally anomalous, the covariance between Hg, Mo, and euxinia (i.e., sulfide) likely indicates that the supply of all three elements to the ocean became enhanced at this time.

Our isotopic data suggest that the most plausible mechanism for enhanced Hg input in this upper interval of the Mt. McRae Shale is either hydrothermal input or oxidative weathering of fresh crustal rocks, which typically display $\Delta^{199}\text{Hg}$ (and $\Delta^{201}\text{Hg}$) values close to zero, consistent with our observations. Fresh crustal rock may also include volcanic ash and fallout from prior volcanic eruptions (see below). While we cannot rule out a hydrothermal contribution, the covariance of the Hg/TOC spike in the upper shale with Mo, Re, U, Se, N, and other redox-sensitive tracers (3, 26, 29, 34, 36) is suggestive of oxidative weathering as the major Hg source during this interval. Contemporaneous volcanic emission of volatile Hg(0) is an unlikely source of Hg in this part of the section, because Phanerozoic studies suggest that the isotopic signature of large-scale subaerial volcanism is a slightly positive $\Delta^{199}\text{Hg}$ resulting from the oxidation of volcanogenic Hg(0) in the atmosphere and subsequent direct atmospheric deposition of positive odd-MIF-bearing Hg(II) (16). It is therefore more likely that the muted odd Hg-MIF signal across this interval reflects the input of lithogenic Hg released from land by oxidative weathering of previously deposited volcanic rocks or volcanogenic sulfide minerals that were not exposed to photochemical processes in the atmosphere and that do not carry any significant Hg odd-MIF (therefore, $\Delta^{199}\text{Hg} = \sim 0\text{‰}$). The Hg data thus further support the inference of a whiff of O_2 during this interval (3).

The Lower Mt. McRae Shale: Evidence of Volcanic Input. In contrast to the whiff interval, the older and stratigraphically lower part of the Mt. McRae Shale lacks enrichments in redox-sensitive trace elements. This interval is believed to have been deposited under an anoxic atmosphere in ferruginous waters (35). The Hg enrichment observed at ~ 177 m amounts to only about a third of the Hg anomaly across the O_2 whiff, and although TOC shows a small peak as well (possibly linked to high productivity), Hg/TOC ratios are again enriched and the maximum Hg/TOC ratio is comparable to the whiff interval (Figs. 1 and 2). Moreover, Hg is notably enriched over Mo in this interval, indicating a decoupling from weathering-induced sulfate input and ensuing water column euxinia. Oxidative weathering of crustal sulfides can be excluded as a viable Hg source during the deposition of the lower shale, because there is no evidence of oxygenation in any other proxies (3, 26, 34–36). The only other significant source of Hg in the late Archean was volcanism, and so the peak in Hg/TOC ratios at 173.5 m likely corresponds to enhanced volcanic Hg input. If so, then the small peak in TOC is perhaps explicable by short-lived fertilization by P derived from volcanic ash.

Throughout the lower core interval, $\Delta^{199}\text{Hg}$ shows positive values consistent with a volcanic contribution (16). Specifically, it has been shown that photo-oxidation of fresh volcanogenic Hg(0) leads to initial atmospheric deposition of Hg(II) carrying a positive $\Delta^{199}\text{Hg}$ signature. The complementary negative $\Delta^{199}\text{Hg}$

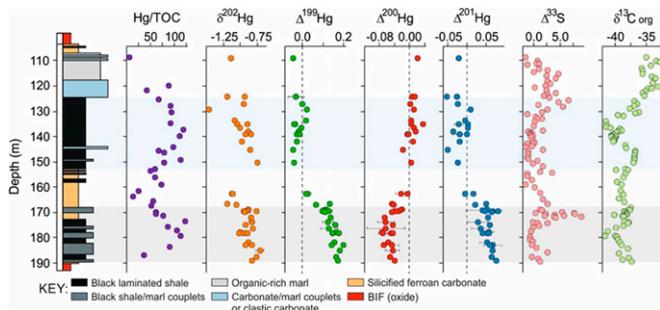


Fig. 2. Lithology and isotopic chemostratigraphy of the Mt. McRae Shale. C and S isotopic data were taken from Kaufman et al. (6).

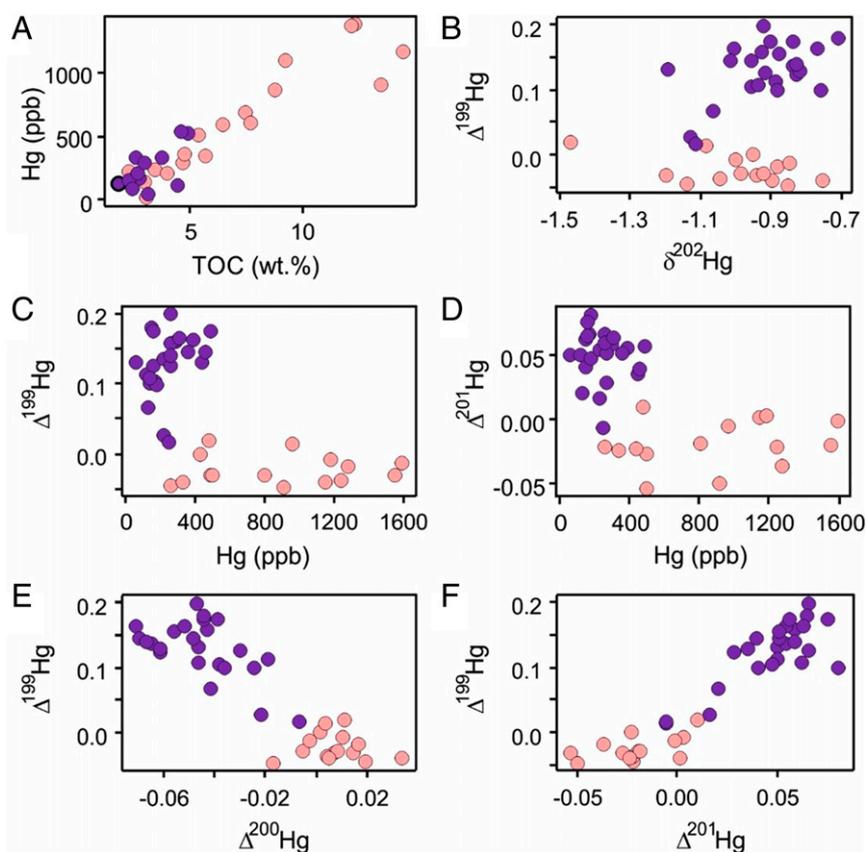


Fig. 3. Cross plots of geochemical data (A–F). Dark purple data points correspond to the lower interval from 180- to 160-m stratigraphic depth; pink data points represent the upper interval above 160 m and include the whiff of oxygen. Apart from Hg/TOC, elemental abundances and isotopes exhibit distinctly different relationships in the two sections of the core (*SI Appendix, Fig. S2*).

is held in residual gaseous Hg(0). When volcanism ends, this residual Hg(0) also undergoes photo-oxidation and rains out, possibly more distal to the volcanic source. A long-lived positive $\Delta^{199}\text{Hg}$ signature in sediments thus requires continuous replenishment of the proximal atmospheric Hg pool by volcanism. The decrease in $\Delta^{199}\text{Hg}$ up-section may thus be explained by decreasing volcanic input to the atmosphere proximal to the sampling site, such that the rainout of background volcanogenic Hg from more distal sources would have become progressively more dominant in the samples. This process would over time have shifted the sedimentary $\Delta^{199}\text{Hg}$ to more negative values and created the gradual diminution of odd-MIF that we observe up-section. Alternatively, it is conceivable that the decrease in $\Delta^{199}\text{Hg}$ represents the buildup of a UV-shielding haze (24) that diminished Hg photochemistry. We cannot exclude this possibility, but the decline in Hg/TOC ratios up-section in the lower shale points toward a diminution of Hg input, consistent with declining volcanism near the basin. Interestingly, the Hg enrichment in the lower core closely underlies a very large positive excursion in the mass-independent fractionation of sulfur (S-MIF) ($\Delta^{33}\text{S}$, Fig. 2). S-MIF is thought to form by photochemical reactions of sulfur-containing volcanic gases in the atmosphere (38), which strongly supports the hypothesis of subaerial volcanic activity. We speculate that the short stratigraphic extent of the S-MIF peak compared to the Hg-MIF signal reflects injection of volcanic gases into higher atmospheric layers, leading to the production of distinct UV effects.

We note that our observations differ from slightly older Archean black shales from the Griqualand West basin in South Africa (2.65–2.5 Ga) (24), which show a short-lived collapse in

$\Delta^{200}\text{Hg}$ and $\Delta^{199}\text{Hg}$ to near-zero relative to high positive background values in both parameters. In that case, the positive background in both $\Delta^{200}\text{Hg}$ and $\Delta^{199}\text{Hg}$ was interpreted as evidence of extensive photochemical destruction of Hg gases in the absence of an ozone shield, while the collapse in Hg-MIF was interpreted as an episode of enhanced organic haze production. In our dataset, $\Delta^{199}\text{Hg}$ is positive while $\Delta^{200}\text{Hg}$ is negative during the lower core section. The origin of $\Delta^{200}\text{Hg}$ is currently not well understood but is thought to be related to Hg(0) oxidation under UV light (39). In Phanerozoic atmospheric samples, it is usually positive (18, 21). The difference between these two Archean datasets suggests a different atmospheric state during the deposition of the Mt. McRae Shale, possibly related to more intense volcanic activity around the 173.5-m horizon where Hg/TOC ratios are highest.

The interpretation of a significant volcanic event around the Hg/TOC peak at 173.5 m is consistent with the duration of the Hg enrichment interval. The average sedimentation rate of the Mt. McRae Shale is estimated to be ~ 4.5 m/My (3, 29, 40), so our lower core interval (22 m thick) could have been deposited over ~ 4.9 My. However, the sedimentation rate of carbonate-bearing rocks is usually higher than that of shales, estimated in the Hamersley Group to be ~ 12 m/My (40), so our lower core interval showing Hg enrichment among ferroan carbonate/black shale couplets may have accumulated rather more rapidly, in less than half this time. This timing is in agreement with the average lifetime of LIPs, most of which span a 1- to 5-My interval (with a maximum lifetime up to 50 My) and in which single magma pulses may have lasted from a few hundred thousand years up to 1 My (41). The Hg/TOC ratios up to 122 are of similar

magnitude as those attributed to LIP events during extinction episodes and ocean anoxic events in the Phanerozoic sedimentary record (16), which further strengthens our interpretation.

Subaerial volcanism preceding an O₂ whiff begs the question about causality: Did a volcanic episode trigger transient O₂ accumulation? We propose that the immediate aftermath of LIP activity may have facilitated oxygenation because 1) O₂ sinks diminished, and 2) nutrient supply increased as LIPs were subject to weathering. Initially, volcanism likely released reducing gases, such as CO or H₂S, that act as O₂ sinks. Such gas emissions are short-lived compared to the much longer effect of weathering fresh volcanic rock (42). The cessation of intense volcanism would thus have switched off this kinetically rapid O₂ sink, thereby promoting O₂ accumulation (12). On longer time scales, weathering and mobilization of nutrients would have gained prominence and enhanced biological productivity through the whiff interval. Freshly emplaced basaltic crust is highly susceptible to chemical weathering and is able to release significant amounts of P. This basaltic P source has been invoked as a fertilization mechanism for the ocean later in Earth's history (9). As the Archean biosphere is thought to have been predominantly P-limited (43, 44), such a nutrient injection may have stimulated biological productivity and increased the rate of O₂ production. Consistent with this logic, our data reveal a conspicuous P spike following the Hg enrichment and elevated Hg/TOC ratios in the lower core and preceding the whiff of O₂ (Fig. 1). This P excursion coincides with a bed of ferroan carbonate, so P enrichment resulting from lithologic changes cannot be excluded, but enhanced P bioavailability following volcanism appears likely and warrants further scrutiny.

Conclusions

This study utilizes Hg abundance and isotopic data that support the existing narrative that a whiff of oxygen was recorded by the upper shale interval of the Mt. McRae Shale. Our data also provide insights into potential causes of this event. Preceding this transient surface oxygenation event, a stratigraphically lower and older section of the Mt. McRae Shale records a Hg/TOC anomaly and isotopic pattern that is strongly suggestive of subaerial volcanism under unfiltered UV radiation of a magnitude and duration comparable to Phanerozoic LIPs. We hypothesize that the weathering of these flood basalts may have delivered nutrients such as P to the ocean and promoted primary productivity and thus the whiff of oxygen in its aftermath. In support of this hypothesis, it is notable that TOC levels increase markedly (~10-fold) from 170 m to 145 m (Fig. 1), peaking where oxygenation proxies such as Mo and Hg abundance are highest. So, while saturation of oxygen sinks is often regarded as the primary cause of the GOE (12), it seems that in the case of this pre-GOE oxygenation event a contributing factor may have also been volcanic-sourced phosphorus fertilization of biogenic oxygen production. While the Mt. McRae Shale is only a regional, short-lived example of a linkage between volcanism and oxygenation, it is conceivable that this linkage operated also on a global, protracted scale in the run-up to the GOE.

Materials and Methods

We analyzed 44 samples that had previously been analyzed for S, Fe, Se, C, and N isotopes and some trace metals (3, 6, 34–36, 45, 46). For each sample, a billet was cut (3 cm × 5 cm × 1 cm) from the drill core using a water-cooled diamond blade tile saw. The billets were then broken into <5-mm chips without metal contact and ground to <100 mesh in silicon nitride ball mill vials. Samples were prepared for Hg isotope analysis in 2007, and again in 2018, following protocols described in detail by Biswas et al. (47) and Blum and Johnson (39). Briefly, Hg was released from between 0.1 and 1.5 g of powdered rock sample by thermal decomposition in a two-stage tube-furnace, carried by gold-trap filtered O₂, and captured in an oxidizing solution of 1% KMnO₄ (wt/wt) in 10% H₂SO₄ (vol/vol). In 2007, the amounts of sample processed yielded 200–400 ng of Hg per preparation. Trap solutions were neutralized by addition of 30% hydroxylamine-hydrochloride (wt/vol)

in accordance with EPA Method 1631 (Rev. E) recommendations and measured for Hg content using gold-amalgamation cold vapor–atomic absorption spectrophotometry (MA2000). Samples were then made ready for isotope measurement by dilution with additional neutralized KMnO₄ solution so that multiple samples could be analyzed at the same run solution concentration. In 2018, smaller amounts of sample material were processed, which yielded 30–180 ng of Hg per preparation, and additional processing followed thermal decomposition and trap neutralization. Hg content of each trap solution was assessed by cold vapor atomic fluorescence spectroscopy (CVAFS) (RA-3320F Gold+, Nippon Instruments) and then purged into a smaller secondary oxidizing trap solution with the same chemical composition as the initial trap. Use of a secondary trap separates Hg from sample matrix residues liberated by thermal decomposition and carried into the initial trap, and also enables preconcentration of Hg into the smallest practical volume so that isotope measurements may be made with the highest precision possible. Verification of secondary trap Hg contents was made by CVAFS measurements, and, as in 2007, final dilutions to common run solution concentrations were made by addition of neutralized KMnO₄ solution.

Process yields for the isotope preparation thermal decomposition step relative to direct-combustion atomic absorption spectrophotometry (AAS) averaged 98% (±10%, 1SD). For samples subjected to additional processing average yield associated with the purging of samples into secondary traps, relative to amount of Hg trapped from thermal decomposition, was 99% (±1%, 1SD). Larger scatter of thermal decomposition yield results may be attributable to the much smaller amounts of material (~0.05 g) processed for THg determination by direct-combustion AAS. The approximately 10-fold larger amounts of material processed per sample for isotope measurement diminishes the likelihood that uneven distribution of Hg in pulverized sample material could influence a THg result. The total Hg process blank associated with sample and standard reference materials (SRMs) prepared for isotope analysis averaged 0.3 ng per preparation, which represents an average contribution of 0.5% (±0.2%, 1SD) to sample or SRM Hg.

Measurements of Hg isotopes were performed with a Nu Plasma (Nu Instruments) multicollector inductively coupled plasma mass spectrometer at the University of Michigan and results are presented following recommendations of Blum and Bergquist (23). Hg was released by SnCl₂ reduction as a cold vapor from a gas–liquid separator of custom design and combined with TI (National Institute of Standards and Technology [NIST] SRM997) aerosol delivered from an Aridus desolvating nebulizer (Teledyne CETAC Technologies). Each analysis consisted of 24 10-s measurements followed by washout to a low, stable background signal. Background signals were assessed with on-peak-zero (OPZ) measurements of neutralized KMnO₄ solution, which were subtracted from signals measured during the subsequent analysis. Instrumental mass-bias was accounted for by using both an exponential fractionation law applied to individual measurements of samples and SRMs, and strict sample-standard bracketing of samples with analyses of NIST SRM3133. Evaluation of potential isobaric interference with the measurement of ²⁰⁴Hg was made by monitoring for any signal attributable to ²⁰⁶Pb, which was never detected.

MDF of Hg isotopes is reported as δ²⁰²Hg in permil (‰) relative to NIST SRM 3133 (Eq. 1). MIF of Hg isotopes is calculated as the difference between the measured δ²⁰²Hg value and that which would be predicted based on mass dependence for a given isotope and is reported as Δ^{xxx}Hg in permil (Eq. 2), where xxx is the mass of each Hg isotope 199, 200, 201, and 204, and β is the mass proportionality constant (0.2520, 0.5024, 0.7520, and 1.493, respectively) (23):

$$\delta^{202}\text{Hg} = \left(\left(\frac{\left(\frac{^{202}\text{Hg}}{^{198}\text{Hg}} \right)_{\text{sample}}}{\left(\frac{^{202}\text{Hg}}{^{198}\text{Hg}} \right)_{\text{NIST3133}}} \right) - 1 \right) \times 1000, \quad [1]$$

$$\Delta^{xxx}\text{Hg} \approx \delta^{xxx} - (\delta^{202} \times \beta). \quad [2]$$

In 2007, limitations imposed by the available collector array made it impossible to simultaneously measure all seven stable Hg isotopes, the two TI isotopes, and a Pb isotope. The default configuration only permitted measurement of consecutive Hg isotopes (¹⁹⁸Hg–²⁰²Hg). A small subset of samples processed at that time were measured again during a second analytical session in which an alternate collector configuration enabled measurement of ¹⁹⁸Hg, ²⁰⁰Hg–²⁰²Hg, and ²⁰⁴Hg, but not ¹⁹⁹Hg. Subsequent to the 2007 analyses, the collector array of the instrument was upgraded. Consequently, in 2018 simultaneous measurements were made for the full range of isotopes, from ¹⁹⁶Hg to ²⁰⁶Pb.

For analyses performed in 2007, instrument sensitivity for Hg was 0.64 V/ppb (total beam) and OPZ measurements indicated that about 1% of sample or bracketing standard signals could be attributed to carryover from the

preceding analysis. Subsequent modifications to the inlet system and instrument interface improved sensitivity and reduced potential carryover to the extent that in 2018 Hg sensitivity was 2.79 V/ppb with a measured blank contribution of about 0.1%.

Estimates of analytical uncertainty (SI Appendix, Table S1) for samples are the larger average 2SD of the following: measurements of multiple preparations of UM-Almaden and NIST3133 used as periodic performance checks during mass spectrometer sessions; and measurements of multiple-sample and SRM process replicate preparations (SI Appendix, Tables S2 and S3).

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Data Availability. All study data are included in the article and/or supporting information.

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