Reel-to-Reel Re-Os Records: Earth System Transactions Preserved in Sediments

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Upper Jurassic Botneheia Formation, Svalbard.
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A unique feature of the Re-Os isotope system is its ability to provide precise and accurate depositional ages from organic-rich sedimentary rocks. Applications include geologic timescale calibration, stratigraphic correlation, and dating key events such as biological innovations, mass extinctions, carbon cycle perturbations, Snowball Earth glaciations, and atmospheric oxygenation. Multiple sediment types reveal temporal variations in the osmium isotope composition of seawater, driven by changes in osmium inputs from continental weathering, seafloor hydrothermal systems, and extraterrestrial material. These variations provide valuable information on climate–tectonic interactions, glacial–interglacial cycles, large igneous province magmatism, bolide impacts, and crustal evolution. Continental processes can be inferred from lake sediment records. These diverse applications highlight the central role of the Re-Os isotope pair in understanding Earth's evolution.

KEYWORDS: sediment; oceans; lakes; climate; glaciation; large igneous provinces; bolide impact; crustal evolution; oxygenation; biological evolution; geologic timescale calibration.

INTRODUCTION

Given the unique organophile and chalcophile nature of its parent and daughter isotopes, the Re-Os isotope system holds unmatched value as a sedimentary geochronometer and geological tracer. Both Re and Os are soluble in oxygenated waters, but in anoxic environments, both metals are fixed by organic matter and sulfide minerals in organic-rich sediments (ORS). Closure of the Re-Os isotope system in ORS (no gain or loss of Re or Os from the sediment) occurs during or shortly after sediment deposition (Ravizza and Turekian 1989; Cohen et al. 1999). The decay of ^{187}Re to ^{187}Os between the time of deposition and today provides a clock that records the depositional age of ORS rocks (e.g., mudstones, black shales, marly carbonates). Re-Os ages from ORS rocks provide critical information on the timing and duration of geological events and processes, particularly for sedimentary sequences lacking biostratigraphy or U-Pb zircon ages from intercalated volcanic ash beds. The ^{187}Os/^{188}Os at the time of deposition can be calculated for ORS (and other sediment types such as Fe-Mn crusts) from a Re-Os isochron diagram or from an individual sample of known age (see *Toolkit* FIG. 6). The sediments inherit this initial ^{187}Os/^{188}Os directly from the local water column. Osmium isotopes, therefore, provide tracer information for processes that alter seawater chemistry, such as climate change, tectonic cycles, bolide impacts, and large igneous province volcanism.

The founding principles for Re-Os geochronology of ORS rocks were established by Ravizza and Turekian (1989). Results at this time were, however, severely limited by low-precision analytical methods. A decade later, results using negative thermal ionization mass spectrometry (NTIMS) combined with Carius-tube digestion in inverse *aqua regia* (normal *aqua regia* has a 1:3 ratio of nitric acid and hydrochloric acid, respectively; inverse *aqua regia* has a 2:1 or 3:1 ratio dominated by nitric acid) produced Re-Os depositional ages with precisions of ±3%–8% for Jurassic shales from the UK (Cohen et al. 1999). This study used only hydrocarbon immature shales, assuming hydrocarbon maturation would disturb the Re-Os isotope system, an assumption later shown to be unfounded (Creaser et al. 2002). A major development arose in 2003 with the discovery that sample digestion using CrO_3-H_2SO_4 selectively liberates hydrogenous Re and Os held within organic matter and sulfide minerals, thereby minimizing release of non-hydrogenous Re and Os from detrital material (Selby and Creaser 2003). Since then, high-precision and demonstrably accurate Re-Os ages from ORS rocks have been produced by multiple laboratories worldwide, with application to problems of global stratigraphic correlation, faunal correlation, geological timescale calibration, paleoenvironmental change, and sedimentary basin evolution. As a result of over 35 years of development, Re-Os ages from ORS rocks, along with U-Pb and Ar-Ar ages from igneous rocks and minerals, are now used as reference ages in the geologic time scale (representation of time based on Earth's rock record using chronostratigraphy and geochronology).

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SEDIMENTARY TIMEKEEPER

Getting the Clock from a Sedimentary Rock: Importance of Sampling Strategies

Precise and accurate geochronology using a Re-Os isochron diagram (see *Toolkit* FIG. 6) begins with thoughtful sample selection. The goal is to identify ORS rocks that have maintained a closed Re-Os isotope system between the time of deposition and today. Drill core is preferred over outcrop samples to minimize post-depositional loss of Re and Os from oxidative weathering. Still, high-quality Re-Os ages have been obtained from some less-weathered outcrops, road cuts, quarry walls, and mines. Geochemistry (redox-sensitive metals and sulfur abundances) and Rock-Eval pyrolysis indices (laboratory process invented in the 1970s at the French Institute of Petroleum to characterize organic carbon and mineral carbon contents of rocks and soils) are used to determine if outcrop samples are likely to yield Re-Os ages (Georgiev et al. 2012).

The development of an isochron requires that samples start with identical initial $^{187}Os/^{188}Os$ yet variable $^{187}Re/^{188}Os$ isotope ratios upon deposition. Because the residence time of Os in seawater is only ~10^4 years, the sampled stratigraphic interval (ideally 5 to 20 cm) must represent a geologically short time interval; otherwise, any temporal variation in seawater $^{187}Os/^{188}Os$ imparts differing initial $^{187}Os/^{188}Os$ among samples and, thus, imprecise Re-Os isochron ages. The hydrogenous component in shales (non-detrital component derived directly from the water) typically comprises an array of different organic molecules and sulfides, and these acquire variable $^{187}Re/^{188}Os$ upon

deposition (DiMarzio et al. 2018). Thus, most shales from reducing environments contain synsedimentary pyrite and/or organic matter with enough variation in $^{187}Re/^{188}Os$ ratios to obtain a precise isochron. Attempts to date terrestrial coal beds confirm spatially variable initial $^{187}Os/^{188}Os$ in the complex mixture of organic matter that accumulates in peat mires or fluvial overbank deposits, violating one of the fundamental requirements for an isochron (Goswami et al. 2018). Shales intercalated with coals may result from marine incursions, however, providing datable material for coals (Tripathy et al. 2015).

Post-depositional processes that might give rise to inaccurate and/or imprecise Re-Os ages are commonly revealed by petrography; notable examples of features left by such processes include cubic pyrites formed during late diagenesis and infilled fractures recording fluid flow. Given the redox-sensitive nature of Re and Os, oxidizing fluids are likely to cause open-system behavior. Fractures, veins, and possible temporal hiatuses should be avoided or carefully tested (FIG. 1). In addition to identifying post-depositional disturbance, petrographic inspection can provide clues to the depositional environment; as examples, fine-grained framboidal pyrite indicates precipitation in an anoxic and sulfidic (euxinic) water column, and various pyrite morphologies (e.g., shale laminae draping around a spheroidal pyrite grain) indicate an early diagenetic origin (Hannah et al. 2004).

Some post-depositional processes, however, do not cause open-system Re-Os behavior. Neither hydrocarbon generation and expulsion nor bioturbation during earliest diagenesis affect the accuracy of Re-Os ages (Creaser et al. 2002;
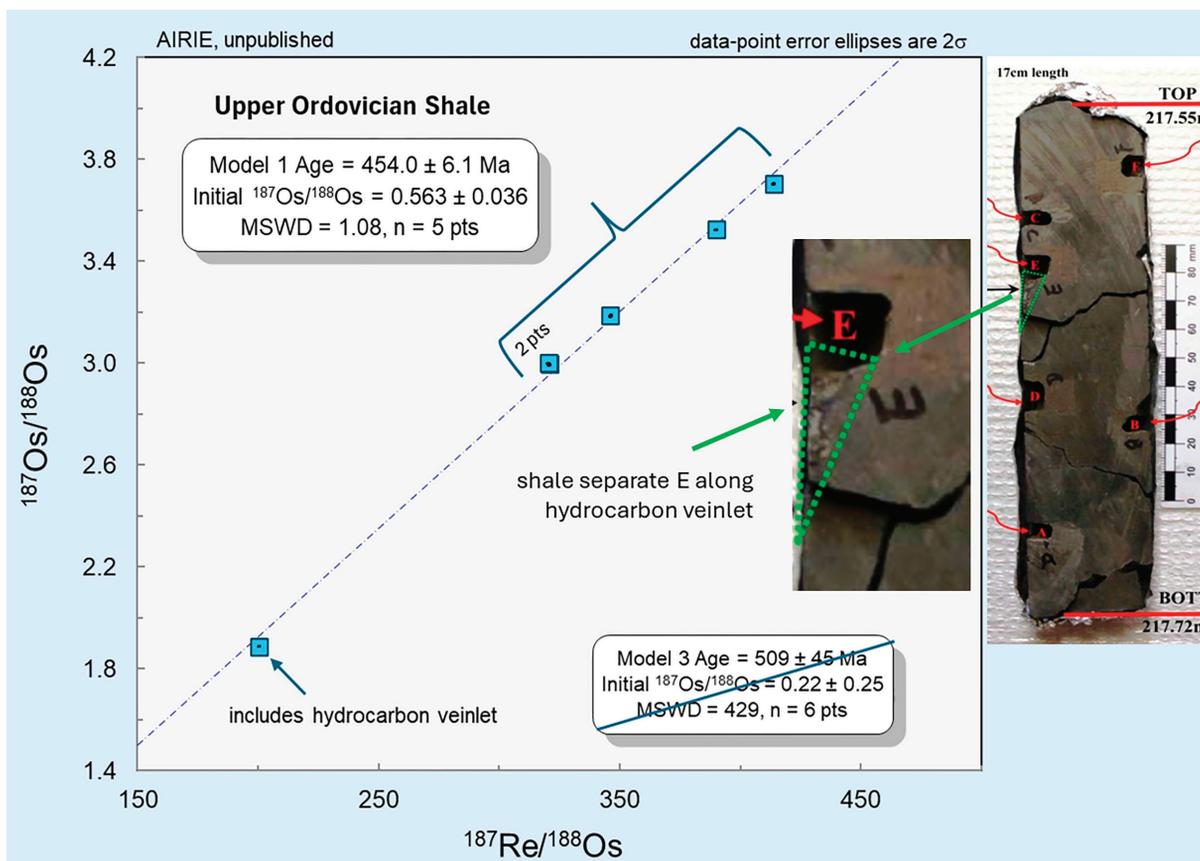

Upper Ordovician Shale

Model 1 Age = 454.0 ± 6.1 Ma
Initial $^{187}Os/^{188}Os$ = 0.563 ± 0.036
MSWD = 1.08, n = 5 pts

2 pts

shale separate E along hydrocarbon veinlet

includes hydrocarbon veinlet

Model 3 Age = 509 ± 45 Ma
Initial $^{187}Os/^{188}Os$ = 0.22 ± 0.25
MSWD = 429, n = 6 pts

AIRIE, unpublished   data-point error ellipses are 2σ

17cm length   TOP 217.55m   BOTTOM 217.72m

FIGURE 1 Example of drill core from an Upper Ordovician shale. Color variations are an artifact of cutting and drying of the core. Six points along the core were selected for analysis (red arrows). Several hundred mg of shale were drilled from each point. The isochron diagram shows five points (two points almost identical) that define a well-fitted linear regression as revealed by its mean square of weighted deviates (MSWD) near 1 (see *Toolkit* for definition of MSWD and model ages). The relatively poor age precision (6.1 Ma, ±1.3%) results from the limited spread in $^{187}Re/^{188}Os$. A sixth point (separate E, lower left point) falls off the isochron because a thin hydrocarbon veinlet was intersected while drilling, contaminating the shale separate.

Park et al. 2024). Precise Re-Os depositional ages have been obtained from ORS rocks that experienced contact and/or regional metamorphism (e.g., Kendall et al. 2004; Yang et al. 2009). Although Re-Os ages are now normally obtained from $CrO_3-H_2SO_4$ digestions (Selby and Creaser 2003), pyrite with indisputably syn-depositional (or early diagenetic) morphologies in ORS rocks also yield accurate and precise Re-Os ages (Hannah et al. 2004).

Setting the Boundaries: Geological Timescale Calibration

Any "new" geochronometer requires cross-calibration with geochronology's "gold standard," which is the combined $^{235}U-^{207}Pb$ and $^{238}U-^{206}Pb$ systems in zircon or monazite. Using the Exshaw Formation (Alberta, Canada) as an example of a black shale with constrained biostratigraphy, known timescale position, and U-Pb monazite geochronology, Selby and Creaser (2005) showed that the Re-Os isotope system in shale could yield a depositional age with < ± 1% (2σ) total uncertainty using Carius-tube $CrO_3-H_2SO_4$ digestion and NTIMS analysis. The age result of 361.3 ± 2.4 Ma overlaps the U-Pb age of a tuff within the Formation (363.4 ± 0.4 Ma) and the known age of the Devonian-Mississippian boundary hosted within the Exshaw Formation, currently constrained at 358.9 ± 0.4 Ma.

The precision now attainable with the Re-Os geochronometer led to the first application of Bayesian-refined Re-Os ages (Xu et al. 2014; Fig. 2). This statistical method is used when the uncertainties of values in a dataset are constrained by independent *a priori* knowledge. Calculated uncertainties for a set of Re-Os ages of samples collected in stratigraphic order from an intact sedimentary section may be refined in this way. The uncertainty of a Re-Os age cannot exceed the ages of samples stratigraphically above or below, as this would violate the known stratigraphy.

More than a decade ago, both correlation of fossil assemblages between polar and equatorial realms and age pins in the Triassic time scale were highly contentious. Xu et
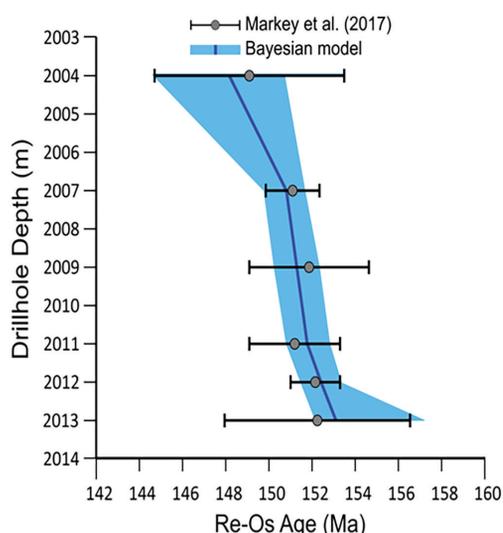

FIGURE 3 Comparison of Re-Os shale and U-Pb zircon ages from the Boreal and Tethyan geographic realms, dating the base and top of the Ladinian Stage as defined by ammonoid stratigraphy. The Boreal and Tethys realms have no common ammonoid species, so their correlation has been controversial. Radiometric ages are needed to validate correlations. MODIFIED FROM XU ET AL. (2014) AND BASED ON REFERENCES THEREIN.

al. (2014) helped break the logjam with seven new Re-Os isochrons through a continuous ORS section that also hosts well-studied Triassic ammonite fossil assemblages. These Re-Os ages helped decide between two competing time scales for the Triassic. Further, the ages allow correlation between the distant realms (Fig. 3) and help tie a large magmatic province (Wrangellia) to a period of intense global warming (the Carnian Pluvial Event), illustrating the significant impact of accurate Re-Os ages from ORS rocks for understanding ancient climate change (Xu et al. 2014). Similarly, new correlations of Late Jurassic ammonite zones have been proposed based on Bayesian-refined Re-Os shale ages from Svalbard. This provides a critical link between different fossil realms, allowing a solution to the problem of faunal provincialism (Park et al. 2024).

Dating the Rock Stars: Re-Os Ages of Famous Events

The large impact of Re-Os shale ages on global stratigraphic correlations is exemplified by the work in Neoproterozoic strata (Kendall et al. 2004, Rooney et al. 2020a). Global events relating to glaciation and deglaciation of multiple "Snowball Earth" events have been refined and correlated worldwide by combining Re-Os geochronology of ORS rocks with U-Pb zircon geochronology. In particular, Re-Os ages helped show that the older Sturtian glaciation lasted an astounding ~56 My (717–661 Ma), highlighting that early eukaryotic multicellular life defied the odds in spectacular fashion to survive this unprecedented climatic catastrophe. The onset of the younger Marinoan glaciation still lacks precise age control, but a Re-Os age has helped constrain deglaciation to ~635 Ma, in agreement with multiple U-Pb ages. Hence, Re-Os shale geochronology has been pivotal in establishing the absolute timing and duration of these global glaciations, which were key events immediately prior to emergence of complex metazoan life and faunal

FIGURE 2 Illustration of Bayesian refinement based on data from a shale in drill core from the Jurassic Hekkingen Formation, SW Barents Sea. SIMPLIFIED FROM MARKEY ET AL. (2017). Circles are the Re-Os isochron ages for six core segments. Horizontal lines show the uncertainties for each age. Because the stratigraphic sequence is known, the uncertainties for each point cannot exceed the age of the data points above and below. Bayesian refinement (see *Toolkit* for references) is shown here by the blue band. Segments at the top and bottom of the section, and where absolute ages are inverted (middle two segments), are constrained on only one side, so refined uncertainties are strongly asymmetrical.
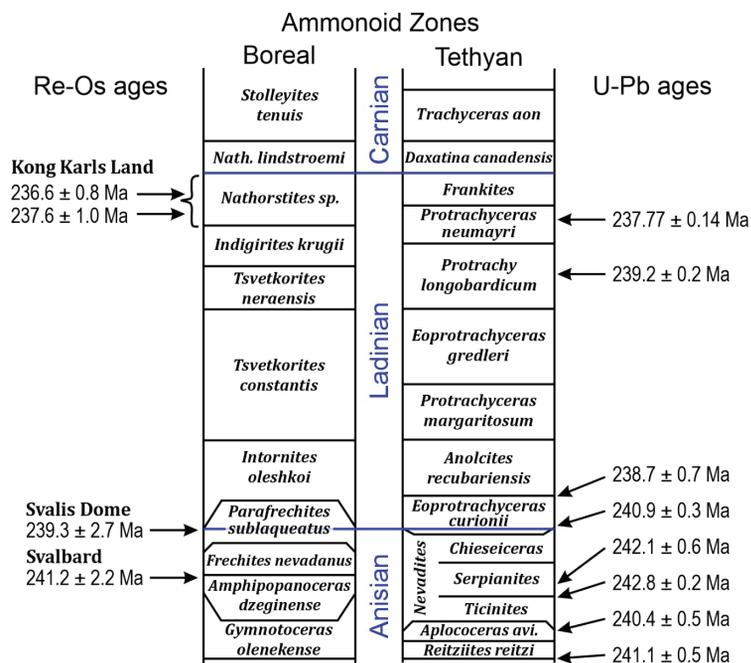
radiations in the Ediacaran and Cambrian, because many of these stratigraphic sections lack volcanic ash beds for U-Pb geochronology.

Sedimentary Re-Os geochronology has provided key age constraints on biological innovations ranging from oxygenic photosynthesis to animal evolution. A Re-Os age of 2316 ± 7 Ma from early diagenetic pyrite from black shales lacking independent geochemical evidence of an anoxic atmosphere provided an important age constraint for the Great Oxidation Event (Hannah et al. 2004). Subsequently, a Re-Os black shale age dated a transient accumulation of photosynthetic O_2 in the atmosphere and shallow oceans at ~2.5 Ga, shortly before the Great Oxidation Event (Kendall et al. 2015). Fossil records for which the Re-Os clock has provided age information include eukaryotic microfossils between ~1590 and ~1440 Ma (Rainbird et al. 2020) and the first Ediacaran animal macrofossils on multiple paleocontinents between ~580 and ~574 Ma (Rooney et al. 2020b).

Re-Os geochronology has shed new light on major Phanerozoic mass extinction events, including the Permo–Triassic extinction that decimated more species than the other "Big Five" extinctions (Georgiev et al. 2011). Before Georgiev et al. (2011) was published, tight age constraints were limited to U-Pb ages for the famous Meishan exposure in China. The extinction horizon is also exposed in East Greenland with correlative sections on the mid-Norwegian shelf. Using drill core, Re-Os geochronology for two Boreal shale sections immediately below the extinction horizon yielded four highly precise ages overlapping multiple U-Pb zircon ages from an ash bed at the Meishan extinction horizon on the opposite side of the globe, confirming the timing and global extent of this greatest extinction event (Georgiev et al. 2011). The initial $^{187}Os/^{188}Os$ ratio of ~0.6 for all four isochrons rules out massive basaltic volcanism or a bolide impact (expected initial $^{187}Os/^{188}Os$ of ~0.13) as the cause of the extinction, while high concentrations of toxic metals in late Permian shales implicate noxious seawater.

Unusual perturbations to biogeochemical cycles, often recorded as carbon isotope excursions, have also received significant attention from the Re-Os community. In addition to dating carbon isotope excursions associated with Phanerozoic deoxygenation events, Re-Os geochronology has constrained the timing of large positive and negative excursions recorded in Neoproterozoic sedimentary rocks worldwide. For example, Re-Os ages from multiple paleocontinents were used to suggest that the most severe negative carbon isotope excursion in Earth's history, the Shuram Excursion, was a globally synchronous event between 574.0 ± 4.7 and 567.3 ± 3.0 Ma (Rooney et al. 2020b).

Another noteworthy application of Re-Os geochronology is determining the duration of a supercontinent cycle. A Re-Os black shale age of 1067.3 ± 13.5 Ma dated the base of the 4-km-thick Shaler Supergroup in northern Canada, whereas U-Pb zircon and baddeleyite ages for the Franklin large igneous province dated the top of the supergroup. Together, these ages yielded a duration of ~350 My between the assembly and breakup of the Rodinia supercontinent (Rainbird et al. 2020).

REEL-TO-REEL TRACER: OSMIUM ISOTOPES

Water column $^{187}Os/^{188}Os$, captured by ORS and other sediment types (e.g., Fe-Mn crusts), is set by the relative contributions of different Os sources and, thus, provides information about Earth system processes. A sediment's $^{187}Os/^{188}Os$ at the time of deposition can be determined from the initial $^{187}Os/^{188}Os$ ratio (y-intercept) of a Re-Os isochron (see *Toolkit* FIG. 6) or calculated from the sediment's present-day $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ if the sediment age can be interpolated from other dated sedimentary horizons or volcanic ash beds, and if it can be shown that the sediment's Re-Os systematics have been undisturbed since the time of deposition.

Tape Recorder of Tectonic, Climatic, and Sea Level Changes

Seawater $^{187}Os/^{188}Os$ ratios are commonly used to assess the sensitivity of continental weathering to climatic and tectonic changes (FIG. 4). This ratio is nearly homogenous (~1.05) in modern deep oceans and reflects a dominant Os contribution from continental weathering. The average $^{187}Os/^{188}Os$ ratio of the upper continental crust (~1.4) is an order of magnitude higher than that of mantle and extraterrestrial materials (~0.13), the other major sources of Os input to seawater. Relative changes in continental weathering intensity in the past can, therefore, be tracked effectively using seawater $^{187}Os/^{188}Os$ ratios (FIG. 4; see *Toolkit* FIG. 13).

Past variations in seawater $^{187}Os/^{188}Os$ have been reconstructed by analyzing hydrogenous Os phases from several archives (e.g., ORS rocks, Fe-Mn crusts and nodules, foraminifera). The Fe-Mn crusts and nodules largely accumulate Os directly from seawater and their diagenetic alteration can
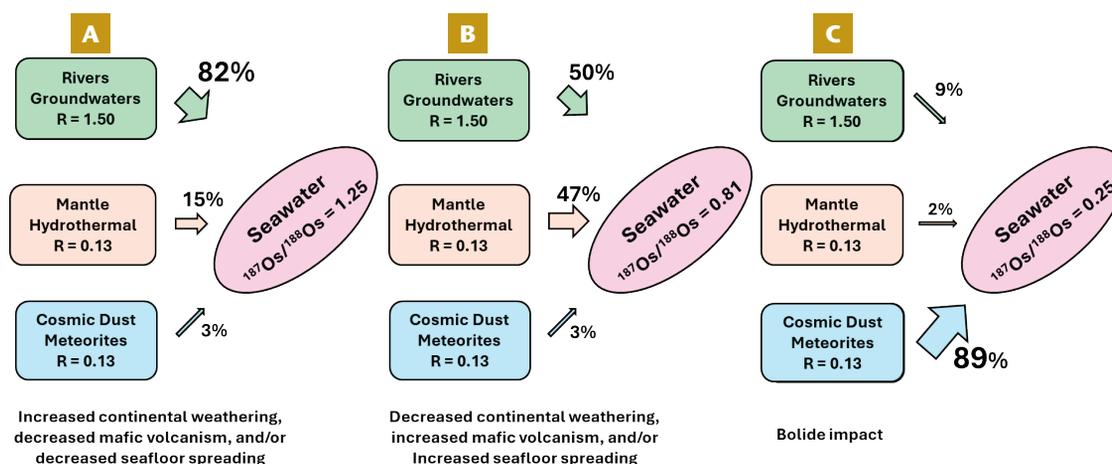

FIGURE 4 Mass balance solutions to illustrate the impact of varied inputs from major Os reservoirs on the $^{187}Os/^{188}Os$ composition of seawater: (**A**) increased relative input of high $^{187}Os/^{188}Os$ material; (**B**) decreased relative input of high $^{187}Os/^{188}Os$ material; and (**C**) a bolide impact. The $^{187}Os/^{188}Os$ ratios (R) for the three reservoirs are as follows: rivers–groundwaters = 1.50; mantle–hydrothermal = 0.13; cosmic dust–meteorites = 0.13.

have minimal effect on $^{187}Os/^{188}Os$ (e.g., Burton et al. 1999). The measured $^{187}Os/^{188}Os$ ratios of surface Fe-Mn deposits match well with the modern seawater value, confirming proxy reliability. The $^{187}Os/^{188}Os$ ratios of these slow-growing (a few mm/My) deposits archive large variations in seawater $^{187}Os/^{188}Os$ on million-year timescales.

Notably, $^{187}Os/^{188}Os$ ratios show a steady rise from 0.4 to 1.05 during the Cenozoic Era, with the highest value being observed for the modern ocean (see *Toolkit* FIG. 12 and *Toolkit* references). This trend is broadly consistent with the corresponding first-order rise in seawater $^{87}Sr/^{86}Sr$ during the Cenozoic and reflects high weathering influxes from young orogenic belts (e.g., Himalayan-Tibetan plateau river basins). This observation underscores the impact of mountain building processes on continental weathering rates, which in turn regulate the global climate. At finer temporal resolution, significant differences are observed between the Cenozoic seawater Os and Sr isotope curves (see *Toolkit* FIG. 12). These differences reflect the much longer seawater residence time for Sr (~10^6 y) than Os (~10^4 y) and temporal changes in oxidation of sulfide minerals, which supply more chalcophile Os than lithophile Sr to seawater (Torres et al. 2014). Sulfide oxidation in river basins produces sulfuric acid, which reacts with carbonates, thus releasing CO_2 to the atmosphere that counterbalances CO_2 consumed by H_2CO_3-mediated silicate weathering. The mismatch between $^{87}Sr/^{86}Sr$ and $^{187}Os/^{188}Os$ seawater trends during the Cenozoic, therefore, has provided deeper insight into fluctuations in the rates of these two weathering processes due to tectonic activity and their net effect on atmospheric CO_2 levels (Torres et al. 2014).

Glacial–interglacial variations in seawater $^{187}Os/^{188}Os$ depict a strong relationship between weathering and climate. Seawater $^{187}Os/^{188}Os$ ratios inferred from marine sediments are systematically lower during glacial events because of slower weathering rates. By contrast, seawater $^{187}Os/^{188}Os$ increased during deglaciation because exposed post-glacial soils and fresh bedrock are readily weathered in a warmer climate and transported by increased run-off. Climate-driven variations in seawater $^{187}Os/^{188}Os$ ratios and sedimentary Os enrichments at kilo-year timescales and their offset between sites have also provided clues about changes in regional-scale weathering patterns and oceanic redox states due to sea-level fluctuations (Paquay and Ravizza 2012). Seawater $^{187}Os/^{188}Os$ further has been used to trace changes in climate and ocean circulation in the wake of the Neoproterozoic Snowball Earth glaciations. These studies reveal that the onset of deglaciation is initially accompanied by high seawater $^{187}Os/^{188}Os$ in continental margin environments, reflecting intense continental weathering of a glacially scoured terrestrial landscape in a high-CO_2 greenhouse climate. Subsequently, continental margin seawater $^{187}Os/^{188}Os$ decreased upon mixing with deeper-ocean waters, which had developed low $^{187}Os/^{188}Os$ during the Snowball Earth with hydrothermal Os inputs into ice-covered oceans (Rooney et al. 2020a).

At the Heart of a Continent: Regional Processes Recorded in Paleolakes

Organic-rich lake sediments provide high-resolution records of changes in paleoclimate, tectonic and landscape evolution, and terrestrial paleoecology within a continent. Unlike oceans, the volume of water in lakes is small relative to their drainage basins. Thus, lacustrine systems are highly sensitive to small fluctuations in both volume and composition of water and sediment influx. Lacustrine records, however, are often marred by limited chronological constraints.

Attempts to date lake sediments using Re-Os geochronology are typically hampered by a narrow range of $^{187}Re/^{188}Os$ ratios and variability in initial $^{187}Os/^{188}Os$ ratios. Still, useful depositional ages have been obtained if sample suites are carefully selected from distal sections farther from shore where lake water $^{187}Os/^{188}Os$ is more likely to be stable. For example, Re-Os dating of shale from the Eocene Green River Formation (Douglas Creek Member), Uinta Basin, Utah, USA yielded a depositional age of 49.2 ± 1.0 Ma, consistent with $^{40}Ar/^{39}Ar$ ages of intercalated tuff horizons (Cumming et al. 2012).

In lacustrine environments, the short Os residence time allows lake sediments to record stratigraphic variations in depositional $^{187}Os/^{188}Os$ at ~10^2 to 10^3 year timescales, thus providing high-resolution records for the overall $^{187}Os/^{188}Os$ of lake inputs. Such changes in input can be orders of magnitude faster than changes in seawater $^{187}Os/^{188}Os$. These rapid variations may be useful for tracking shifts in drainage geology triggered by regional climate change or tectonic variations that change the relative contribution of Os from different bedrock sources. Variability in initial $^{187}Os/^{188}Os$ (1.37–1.57; from individual samples) was observed for Green River sediments (Douglas Creek Member; ~49 Ma), suggesting (i) variations in continental runoff and (ii) measurable changes to overall lake water chemistry (Cumming et al. 2012).

Osmium isotope records from ORS rocks have the potential to discriminate between terrestrial and marine depositional settings, and changes in marine basin connectivity to the open ocean. Significant deviations of depositional $^{187}Os/^{188}Os$ from the established concurrent seawater $^{187}Os/^{188}Os$ record may indicate non-marine sediment deposition. For example, a change from a marine to a lacustrine setting would be revealed by a change in depositional $^{187}Os/^{188}Os$ toward relatively higher values compared with independent estimates of coeval marine $^{187}Os/^{188}Os$ (e.g., Poirier and Hillaire-Marcel, 2011). Highly restricted marine basins, with limited exchange of water with the open ocean, may generate ambiguous $^{187}Os/^{188}Os$ records with similarly high values and large short-term variability.

Knockout Punches: Bolide Impacts and Large Igneous Provinces

Unlike conventional isotopic tracers like Sr, the large difference in $^{187}Os/^{188}Os$ between mantle/extraterrestrial Os (~0.13) and continental Os (~1.4) enables the Re-Os isotope system to identify periods of time in which the mass balance of Os in the oceans was dominated by mantle or extraterrestrial input, such as large bolide impacts or short-term eruption of large igneous provinces (LIPs), which are enormous volumes of mafic magma erupted over geologically short periods of time, typically ~10^5–10^6 years. The Cretaceous/Paleogene (K-Pg) boundary at ~66 Ma is one such interval widely attributed to a large bolide impact (see *Toolkit* FIG. 12C). An inferred seawater $^{187}Os/^{188}Os$ approaching meteoric values measured at globally widespread exposures of the K-Pg boundary supports this hypothesis (FIG. 4; Koeberl and Shirey 1997; see also references in *Toolkit*).

Mesozoic Oceanic Anoxic Events (OAEs) are characterized by periods of low seawater O_2, climatic warming, carbon burial, and major changes in oceanic fauna. A triggering mechanism for OAEs is commonly proposed to be the eruption of LIPs. Osmium isotopes played a pivotal role in linking LIPs to OAEs, with the discovery that very low, mantle-like $^{187}Os/^{188}Os$ ratios coupled with large Os enrichments characterize oceanic sediments deposited during OAE2 at ~93 Ma (Cenomanian–Turonian boundary; Turgeon and Creaser 2008). Further work verified this
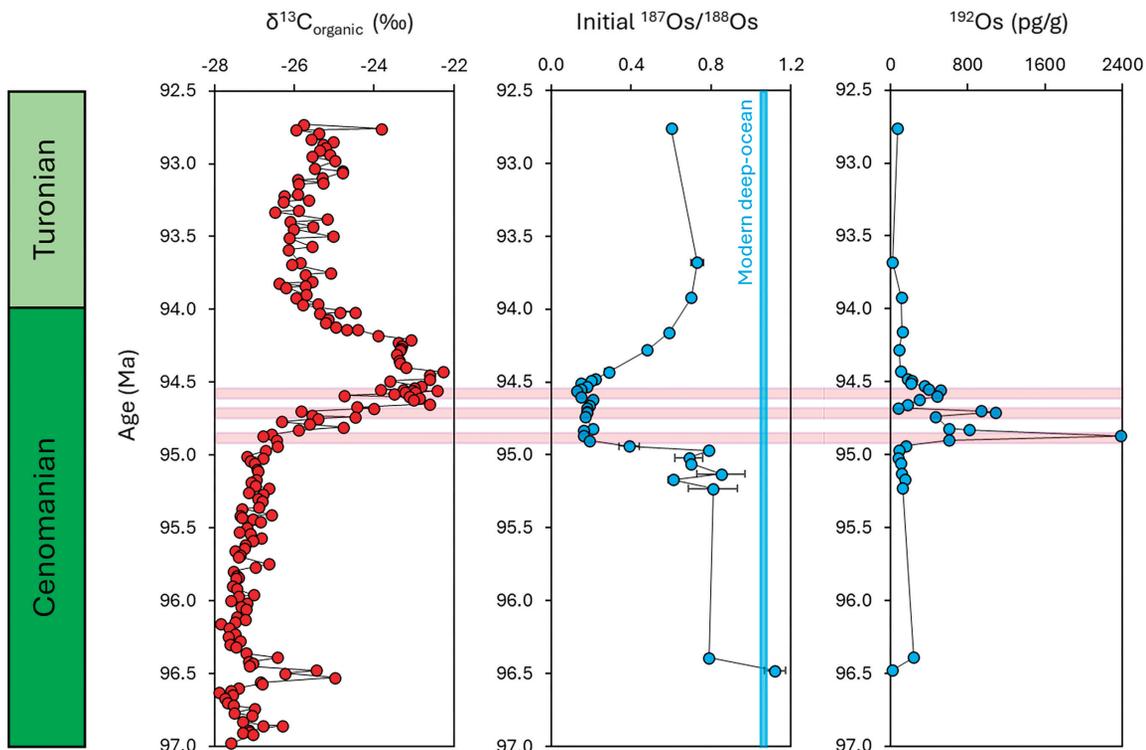
FIGURE 5 Large igneous province (LIP) magmatism revealed by low $^{187}Os/^{188}Os$ and elevated osmium concentrations (represented by the non-radiogenic isotope ^{192}Os) near the Cenomanian–Turonian boundary in the Iona-1 core, Western Interior Seaway. Excursions to higher ^{192}Os concentrations (red bars) may represent pulses of more intense magmatic activity.

The lowermost Os excursion (bottom red bar) occurs before a significant change in organic carbon isotope compositions ($\delta^{13}C$), highlighting the rapid response time and greater sensitivity of the seawater Os reservoir and its isotopic composition to the effects of LIP magmatism compared to the oceanic carbon reservoir. DATA FROM SULLIVAN ET AL. (2020).

initial discovery, extended the effect globally (Du Vivier et al. 2015), and identified three distinct pulses of unradiogenic LIP-derived Os into the oceans during the ~450 Ka duration of OAE2 (FIG. 5; Sullivan et al. 2020). However, distinguishing between bolide impact and LIP-derived Os is not possible using Os isotopes alone as both have ratios of ~0.13 (FIG. 4; see *Toolkit* FIG. 5) and, thus, require other data such as highly siderophile element abundances (Sullivan et al. 2020). After the discovery of low $^{187}Os/^{188}Os$ ratios across OAE2, other Cretaceous OAEs also yielded evidence of LIP-derived Os. In contrast, the Toarcian OAE (T-OAE) is characterized by elevated $^{187}Os/^{188}Os$ during OAE sediment deposition, which likely records intense continental weathering in a volcanogenic-induced greenhouse climate, without significant direct input of Os from LIPs (Them et al. 2017).

Evolution of our Blue Planet Through Time: The Seawater $^{187}Os/^{188}Os$ Perspective

Seawater $^{187}Os/^{188}Os$ ratios inferred from Precambrian ORS rocks have provided insight into a fundamental transition in Earth's history: the onset of atmospheric oxygenation and oxidative continental weathering (Hannah et al. 2004; Kendall et al. 2015). An atmospheric O_2 level of perhaps >0.1% PAL (present atmospheric level) is needed to weather the Earth's upper crust, allowing oxidation of Os with elevated $^{187}Os/^{188}Os$ to be transported to the oceans. Hence, seawater $^{187}Os/^{188}Os$ that is higher than mantle and extraterrestrial $^{187}Os/^{188}Os$ is evidence for photosynthetic O_2 accumulation and oxidative weathering.

The oldest known instance of oxidative weathering and transport of crustal Os may be the 2.5 Ga Mt. McRae Shale, although the initial $^{187}Os/^{188}Os$ (0.34 ± 0.19) derived from these black shales is only marginally higher than the mantle value of ~0.11 at 2.5 Ga (Kendall et al. 2015). Other ORS

rocks from the late Archean and early Paleoproterozoic, including during the Great Oxidation Event (Hannah et al. 2004; Yang et al. 2009), yield seawater $^{187}Os/^{188}Os$ equivalent to mantle values. One possible interpretation is that oxidative weathering of the late Archean and early Paleoproterozoic crust provided a much smaller flux of Os to the oceans than mantle Os inputs at seafloor spreading centers. It must also be recognized that the $^{187}Os/^{188}Os$ of the upper continental crust was lower at this time because less ^{187}Re had decayed to ^{187}Os. Most Archean ORS rocks have low authigenic Re enrichments because low atmospheric O_2 (<10^{-4}% PAL) limited chemical weathering and river transport of Re to the oceans, and widespread ocean anoxia caused the small amounts of oceanic Re to be removed over a wide seafloor area. Consequently, Archean ORS rocks typically did not develop high $^{187}Os/^{188}Os$ because decay of ^{187}Re to ^{187}Os was limited. Hence, continental weathering may have continued to provide Os with low $^{187}Os/^{188}Os$ to early Proterozoic oceans, even during and shortly after the Great Oxidation Event (Hannah et al. 2004).

The observation that seawater $^{187}Os/^{188}Os$ is clearly higher than the mantle is first observed in the mid-Proterozoic and becomes common in the Neoproterozoic and Phanerozoic (see *Toolkit* FIG. 12). Three main factors likely contributed to these temporal changes. First, the continental crust evolved towards higher $^{187}Os/^{188}Os$ through time via ^{187}Re decay to ^{187}Os. Second, secular mantle cooling likely decreased the seafloor hydrothermal flux of Os to the oceans, making the continental contribution more important. Third, increasing subaerial exposure and weathering of younger Proterozoic ORS rocks with greater authigenic Re enrichments produced increasingly elevated Re/Os and $^{187}Os/^{188}Os$ ratios in river waters delivered to the oceans.

Co-evolution of the atmosphere, hydrosphere, crust, and mantle, therefore, have modulated first-order temporal changes in seawater $^{187}Os/^{188}Os$ through time.

FUTURE DIRECTIONS

Many novel insights into Earth system processes have been made with the Re-Os isotope system, but there remain ample opportunities for current and future generations of geoscientists to make important contributions. Gaps in the seawater $^{187}Os/^{188}Os$ curve need to be filled, especially for the Precambrian, but even the Phanerozoic curve still has low temporal resolution compared with the seawater Os residence time. Sedimentary deposits from rivers may contain information about ancient river $^{187}Os/^{188}Os$ and provide new insights into paleoenvironments and variations in seawater and lacustrine $^{187}Os/^{188}Os$. Mass-dependent variations of Re and Os isotopes in nature are only just starting to be explored as tracers of environmental processes such as oxidative weathering. There are many geological processes/events and biological innovations/catastrophes throughout Earth's history whose timing and duration could benefit from Re-Os depositional ages. More precise Re-Os ages for ORS rocks are possible if the spread of $^{187}Re/^{188}Os$ ratios on isochron diagrams can be maximized by targeting individual organic matter and sulfide phases. Standardized (community-wide) analytical and data reduction procedures for Re-Os geochronology and isotopic tracing will improve overall data quality and the precision and accuracy of depositional ages, as well as encourage and support entry of the next generation of Re-Os isotope geochemists.

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