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Jeremy D. Owens
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1 Introduction

The reduction–oxidation state of the ocean–atmosphere system has undergone significant changes throughout Earth's history (Lyons et al., 2014). The broad-scale oxygenation history of the atmosphere is well documented (Berner, 2006; Lyons et al., 2014) and, generally, the oceans follow a similar pattern. However, there are numerous punctuated events throughout the geological record that document variability in the coupled ocean–atmosphere system (Saltzman and Thomas, 2012). Many of these events occurred in the Phanerozoic eon with associated biological crises, e.g., (mass) extinctions (Hannisdal and Peters, 2011). A wealth of geochemical proxies have been developed to potentially track past ocean conditions using sedimentary archives that transfer information from marine seawater to sediments (Tribovillard et al., 2006). Our geochemical redox toolkit has expanded greatly in the past decade with the utilization of Fe speciation, redox-sensitive trace elements, and isotopic analysis of many elements from a variety of lithological archives (Tribovillard et al., 2006; Anbar and Rouxel, 2007; Raiswell et al., 2018).

Molecular oxygen is essential for many metabolic pathways and is important in regulating elemental cycles that are relevant to climatic and biological feedbacks (Anbar and Knoll, 2002; Berner, 2006). Relatively small increases in the geographical extent of reducing conditions can have profound effects on the availability of bioessential elements (i.e., Fe, Mo, V, and Zn; Scott et al., 2008; Reinhard et al., 2013; Owens et al., 2016) in the oceans, which in turn affects enzymatic processes (Anbar and Knoll, 2002; Saito et al., 2008; Glass et al., 2009). The sequence of chemical reactions/processes following oxygen depletion is important for marine organisms that can utilize various electron acceptors to create free energy (Fig. 1A; Froelich et al., 1979).

Fingerprinting individual portions of the redox ladder or elemental pathways are ideal to reconstruct water column and sedimentary depositional conditions. In modern settings, this is possible (Canfield and Thamdrup, 2009), but owing to proxy specificity/limitations, burial diagenesis, and sedimentary transfer mechanisms, it is difficult to precisely fingerprint each process for ancient sedimentary rocks. Berner (1981) prescribed a general classification that separated the redox ladder into two zones: oxic and anoxic. The anoxic zone was delineated further into three categories: post-oxic (nonsulfidic), sulfidic, and methanic. Proxy development and application have led to the ability to accurately identify sulfidic conditions, with the means to also delineate sulfidic water-column (euxinic) from sulfidic sedimentary pore fluids (Scott and Lyons, 2012; Hardisty et al., 2018). However, unambiguously fingerprinting the initial global extent of deoxygenation or more broadly post-oxic conditions

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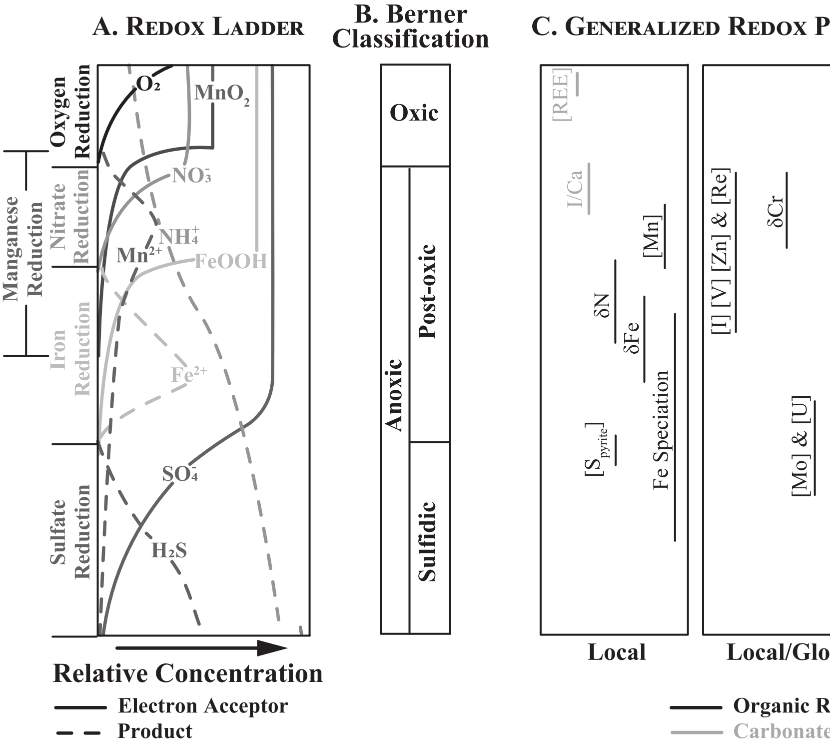

Figure 1 Conceptual figure that connects redox processes and potential proxy records. (A) Redox la
(B) Simplified redox classification modified from Berner (1981), which is related to (A). (C) Prox
ladder and are generally related to the redox scheme of (A) and (B). Several redox proxies are co
processes that require supporting evidence for interpretation. The label color of εTl corresponds to n
(C) represent proxies that have been developed or applied mostly to shales and the gray lines de
indicates the approximate region in which the proxy responds to the correspond

has been more difficult due to a lack of proxy specificity. One of the first minerals to respond to the earliest depletion of oxygen is manganese (Mn) oxides (Rue et al., 1997). However, tracking Mn concentrations only records the local process and requires investigating the global sedimentary record to reconstruct the response to ocean oxygen perturbations, which is not possible for the geological record. This is further complicated by the fact that Mn lacks multiple long-lived stable isotopes to generate an accurate mass balance framework.

Manganese oxides are an important marine sink and represent an oxic flux for many transition elements as they adsorb onto precipitated particles in the water column and on the seafloor (Hein et al., 2000 and references therein). For precipitation *and* long-term burial, Mn oxides require oxygen; as Mn oxides are one of the first minerals to dissolve under low oxygen conditions, they have the capacity to release adsorbed elements (Rue et al., 1997). The post-transition element thallium (Tl) readily adsorbs onto Mn oxides. Birnessite, a low-temperature Mn oxide mineral, imparts a large isotopic offset (fractionation) (Peacock and Moon, 2012). This Tl isotope fractionation represents the largest fractionation from seawater; thus it is the dominant control on the global Tl seawater signature in oxygenated oceans. The residence time of Tl is ~18.5 kyr (Fig. 2; Rehkämper and Nielsen, 2004; Baker et al., 2009; Nielsen et al., 2017; Owens et al., 2017), which is longer than ocean mixing times but is relatively short compared to that of other elements. The response to Mn oxides and its residence time makes it a promising element to track initial oxygen perturbations. Importantly, Mn oxides are likely perturbed during short-term climate events when the amount of oxygen in the oceans fluctuates, which has the potential to shift the global Tl isotope signature. This has been observed recently across two Phanerozoic oceanic anoxic events and one Precambrian oxygenation event.

2 Marine Elemental Cycle

Thallium concentrations and isotopes have been utilized for several decades (Shaw, 1952; Matthews and Riley, 1970; McGoldrick et al., 1979; Flegal and Patterson, 1985; Bidoglio et al., 1993; Rehkämper et al., 2002, 2004; Nielsen et al., 2004, 2005, 2006a; Rehkämper and Nielsen, 2004; Xiong, 2007), but the application of Tl isotopes as an ancient paleoceanographic tool is relatively recent (Nielsen et al., 2009, 2011b; Owens et al., 2017). This has been possible because of the numerous Tl isotope measurements of Earth materials (Rehkämper et al., 2002, 2004; Rehkämper and Nielsen, 2004; Nielsen et al., 2005, 2006b, 2017; Baker et al., 2009; Prytulak et al., 2013), which have provided a relatively well-constrained marine isotope mass balance (Rehkämper and Nielsen, 2004; Baker et al., 2009; Nielsen et al., 2017;

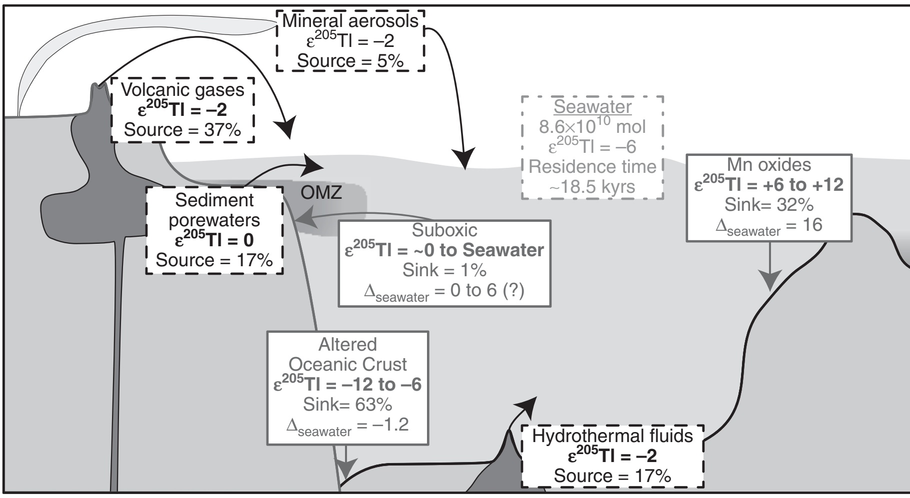

Figure 2 Marine Tl mass balance that includes the most updated data (Baker et al., 2009; Nielsen 2017). Black boxes represent the source fluxes with isotopic values (ε^{205}Tl) and the percentage of th represent sinks from the ocean with isotopic values (ε^{205}Tl), percent of the total output flux, and t between ε^{205}Tl value and the seawater value labeled as $\Delta_{seawater}$). Note that the averages for some of (see Owens et al., 2017). Total flux is 484.3×10^4 moles per y

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Owens et al., 2017b). Thallium has two isotopes, with atomic masses of 203 and 205, and their relative abundances represent ~30% and ~70% of the total, respectively. The isotopic ratios are reported relative to the NIST SRM 997 Tl standard:

$$\varepsilon^{205}\mathrm{Tl} = 10{,}000 \times (^{205}\mathrm{Tl}/^{203}\mathrm{Tl}_{\mathrm{sample}} \text{-} ^{205}\mathrm{Tl}/^{203}\mathrm{Tl}_{\mathrm{NIST\ 997}})/(^{205}\mathrm{Tl}/^{203}\mathrm{Tl}_{\mathrm{NIST\ 997}}).$$

The terminology used for Tl isotope ratios is different from the standard δ-notation (variations in parts per 10,000 compared to 1,000, respectively). Generally, 2-sigma errors are reported for repeated dissolutions of standard reference materials.

The continental crust is the largest reservoir of Tl, as concentrations are high (Shaw, 1952; Nielsen et al., 2017). This is due to Tl being incompatible during mantle melting (Nielsen et al., 2014), as the depleted mantle has very low concentrations (Salters and Stracke, 2004). One direct measurement of a mantle xenolith has a value of −2.0 ± 0.8 (Nielsen et al., 2015), which is consistent with mid-ocean ridge basalt measurements of −2.0 ± 1.0 with very low concentrations (Nielsen et al., 2006a). Furthermore, samples of variable igneous origins, but importantly devoid of sedimentary inputs, have been analyzed and the combined data suggest the continental crust and bulk mantle Tl isotope values are indistinguishable, with ε^{205}Tl values of −2.0 with a range of ± 1.0 (as reviewed in Nielsen et al., 2017). A recent study shows mineral separates from igneous and metamorphic rocks have a wide range of Tl isotope composition but many do cluster near −2.0, e.g., the whole rock value (Rader et al., 2018). Thus, fractionation from bulk Earth materials is unlikely because of near-quantitative transfer of Tl from the mantle to the crust.

Volcanic gases, riverine, hydrothermal fluid, and mineral aerosols (e.g., dust) are the dominant source fluxes into the ocean and are directly related to the mantle or weathering of the continental crust (Nielsen et al., 2005, 2006a, 2006b, 2007, 2016; Prytulak et al., 2013). The average Tl isotope compositions for these four sources are indistinguishable from those of the continental crust, as they all record ε^{205}Tl values of −2.0, which represent ~83% of the total flux to the oceans (484.3×10^4 moles/yr; Rehkämper and Nielsen, 2004; Nielsen et al., 2005, 2006b, 2017; Baker et al., 2009). The last significant source flux is from reducing sedimentary pore fluids, which are currently estimated to be ~17% of the total input flux and have an isotopic value of 0 but generally display a larger isotopic range (Rehkämper and Nielsen, 2004; Nielsen et al., 2011b, 2017). The isotopic range is likely due to mixing, as Mn oxide dissolution might be captured in sulfidic pore fluids if these processes occur nearby, and/or due to nonquantitative Tl removal during pyrite formation (Owens et al., 2017). The isotopic sources of Tl isotopes are generally homogeneous. However, recent

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data document mineralogical variations (Rader et al., 2018), but this would require differential weathering and/or variable crustal mineralogy throughout Earth history to have a significant effect on the global marine Tl isotope composition.

The modern open-ocean seawater Tl isotope composition is homogeneous, with an ε^{205}Tl value of −6.0 ± 0.6 (Rehkämper et al., 2002; Nielsen et al., 2006b; Owens et al., 2017), with a relatively constant global concentration of 13.3 ppb (Flegal and Patterson, 1985; Rehkämper et al., 2002; Nielsen et al., 2006b; Owens et al., 2017). Thus, the modern marine isotopic composition is depleted (i.e., more negative) compared to that of the average continental crust and mantle. This is because the two dominant sinks of Tl, Mn oxide adsorption and incorporation during low-temperature alteration of oceanic crust (AOC; Nielsen et al., 2017), have large and opposing isotope compositions. The largest output flux is AOC, which accounts for ~65% of the Tl burial and has an average isotopic value of ~−7.5 (range between −6 and −12 ε units; Rehkämper and Nielsen, 2004; Nielsen et al., 2006b, 2017). Thus, the isotopic fractionation of AOC from modern seawater values is relatively small, with a difference of ~−1.5 ε units (e.g., the difference between AOC and seawater). However, there is a large isotopic range for AOC Tl isotopes related to the depth of the altered material, with greater depths exhibiting smaller fractionations (Nielsen et al., 2006b; Coggon et al., 2014). The mechanism controlling the incorporation of isotopically light Tl during alteration of oceanic crust remains ambiguous but could be kinetic in nature (Nielsen and Rehkämper, 2012b) or caused by microbially mediated sulfide precipitation (Coggon et al., 2014). The other significant Tl sink is associated with low-temperature authigenic Mn oxides (Rehkämper and Nielsen, 2004), specifically birnessite (Peacock and Moon, 2012). Manganese oxides have an average ε^{205}Tl composition of ~+10 with a range between +6 and +12, and Mn oxide preservation accounts for ~30% of the burial. High-temperature hydrothermal Mn oxide precipitates such as the mineral todorokite display no fractionation from seawater or hydrothermal fluids (Peacock and Moon, 2012; Nielsen et al., 2013). The average Mn oxide burial value of +10 provides an isotopic difference from seawater of ~+16. This suggests that small changes in the amount of Mn oxide burial can have a significant effect on the global seawater Tl isotope composition; thus, Tl isotopes can potentially track changes in the local or global burial flux of Mn oxides depending on the connectivity of a sedimentary basin with the open ocean.

There are two additional, albeit minor Tl sinks from the ocean and are estimated to represent 5% of the burial flux (Owens et al., 2017). They are associated with reducing bottom water conditions, specifically low oxygen (suboxic) and anoxic/euxinic settings. The fluxes and isotopic compositions for low oxygen environments are limited in the modern ocean. Limited data from reducing sediments suggest a range of values but an average near 0 (Nielsen et al., 2011b). This range of isotopic values in reducing sediments is likely due to Mn oxide reduction near sulfidic pore fluids; further research is needed, however, to constrain Tl behavior in these settings as a recent study suggests a potential to capture seawater Tl isotope values (Fan et al., in press). In addition, several estuaries or tidally influenced sediments have been analyzed for Tl concentrations (Böning et al., 2018 and references therein), but the global record remains unclear and lacks isotopic analysis. Euxinic sediments capture the oxic seawater value (Section 3) and the flux in these environments was estimated using Tl/S relationships in the Black Sea (Owens et al., 2017), but detailed research is needed to confirm the calculations of this flux.

There are no known enzymatic pathways that utilize and fractionate Tl. There are several known plant species, however, that accumulate thallium, likely because of the similar ionic radius of potassium and there is a fractionation within plants (Rader et al., 2019). With our current understanding, it is unlikely that biological cycling and perturbations to the marine biosphere have a significant effect on the oceanic Tl isotope mass balance. Furthermore, the modern vertical and horizontal ocean transects of Tl isotopes and concentrations in the South Atlantic document no observable fractionations, as the surface and deep waters record values that are analytically indistinguishable (Owens et al., 2017).

Therefore, temporal changes in the marine Tl isotope composition are most likely controlled by the ratio between the two marine output fluxes (Nielsen et al., 2009, 2011b; Owens et al., 2017), which are highly fractionated (Rehkämper et al., 2002; Rehkämper and Nielsen, 2004; Nielsen et al., 2006b, 2017). Importantly, AOC fluxes are likely globally controlled by ocean production rates driving oceanic crust cooling that change over long timescales – many millions of years. Therefore, short-term perturbations to the global marine Tl system are most likely driven by changes in the precipitation/dissolution, preservation, and burial flux of Mn oxides on the seafloor, a process that requires free oxygen. Thus, a decrease in the burial of the positively fractionated Mn oxides will shift the seawater composition toward more positive values.

3 Sedimentary Thallium Isotope Signature

Thallium exists in two valence states: Tl^{+} and Tl^{3+}. The oxidized form is uncommon in natural environments because of the high redox potential, but it is likely that this form of Tl plays a significant role in the observed strong adsorption onto authigenic Mn oxides (Matthews and Riley, 1970; McGoldrick et al., 1979; Bidoglio et al., 1993; Hein et al., 2000; Peacock and Moon, 2012; Nielsen et al., 2013). The first studies to reconstruct ancient marine Tl isotope compositions analyzed ferro-manganese crusts (Rehkämper et al., 2004; Nielsen et al., 2009, 2011a); this assumes a constant and near modern isotopic fractionation in order to reconstruct seawater values (Rehkämper et al., 2002). There is currently no evidence to suggest this offset varies, systematically or otherwise, but the isotopic range for the Cenozoic era is between ~4 and 14 ε units. In addition, the utility of Fe–Mn crusts is limited because of the limited temporal preservation (maximum ages of ~70 million years) and age constraints (Nielsen et al., 2009). Thus, it was essential to develop an additional archive to increase the utility of Tl isotopes. However, a high-resolution ferro-manganese Tl isotope record has been generated for the Cenozoic era and provides evidence for large isotopic variations (Nielsen et al., 2009).

The first Tl isotope data analyzed from organic-rich sediments were generated from mechanically separated pyrite grains (Nielsen et al., 2011b), which provided the motivation to analyze Tl isotopes in environments that precipitated pyrite in the water column and thus had the potential to capture and record local and potentially global environmental conditions. A modern study of Tl isotopes of seawater and sediment core tops from the two largest modern euxinic basins, Cariaco Basin and the Black Sea, was conducted as a first assessment to reconstruct seawater values (Owens et al., 2017). The overlying oxic seawater values in the Cariaco Basin values are −5. 6 ± 0.7, which are within analytical uncertainty of open ocean values, while the Black Sea values are −2.2 ± 0.3 (one sample), which are similar to input fluxes (Owens et al., 2017). Core top samples from the Cariaco Basin documented an average $\varepsilon^{205}Tl_{leach}$ −5.4 ± 0.6 for five samples (excluding one sample), while the Black Sea documented average values of −2.3 ± 0.6 for the leached fraction of five samples. This initial research documented that the leached fraction (see Section 5 for more details) of the sedimentary core tops from both basins captures, within analytical uncertainties, the overlying oxic seawater value from each basin. The Tl isotope difference for each locality is likely due to basin restriction. The Cariaco Basin is considered a more open-ocean archive and the Black Sea is severely restricted, and when coupled to the relatively short residence time of Tl allows for isotopic variation between these two basins. In addition, recent work highlights the utilization of anoxic but noneuxinic sediments to capture seawater values (Fan et al., in press) from the Santa Barbara Basin, where sulfide is limited to the pore fluids. Limited data from reducing sediments overlain by an oxic water-column do no capture seawater values (Nielsen et al., 2011b). The difference in these depositional environments suggests that the distance between Mn oxide dissolution and pyrite formation is important and needs to be investigated in greater detail (see Section 6 for more discussion).

Moreover, Tl concentrations below the chemocline (euxinic) decrease rapidly with depth (Owens et al., 2017). This drawdown of Tl is not likely due to direct Tl sulfide precipitation, as the solubility in aqueous solution is high (Nielsen et al., 2011b). More likely, it reflects Tl partitioning into Fe sulfides that precipitate in the water column, as Tl is known to have a strong affinity for such minerals (McGoldrick et al., 1979; Nielsen et al., 2011b, 2014). The near-quantitative removal of Tl from euxinic seawater (Owens et al., 2017) likely accounts for the indistinguishable Tl isotope compositions observed for sediments deposited under euxinic conditions and the overlying oxic waters. Thus, it is important to constrain local redox conditions using other proxies that are not susceptible to global redox perturbations, such as Fe speciation, Mn concentrations, or other evidence for local oxide-bearing minerals (Owens et al., 2016; Ostrander et al., 2017; Them et al., 2018). Most significantly, this work documents the ability of sediments deposited under euxinic and, potentially ferruginous, conditions to capture the overlying oxic seawater values. When possible, sediments from multiple ocean basins should be analyzed to confidently capture global seawater perturbations (Ostrander et al., 2017; Them et al., 2018). This is not always possible, however, owing to biases in the preservation of strata in the geological record; thus, invariant stratigraphic trends should be interpreted with caution, as they could be due to basin restriction (i.e., modern Black Sea) or coupled with additional proxies.

4 Brief Analytical Guide

An operationally defined chemical separation (leaching method) has been developed using modern euxinic sediments to extract the oxic seawater value. This was required to separate the authigenic Tl (likely complexed with pyrite) from the lithogenic (likely bound to silicates) fraction, as the bulk values did not capture oxic seawater value but rather a mixture of the two isotopic pools (Owens et al., 2017). This is classically observed in the Cariaco Basin, as the bulk sediment values are −2.5 ε units, while the authigenic values are −5.5 ε units and ~63% of the total Tl concentration and the lithogenic values are −2.0 ε units and 37% (Owens et al., 2017). This relationship is not observed in the Black Sea, however, as the lithogenic and oxic seawater are nearly the same (i.e., within analytical error; Owens et al., 2017) but the percentage of authigenic to total Tl is similar to that of the Cariaco Basin (Owens et al., 2017). Authigenic concentrations of ancient marine sediments have been greater than the modern values, and therefore the bulk values would be less affected by

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lithogenic contamination, but the Tl leach method is still required to compare similar Tl isotope fractions. For detailed information on the method, refer to Owens et al. (2017). The chemically separated solutions are then purified using an established anion-exchange protocol (Rehkämper and Halliday, 1999; Rehkämper et al., 2002; Nielsen et al., 2005, 2009; Baker et al., 2009; Nielsen and Rehkämper, 2012a). Ostrander et al. (2017) documented that only a single microcolumn is required for samples with high Tl to Pb ratios. The purified solution is then analyzed using a multicollector–inductively coupled plasma–mass spectrometer (MC-ICP-MS). The leaching method on the USGS SCo-1 standard has an average ε^{205}Tl of −2.99 with a long-term reproducibility better than 0.3 ε units (Ostrander et al., 2017, 2019; Owens et al., 2017; Them et al., 2018), which is within or slightly better than bulk ε^{205}Tl values (Nielsen et al., 2014).

5 Case Studies

While the proxy is in its infancy and there are many new avenues to explore, there have been several applications of Tl isotopes in ancient marine shales to reconstruct the global burial of Mn oxides to track the initial marine oxygen perturbation. Nielsen et al. (2009) reconstructed the Tl isotope record for the Cenozoic era by analyzing Mn oxide crusts, which documents a secular trend to heavier values over the past ~60 Myr. The nearly 10-ε unit shift between 55 and 45 million years has been interpreted as an increased Mn oxide burial, as there is no evidence for changes in AOC because spreading rates did not change dramatically (Nielsen et al., 2009). Ideally, this will be confirmed using additional archives to constrain the global seawater record and constrain the fractionations associated with Mn oxide burial. In addition, the combination of Tl isotopes and euxinic proxies (i.e., molybdenum isotopes and concentrations, carbonate-associated sulfur isotopes, etc.) have the potential to delineate post-oxic (non-sulfidic anoxia) and euxinic conditions. Thus, a more holistic reconstruction of the global redox landscape is possible using a combination of redox proxies to illuminate the timing and magnitude of redox perturbations. It is important to constrain the relationship between ancient redox conditions and volcanism, carbon isotope excursions, and extinction events in the geological record (Fig. 3).

The geologically youngest application of organic-rich shales that capture seawater Tl isotopes to date has been across Cretaceous Oceanic Anoxic Event 2 at the Cenomanian/Turonian Boundary Event (~94 Ma). This event has been well studied with organic-rich mudstone deposition recorded from multiple ocean basins and a documented redox perturbation (Owens et al., 2018