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Correlation of Permo-Triassic Sections in Eastern Greenland and Western Canada Based on Re-Os and Stable Isotope Data

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Chemostratigraphy has been widely employed to determine the cause of Late Permian environmental perturbations that set in motion the incremental steps towards the largest mass extinction of the Phanerozoic. Chronostratigraphy has constrained timing and duration of teetering geological and biological conditions that culminated in the mass extinction.

The Re-Os isotope method is a powerful geochemical tracer that ideally derives four separate types of information from the sedimentary record. First, the radioactive decay of ¹⁸⁷Re to ¹⁸⁷Os with time provides a geologic clock for the depositional age of the rock. Second, Re and Os concentrations help constrain the depositional environment - both Re and Os are redox sensitive and therefore significantly enriched in anoxic and euxinic sediments. High Re/Os ratios may further indicate severe oxygen depletion. Third, the initial ¹⁸⁷Os/¹⁸⁸Os ratio (or Os_i) of the sediment reflects the Os isotopic composition of paleoseawater and is sensitive to changes in the rates of continental weathering, the material dominating weathering cycles, submarine volcanism, and meteorite impacts. Fourth, because both Re and Os are readily remobilized upon post-depositional exposure(s) to oxygen, the degree of isochroneity directly correlates with the degree of chemical disturbance/preservation in the rocks. That is, the degree of isochroneity indicates the reliability of other geochemical proxies for depositional conditions. Furthermore, combining Re-Os studies with stable isotope and trace metal analyses provides a multi-faceted geochemical characterization of the sedimentary environment. When put into stratigraphic and paleontological perspective, the different facets contribute to accurate reconstruction of paleoceanographic depositional conditions.

Here we discuss Re-Os isotope data for Upper Permian

to Lower Triassic successions from three Boreal localities: East Greenland (GRL), mid-Norwegian shelf (MNS), and Opal Creek, Alberta, Canada (OPC). The GRL and MNS shale-siltstone-dominated sections were deposited on facing sides of a drowned shallow continental shelf in the Permo-Triassic Greenland-Norway seaway (Bugge et al., 2002; Stemmerik, 2001; Wignall and Twitchett, 2002). In the Late Permian, this elongate seaway probably connected the Panthalassa sea with the Tethys ocean and provided a pathway for water exchange (Sengör and Atayman, 2009). The OPC silty shale-dominated succession in western Canada was deposited on a deep water outer shelf or slope in the Panthalassa sea (Henderson, 1997).

Drillcores sampled Wuchiapingian to Changhsingian organic-rich shale from the Ravnefjeld Formation in GRL (Piasecki and Stemmerik, 1991; Surlyk et al., 1986) and the Lower Turbidite Unit in MNS (Bugge et al., 2002). Five stratigraphically restricted intervals, four from MNS and one from GRL yield four indistinguishable Re-Os isochron ages (2-sigma) that constrain the time of shale deposition to ~252 Ma and the Os_i of seawater in the Late Permian to ~0.6 (Georgiev et al., 2011). In addition to drillcore samples, we also studied Upper Permian shales and siltstones from outcrops in GRL. Re-Os data from shale-outcrop occurrences in the Ravnefjeld Formation scatter significantly around the isochron defined by correlative shale drill core samples. Georgiev et al. (2012) document alteration of primary Re-Os systematics by recent chemical weathering and oxidation of outcrop shales. Similarly, new analyses of outcrop siltstones from the Schuchert Dal Formation yield imprecise Re-Os ages.

Re-Os isochroneity is achieved when a suite of samples with varying Re/Os ratios is deposited in a geologically short time with relatively constant seawater Os_i, and the samples are not subsequently disturbed (e.g., exposed to oxidative processes). Even when Re-Os isochroneity is

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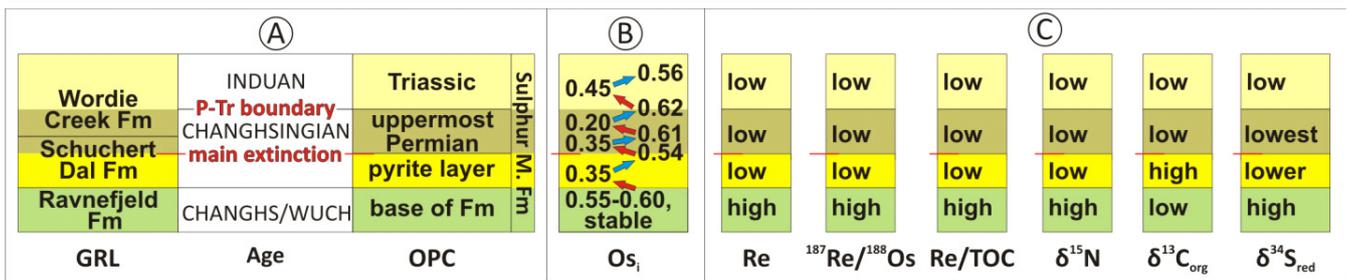


Fig.1. (A) Schematic stratigraphy and proposed correlations; (B) Os_i variation with depth; and (C) Systematic changes in elemental and isotopic parameters in the GRL and OPC sections. In OPC, the pyrite layer and overlying siltstones deposited before the extinction are displayed as a single unit (yellow color). MNS section not shown.

imperfect, Os isotope chemostratigraphy can reveal global changes in the major contributing sources of Os to paleoseawater and constrain the depositional environment of the rock. Here we present two examples from the Permo-Triassic transition, in which chemostratigraphic trends are correlative (Fig. 1A).

In GRL, where outcrop-shales did not yield meaningful isochrons, we calculated Os_i ratios for each outcrop sample using the same Late Permian age as input. Thirty-two out of thirty-four outcrop shales from the Ravnefjeld Formation have clearly impossible or unrealistic Os_i ranging from -10 to 0 and from 1 to 10, demonstrating chemical disturbance of these shales. In contrast, all eleven outcrop-shales from the Schuchert Dal Formation have geologically plausible Os_i ratios with a much smaller range, from 0.40 to 0.75. This smaller variation in the calculated Os_i may indicate a lesser degree of chemical disturbance in the Schuchert Dal compared to Ravnefjeld shales. Alternatively, the variation in the Os_i may be primary, documenting notable variation in the Os isotopic composition of seawater during the latest Changhsingian.

In the OPC, the Os isotope chemostratigraphy presents supporting evidence for highly unstable seawater chemistry in the latest Changhsingian (Fig. 1B). The OPC siltstones-shales we analyzed are from the Sulphur Mountain Formation in the Opal Creek section, western Canada. Previous work on latest Changhsingian strata at OPC show a moderate drop of Os_i from ~ 0.55 at the main extinction interval to 0.35 minima 20 cm up, followed by a gradual rise to values of 0.62 at the Permo-Triassic boundary (Schoepfer et al., 2012). Our data expands and partially overlaps the interval studied in Schoepfer et al. (2012). We analyzed a vertical profile of Upper Permian and Lower Triassic siltstones and shales, sampling the base of the formation (Wuchiapingian or Changhsingian), a distinct pyrite layer thought to represent the onset of latest Permian water column euxinia, siltstones pre-dating the extinction, the main extinction interval and Permo-Triassic boundary (latest Changhsingian), and the Early Triassic portion of the section. The limited number of samples available in both studies prevents construction of

a complete Os chemostratigraphic profile. However, several important observations stand out from our new data. The base of the OPC section has high Re contents and high $^{187}Re/^{188}Os$ ratios compared to all overlying latest Permian and Induan siltstones. A few centimeters above the base, the pyrite layer has a relatively low Os_i of ~ 0.35 that gradually recovers to ~ 0.55 into the Changhsingian until the mass-extinction interval. Above the main extinction interval and above the dip to less radiogenic values of ~ 0.35 described by Schoepfer et al. (2012), one of our analyzed siltstones exhibits a very low Os_i of ~ 0.19 to ~ 0.24 (two methods for powder preparation sampled mostly overlapping but slightly offset vertical intervals covering a depositional span of ~ 1 cm). These markedly low values may represent a significant and rapid contribution of depleted mantle Os and/or meteorite components into latest Permian seawater. Importantly, both this contribution and the earlier and less prominent Os_i dip to ~ 0.35 in siltstones followed the main extinction. After another dip from 0.62 to 0.48 at the Permo-Triassic boundary noted in Schoepfer et al. (2012) and supported by our data, the Os_i of our analyzed Early Triassic shales varies between ~ 0.45 to ~ 0.58 .

Comparing Re-Os data from the three studied localities reveals potential for important global correlations (Fig. 1). In GRL, MNS, and OPC the latest Wuchiapingian to Changhsingian sediments have relatively high Re contents (tens to hundreds of ppb), high Re/TOC ratios (generally 40-80), relatively high $^{187}Re/^{188}Os$ ratios (>1500), and confined and moderately radiogenic Os_i ratios of ~ 0.55 to 0.60. Sometime later in the Changhsingian, a dramatic change in the Re-Os seawater-sediment cycle occurred. All studied latest Changhsingian sedimentary rocks from GRL and OPC have low Re contents (<11 ppb), low Re/TOC ratios (<15) low $^{187}Re/^{188}Os$ ratios (<500), and highly variable Os_i ratios. In OPC, this change coincides with deposition of the pyrite layer and the first dip to very low Os_i ratios. Directly above the pyrite layer, Re content of the sediments is about 0.5 ppb and gradually rises to 11 ppb at the Permo-Triassic boundary. Right at the boundary the sediments record another drop in Re content to $\sim 3-5$

ppb, and this Re concentration is maintained in the lower Triassic samples. In GRL, the expanded thickness of the upper Permian- lower Triassic successions (hundreds of meters) precluded our sampling the transition and reconstructing the full detailed record of Os.

The variations in the Re concentration data can be explained by a massive and global drawdown of Re from seawater under anoxic conditions during the latest Wuchiapingian and/or Changhsingian. For the OPC, anoxia culminated with the continuous pyrite layer that coincides with the first evidence for mantle/meteorite Os input to Late Permian seawater. The pyrite layer and the immediately overlying Re-deficient siltstones also record sudden and major swings in ^{34}S , ^{13}C (organic and inorganic) and ^{15}N isotopes (unpublished and published data). In GRL, the direction and magnitude of the changes in stable isotope compositions upward from the Ravnefjeld, through the Schuchert Dal, and into the earliest Triassic Wordie Creek Formations closely parallel those in the Opal Creek section in western Canada (Fig. 1C).

Systematic changes in Re-Os, stable isotope ratios, and trace metal inventories in the relatively condensed (OPC) and expanded (GRL) stratigraphic records argue for a shared trigger for mass extinction between these two geographically separated regions. Based on new data and correlations, we propose that a transient state of global oceanic anoxia was further intensified by the initiation of Siberian Trap volcanism. Anoxic waters reached productive shelf environments, causing a severe productivity crisis and a profound change in ocean metal inventory. These changes are also captured in the stable isotope record. Subsequent and stronger magmatic pulses recorded by low Os, followed the main extinction.

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Key words: Permo-Triassic extinction, Re-Os, stable isotopes, anoxia, Siberian traps

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