

# Nutrient Cycling in the Phosphoria Sea

Brett Smith<sup>1</sup>, Jana Meixnerova<sup>1,2</sup>, Michael Kipp<sup>1,2</sup>, Eva Stüeken<sup>2,3</sup>, Roger Buick<sup>1,2</sup>

<sup>1</sup>Department of Earth and Space Sciences & Astrobiology Program, University of Washington

<sup>2</sup>Virtual Planetary Laboratory - NASA Astrobiology Institute

<sup>3</sup>Department of Earth & Environmental Sciences, University of St. Andrews



## Background

The Phosphoria Formation was deposited in an epicontinental seaway – known as the Phosphoria Sea – located on the western margin of the Pangaeon supercontinent in the Middle Permian (Wardlaw et al. 1995; Fig. 1). The Phosphoria Formation is comprised predominantly of chert and organic-rich shale, and currently stretches across a vast portion of the western United States (Fig. 1, inset). The abundance of phosphorus in some of the organic-rich shale horizons has led to continued interest in these deposits as a source of phosphorus for agricultural fertilizers, among other products. Mining of the Phosphoria Formation today constitutes 12-14% of annual US phosphate production, and the remaining reserves comprise ~30% of the US phosphorus inventory (Jasinski et al. 2004).

Since the original exploration of the Phosphoria Formation in the early 20<sup>th</sup> century, several questions have remained regarding the depositional environment in which it originated. While early models wrestled with difficult physical, chemical or biological explanations needed to account for the inferred extreme depositional rates of phosphate (e.g. Pardee 1917; Mansfield 1927), the recognition of upwelling as an important nutrient transport process in the oceans (Kazakov 1937) eventually helped inform the understanding of phosphogenesis in the Phosphoria Sea (e.g. McKelvey 1946). In the past half century, there has been a considerable effort to reconcile the geochemistry of the Phosphoria Formation with an upwelling-based model for nutrient transport into the basin (e.g. Piper and Link 2002; Hiatt and Budd 2003).

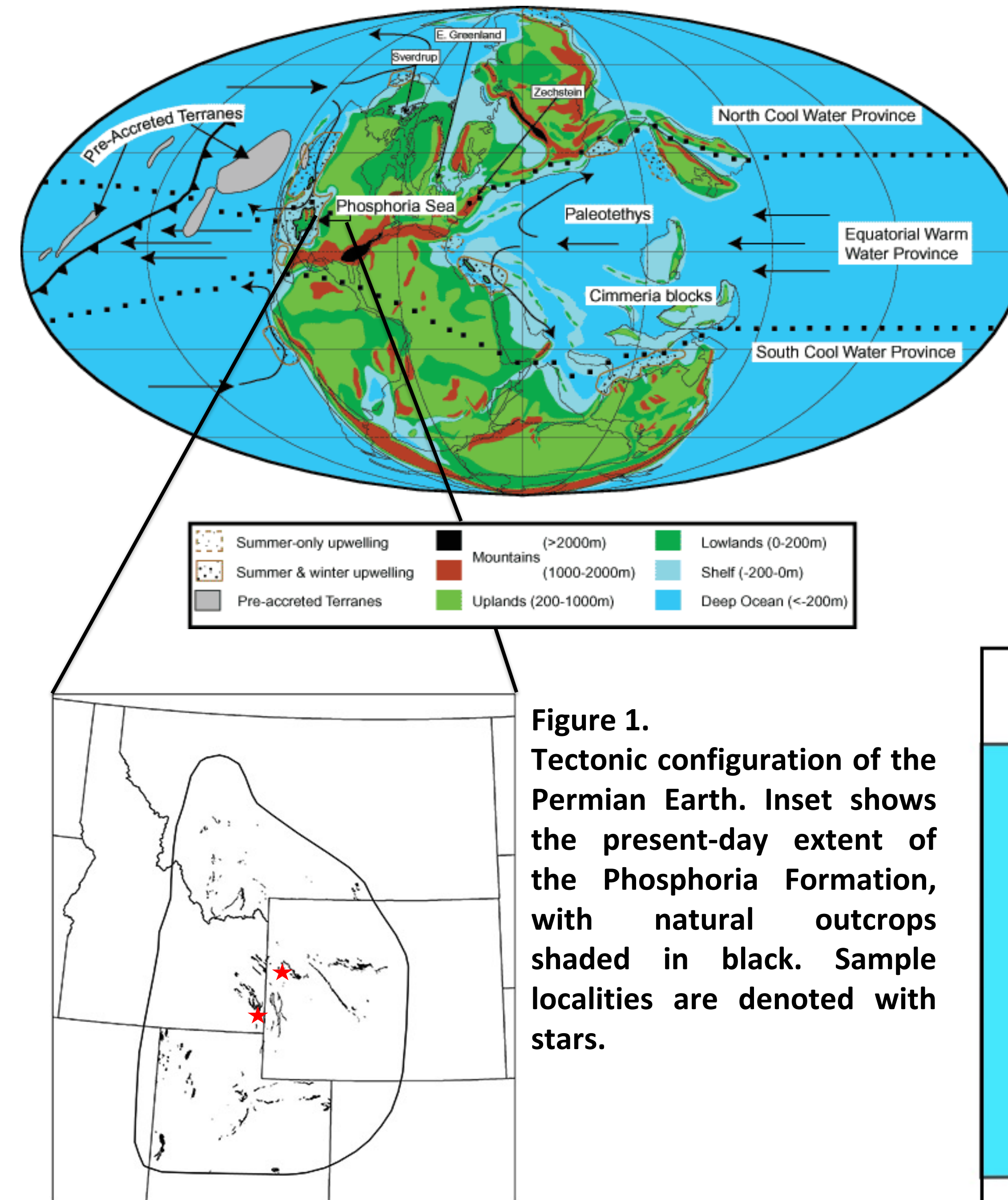
One aspect of the upwelling model that has not yet been evaluated is the status of the nitrogen cycle in a basin featuring vigorous phosphogenesis. Since upwelling transports nitrogen along with phosphorus, it is conceivable that this essential macronutrient would also have been present in abundance in the Phosphoria Sea. However, the inference of persistent denitrifying conditions in the water column (Piper 2001) also leaves open the possibility that nitrogen was rapidly removed from the system. Here we present nitrogen isotopic data spanning the Retort phosphatic shale member of the Phosphoria Formation, and consider the implications for the status of nitrogen cycling at the time of deposition. We also lay out plans for future work that will aim to more broadly characterize water-column and sedimentary redox conditions during phosphogenesis in the Phosphoria Sea.

## Methods

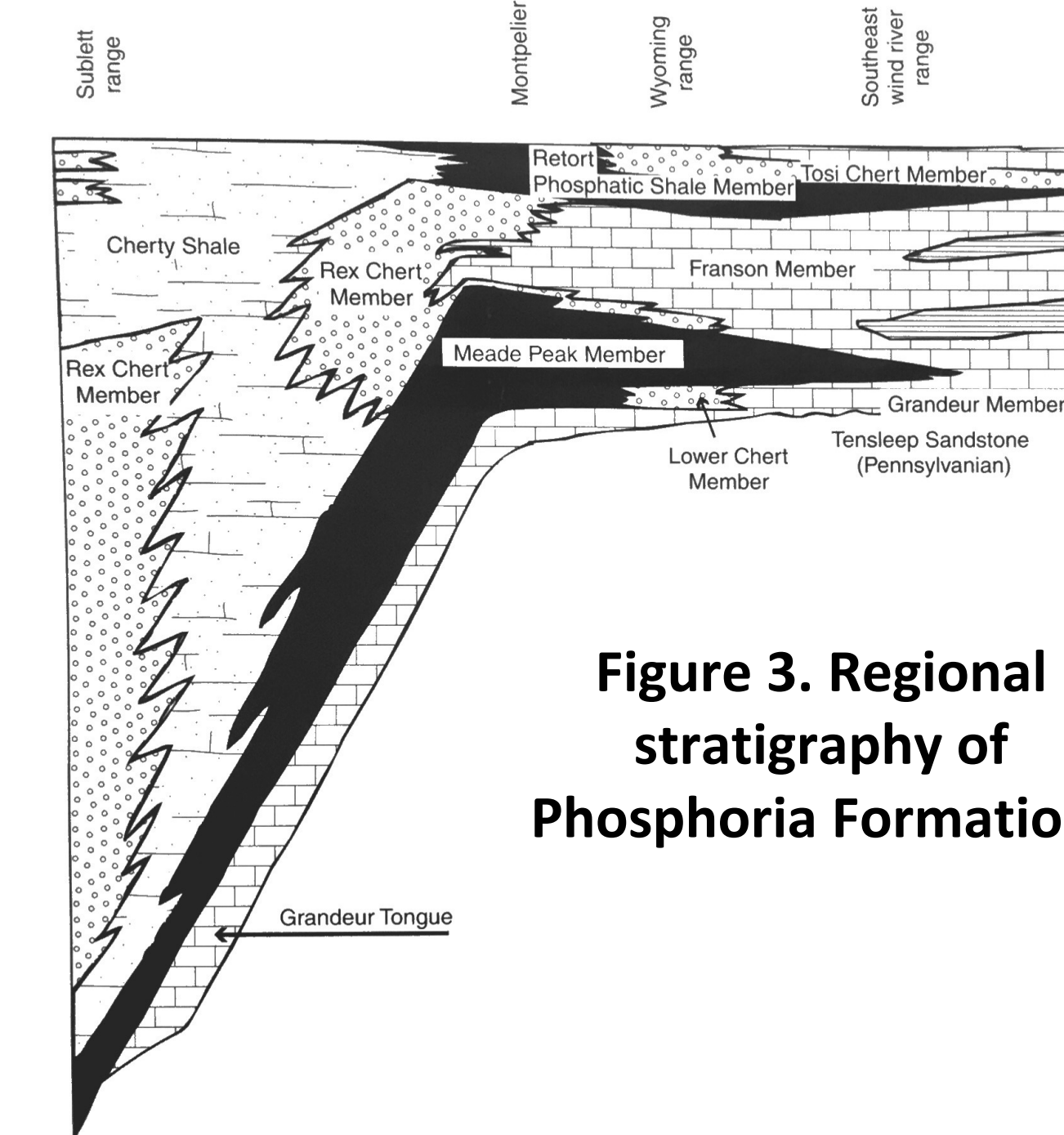
Samples were collected from an exposure of the Retort phosphatic shale near Montpelier, ID, as well as from natural outcrops of the Tosi Chert near Afton, WY (Figs. 1, 2). All samples were analyzed on a Costech ECS 4010 Elemental Analyzer coupled to a Thermo Finnigan MAT 253 continuous flow isotope-ratio mass spectrometer. We report all data in standard delta notation, with  $\delta^{13}\text{C}$  values relative to Vienna PeeDee Belemnite and  $\delta^{15}\text{N}$  values relative to air.



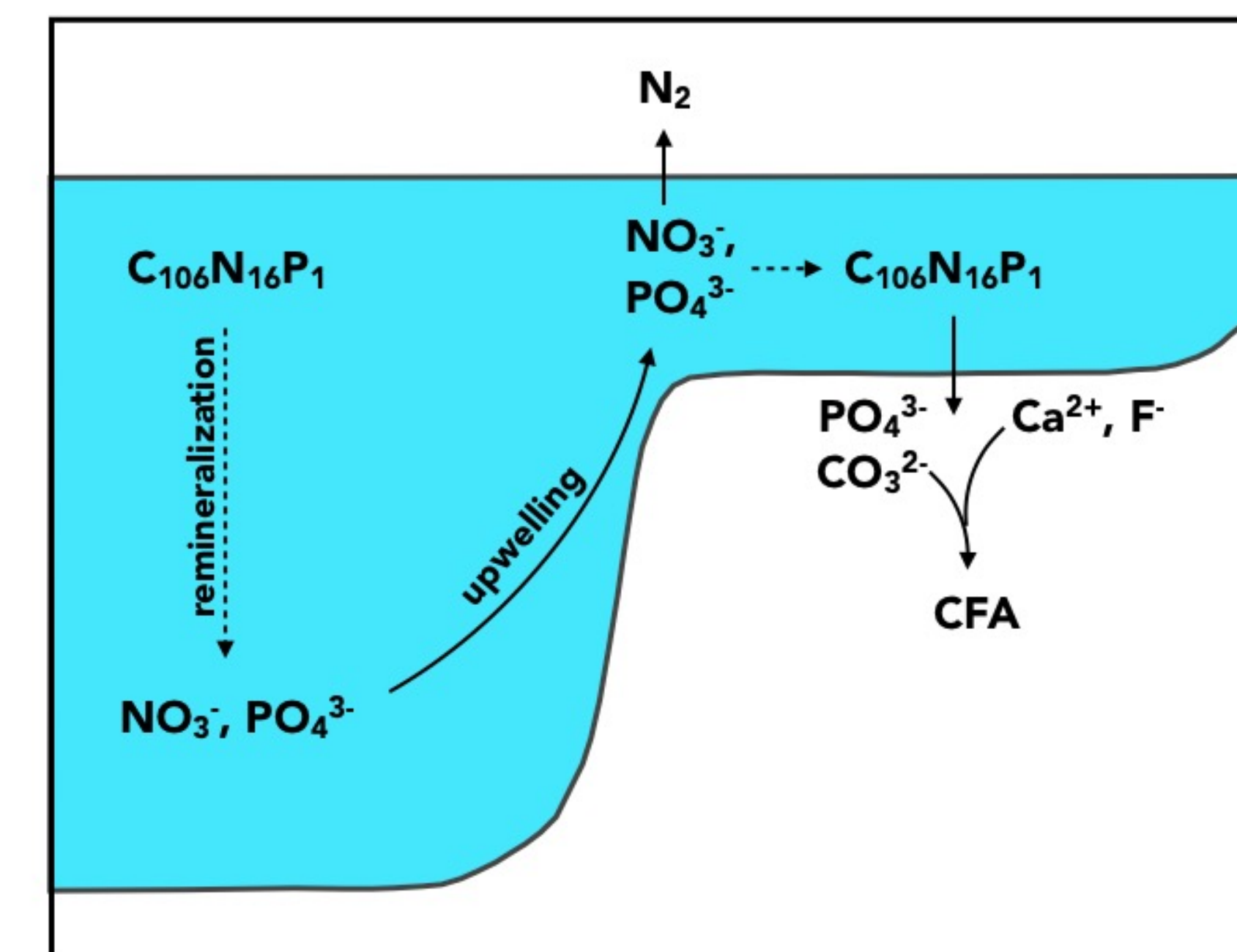
**Figure 2.** Abandoned mining exposure of Retort phosphatic shale near Montpelier, ID. Organic-rich horizons are seen inter-fingered with cherty shale. The Triassic Dinwoody Formation sits unconformably atop the Retort member.



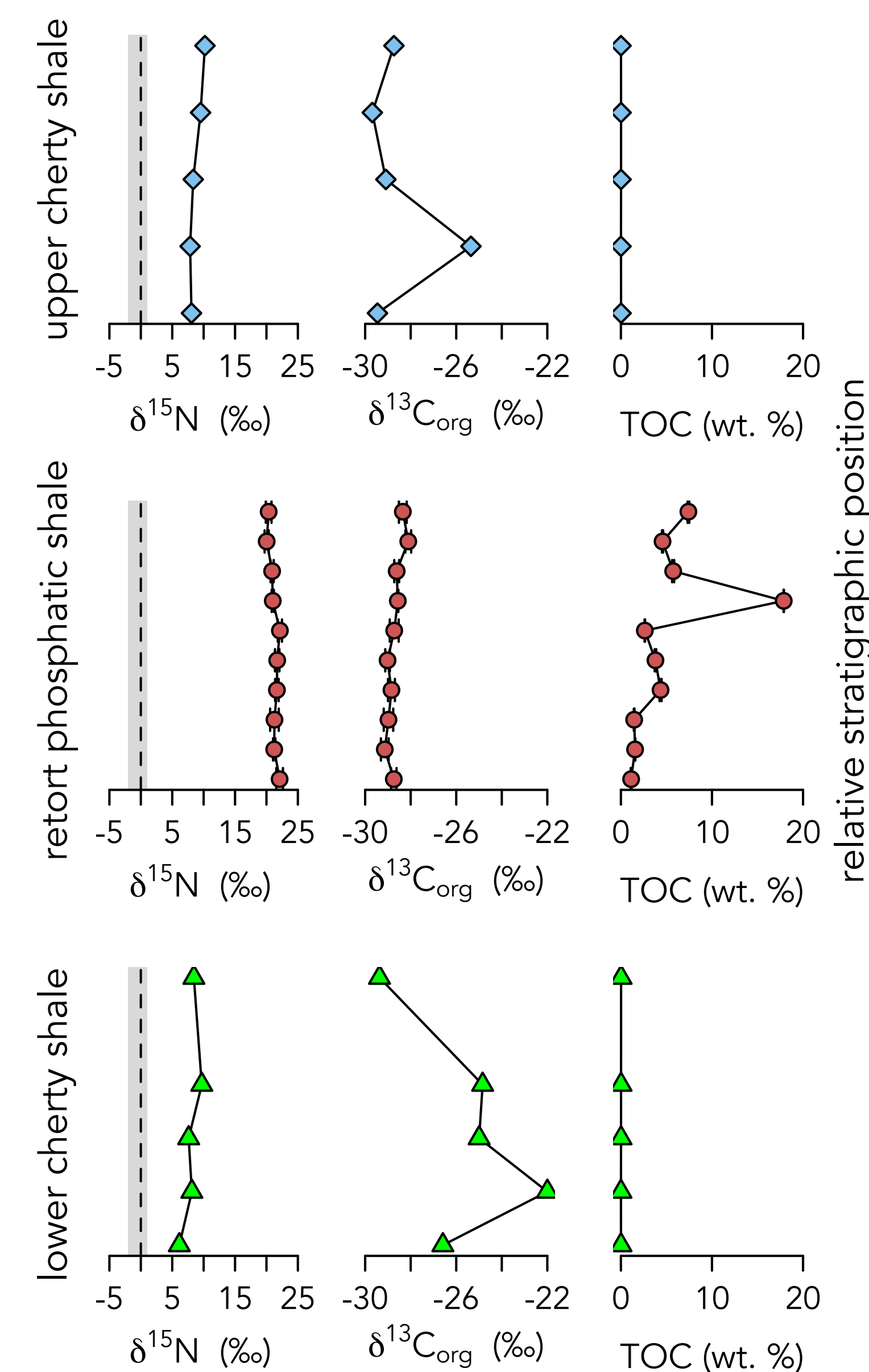
**Figure 1.** Tectonic configuration of the Permian Earth. Inset shows the present-day extent of the Phosphoria Formation, with natural outcrops shaded in black. Sample localities are denoted with stars.



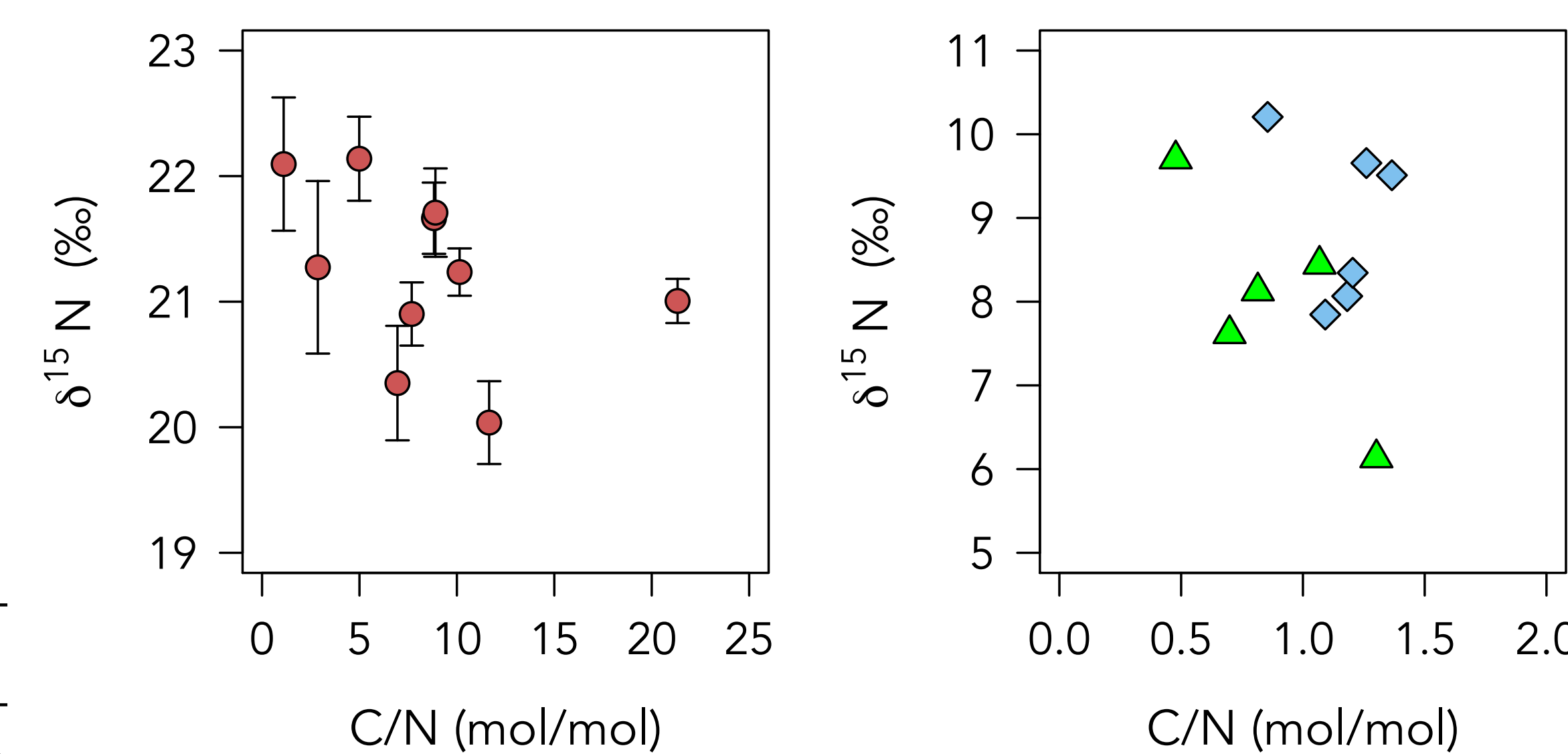
**Figure 3.** Regional stratigraphy of Phosphoria Formation.



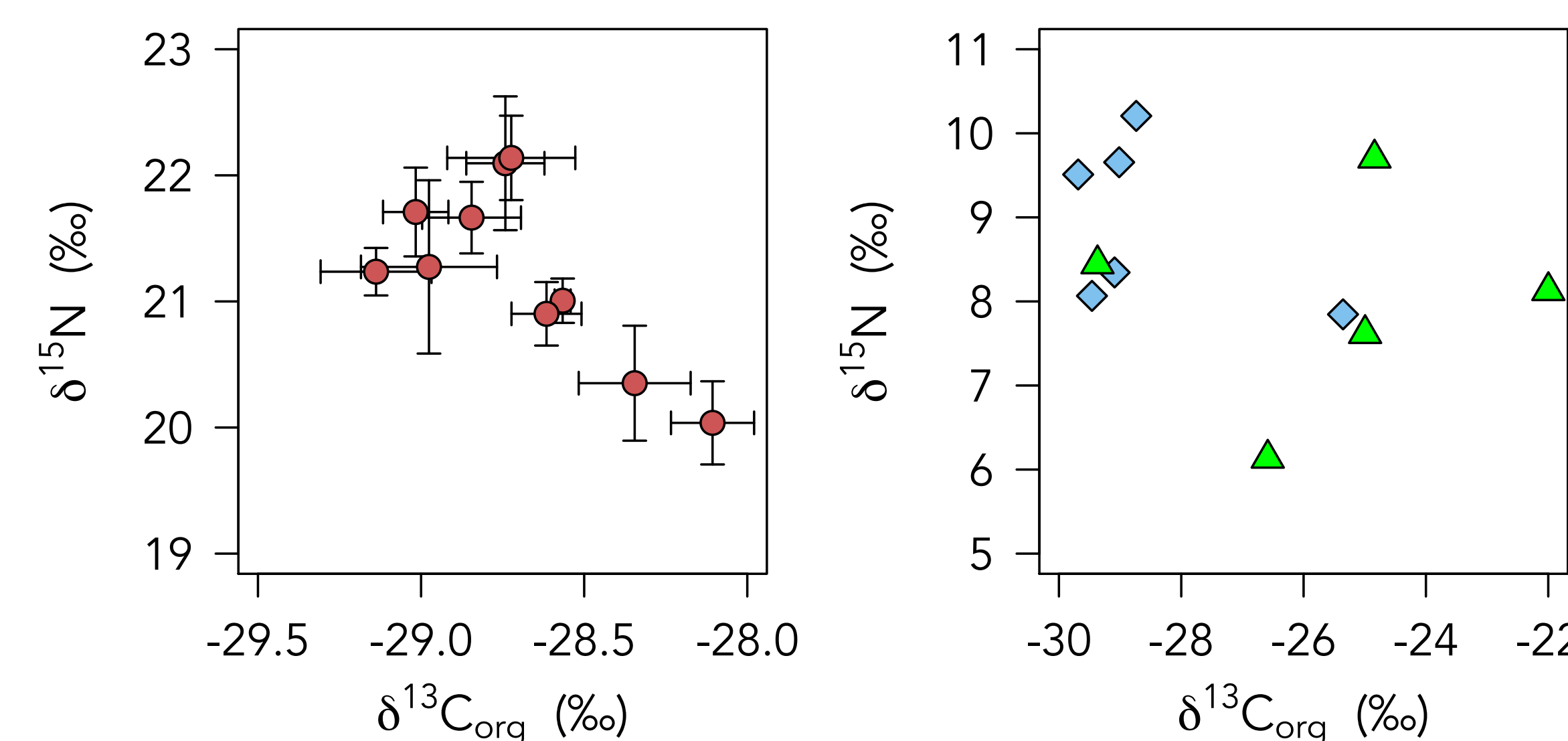
**Figure 4.** Upwelling model for deposition of the Phosphoria Formation.



**Figure 5.** Nitrogen and carbon isotope chemostratigraphy.



**Figure 6.** Assessment of alteration:  $\delta^{15}\text{N}$  vs. C/N ratios.



**Figure 7.** Assessment of alteration:  $\delta^{15}\text{N}$  vs.  $\delta^{13}\text{C}$  ratios.

## Results & Discussion

The Retort phosphatic shale member showed extremely high  $\delta^{15}\text{N}$  values, in contrast to the Tosi Chert (Fig. 4). The highest  $\delta^{15}\text{N}$  values observed in the modern ocean are generally seen near upwelling zones (Tesdal et al. 2013) where high rates of export production create a large oxygen demand, *i.e.* an oxygen minimum zone (OMZ). Denitrification rates are rapid in OMZ's, leading to isotopic enrichment of residual nitrate. The finding of extremely high  $\delta^{15}\text{N}$  values in the Retort member thus seems to implicate vigorous water-column denitrification. However, there may be additional processes contributing to the elevated  $\delta^{15}\text{N}$  values.

Restricted exchange between the open ocean and the Phosphoria Sea could have enabled extreme enrichments in  $^{15}\text{N}$ . Such a scenario would involve continuous resupply of nutrients into the basin from upwelling deep waters, followed by vigorous denitrification. Indeed, tectonic, sedimentologic, and geochemical arguments have been used to argue for basinal restriction in the Phosphoria Sea (reviewed in Hein et al. 2004). Interestingly, this depositional environment bears resemblance to phosphate-bearing horizons of the ~2 Ga Aravalli Spgp, where extremely high  $\delta^{15}\text{N}$  values have been observed in P-rich beds that are thought to have been deposited in an epicontinental seaway (Papineau et al. 2009).

A lack of correlation between  $\delta^{15}\text{N}$  and C/N (Fig. 4), as well as between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  (Fig. 5), suggests that these samples were not significantly affected by diagenesis, metamorphism, or recent weathering after exposure. One possible alteration mechanism that we cannot explicitly rule out for the observed high  $\delta^{15}\text{N}$  values in bulk samples is subsequent fluid movement through the Retort member, which could have introduced isotopically heavy silicate-bound nitrogen. This post-depositional introduction of nitrogen could alter the bulk rock  $\delta^{15}\text{N}$  values, but could be ruled out with future analyses of kerogen isolates.

## Future Work

A follow up trip back to the Phosphoria Fm is being planned in order to obtain more samples, particularly from the Meade Peak phosphatic shale member. This will add spatial and temporal resolution to our dataset.

Kerogen extracts from all samples will be analyzed for nitrogen isotopes to quantify any post-depositional alteration of primary  $\delta^{15}\text{N}$  signatures. This would allow us to know if heavy nitrogen was introduced by metasomatic fluids.

The full sample set will also be analyzed for sulfur isotope ratios in sedimentary sulfides to better constrain depositional redox conditions and the potential influence of sulfate-reducing bacteria in phosphogenesis (e.g. Lepland et al. 2014).

Lastly, we would like to look at thin sections, potentially in conjunction with micro-scale analyses to see where phosphate resides in these rocks, and whether there are noticeable signs of metamorphic or metasomatic alteration.

## Acknowledgments

We thank Andy Schauer and the UW IsoLab for technical support. Funding for this work is provided by NASA Exobiology grant NNX16AI37G and the NSF Graduate Research Fellowship Program.

## References

- Hiatt EE and Budd DA. (2003). GSA Special Paper 370.
- Hein JR, et al. (2004). In: Hein, JR (ed.), Elsevier, Amsterdam.
- Jasinski SM, Lee WH, Causey JD. (2004). "The history of production of the Western Phosphate Field" In: Hein, JR (ed.), Elsevier, Amsterdam, p. 45-59.
- Lepland A, et al. (2014). *Nature Geoscience*. 7(1): 20-24.
- Kazakov AV (1937). 17<sup>th</sup> session of the International Geological Congress, Leningrad, p. 95-113.
- Mansfield GR. (1927). USGS Professional Paper 152.
- McKelvey VE. (1946). USGS Open-File Report.
- Papineau D, et al. (2009). *Precambrian Research*. 171: 37-56.
- Pardee JT. (1917). USGS Bulletin 640, p. 195-228.
- Piper DZ. (2001). *Economic Geology*. 96: 599-620.
- Piper DZ and Link PL. (2002). *AAPG Bulletin*. 86: 1217-1235.
- Tesdal JE, et al. (2013). *Biogeosciences*. 10: 101-118.
- Wardlaw BR, et al. (1995). "Permian of the western United States" In: Scholle PA, Peryt TM, Ulmer-Scholle DS (eds.), Springer-Verlag, Berlin, p. 23-40.