Reassessing the nitrogen isotope composition of sediments from the proto-North Atlantic during Oceanic Anoxic Event 2

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Introduction

Sediment records of the stable isotopic composition of nitrogen ($\delta^{15}N$) show exceptionally light $\delta^{15}N$ values at several sites in the proto-North Atlantic during Oceanic Anoxic Event 2 (OAE2) (~94 Ma). The low $\delta^{15}N$ during the event is generally attributed to an increase in N_2-fixation[1,2]. Surprisingly, published $\delta^{15}N$ values for OAE2 vary widely, even for similar locations. Using analyses of $\delta^{15}N$ for sediments from three open-ocean and two coastal sites, we show that this reported variation is likely related to the treatment of sediment samples with acid prior to the $\delta^{15}N$ analysis. Here, a compilation of pre-OAE2 and OAE2 mean values of $\delta^{15}N$ measured in unacidified samples for the proto-North Atlantic is presented (fig. 1). A box model of total N and ^{15}N cycling is used to further detect N fluxes contributing to the $\delta^{15}N$ signal.

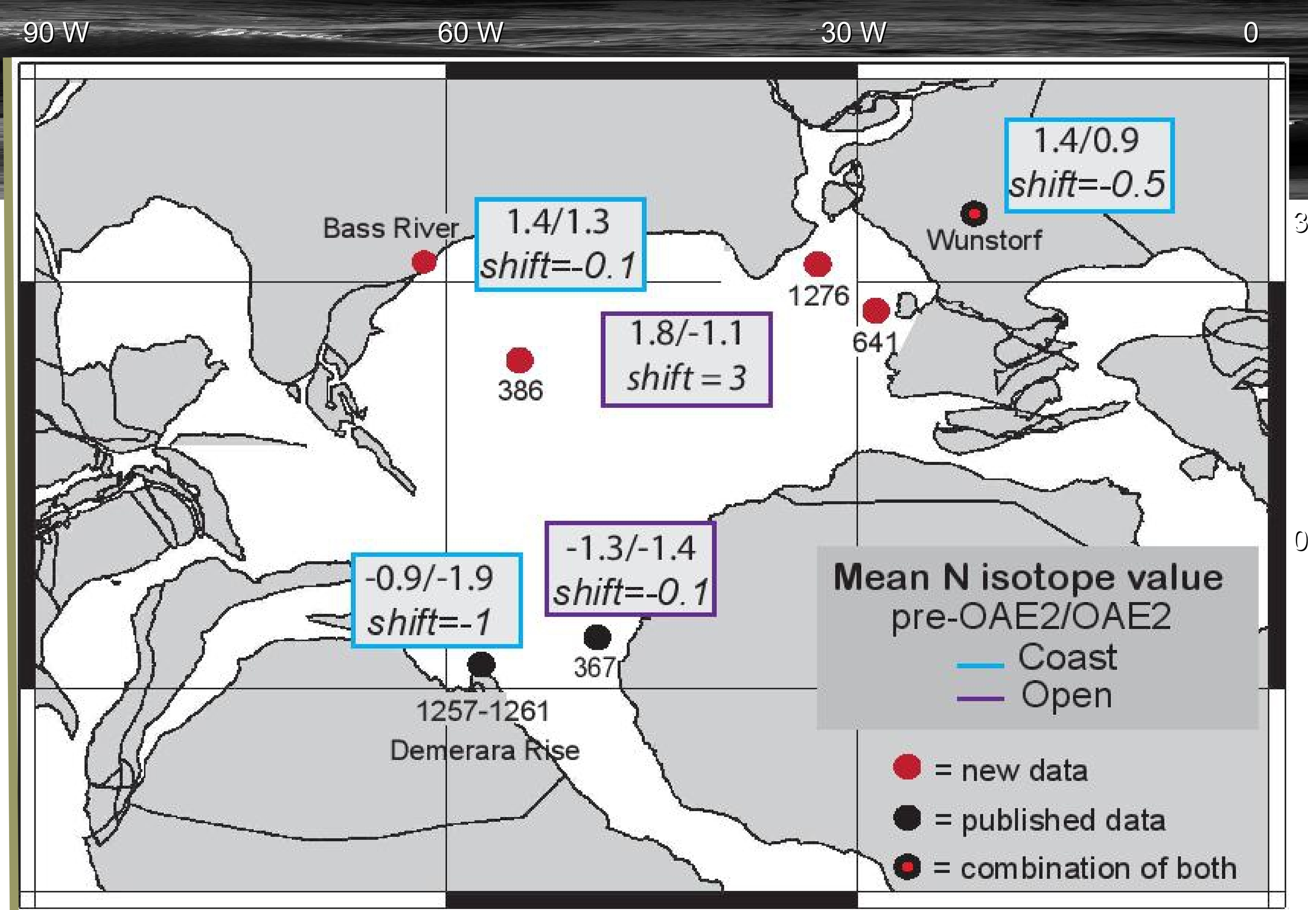

Figure 1. Map of the proto-North Atlantic during OAE2, indicating the location of the sites where $\delta^{15}N$ were not measured in samples treated with acid. Published data are from [1,2,3,4].

Results

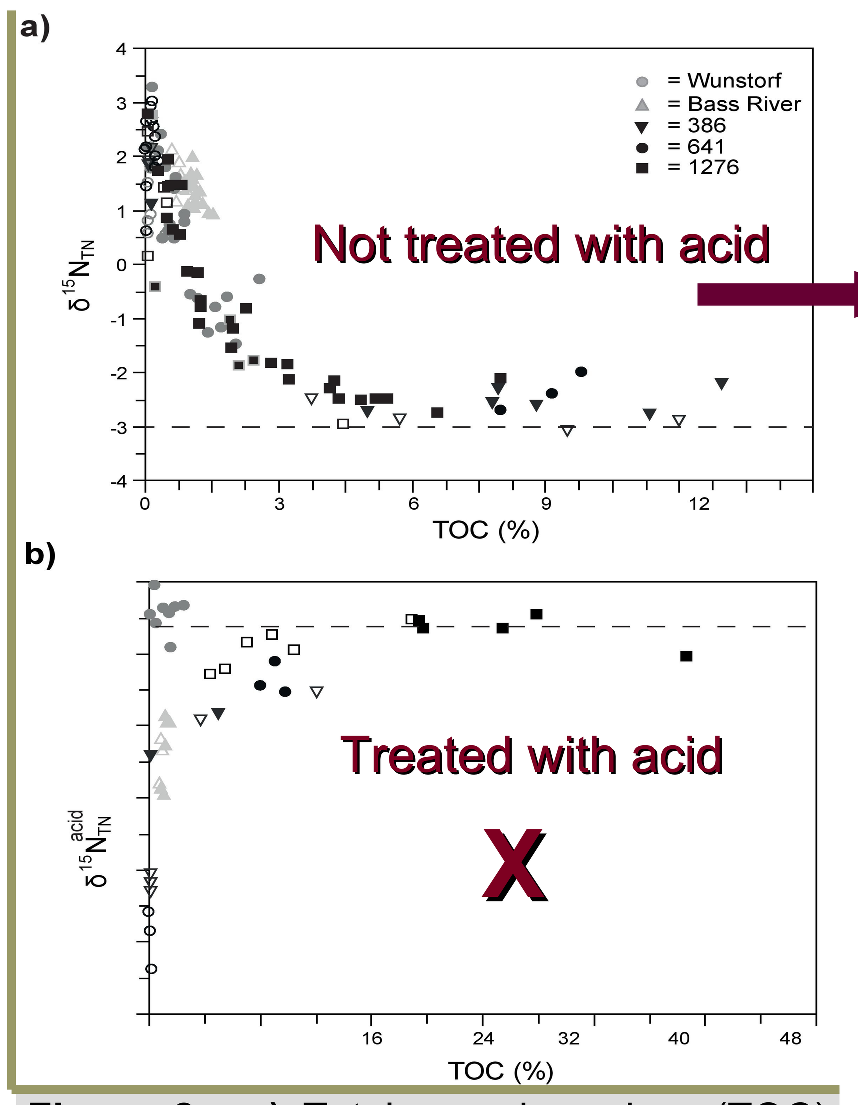

Figure 2. a) Total organic carbon (TOC) versus all new $\delta^{15}N$ measurements in the proto-Noth Atlantic. Open and closed symbols indicate pre-OAE2 and OAE2 sediments, respectively. **A lower limit of -3 ‰ can be observe in the $\delta^{15}N$ signal. b)** Relation between TOC content and the $\delta^{15}N$ signal measured in samples treated with acid. Most values fall below the $\delta^{15}N$ reference of -3 ‰..

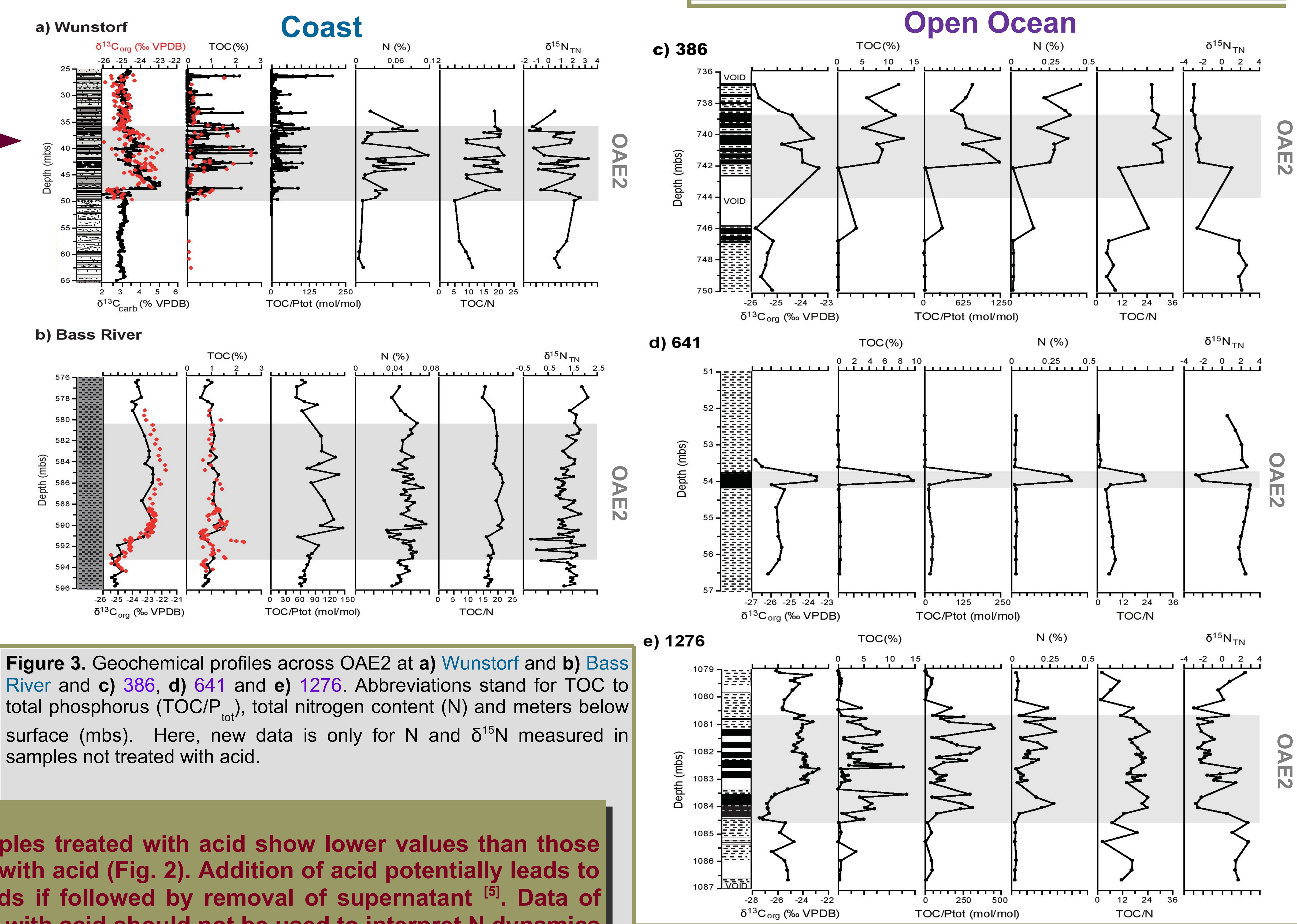

Figure 3. Geochemical profiles across OAE2 at **a)** Wunstorf and **b)** Bass River and **c)** 386, **d)** 641 and **e)** 1276. Abbreviations stand for TOC to total phosphorus (TOC/P_{tot}), total nitrogen content (N) and meters below surface (mbs). Here, new data is only for N and $\delta^{15}N$ measured in samples not treated with acid.

New $\delta^{15}N$ data measured in samples treated with acid show lower values than those measured in samples not treated with acid (Fig. 2). Addition of acid potentially leads to selective removal of N compounds if followed by removal of supernatant [5]. Data of $\delta^{15}N$ measured in samples treated with acid should not be used to interpret N dynamics in past environments.

All sites show similar trends in $\delta^{15}N$, with the OAE2 perturbation being most pronounced in the central open ocean (Fig. 3). In the euxinic southern proto-North Atlantic, the absolute shift in $\delta^{15}N$ is, however, smaller than in the central open ocean.

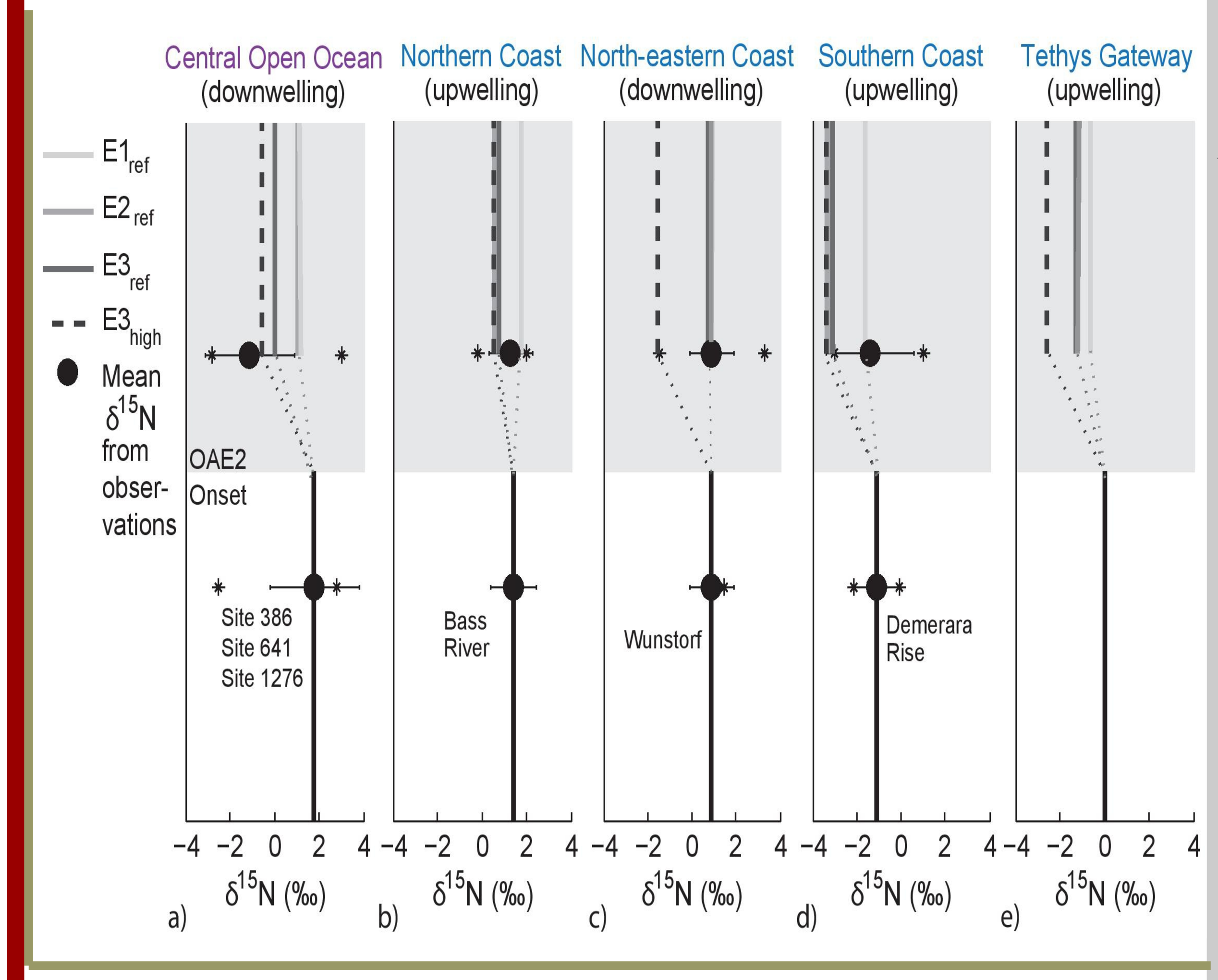

Figure 4. Model results for Experiments 1 to 3, simulating the mean shift in $\delta^{15}N$ from pre-OAE2 to OAE2 in the different areas of the proto-North Atlantic:

E1 = No fractionation due to primary productivity
E2 = Fractionation effect by primary productivity due to incomplete uptake of ammonium. Ammonium input to surface waters is assumed to be only from upwelling.
E3 = Same as E2, but the input to surface waters is assumed to be from upwelling and lateral transport.
"ref" = reference model[6]
"high" = model with higher rates of denitrification and nitrification.

Best results are from $E3_{high}$

Standard deviation (horizontal black lines) and the lowest and highest value during OAE2 (stars) are also plotted.

Conclusions

- **$\delta^{15}N$ data should not be measured in samples treated with acid.**
- **$\delta^{15}N$ values for OAE2 in the open ocean are the lowest, but never lower than -3 ‰.**
- **Intra-basinal transport of ammonium was important during OAE2 and contributed, besides, N2-fixation, to lower the $\delta^{15}N$ signal in the proto-North Atlantic.**

Acknowledgments

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