Large mass-independent oxygen isotope fractionations in mid-Proterozoic sediments: Strong evidence for a low-oxygen atmosphere

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Abstract:

Earth's ocean-atmosphere system has undergone a dramatic but protracted increase in oxygen (O_2) abundance. This environmental transition ultimately paved the way for the rise of multicellular life and provides a blueprint for how a biosphere can transform a planetary surface. However, estimates of atmospheric oxygen levels for large swaths of Earth's history still vary by orders of magnitude—foremost for Earth's middle history. Historically, estimates of mid-Proterozoic (1.8–0.8 Ga) atmospheric oxygen levels are inferred based on the kinetics of reactions occurring in soils or in the oceans, rather than being directly tracked by atmospheric signatures. Rare oxygen isotope systematics—based on quantifying the rare oxygen isotope ^{17}O in addition to the conventionally determined ^{16}O and ^{18}O—provide a means to track atmospheric isotopic signatures and thus potentially provide more direct estimates of atmospheric oxygen levels through time. Oxygen isotope signatures that deviate strongly from the expected mass-dependent relationship between ^{16}O, ^{17}O, and ^{18}O develop during ozone formation, and these 'mass-independent' signals can be transferred to the rock record during oxidation reactions in surface environments that involve atmospheric O_2. The magnitude of these signals is dependent upon pO_2, pCO_2, and the overall extent of biospheric productivity. Here, we use a stochastic approach to provide a new estimate of atmospheric pO_2 from the mid-Proterozoic $\Delta^{17}O$ record, relying on the fact that pO_2 and biospheric productivity must be coupled in order to limit redundancy in our inversion results. Using this approach we find strong evidence for atmospheric oxygen levels less than ~1% of the present atmospheric level (PAL) for at least intervals of the mid-Proterozoic.

Introduction:

The mid-Proterozoic (1.8 to 0.8 billion years ago, Ga) is generally regarded as a transitional time between the anoxic surface conditions of the Archean and the relatively well-oxygenated conditions that characterized much of the late Neoproterozoic and Phanerozoic (Canfield, 1998,

2005; Derry, 2015; Holland, 2006; Kump, 2008; Laakso and Schrag, 2017). However, there is a wide range of estimates for surface oxygen during the mid-Proterozoic, from < 0.1% to 40% of the present atmospheric level (PAL) (Kump, 2008; Lyons et al., 2014). If estimates of mid-Proterozoic pO_2 levels near or below ~1% (PAL) are correct, environmental conditions present for the majority of Earth's history are likely to have limited ecosystem complexity and inhibited the emergence of mobile multicellular heterotrophs (e.g., animals) (Reinhard et al., 2016). The potential for low pO_2 levels during the mid-Proterozoic also has important implications for oxygen-based frameworks for remote life detection on terrestrial planets (Reinhard et al., 2017). In particular, if we use Earth as an analogue and take lower Proterozoic pO_2 estimates, it is possible that atmospheric oxygen levels on terrestrial planets can stabilize for billion-year time scales at or below the detection limits for near-term observational techniques (Reinhard et al., 2017). The importance of the mid-Proterozoic for the secular history of Earth's biotic and environmental evolution thus provides strong motivation to critically assess claims of low surface oxygen levels through this interval.

Historically, mid-Proterozoic atmospheric oxygen levels were assumed to be ~10% PAL based on geochemical signatures in paleosols and marine redox records (Holland, 2006; Kump, 2008). There are several reports of Proterozoic paleosols with quantitative iron oxidation, implying atmospheric oxygen levels above ~1% PAL (Pinto JP, 1988; Zbinden et al., 1988). The presence of anoxic deep oceans (e.g., (Lyons et al., 2014; Poulton et al., 2010) has been assumed to roughly constrain maximum atmospheric oxygen levels at ~40% (Canfield, 1998; Kump, 2008). However, these traditional bounding pO_2 estimates have recently been questioned (Planavsky, 2018). Critically, the only definitive mid-Proterozoic paleosols that have formed directly from parent rock, are characterized by iron loss (Mitchell and Sheldon, 2009, 2010, 2016), pointing to low oxygen levels. A suite of other proxies has also suggested atmospheric oxygen levels less than ~10% PAL or even ~1% PAL, for at least intervals of the mid-Proterozoic. For instance, sedimentary Cr isotopes and carbonate trace element patterns have been suggested to indicate atmospheric oxygen levels less than 1% PAL, perhaps as low as 0.1% PAL or lower (Bellefroid et al., 2018; Cole et al., 2016; Gilleaudeau et al., 2016; Liu et al., 2016), consistent with updated currently available mid-Proterozoic paleosol records (Planavsky et al., 2018). However, records of both low and high mid-Proterozoic oxygen levels (Zhang et al., 2016) have been questioned and critiqued (Planavsky et al., 2016).

Some of the debate surrounding Proterozoic oxygen levels emerges naturally from the diverse suite of proxies being applied to the problem. The majority of paleo-oxygen barometers do not directly track an atmospheric signal—instead, they track an oxidation reaction occurring in a soil (or the oceans) or they attempt to link a marine redox structure to an atmospheric oxygen level. These approaches, even those that rely on fossilized soil horizons in more direct contact with the overlying atmosphere, can only indirectly track pO_2 and rely on a large number of assumptions. For instance, to link a paleosol record to atmospheric oxygen level one must assume a background pCO_2, local rainfall and infiltration rates, and a denudation rate, in addition to assumptions regarding the presence/absence and/or activity of a local terrestrial biosphere. To link a marine redox sensitive metal signature to an atmospheric pO_2 estimate one needs to link local or global ocean redox to atmospheric composition, and is thus reliant on a series of assumptions regarding ocean circulation and nutrient inventories. Not surprisingly, different researchers have reached very different conclusions about Proterozoic oxygen levels using

essentially the same numerical frameworks and empirical records. The strong potential for diagenetic overprinting of depositional signatures in paleoredox proxies only adds to uncertainty and continuing debate.

The sedimentary rare oxygen isotope record presents a means to more directly track mid-Proterozoic atmospheric oxygen levels. The majority of reactions on Earth induce stable isotope fractionations that are dictated almost entirely by mass differences between isotopes (Urey, 1947). However, for systems with more than two isotopes there are some processes that can create pools that are anomalously enriched or depleted in certain isotopes relative to what would be expected for a purely mass-dependent process, leading to so called 'mass-independent' or 'non-mass-dependent' (NMD) isotope effects (e.g., Thiemens, 2006).

Ozone formation is the first and one of the most intensively studied of the these NMD isotope effects (Thiemens and Heidenreich, 1983). Ozone formed in the stratosphere is anomalously enriched in ^{17}O, which is denoted as a positive $\Delta^{17}O$ value. This positive $\Delta^{17}O$ signal is transferred via photochemistry to atmospheric CO_2, while the complementary negative $\Delta^{17}O$ signal is stored in residual stratospheric O_2. This residual negative $\Delta^{17}O$ signal can then be transferred to the rock record via oxidation reactions during weathering (e.g., pyrite oxidation). The magnitude of this $\Delta^{17}O$ anomaly is dependent most strongly on the amount of atmospheric O_2 and CO_2 and how quickly the anomalous O_2 produced during photochemistry is reset by biological cycling (Cao and Bao, 2013; Luz et al., 1999). Therefore, the $\Delta^{17}O$ composition of sedimentary sulfate minerals at any given time and location primarily reflects: (1) atmospheric O_2 levels; (2) atmospheric CO_2 levels; and (3) global primary productivity. Importantly, diagenetic processes and/or metamorphic overprinting should only act to erase $\Delta^{17}O$ anomalies, making this proxy arguably more robust than traditional redox proxies.

Here, we revisit previous modeling of the Proterozoic sulfate mineral $\Delta^{17}O$ record (Crockford et al., 2018) in order to more precisely reconstruct atmospheric pO_2 during an interval of mid-Proterozoic time. We utilize a stochastic approach, building from statistical analysis of output from the global biogeochemical model CANOPS (Ozaki et al., 2019; Ozaki et al., 2011), to filter the large number of mathematically possible solutions for any given $\Delta^{17}O$ value according to only those solutions that allow for mass balance between biospheric productivity and atmospheric pO_2. This results in a dramatically reduced number of possible O_2-CO_2-productivity combinations consistent with a given $\Delta^{17}O$ measurement, and a much more precise range of atmospheric pO_2 values.

The mid-Proterozoic $\Delta^{17}O$ record:

Sulfate minerals extracted thus far from mid-Proterozoic carbonates have been found to be heavily contaminated with recent atmospheric sulfate and thus cannot be used to track atmospheric signals (Peng et al., 2014). However, sulfate from a limited number of mid-Proterozoic evaporite successions appears to preserve $\mathbf{\Delta}^{17}O$ signals from atmospheric O_2, presumably acquired during terrestrial pyrite oxidation (Crockford et al., 2018) in which roughly 10% of oxygen that becomes incorporated into sulfate during pyrite oxidation is atmospherically derived (Balci et al., 2007; Kohl and Bao, 2011). Although $\mathbf{\Delta}^{17}O$ signals in examined evaporite successions are highly variable, there are distinctively negative $\mathbf{\Delta}^{17}O$ signals relative to the Phanerozoic sulfate record (Crockford et al., 2018) (Fig 1).

Variability on the formation scale is expected, given that any surface sulfur cycling will tend to homogenize and erase $\mathbf{\Delta}^{17}O$ signals. In particular, activation of S to SO_3^{2-} during microbial sulfate reduction leads to extremely rapid O isotope equilibration with isotopically 'normal' ambient H_2O within the cell (e.g., (Antler et al., 2013). Therefore, sulfate reduction and sulfide oxidation will decrease the magnitude of $\mathbf{\Delta}^{17}O$ signals. Marine environments, even those that are strongly redox stratified (e.g., the Black Sea), are characterized by extensive sulfide re-oxidation (Yakushev and Neretin, 1997). Evaporative successions can similarly be marked by high rates of sulfur redox cycling (e.g., (Petrash et al., 2012)). With these observations in mind, it is not surprising that there is variation within a given evaporite unit and that the most anomalous $\mathbf{\Delta}^{17}O$ signals have thus far been found in lacustrine—rather than marine—evaporite successions (Crockford et al., 2018). The most negative $\mathbf{\Delta}^{17}O$ signals found to date with the exception of Cryogenian barite and CAS (cf. (Bao et al., 2008, Bao et al., 2009; Crockford et al., 2016, 2017) (Fig. 1) —$\mathbf{\Delta}^{17}O$ values of -0.9‰—are in the lacustrine 1.4 Ga Sibley Formation (Crockford et al., 2018). Because this minimum value is likely our best estimate of a true atmospheric signal (Crockford et al., 2018; Planavsky, 2018), in what follows we develop an approach that is designed to translate this value into a quantitative estimate of atmospheric pO_2.

Translating $\Delta^{17}O$ signals to pO_2 estimates:

We use the 4-box atmosphere-ocean-biosphere model (Fig. 2) from Cao and Bao (2013) to estimate atmospheric chemistry from $\Delta^{17}O$ values. The model is designed to predict tropospheric $\Delta^{17}O$ solutions with different pO_2, pCO_2, O_2 residence times and global biospheric productivities. $\Delta^{17}O$ values of stratospheric O_2 and CO_2 vary with changing pO_2/pCO_2 ratios, following experimental results from the O_2-O_3-CO_2 photochemical reaction system (Shaheen et al., 2007). The pO_2/pCO_2 ratio affects both the lifespan of $\Delta^{17}O$ anomalies in the troposphere and the magnitude of the stratospheric $\Delta^{17}O$ anomaly (Cao and Bao, 2013). When O_2 with a $\Delta^{17}O$ anomaly is mixed down into the troposphere it can be consumed by aerobic respiration and replaced by isotopically 'normal' O_2 produced from photosynthesis (e.g., Luz et al., 1999). Because we assume steady state, the model effectively links the amount of recycled oxygen to the oxygen released through primary production within the biosphere. In a low-oxygen system this value will be less than gross primary productivity (GPP), as some oxygen released in the marine realm will be consumed through respiration without interacting with the atmospheric reservoir (e.g., Reinhard et al., 2013). However, in order to be conservative in our estimates we assume the oxygen flux is equal to GPP. Although the amount of primary productivity in the terrestrial realm in the Precambrian is debated, we include a recent estimate of terrestrial productivity from cyanobacterial mats (1.74 Gt C; Zhao et al., 2018). However, we assume this terrestrial cyanobacterial productivity results in an insignificant amount of organic carbon burial. Overall, the $\Delta^{17}O$ value of O_2 in the troposphere reflects the mass balance between sourcing of anomalous O_2 from photochemistry in the stratosphere (the magnitude of which varies with the size of the atmospheric CO_2 reservoir) and O_2 recycling within the biosphere (Fig. 2). The tropospheric $\Delta^{17}O$ anomaly can then be transferred to the rock record during pyrite oxidation and subsequent sulfate burial, linking Earth's stratosphere with the rock record.

Within this framework, there are numerous hypothetical O_2, CO_2, primary productivity combinations that could be consistent with a single sedimentary $\Delta^{17}O$ value (Cao and Bao, 2013; Crockford et al., 2018). Although results from the Sibley Group have provided strong arguments

for a less productive mid-Proterozoic biosphere (Crockford et al., 2018), not all of these *GPP*-pO_2-pCO_2 mathematical solutions will represent mechanistically accessible Earth states—e.g., Earth system states that are stable on geologic timescales and are thus consistent with the mid-Proterozoic sedimentary record. In order to estimate which combinations of atmospheric O_2, CO_2, and global primary productivity represent possible 'alternative Earths', we rely on previous estimates of atmospheric CO_2 (Crockford et al., 2018; Isson and Planavsky, 2018; Kah and Riding, 2007; Sheldon, 2006) for reviews and pCO_2 estimate compilations). In a new contribution, we use the results from a stochastic exploration of the global biogeochemical model CANOPS (Ozaki et al., 2019; Ozaki et al., 2011) to filter out combinations of pO_2 and global primary productivity that satisfy $\Delta^{17}O$ results but that do not provide redox balanced Earth states. In other words, although there are uncertainties in global organic carbon burial efficiency and estimates of reductant outgassing, at any given pO_2 there are only a limited range of global primary productivities that results in global redox balance (Derry, 2015; Laakso and Schrag, 2014, 2017; Ozaki et al., 2019). We estimated plausible ranges of biospheric productivities for different pO_2 values using a statistical analysis of the CANOPS biogeochemical model (Ozaki et al., 2019), which allows us to assess a wide range of global carbon cycle and reductant fluxes. We use the CANOPS outputs to define upper and lower bounds on possible primary productivities at a given atmospheric pO_2 (Fig. 2). The rationale behind this approach is simple—in a mass balanced Earth system there must be a link between the globally integrated rate of biospheric primary productivity, organic carbon burial, and atmospheric oxygen levels (Derry, 2015; Laakso and Schrag, 2014, 2017; Ozaki et al., 2019).

In practice, our approach occurs in two steps. First, pO_2 and pCO_2 combinations are randomly selected (assuming uniform distributions for both; pO_2 0 to 40 % PAL; pCO_2 2-500 × PIAL) and primary productivity is computed for each pCO_2 and pO_2 combination using our observed minimum $\Delta^{17}O$ value ($\Delta^{17}O$ = -0.88 ‰) as a constraint on our atmosphere-ocean-biosphere model (Fig. 2). This step results in a wide range of possible atmospheric oxygen levels. To refine these estimates, we then filter the dataset for combinations of atmospheric pO_2 and global primary productivity that do not yield redox balanced solutions in the CANOPS global biogeochemical model. This filtering step dramatically reduces both the range of pO_2 estimates and the modal values—with essentially all estimates from our approach falling between slightly below 0.1% PAL to just above 1% PAL (Fig. 3). Although possible pO_2 values still span over an order of magnitude, this range is considerably more precise than that conventionally invoked for the mid-Proterozoic Earth (Lyons et al., 2014). Upon publication the code will be posted on GitHub. The details of the CANOPS simulations in an anoxic ocean (suitable for our 0.01% to 40% PAL pO_2 range) have been recently described in detail in Ozaki et al., (2019).

Discussion:

Our analysis provides new evidence for low mid-Proterozoic atmospheric oxygen levels (95% of the outputs from the Monte Carlo simulation where < 1% PAL). Given the strong potential to erase $\Delta^{17}O$ anomalies (through surface sulfur cycling) and the stratigraphic rarity of rocks that best preserve atmospheric $\Delta^{17}O$ signals—lacustrine evaporites—we only reconstruct meaningful maximum pO_2 levels from a single interval of mid-Proterozoic time using this approach. However, we argue that this snapshot offers the single most robust constraint on surface oxygen levels in Earth's middle history. First, later diagenetic alteration will erase $\Delta^{17}O$ signals for low oxygen, which is in strong contrast to most oxygen proxies for which signals implying low

oxygen can potentially be caused by alteration. That is, the $\Delta^{17}O$ system is the only currently available geochemical tracer applicable to the post-Archean rock record that is not susceptible to 'false positives' for low O_2, which on its own makes our pO_2 reconstruction arguably the most robust estimate of mid-Proterozoic atmospheric composition. Further, as stressed above, the $\Delta^{17}O$ system is the only known oxygen barometer that records a direct atmospheric signal—with the notable exception of the $\Delta^{33}S$ system, which has transformed our understanding of atmospheric composition during Archean time (4.0-2.5 Ga) (Bekker et al., 2004; Farquhar et al., 2000; Pavlov and Kasting, 2002). The translation of a sulfate $\Delta^{17}O$ value into an atmospheric pO_2 estimate requires a model, and thus the leveraging of several assumptions. However, the use of computationally tractable biogeochemical models allows for formal assessment of uncertainty, and results in a significant refinement of the estimated pO_2 range and overall values that are significantly lower than traditional estimates for the mid-Proterozoic (Holland, 2006). We consider this approach a useful strategy to build on moving forward.

Our new atmospheric pO_2 estimate for ~1.4 Ga contrasts with some recent, roughly contemporaneous pO_2 estimates. For example, our estimate is higher than estimates inferred from an early Cr isotope study (<0.1% PAL; Planavsky et al., 2014), but much lower than estimates from several marine redox records (<5% PAL; Zhang, 2016). It is possible that the disagreement among proxies simply reflects time-variable atmospheric oxygen levels, as temporally variable oxygen levels are excepted with a small atmospheric oxygen reservoir. However, we emphasize that the empirical and quantitative approaches utilized in reconstructions of mid-Proterozoic pO_2 that yield estimates outside of 0.1% to 1% PAL range have been strongly critiqued (e.g., Diamond et al., 2018; Planavsky et al., 2016; Zhang et al., 2016). Nevertheless, our estimate is consistent with a number of other proxy reconstructions. For instance, more recent interpretations of the Proterozoic Cr isotope record, surface oxygen estimates based on cerium oxidation kinetics, and other works revising classical estimates from Proterozoic paleosols are all consistent with a mid-Proterozoic atmospheric pO_2 between 0.1—1% PAL (Bellefroid et al., 2018; Cole et al., 2016; Gilleaudeau et al., 2016; Liu et al., 2016).

Robust evidence for low Proterozoic oxygen levels carries important implications for how we think about long-term ecosystem evolution and the development and maintenance of remotely detectable atmospheric biosignatures. It is outside of the scope of this paper to discuss these topics in detail. However, it has been argued that an Earth system with surface oxygen levels less than ~1% PAL may not be well-suited to foster the diversification and expansion of animal-rich ecosystems (Reinhard et al., 2016). Minimum oxygen requirements for many animals are likely less than 1% PAL (Sperling et al., 2016; Sperling et al., 2015), but at such low baseline levels of oxygen and productivity would render most marine environments challenging for early metazoan organisms (Reinhard et al., 2016). Second, this work supports the idea that terrestrial planets can be stable under 'weakly oxygenated' states, which may be near or below the detection limit of current observational technology in many cases. This provides an impetus to bolster the UV capabilities of space-based mission concepts such as HabEx or LUVOIR (Schwieterman, 2018).

Conclusions:

Here we have provided new constraints on the mid-Proterozoic Earth system by developing a new quantitative framework for interpreting the sedimentary $\Delta^{17}O$ record. Building from previous work (Crockford et al., 2018) that has provided evidence for a less productive mid-

Proterozoic biosphere, we translate sulfate $\Delta^{17}O$ values into a range of possible atmospheric oxygen levels using a stochastic approach. We explore the range of previously proposed pCO_2 and pO_2 estimates and solve for the extent of productivity needed to explain minimum mid-Proterozoic $\Delta^{17}O$ values for each unique pCO_2 and pO_2 combination. Following upon several models that have stressed the link between nutrients, productivity and atmospheric oxygen levels (Derry, 2015; Laakso and Schrag, 2014, 2017; Ozaki et al., 2019), we then filter these initial model outputs for pO_2 and productivity combinations that yield stable Earth system states in the global biogeochemical model CANOPS. Using this approach, we arrive at an estimate of atmospheric pO_2 at ~1.4 Ga of 0.1-1% PAL (with more than 95% of outputs below 1% PAL). Although this approach provides only a snapshot of Earth's evolving atmospheric chemistry, represents the first quantitative Proterozoic pO_2 estimate from an isotopic signal directly related to atmospheric oxygen levels. This bolsters the case that environmental conditions inhibited the rise and diversification of complex multicellular heterotrophs. Evidence for low levels of atmospheric oxygen in Earth's middle history also has implications for the development and implementation of tools for remotely detection of atmospheric biosignatures on terrestrial planets and further highlights the importance of ozone quantification for exoplanet exploration (Schwieterman, 2018).

Figures:

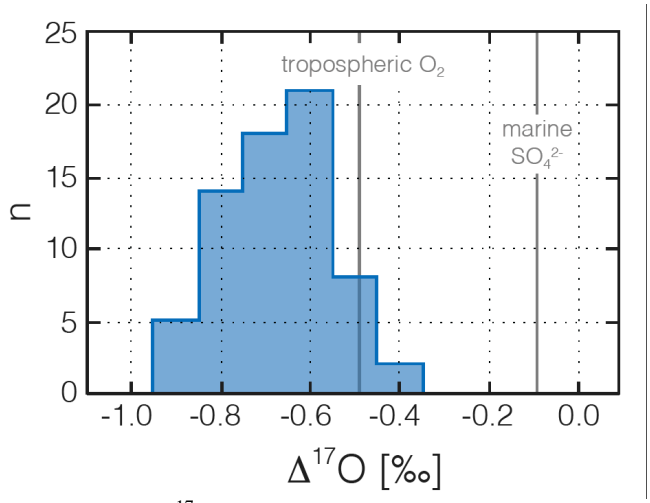

Figure 1. Histogram of gypsum $\Delta^{17}O$ values from the ca. 1.4 Ga lacustrine Sibley Basin in Ontario Canada. This lacustrine setting seems to be characterized by limited sulfur cycling (sulfur reduction and re-oxidation (see Crockford et al., 2018), allowing for the effective preservation of atmospheric $\Delta^{17}O$ anomalies. For comparison, the lines show the compiled values of modern marine sulfate (dark blue line) and modern tropospheric O_2 (light blue line). Note that only a portion (roughly 10%) of atmospheric oxygen is incorporated into sulfate during pyrite oxidation. Data adapted from Crockford et al., (2018).

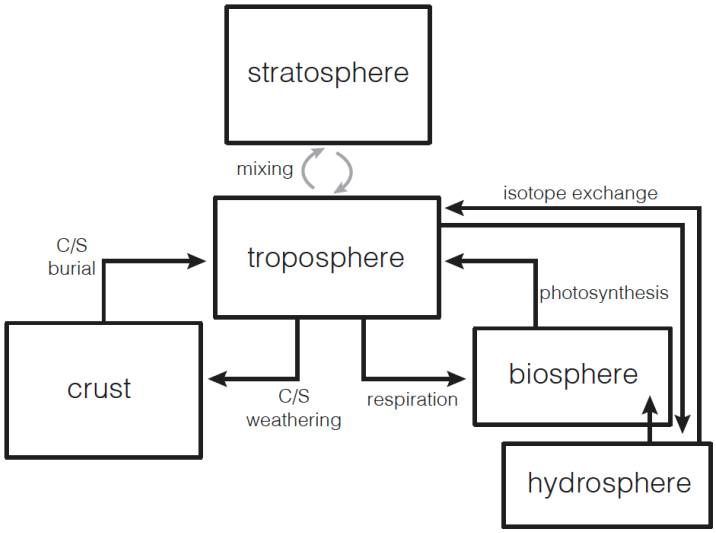

Figure 2. Schematic overview of the box model used to explore the ^{17}O system. ^{17}O anomalies are created in the stratosphere the the Chapman cycle. Negative ^{17}O anomalies (negative $\Delta^{17}O$) are transferred to O_2 and positive ^{17}O anomalies (positive $\Delta^{17}O$) are transferred to CO_2. The O_2 with negative $\Delta^{17}O$ can be mixed into the troposphere where it can be erased (reset to the terrestrial mass fractionation line) through aerobic respiration or transferred to rock record via weathering of reduced mineral phases (e.g., pyrite oxidation to form sulfate). The magnitude of $\Delta^{17}O$ in sulfate will be dependent on the CO_2 / O_2 mixing ratio and the extent of biospheric productivity.

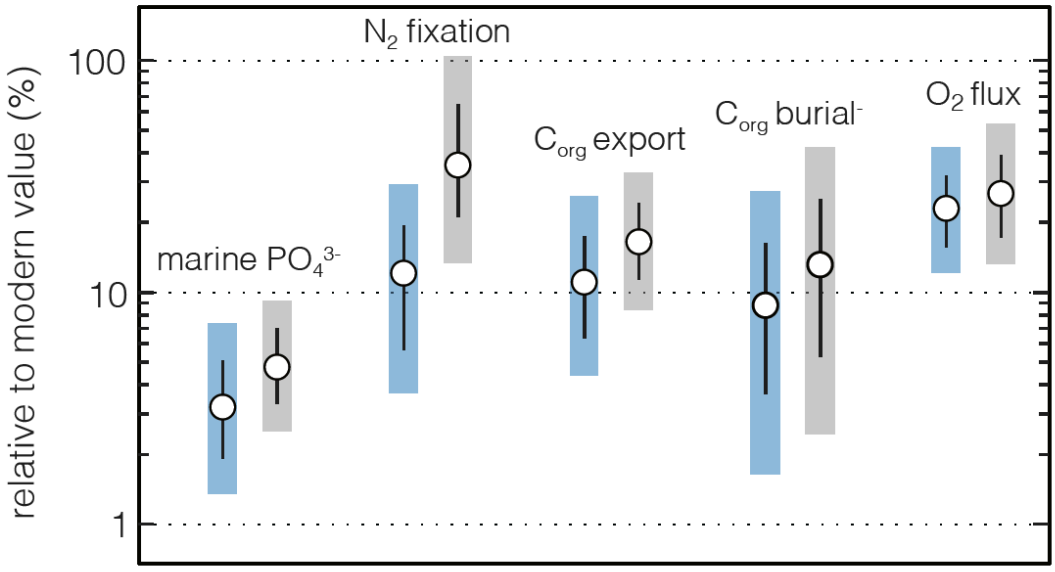

Figure 3. Example of the steady state environmental parameter space from the CANOPS Monte Carlo simulation at 1% PAL pO_2 (light blue) and 10% PAL pO_2 (light grey). Marine phosphate levels, the extent of N fixation, the marine export flux, organic carbon burial and the O_2 are all significantly less than those of the modern Earth.

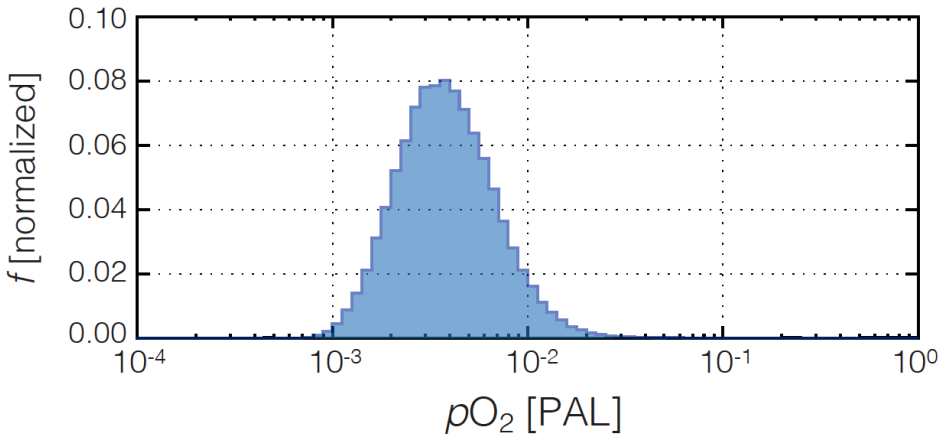

Figure 4. Atmospheric oxygen estimates consistent with the CANOPS-filtered sulfate $\Delta^{17}O$ values from our stochastic method. Although there are a wide range of numerically possible O_2, CO_2, primary productivity combinations that are consistent with a single sedimentary $\Delta^{17}O$ value, most of these combinations are not possible (i.e., stable) alternative Earth states. The stable Earth states that that are consistent with the Sibley $\Delta^{17}O$ values have low (<1% PAL; < 10^{-2} PAL) atmospheric oxygen levels.

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