

## Re-examination of bistability of atmospheric oxygen level

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Atmospheric oxygen concentration has increased during the Earth history. Approximately 2.4-2.0 billion years ago, it increased from less than  $10^{-5}$  PAL (Present Atmospheric Level) to 0.01-0.001 PAL (e.g., Lyons et al., 2016). This is known as “Great Oxidation Event (GOE)”. Because there may be two stable steady states in the atmospheric oxygen level, the GOE could be understood as a switch of the atmospheric oxygen level from low- (less than  $10^{-5}$  PAL) to high- ( $10^{-2}$  PAL) steady state (Goldblatt et al., 2006). According to Goldblatt et al. (2006), the bistability arises from ultraviolet shielding of the troposphere by ozone: once oxygen levels exceed  $10^{-5}$  PAL, the ozone starts to form and reduce the rate of methane oxidation, which reduces oxygen sink and promoted rises of oxygen levels to form ozone layer. This positive feedback may have caused the GOE (Goldblatt et al., 2006). Although they used the results of a one-dimensional atmospheric photochemical model of Pavlov et al. (2003), the oxygen levels necessary for reducing ultraviolet is shown to be  $10^{-3}$  PAL in the original model (Kasting, 1987). We suppose that the difference may be derived from some technical errors during data processing because Goldblatt et al. (2006) used the result of Pavlov et al. (2003) and others, instead of using the model by themselves. In this study, I therefore use the photochemical model of Pavlov et al. (2003) to obtain a complete data set from which the bistability of atmospheric oxygen level is reevaluated. Based on the results of parameter studies, we calculated methane oxidation rates with the oxygen concentration and the methane concentration, and recalculated stable states of atmospheric oxygen levels using a redox balance model for the Earth's surface system (Goldblatt et al., 2006). We found that the methane oxidation rate increases as the oxygen concentration becomes higher in the range of  $10^{-4}$ - $10^{-7}$  PAL, but it decreases in the range of  $1$ - $10^{-4}$  PAL. It is natural that the methane oxidation rate becomes higher as the oxygen concentration increases, hence the behavior in the range of oxygen levels of  $1$ - $10^{-4}$  PAL looks strange. It would be the effect of decrease in OH radicals owing to ultraviolet shielding by development of ozone layer. In order to ascertain the relationship between the decrease in the methane oxidation rate and the formation of the ozone layer, the photodissociation of water vapor due to ultraviolet is investigated. In the range of oxygen level of  $1$ - $10^{-4}$  PAL, it is shown that the photodissociation of water vapor at an altitude of 30 km or less is remarkably suppressed. Hence it is confirmed that the generation of OH radicals decreases remarkably because of the development of ozone layer above the oxygen levels of  $10^{-4}$  PAL. Using the methane oxidation rate calculated in this study, it is shown that there is a critical condition at which transition of stable steady state of oxygen levels occurs. But, unlike the result of Goldblatt et al. (2006), the recalculated stable states of oxygen levels represent no bistability. This is probably because this study used data obtained from the same model under the same conditions for the range of oxygen levels of  $1$ - $10^{-7}$  PAL, while Goldblatt et al. (2006) used data taken from some different references which may have adopted different models with different photochemical reaction systems and under the different conditions for the range of oxygen levels of  $1$ - $10^{-12}$  PAL. Based on this result, increase in oxygen production due to increase in primary productivity would have been responsible for the rise of oxygen in the early Paleoproterozoic.

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