

## Isotopic fractionation of oxygen during sediment respiration

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The apparent community respiration fractionation factor for deep-sea sediments has a predicted value of 9‰ (Bender, 1990). This value is based on a model of sediment oxygen consumption that satisfies the assumption of first order kinetics with respect to carbon (i.e. a pore water oxygen profile which decreases exponentially with depth below the sediment-water interface). This implies that the organic matter oxidation rate is carbon limited. Bender suggests the geometry of the sediments (a partially-closed system) prevents the expression of the full microbial respiration fractionation which has been determined to be 19.1‰ ( $\alpha = 0.980$ ) for free-living bacteria (Kiddon *et al.*, 1993). The apparent fractionation in sediments (9‰ or  $\alpha = 0.991$ ) has a square-root relation to the fractionation factor for bacterial cultures as a result of the assumption of an exponential oxygen decrease in the sediments.

Brandes and Devol (1996) have presented oxygen isotope data for benthic chamber deployments in Puget Sound, Washington. Their results indicate an apparent sedimentary respiration fractionation factor of 3‰ ( $\alpha = 0.997$ ). The Puget Sound sediments are sites of rapid organic matter diagenesis and complete oxygen consumption within the top centimeter of the sediments. Brandes and Devol argued that the apparent fractionation is dramatically reduced from Bender's value of 9‰ (or from the free-living bacterial fractionation of 18‰) due to complete oxygen removal and due to the diffusive limitation present in a sedimentary system. Their model parameterizes intense diagenesis in discrete sediment micro-sites wherein oxygen is completely consumed. The apparent fractionation is small because oxygen concentrations go to zero at the micro-site. They suggest this small fractionation arises as a result of oxidant limitation. When the diffusive oxygen flux is insufficient to balance the respiratory demand all oxygen molecules are consumed and there is no distinction between the heavy and the light isotopes.

### Methods and results

In order to further examine the oxygen isotope fractionation a resulting from benthic metabolism we

measured changes in dissolved oxygen concentration and isotopic composition ( $\delta^{18}\text{O}$ ) in the overlying waters of sediment core incubations. Triplicate sediment cores were collected from four depths (800, 1770, 2000 and 2600 m) on the deep continental margin off Washington State during the summer of 1997. Cores were incubated *in situ* temperatures for two to three days. Oxygen concentrations were measured at 0, 12, 24 and 48 or 72 hours; samples for stable isotope analysis were taken at the initial and final time points. In all cases, dissolved oxygen concentrations in the overlying water decreased and the  $\delta^{18}\text{O}$  of the dissolved oxygen increased over the course of the experiment. The initial overlying water had an oxygen concentration of 338  $\mu\text{mol L}^{-1}$  and an isotopic composition of 0.51‰. At the end of the experiment, oxygen concentrations had decreased by 18 to 55% and the final overlying water  $\delta^{18}\text{O}$  values ranged from 1.70‰ to 5.89‰ (Fig. 1). The sediment core incubation is a closed system and thus can be approximated by Rayleigh fractionation kinetics. We have plotted the change in  $\delta^{18}\text{O}$  composition as a function of the fraction of the initial oxygen remaining for various values of the fractionation factor ( $\alpha$ ). The per mil fractionation for a given oxygen consumption increases dramatically as the fractionation factor increases. Based on this calculation, the isotopic changes during the core incubation experiments (indicated by the open symbols in Fig.1) correspond to an average apparent sedimentary respiration fractionation factor of 8‰ ( $\alpha = 0.992$ ).

### Discussion: oxidant vs substrate limitation

In suboxic and highly respiring sediments, the supply flux of oxygen is lower than the sedimentary oxygen demand (i.e. oxidant limitation) and the apparent fractionation during respiration should be lower (potentially much lower) than 9‰. Based on data in Brandes and Devol, most continental margin sediments appear to be oxidant limited. In shallow, highly respiring sediments where oxygen supply is extremely low the apparent fractionation is very small (i.e. the fractionation approaches 0‰ or  $\alpha =$

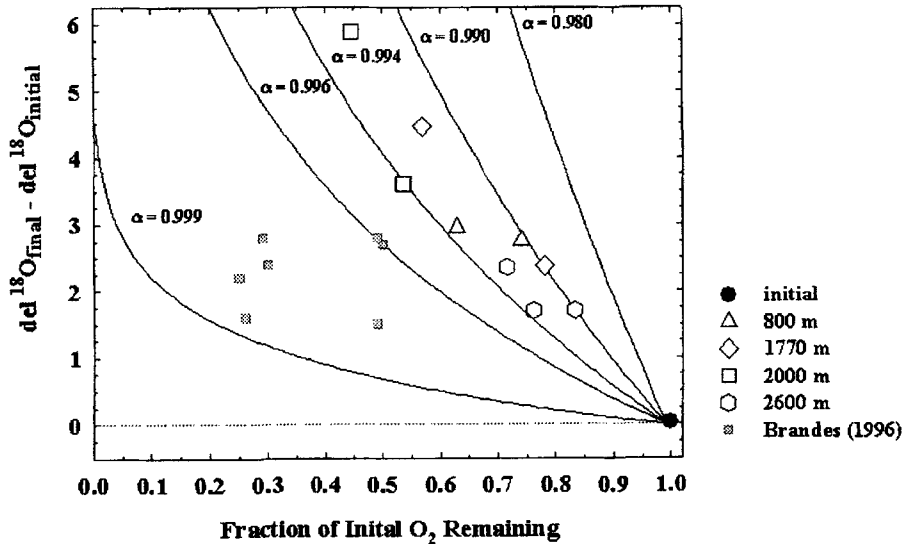


FIG. 1. Fractionation of dissolved oxygen during sediment core incubations. Per mil fractionation of dissolved oxygen in the overlying water is plotted versus the normalized oxygen concentration. Lines indicate predicted  $\delta^{18}\text{O}$  compositions based on Rayleigh fractionation kinetics for the indicated values of the fractionation factor ( $\alpha$ ). The shaded squares are replotted from Brandes and Devol, 1996.

1.000). As the system becomes substrate limited and the oxygen limitation is relieved, the isotopic fraction approaches Bender's theoretical fractionation of 9‰. Our experiment was designed to examine a substrate limited case. To eliminate (to the extent possible) any oxidant limitation we equilibrated the overlying water with the atmosphere to give an initial oxygen concentration of roughly four times the *in situ* concentrations. The sediment organic carbon contents in these cores are typical for sediments from the Washington continental margin and range from 1.1 to 2.4 wt.%. These carbon contents are essentially constant with depth in the sediments; however, measured porewater oxygen profiles show that oxygen concentrations approach zero at a depth of approximately three centimeters, indicating that there is still some fraction of reactive organic matter present. Our reported fractionation factor of 8‰ is similar to the 9‰ predicted by Bender (1990). This amount of fractionation may be representative of sediments in which carbon oxidation is substrate (i.e. carbon) limited. Bender's predicted value is for deep-sea sediments where oxygen penetration depths are considerably greater than 3 cm, however our oxygen

concentrations are considerably higher than *in situ* and one might expect that in this experiment, the apparent fractionation will fall closer to 9‰ than to the value of 3‰ reported by Brandes and Devol.

Taken together, our data and that of Brandes and Devol suggest there should be a continuum from oxidant limitation in shelf and upper-slope sediments to substrate limitation in deeper sediments. Sediments will become progressively more substrate limited going off shore into deeper waters with greater oxygen supply and a more refractory pool of organic carbon available. The switch from oxidant to substrate limitation should be accompanied by an increase in the fractionation of oxygen during benthic metabolism.

## References

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