

PHANEROZOIC ATMOSPHERIC OXYGEN: NEW RESULTS USING THE GEOCARBSULF MODEL

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ABSTRACT. Modifications of the GEOCARBSULF model for Phanerozoic atmospheric oxygen have been made to account for new carbon isotopic data, reconsideration of the fractionation of carbon isotopes between carbonate and organic matter deposited in sediments, and different rates of weathering of volcanic rocks versus granitic rocks. Results indicate distinctly higher O_2 values than GEOCARBSULF for the Mesozoic and Cenozoic, lack of an appreciable drop in O_2 below 15 percent at any time, and a small late Cenozoic decline of O_2 to the present.

MODIFICATION OF THE GEOCARBSULF MODEL

Since publication, several modifications of the GEOCARBSULF model (Berner, 2006a), as they affect atmospheric O_2 , have been made. (Other than the changes stated here, all other aspects of the GEOCARBSULF model remain the same.) New carbon isotopic data for the Permian plus Carboniferous (Grossman and others, 2008) and Devonian (van Geldern and others, 2006) have become available. Grossman and others provide carbon isotopic measurements of over 2000 Permian and Carboniferous brachiopod shells. The running average values of their data (4 Ma window, 2 Ma steps) (Grossman and others, 2008, fig. 8) have been further smoothed here (12 Ma window, 10 Ma steps). Results are shown in figure 1. The further smoothing is done here to be in line with GEOCARB modeling, which is based on data input each 10 million years. Updating of the carbon isotopic data for the Permo-Carboniferous is of great importance to GEOCARBSULF modeling because it is during this time that the largest excursion of atmospheric O_2 from the present value has been calculated (for example, Berner, 2006a).

The difference in the carbon isotopic composition between carbonate and organic matter deposited over geologic time has been reconsidered based on the relative importance of the rate of burial of terrestrial organic matter versus that of marine origin. The compilation of Hayes and others (1999) of differences in $\delta^{13}C$ between carbonates and organic matter over the Phanerozoic, as used in GEOCARBSULF, is based solely on marine organic matter. However, the burial of terrestrially-derived organic matter cannot be neglected and it is normally of different isotopic composition than marine organic matter. The importance of terrestrial burial is shown in table 1. Under present day conditions there is approximately equal burial of terrestrial and marine organic matter. Because one cannot readily deduce the contribution of terrestrial organic matter burial over time, O_2 -dependent carbon isotopic fractionation (Berner, 2006a) is used here. The relation is:

$$\alpha_C(\text{‰}) = 27 + J(O_2/38 - 1) \quad (1)$$

where: α_C represents $\delta^{13}C$ (carbonates) – $\delta^{13}C$ (organic matter), J is an empirical coefficient (here assumed = 4), O_2 is the mass in moles of O_2 in the atmosphere at some past time and 38 is the present mass. This expression results in values of α_C over time in agreement with an approximately even mixture of marine organic matter (Hayes and others, 1999; Falkowski and others, 2005) and terrestrial organic matter as represented by land plant fossils (Beerling and others, 2002).

Some other changes have been made in the GEOCARBSULF model that affect calculated values of atmospheric CO_2 but have an almost negligible effect on O_2 . The

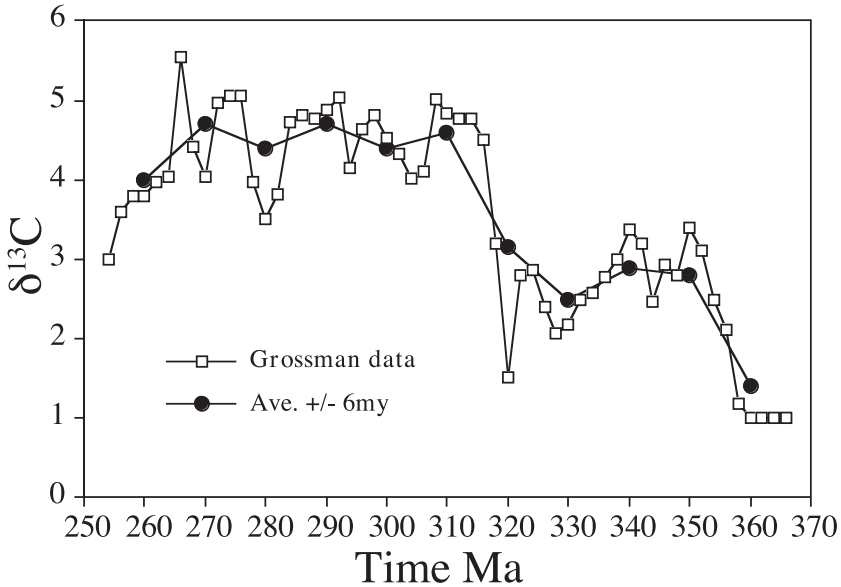


Fig. 1. Curve fit to the $\delta^{13}\text{C}$ data of Grossman and others (2008) for Permian and Carboniferous brachiopods.

most important factor is consideration of terrestrial volcanic weathering rate as different from the weathering rate of other silicates (Berner, 2006b, 2008).

REVISED PHANEROZOIC O_2 VALUES

The revised plot of atmospheric O_2 versus time is shown in figure 2 where it is compared with the curve published in the GEOCARBSULF paper. Notable changes are higher values for the level of O_2 over the past 300 million years, lack of an

TABLE 1

Terrestrial vs Marine organic matter burial

Location	Organic C Burial (10^{12} g/yr)	Reference
<i>Terrestrial Burial</i>		
Lakes (pre-Agric.)	42	Dean and Gorham (1998)
Lakes (pre-Agric.)	43	Stallard (1998)
Swamps	94	Stallard (1998)
Floodplain soils	82	Stallard (1998)
Northern Peatlands	147	Stallard (1998)
Northern Peatlands	96	Dean and Gorham (1998)
Average TOTAL	350 (220 without northern peatlands)	
<i>Marine Burial</i>		
Shelves and slopes	290	Mackenzie (1981)
Shelves and slopes	115	Berner (1982)
Pelagic sediments	5	Berner (1982)
Average TOTAL	200	

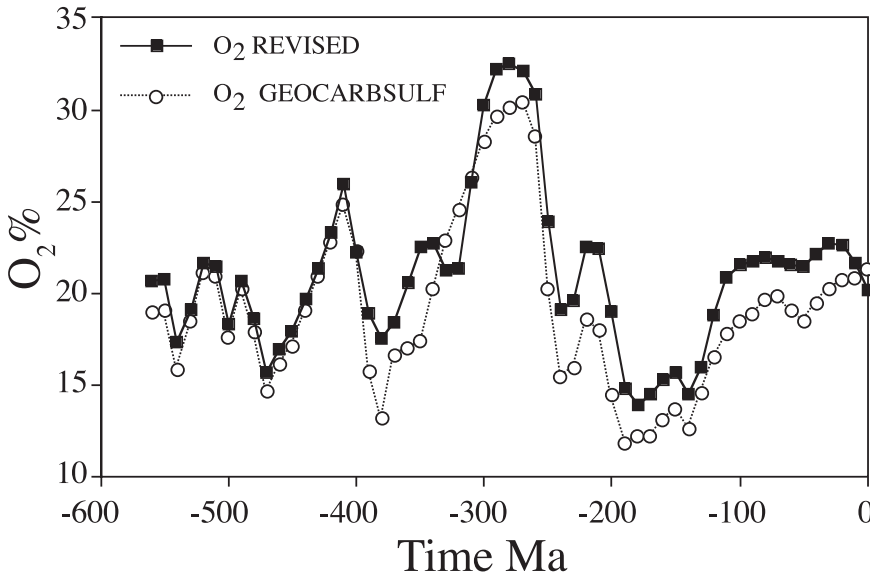


Fig. 2. Results for atmospheric O_2 over time based on the calculations of the present paper (REVISED) compared to those for the original GEOCARBSULF paper (Berner, 2006a).

appreciable drop in O_2 below 15 percent for all time, and a small drop in O_2 during the late Cenozoic. The higher values during the Mesozoic (202-65 Ma) are notably in agreement with the earlier work of Berner and Canfield (1989) that is based on a totally independent, non-isotopic method for estimating O_2 variation over time.

The lack of a drop below 15 percent O_2 appears to be in accord with the experimental results of Belcher and McElwain (2008) because they found that below 15 percent O_2 a variety of materials will not burn and because evidence of fires, in the form of charcoal, is found throughout the geological record since the rise of land plants at about 400 Ma (Scott and Glasspool, 2006). Agreement with the Belcher and McElwain results, however, may be fortuitous because the correctness of their burning method has been criticized (Wildman and others, in preparation¹) and modeling is subject to appreciable error (Berner, 2006a).

The small drop in O_2 over the past 30 million years, as opposed to a rise found by GEOCARBSULF, is due to the use of an essentially constant carbon isotope fractionation α_C (27.4‰ – 26.9‰) over this period whereas the marine fractionation data of Hayes and others (1999), used in GEOCARBSULF, shows a pronounced decrease from 30 permil to 22.5 permil. The drop in O_2 is similar to a drop over the past 40 million years found by Falkowski and others (2005) based on different carbon isotopic data. However, the author feels that additional independent work is needed to test whether this relatively recent drop in O_2 is definitive or not.

The very high O_2 values reported for the Mesozoic by Arvidson and others (2006), even exceeding the Permo-Carboniferous (260-300 Ma) maximum (Bergman and others, 2004), are not found in the present study. This disagreement may well be due to these authors ignoring changes in sedimentation rate as it affects the protection and

¹ Wildman, R. A., Belcher, C. M., Berner, R. A., Dickinson, B., Falkowski, P. G., Huey, R. B., McAllister, S., McElwain, J. V., Ward, P. D., and Wildman, C. B., in preparation, Two opposing perspectives on the applicability of burning experiments to ancient wildfires: To be submitted to *Geology*.

burial of organic matter. The importance of considering total sedimentation rate, as it affects organic matter preservation in sediments and net O₂ production, is discussed in detail by Berner and Canfield (1989) and Berner (2006c).

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