

Eocene/Oligocene alkenone-based CO₂ estimates

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One technique that holds great promise toward revealing the long-term history of atmospheric CO₂, utilizes the δ¹³C value of sedimentary organic molecules known as alkenones (biomarkers derived exclusively from haptophyte algae). Estimates of paleo-*p*CO₂ derived from this biomarker are based on records of the total carbon isotopic fractionation that occurs during carbon fixation (ε_{*p*}; in ‰). ε_{*p*} is a function of surface-water [CO_{2aq}], growth rate, and cell geometry, and in field populations, it is particularly sensitive to phosphate concentrations, presumably reflecting the influence of nutrients on growth rates. Therefore, if temporal variations in growth rate and cell geometry are minimal, ε_{*p*} values provide the potential to evaluate paleo-*p*CO₂ concentrations and trends. Alkenone-based ε_{*p*} records have been used to estimate Miocene *p*CO₂. These records provide evidence that *p*CO₂ was lower than previously anticipated and suggest that CO₂ played a secondary role in forcing the large-scale climate change during the Neogene.

The effort to extend alkenone-based CO₂ records into the Paleogene is ongoing, with our initial efforts focused on the late Eocene through the Oligocene. The Eocene-Oligocene boundary (E/O) is characterized by a "step-like" cooling event that represents a critical shift in Earth's climatic character. Foraminifera δ¹⁸O mark a ~4°C cooling of the deep ocean in less than 350 kyr associated with a rapid expansion of continental ice sheets on Antarctica.

Alkenone δ¹³C values were measured from four ocean locations encompassing a range of growth environments (DSDP sites 277, 516, 612, and ODP site 803). Our preliminary results indicate that Eocene/Oligocene alkenone δ¹³C values are similar to, or lower than, the lowest values recorded from similar environments in the modern ocean. The most depleted values are recorded during the E/O transition. *p*CO₂ can be estimated if we assume ancient phosphate concentrations were similar to modern distributions, δ¹³C of aqueous CO₂ at each site was ~ -10‰, and apply reasonable ocean temperatures. Our results suggest that late Eocene atmospheric carbon dioxide concentrations were 2.5 to 3 times higher than modern levels, and declined to concentrations similar to modern values by the early Oligocene. CO₂ levels appear to rise during the E/O transition suggesting that rapid global cooling and expansion of Antarctic ice sheets may have altered the global carbon cycle by reducing chemical weathering rates, allowing *p*CO₂ to increase to concentrations above those recorded for the late Eocene.

Meteorites and the Composition of the Earth

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The composition of the Earth's mantle down to 100 km can be reasonably well inferred from the analyses of spinel- and garnet-lherzolites in a variety of geological settings. It is very likely that the bulk Earth mantle has the same composition [1]. Among the various types of chondritic meteorites the group of carbonaceous chondrites, and in particular the CV-chondrites, show some compositional similarities to the composition of the Earth's mantle: (a) The Earth and most groups of carbonaceous chondrites are enriched in refractory elements, other types of chondrites are depleted. (b) The Earth and carbonaceous chondrites (CC) have higher Mg/Si-ratios than CI. Ordinary and enstatite chondrites have significantly lower ratios. (c) The Earth and carbonaceous chondrites have a similar depletion pattern of moderately volatile elements, in particular both are depleted in alkali elements and Mn. Enstatite and ordinary chondrites are also depleted in volatile elements, but their patterns are very different. (d) CC plot on an „isochron“ in a ⁵³Cr/⁵²Cr - ⁵⁵Mn/⁵²Cr diagram defining an age of 4.568 Gy ± one million years [2]. The Earth falls on the same isochron, assuming no Mn but a major fraction of Cr in the core, indicating that the fractionation of moderately volatile elements occurred at the beginning of the solar system for both reservoirs, the material that made up the Earth and the source region of carbonaceous chondrites. Differences between Earth and CC include: (a) The Fe/Mg ratio of bulk Earth is above CI, and below CI in CV. Removal of parts of the silicate Earth after core formation by large impacts may be responsible. (b) The Earth is different in oxygen isotopic composition. Individual components of CC span an extremely wide range in oxygen isotopes so that the bulk value is of little significance. In contrast, both the Earth and the Moon, the largest and the third largest body in the inner solar system for which oxygen isotopes are known represent more than 50 % of the mass of the inner solar system and they have exactly the same oxygen isotopic composition [3], possibly the oxygen isotopic composition of the bulk solar system, i.e. the Sun. (c) CC have isotope anomalies in ⁵⁴Cr [4]. Isotopically unusual material may have been mixed to the CC-source after proto-Earth material had accumulated to larger objects.

- [1] O'Neill H.St.C. and Palme H. (1998) *The Earth's Mantle: Structure, Composition and Evolution- the Ringwood Volume* (ed. I. Jackson) pp. 3-126. Cambridge: University Press. [2] Shukolyukov A. & Lugmair G. (2001) *Meteoritics and Planet. Sci.*, **36**, A188. [3] Wiechert U et al. (2001) *Science* **294**, 345. [4] Podosek et al. (1997) *Meteoritics and Planet. Sci.* **32**, 617.