

## Compound-specific isotope analysis across the Frasnian-Famennian boundary

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The Frasnian-Famennian extinction events represents one of the big five mass extinction events during the Phanerozoic with the decline of the Devonian stromatoporoid-coral reef ecosystem representing one of the most prominent crises in reef history. Inorganic carbon isotope investigations of Frasnian-Famennian boundary sections show two +3‰ excursions during the late Frasnian with the second excursion marking the Frasnian-Famennian boundary. The  $\delta^{13}\text{C}$  excursions are observed on a global scale and in part coincide with the deposition of black shales (Kellwasser horizons). An increased burial of  $^{13}\text{C}$  depleted organic carbon was interpreted to enrich surface waters in  $^{13}\text{C}$  and to lower oceanic dissolved  $\text{CO}_2$  and atmospheric  $\text{CO}_2$  concentrations (Joachimski and Buggisch 1993). The latter may result in climatic changes that may have stressed in particular the shallow water ecosystems.

### Results

Organic carbon was investigated in a basinal Frasnian-Famennian boundary section from the Holy Cross Mountains (Poland). The conodont alteration index (1 to 1.5), vitrinite reflectance data ( $R\% = 0.5$ ) and  $T_{\text{max}}$  (418–435°C) document the immature character of the organic material that consists of 75 to 95% of bituminite and up to 20% of alginite with only minor amounts of vitrinite. TOC values range from 0.2 to 6.4% with most samples having around 2% TOC. The  $\delta^{13}\text{C}_{\text{TOC}}$  record shows a +3‰ excursion across the Frasnian-Famennian transition starting at -31‰ in the latest Frasnian and peaking at +28‰ immediately above the Frasnian-Famennian boundary.  $\delta^{13}\text{C}_{\text{TOC}}$  decreases to -30‰ during the earliest Famennian. Thus,  $\delta^{13}\text{C}_{\text{TOC}}$  parallels the inorganic carbon isotope pattern measured in carbonate-rich sections. Short-chain n-alkanes (n-C<sub>15</sub> to n-C<sub>31</sub>) and acyclic

isoprenoids pristane and phytane are depleted by -2.7 to -2.5‰ in comparison to TOC, but parallel the  $\delta^{13}\text{C}_{\text{TOC}}$  record perfectly. Isotopic compositions of pristane and phytane do not differ significantly, are well correlated and thus are used as estimate of the isotopic composition of primary organic carbon ( $\delta^{13}\text{C}_p$ ). Most important, the general pattern of  $\delta^{13}\text{C}_p$  and  $\delta^{13}\text{C}_{\text{carb}}$  does not differ substantially with both records showing a +3‰ excursion.

The isotopic composition of primary organic carbon is mainly determined by the  $\delta^{13}\text{C}$  of the carbon source and by the photosynthetic fractionation factor  $\epsilon_p$ .  $\epsilon_p$  may depend on the growth rate of phytoplankton and the concentration of oceanic dissolved  $\text{CO}_2$  (e.g. Laws *et al.*, 1995; Bidigare *et al.*, 1997). The measured  $\delta^{13}\text{C}_{\text{carb}}$  record reflects an increase in  $\delta^{13}\text{C}$  of DIC as consequence of an enhanced  $\text{C}_{\text{org}}$  carbon burial rate. Since an intensification of  $\text{C}_{\text{org}}$  burial is expected to lower the  $\text{CO}_2$  concentration of surface waters and of the atmosphere,  $\epsilon_p$  should change as well assuming that phytoplankton growth rate had been more or less constant. Accordingly,  $\delta^{13}\text{C}_p$  should become more enriched in  $^{13}\text{C}$  than  $\delta^{13}\text{C}_{\text{carb}}$ . The fact that the  $\delta^{13}\text{C}_p$  excursion parallels the  $\delta^{13}\text{C}_{\text{carb}}$  record demonstrates that  $\epsilon_p$  did not change. This is to be expected if  $\text{CO}_2$  concentrations were relatively high (>2000 ppmV) since  $\epsilon_p$  is assumed not to vary at high  $\text{CO}_2$  concentrations. The Devonian atmospheric  $\text{CO}_2$  concentration was modeled to be higher than 2500 ppmV (Bernier 1994) and thus, oceanic dissolved  $\text{CO}_2$  concentrations would have been above the threshold to affect  $\epsilon_p$  by changes in the  $\text{CO}_2$  concentration, i.e. due to a change in  $\text{C}_{\text{org}}$  burial. In conclusion, compound-specific isotope analysis that were used in the Mesozoic to decipher changes in  $\epsilon_p$  and oceanic  $\text{CO}_2$  concentration (Hayes *et al.* 1989) will not help during time periods when  $\text{CO}_2$  concentrations were higher than 2000 ppmV.

**References**

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