



A comparison between two Late Devonian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curves over separate intervals of apparent perturbations in global carbon cycling

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The Late Devonian mass extinction event, which occurred just prior to the Frasnian-Famennian boundary, has frequently been linked to the spread of anoxic bottom waters and/or elevated productivity in epicontinental seas due to the close association of the extinctions with two regionally (perhaps globally) extensive black shale horizons and positive $\delta^{13}\text{C}$ excursions in marine carbonates. However, other intervals during the Devonian also witnessed dramatic changes in global carbon cycling but are not associated with major extinctions. For example, recent work on early-middle Frasnian carbonate successions in Poland, Belgium and China, has revealed a prominent positive shift in $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{13}\text{C}_{\text{org}}$ at the base of the *Palmatolepis punctata* conodont zone (earliest middle Frasnian), which marks the beginning of a prolonged positive carbon isotope anomaly that almost lasted the entire duration of the *Pa. punctata* zone. This positive $\delta^{13}\text{C}$ anomaly is associated with evidence for transgression-related eutrophication, elevated primary productivity, oxygen-deficiency in bottom waters and faunal turnover but does not coincide with elevated extinction rates, despite the apparent intensity of the perturbations in the biosphere (Racki *et al.*, 1994; Piszczowska *et al.*, in press; Yans *et al.*, in press).

In this study, seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curves were constructed for both the Frasnian-Famennian and early-middle Frasnian boundary intervals in order to investigate any changes in the balance between the continental and hydrothermal fluxes of Sr to the

oceans over these times. High resolution Sr isotope data is lacking for both intervals although many causal mechanisms for the widespread accumulation and preservation of organic-rich deposits involve changes in the continental flux of nutrients to the oceans.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured in the denticle material of apparently unaltered conodont elements collected from continuous carbonate successions in the Holy Cross Mountains of Poland. Interestingly, seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values appear to have been relatively stable at ~ 0.70805 over the Frasnian-Famennian extinction interval. This is in contrast with published data for this interval which show a major increase in oceanic $^{87}\text{Sr}/^{86}\text{Sr}$ values in the earliest Famennian but which are based on less reliable whole-rock carbonate samples. In contrast, the early-middle Frasnian data record a marked rapid rise in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the base of the *Pa. punctata* zone. Values were relatively constant during the *Pa. transitans* zone (~ 0.70794), they began to increase in the early *P. punctata* zone and reached a value of ~ 0.70814 in the late part of this zone. The most likely cause of the increase in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values is an increase in the continental (weathering) flux of Sr to the sea and this is supported by the fact that the shift in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values coincides with the reported positive shift in $\delta^{13}\text{C}$ and increase in primary productivity, which suggests an increase in nutrient influx into the shallow marine realm. A possible cause of this increase in continental weathering is the denudation of a new Acadian-Eovariscan orogen which would have been mostly weathering in the humid-equatorial region.

This study highlights the need for further investigation into other Devonian black shale events in order to put the late Devonian mass extinction, and associated environmental changes, in its proper temporal context.