# Geochemical perturbations in the ocean/atmosphere system during the Middle Devonian to Visean: the state of the art

M. M. Joachimski

Institut für Geologie und Mineralogie, Universität Erlangen, 91054 Erlangen, Germany

The Middle Devonian to Lower Carboniferous represents one of the four time windows selected by IGCP Project 386 to quantify variations in the geochemical fluxes as consequence of global change. The Middle Devonian to Visean is an intriguing period since it represents the transition of the Devonian greenhouse into the Carboniferous cold-house mode. The intense colonization of the continents by vascular land plants started during the Middle to Late Devonian. As a consequence continental weathering may have increased due to developing soils and higher nutrient fluxes to the oceans may have initiated enhanced primary productivity and the deposition of black shales. The burial of organic carbon in the oceans and the growth of the terrestrial organic carbon reservoir may have contributed to a drawdown of atmospheric $p_{CO_2}$ and to climatic cooling. Finally, a global mass extinction event occurred in the late Frasnian. The currently available geochemical data base is reviewed with respect to the possibility to quantify short-term or long-term variations in the geochemical fluxes during this time period.

## Geochemical data set

Strontium, oxygen and carbon isotope data were measured on well preserved brachiopod shell calcite, micrites or whole rock samples. The time resolution of the brachiopod isotope records is mostly not adequate to the resolution attainable by whole rock or micrite analysis, but the quality of the brachiopod isotope data is generally better. The brachiopod $^{87}Sr/^{86}Sr$ curve (e.g. Diener *et al.* 1996, Veizer *et al.*1997) is well established and characterized by homogenous ratios around 0.7078 during the Middle Devonian, a prominent increase near the Givetian-Frasnian transition to 0.7082, homogenous ratios of 0.7082 up to the Devonian-Carboniferous transition and a decline to 0.7076 in the Tournaisian and Visean. In contrast, the oxygen and carbon isotope records show rather large variations either for individual sample populations or through time. The variations in $\delta^{18}O$ cannot be explained by changes in temperature or salinity. For example, the dramatic decrease in $\delta^{18}O$ from $-5$ to $-10$‰ during the Frasnian translates into a 20°C temperature increase in sea surface waters. Further, this shift is not confirmed by conodont phosphate $\delta^{18}O$ data (Luz *et al.*, 1984). Accordingly, the preservation of some investigated shells is questionable. The brachiopod $\delta^{13}C$ record reflects variations from $-1$‰ to +5‰. Due to the minor time resolution of the brachiopod $\delta^{13}C$ record, short-term global excursions as recorded by the investigation of micrites (e.g. Frasnian-Famennian) are not detected. In conclusion, the brachiopod oxygen and carbon isotope data base is not yet adequate to allow a quantification of geochemical perturbations in the ocean/atmosphere system. High resolution $\delta^{13}C$ curves based on the investigation of micrites are available for certain time intervals (Joachimski and Buggisch, 1993) and may allow a quantification of the fluxes if the excursions are proven to occur on a global scale.

The sulphur isotope data base for seawater sulphate has not really changed since the first compilation by Claypool (1980). The prominent feature is an increase in $\delta^{34}S$ starting in the Middle Devonian and reaching a maximum near the Frasnian-Famennian transition. $\delta^{34}S$ decreases during the Upper Devonian and Lower Carboniferous.

The Frasnian-Famennian biotic crisis represents one of the big five mass extinction events and was repeatedly related to a bolide impact. Although there is evidence for several impacts during the Middle Devonian to Visean, there is no compelling evidence that proves that either the Frasnian-Famennian or the Devonian-Carboniferous extinction event were triggered by a bolide impact. No unequivocal iridium anomaly, microtektite occurrence, platinum group element enrichment or negative carbon isotope excursion was reported for these boundary events. Until unequivocal evidence for an impact is shown, endogenic causes have to be favoured as possible causes of the mass extinctions.

## Conclusion

In conclusion, more high quality oxygen, carbon and sulphur isotope data are needed in order to enable modelling of variations in the chemical fluxes. Especially high resolution isotope data sets are needed.

## References

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