THE LATE DEVONIAN MASS EXTINCTION – IMPACT OR EARTH-BOUND EVENT? M.M. Joachimski and W. Buggisch, University of Erlangen, Institute of Geology, Schlossgarten 5, 91054 Erlangen/Germany, joachimski@geol.uni-erlangen.de

Introduction: The Frasnian-Famennian (F-F) faunal crisis represents one of the 'Big Five Mass Extinctions' in Earth History. Studies have been published that favor either a collision with an extraterrestrial bolide [e.g. 1] or changes in the oceanographic and climatic systems [e.g. 2]. However, no unequivocal evidence on the origin of the Late Devonian faunal breakdown was reported. E.g. iridium anomalies reported from Australia [3] and Southern China [4, 5] post-date the F-F boundary by 1.5 to 2 Ma. Microtekites from Belgium boundary sections [6, 7] were seen in context with the 368 ±1 Ma old Siljan Ring impact structure. However, the cosmic origin of these spherules has been questioned [8] and the microtektites were found above the F-F boundary and clearly post-date the extinction event. Negative carbon isotope excursions were interpreted as evidence for a sudden biomass crash hat may have been triggered by a bolide impact [9, 10]. In contrast, two positive $\delta^{13}C$ excursions measured in the late Frasnian and at the F-F boundary [2, 11] seem not to support the idea of a dramatic decline in primary productivity. This contribution presents a comprehensive geochemical and stable isotope data set that may help to unravel the mechanisms responsible for the Late Devonian mass extinction.

Results: Carbon isotope analysis on carbonate-rich F-F boundary sections from Nevada, Central Europe, Northern Africa and Australia reveal two +3‰ excursions in the late Frasnian that can be correlated with the deposition of the Kellwasser Horizons. $\delta^{13}C$ values measured on total organic carbon as well as on individual biomarkers (n-alkanes, isoprenoids and hopanes) reveal comparable $\delta^{13}C$ records with two +3‰ excursions. Since the amplitudes of the $\delta^{13}C$ records measured in sections from different palaeogeographic units are well comparable, changes in the carbon isotopic composition of the oceanic dissolved inorganic carbon (DIC) reservoir have to be assumed. The positive shifts in $\delta^{13}C$ are induced by an increase in the organic carbon burial rate during the deposition of the Kellwasser horizons. These results seem to contradict time-equivalent negative excursions in $\delta^{13}C$ measured in Chinese F-F boundary sections [9,10]. The negative excursions are observed in organic carbon-rich and carbonate-poor sediments. Following, we favor a diagenetic orgin of these depleted signatures due the incorporation of light carbon from the oxidation of organic carbon during the recrystallisation of the carbonates. This interpretation is supported by the fact that well-preserved brachiopod shells show no depletion in ^{13}C [12].

The increase in the organic carbon burial rate is not only documented by the positive shifts in $\delta^{13}C$ but as well by the deposition of the Kellwasser Horizons in epicontinental basins and on deeper swells. In addition, the identification of biomarkers diagnostic for green sulfur bacteria in a boundary section from Poland [13] reveals that photic zone anoxia may have prevailed at least seasonally in certain areas of the Prototethys. Sulfur isotope ratios measured on sulfides and organically-bound sulfur show a +27‰ excursion across the F-F boundary indicating enhanced bacterial sulfate reduction and sulfide sedimentation.

Modelling the $\delta^{13}C$ record reveals that the fraction of organic carbon on total carbon burial must have increased from 20 to 30% in order to account for the +3‰ shifts. The estimation of the duration of enhanced organic carbon burial resulted in a 0.4 Ma time period for the Lower Kellwasser Horizon and a 1.0 to 1.5 Ma period at the F-F boundary. The additional organic carbon burial was calculated as 1.4 to 1.6 x 10^6 mol C for the Lower Kellwasser and 3.1 to 4.6 x 10^6 mol C for the F-F boundary. It is expected that this carbon withdrawal from the Devonian ocean-atmosphere system resulted in a decrease in atmospheric CO_2 concentration and culminated in global climatic cooling.

The comparison of the $\delta^{13}C$ records measured on inorganic carbon and biomarkers derived from primary producers shows parallel trends [13]. However, a larger amplitude in $\delta^{13}C$ of individual biomarkers is expected in case of a significant drawdown of atmospheric CO_2. This assumption is based on the fact that the carbon isotopic fractionation during the photosynthetic uptake of CO_2 is dependent on the CO_2 concentration of ambient seawater and on the growth rate of primary producers. Assuming constant growth rate and that the enhanced organic carbon burial resulted in a drawdown of atmospheric pCO_2, photosynthetic fractionation should decrease and result in a greater enrichment of ^{13}C in organic carbon relative to inorganic carbon. The fact that we do not observe a further enrichment in ^{13}C of primary organic carbon does not seem to support the conclusion that atmospheric pCO_2 was reduced as consequence of an enhanced organic carbon burial. However, calculated photosynthetic fractionation is 23 to 24‰ which is very close to the expected maximum fractionation of 25‰ [14]. Following, we assume that photosynthetic fractionation was at a maximum level during the Upper Devonian as a consequence of high atmospheric and oceanic dissolved CO_2 contents [15]. Accordingly, any superimposed change in pCO_2 or growth rate was not recorded in the isotopic composition of primary organic carbon.

Climatic cooling is considered as another consequence of the enhanced organic carbon burial. Oxygen isotope analyses on conodont and fish apatite reveal an increase in $\delta^{18}O$ from values around +17.5‰ to +19‰ (SMOW) parallel to the positive shifts in $\delta^{13}C$. Assuming a $\delta^{18}O$ value for Devonian sea water of -1‰, the positive $\delta^{18}O$ shifts translate in a decrease in sea-surface temperature from 32 to 25°C. Although this drop in sea-surface temperature awaits confirmation by the investigation of apatite from further F-F boundary sections, a significant climatic cooling is indicated.

Conclusions: The geochemical data base for the Late Devonian extinction event shows no evidence for a bolide impact as potential cause of the mass extinction. Instead, repeated changes in the carbon cycle of the ocean-atmosphere system are indicated by positive carbon excursions. The enhanced organic carbon burial is indicated by the higher $\delta^{13}C$ values, deposition of the Kellwasser horizon and a positive excursion in $\delta^{34}S$ of sulfides and organically-bound sulfur A decrease in atmospheric and oceanic dissolved CO_2 contents is expected and may have culminated in global climatic cooling. A decrease in tropical sea-surface temperature of 7°C is indicated by preliminary conodont and fish apatite $\delta^{18}O$ data.

The paleontological data base seems to support the conclusion that climatic cooling may have represented a potential mechanism for the Late Devonian mass extinction [e.g.16]. Organisms living in the tropical to subtropical pelagic and shallow-water ecosystems were heavily decimated. Organisms thriving in higher latitudes or in deeper waters were only slightly affected. Further, late Frasnian faunal groups that were adapted to cooler temperatures migrated into tropical latitudes during the early Famennian. This pattern suggests that climatic cooling in conjunction with significant oceanographic changes may represent a powerful scenario to account for the Late Devonian mass extinction.

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