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Climate and Ice Volume History of the Mid-Paleozoic: Insights from oxygen isotope proxies

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Oxygen isotopes have been successfully applied to studies on Cenozoic climate and ice volume history (ZACHOS *et al.* 2001). The use of oxygen isotopes in older time periods is hampered by potential diagenetic resetting of the oxygen isotope signals. Brachiopod shells have been preferentially used to reconstruct Paleozoic paleotemperatures due to their low-magnesium calcitic shell mineralogy that is assumed to be relatively resistant to diagenetic recrystallisation. In comparison to biogenic calcite, biogenic apatite represents an alternative mineralogical phase for oxygen isotope analysis since apatite is very resistant to diagenetic exchange of phosphate-bound oxygen. Devonian and Carboniferous conodonts, microfossils composed of carbonate–fluor apatite were studied for oxygen isotopes in order to reconstruct climatic changes and the onset of the Late Paleozoic Glaciation (LPG).

Devonian conodonts were studied from several sections in Germany, the Czech Republic, France, the USA and Australia spanning the time interval of latest Silurian (Pridoli) to Late Devonian (Famennian). Late Silurian to Lochkovian sea surface temperatures (SST) are relatively high. Average SSTs start to decrease in the early Pragian and show minimum and about 8°C cooler SSTs in the late Emsian to Givetian. Temperatures reconstructed for the middle to late Frasnian and early Famennian were again significantly warmer indicating considerable warming of low latitudes during the Frasnian. During the middle to late Famennian a moderate cooling trend is apparent culminating in the short-term glaciation at the Devonian–Carboniferous boundary, documented by a positive $\delta^{18}\text{O}$ excursion in conodont apatite (KAISER *et al.* 2006, BUGGISCH *et al.* 2008). The reconstructed Devonian paleotemperature record contradicts earlier views that the Middle Devonian represented a supergreenhouse.

The climax of coral–stromatoporoid reef development was during the Middle Devonian, an interval characterized by cool to intermediate tropical SSTs. Coral–stromatoporoid reefs were rare in the Early Devonian, finally becoming extinct in the latest Frasnian. Microbial reefs were abundant in the Early and Late Devonian suggesting that warm to very warm SSTs in the Early and Late Devonian were unfavourable for the development of coral–stromatoporoid reefs, but promoted growth of autotrophic reefs. Our data suggest that SST exerted a control on Devonian reef development and that climatic warming in the Late Frasnian in conjunction with short-term cooling pulses may have contributed to the extinction of coral–stromatoporoid reef ecosystems during the Frasnian–Famennian life crisis (JOACHIMSKI *et al.* 2009).

Carbon isotopes of whole rock carbonates and oxygen isotopes of conodont apatite from Late Devonian to Early Pennsylvanian sections in Europe, Russia and Laurentia were measured in order to reconstruct variations in the carbon cycle, marine paleotemperature, and ice volume during the Mississippian (BUGGISCH *et al.* 2008) and Pennsylvanian Conodont apatite oxygen isotope values show two major positive shifts of +2‰ and +1.5‰ V-SMOW in the late Tournaisian and Serpukhovian, respectively, that are interpreted to reflect climatic cooling and changes in ice volume. Carbon isotope ratios of inorganic and organic carbon show a major positive excursion with an amplitude of +6.5‰ V-PDB in the Tournaisian and a positive shift of up to +5‰ V-PDB in the Serpukhovian. The positive carbon isotope excursions coincide with the deposition of organic carbon-rich black shales which indicate that organic carbon burial, lowering of atmospheric $p\text{CO}_2$, and climatic cooling may have occurred during these time intervals. However, while in the Tournaisian the positive shifts in apatite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ coincide, the Serpukhovian positive shift in $\delta^{18}\text{O}$ precedes the positive shift in $\delta^{13}\text{C}$ and raises the question as to whether changes in the global carbon cycle were the ultimate cause of the inferred climatic changes. The conodont apatite oxygen isotope values suggest that a first major cooling and potential glaciation event occurred in the Tournaisian with ice masses persisting into the Viséan. The second glaciation event occurred in the Serpukhovian and culminated in the first glacial maximum of the LPG.

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