Paper Number: 3349

Geochemical signature of the Late Devonian events in the Rhenish Massif, the Holy Cross Mountains and the Carnic Alps

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Late Devonian was a time of global ocean and climate perturbation recognized by faunal, lithological and geochemical changes. These changes are best exemplified by the occurrence of e.g. Dasberg, Annulata and Hangenberg events, which are globally recorded as black, organic-rich shales.

Several geochemical techniques were employed to stratigraphic correlations and paleoenvironment interpretations of the Upper Devonian interval in the Rhenish Massif (Germany), the Holy Cross Mountains (Poland) and the Carnic Alps (Italy and Austria).The high-resolution inorganic and organic redox indicators for the all black shale horizons revealed that bottom water redox conditions where not stable and changed periodically.

The Hangenber black shales (HBS), as an example, is characterized by U/Th values above 1.2 in the lower part of the all HBS sections, high total organic carbon contents (TOC) above 10% and δ^{98}Mo around 1.4‰. All data indicate anoxic/euxinic depositional conditions. In the middle and upper part of the HBS U/Th values drop below 1.25, TOC ranged from 8% to 1% and δ^{98}Mo values drop to 0.7‰. Such data suggest that anoxic conditions were intermittently interrupted by less restricted redox conditions. Evidence for the return of anoxic/euxinic conditions during the deposition of the upper part of the HSB was documented only in the Holy Cross Mountains, where the black shale seems to be the most complete. Sulphur isotope values reiterate the pattern of inorganic redox indicators suggesting restricted bottom water conditions especially occurred during deposition of initial stage of the shales. The positive $\delta^{13}C_{org}$ excursion up to 4‰ is noticed only in the Rhenish Massif sections. In contrast to German sections, the $\delta^{13}C_{org}$ values of the HBS at the Carnic Alps and the Holy Cross Mountains outcrops show a negative excursion following with the $\delta^{13}C_{org}$ increase (ca. 3‰). This carbon isotopic drop seems to be associated with the occurrence of volcanogenic material detected in the middle part of the HBS in Kowala section, together with the absence of calcium carbonate observed in the top of the HBS.

Our results imply that not only anoxia but also volcanic activity potentially influenced the Hangenberg mass extinction event.

Authors acknowledge financial support from the Polish National Science Centre grants 2011/03/B/ST10/04602 and 2011/01/B/ST10/01106.