Changes in shelf phosphorus burial during the Hirnantian glaciation and its implications

Johann Müller[a], Michael Joachimski[a], Oliver Lehnert[a], Peep Männik[b] and Yadong Sun[c]

[a] GeoZentrum Nordbayern, Crustal Dynamics, Friedrich-Alexander University of Erlangen-Nürnberg, Schlossgarten 5, D-91054 Erlangen, Germany

[b] Department of Geology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

[c] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, 388 Lumo Road, Wuhan 430074, China

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ABSTRACT

The Late Ordovician mass extinction occurred during an icehouse interval, accompanied by the glaciation of the supercontinent Gondwana, which was located at the South Pole at that time. As suggested by sequence stratigraphy of near- and far-field sedimentary successions as well as stable oxygen isotope studies, ice sheets reached their maximum extent in the late Hirnantian *M. persculptus* graptolite zone. As a result, the global sea-level dropped significantly during the Hirnantian Glacial Maximum (HGM). This led to exposure and erosion of sediments on the tropical shelves of Laurentia and Baltica. Where shelves remained submerged, water depths were probably very shallow.

Local redox proxies, such as I/Ca ratios or iron speciation, indicate that shelf environments were well oxygenated. At the same time, stable uranium isotopes, measured on shallow-water carbonate samples, indicate a global expansion of the seafloor overlain by anoxic water. This implies that the observed increase in anoxia was confined to the open ocean and that there was a redox gradient between coastal and oceanic environments. Unfortunately, the lack of Late Ordovician deep water sedimentary records makes it impossible to directly measure open-ocean redox conditions. In general, Late Ordovician deoxygenation is in stark contrast to other oceanic anoxic events of the Phanerozoic, which occurred during greenhouse conditions and are associated with rising water temperatures.

Under present interglacial conditions, with a relatively high sea-level, it is estimated that about 70% of the nutrient phosphorus delivered from the continents is retained in shelf sediments. Hence, shelf environments act as a nutrient filter. However, during times of low sea-level, this filter is switched off due to the bypassing of incoming riverine dissolved load through river canyons. As a result, excess phosphorus is released into the open ocean leading to eutrophication. This has previously been proposed for the Last Glacial Maximum (LGM) and is supported by geochemical data. We suggest that this scenario may also be applicable to the HGM and serve as an explanation for increasing anoxia during cold climatic conditions.

To test this, we measured phosphorus concentrations across the HGM on carbonate samples collected from two low-latitude successions (Ruisseau aux Algues on Anticosti Island and Valga-10 core section from Estonia, both interpreted as shelf environments). To eliminate the detrital, non-reactive phosphorus fraction, we used the SEDEX sequential extraction method, which allows to separately measure reactive (P_{react}) and organic phosphorus (P_{org}). In order to evaluate the burial efficiency of phosphorus, we determined total organic carbon (C) concentration and calculated C/P_{org} and C/P_{react} ratios.

We observe a decreasing trend in P_{react} towards the HGM and a minimum during the subsequent initial transgression. Low C/P_{react} and C/P_{org} in the range of the Redfield ratio indicate efficient burial under oxygenated conditions. Therefore, we can rule out that phosphorus regeneration, which is stronger under anoxic conditions, caused the observed minimum. This means that P_{react} is a direct measure of primary productivity and phosphorus burial.

Using the P_{react} data and an estimate for the shelf area, we modelled the global burial flux of phosphorus into shelf sediments. Due to the overall reduction in shelf area during the HGM and the low P_{react} contents, the modelling suggests that the shelf burial flux was approximately halved. If the phosphorus input had remained constant across the interval, which is reasonable given that the erosion of exposed shelf sediments compensated for a reduction in continental weathering during the cold and arid climate, the excess phosphorus would have entered the open ocean stimulating primary productivity. Ultimately, enhanced productivity would have resulted in a high organic matter sinking flux and oxygen depletion by aerobic respiration. In summary, our data and modelling support the proposed scenario of an inefficient nutrient filter.

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Corresponding author:
Johann Müller
johann.jm.mueller@fau.de

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