Geochemical changes through the Ordovician-Silurian boundary beds in the Taagepera core, South Estonia

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The end-Ordovician Hirnantian time is characterized by considerable environmental changes – glaciations in high latitudes and remarkable sea level fall. At that time also one of the greatest extinctions of fauna in the Palaeozoic took place (Brenchly *et al.*, 1995). The purpose of the present investigation is to trace geochemical changes by X-ray fluorescence analysis of the main components and trace elements, and $\delta^{13}C$ measurements in 67 samples from the Taagepera core. Taagepera core is situated in South Estonia (Geology and ..., 1997, page 17). At the end of the Ordovician and the beginning of the Silurian, there was a deep shelf area with the most complete sedimentary record in Estonia. The Ordovician part of the investigated section is mainly represented by argillaceous limestones, the Silurian one by marlstones. Pre- and post Hirnantian rocks are predominantly greenish grey, with purple patches, Hirnantian rocks are grey. Two extinction levels of Ordovician biota occure at the lower and upper boundaries of Hirnantia beds – at 424.0 and 411.1 m (J. Nõlvak pers. comm.). Detailed stratigraphy see in Kaljo *et al.*, (1998, this volume).

The Mn content in limestones of Taagepera core ranges from 2000 to 4000 ppm. These high Mn contents cannot be explained by early diagenetic recrystallization of carbonates in seawater rich in oxygen, but in waters with low oxygen, capable of dissolving much of Mn. Supposedly, the Palaeozoic ocean had below the surficial mixing zone vertically extensive water masses with low oxygen contents. Early diagenesis of deep shelf carbonates in these waters could be responsible for high Mn values in the investigated section. Mn distribution is facies-dependent (200–300 ppm in shallow shelf sediments), therefore late diagenetic recrystallization seems unlike. Good preservation of fossiles indicates absence of serious late diagenetic changes as well. The absence of low-Mn carbonates in the Taagepera section suggests that Hirnantian sea level fall was not big enough to shift the shallow sea facies to the Baltic deep shelf area. At the same time, the formation of dry land on the former shallow shelf in North Estonia in late Hirnantian is well recorded in 15–30 m deep erosion channels developed there. Mn contents in lower Hirnantian decrease from the previous average of 3000 ppm to 2000 ppm, which probably reflects facies movements within the low oxygen zone.

The first environmental changes, already before the Hirnantian and the first faunal extinction event, could be traced at a depth of 426.3 m in the lower part of 80 cm thick red limestone. This sample is anomalously rich in terrigenous material and from that level a continuous rise in MgO begins, up to complete dolomitization of rock at 424.75 m. At the same level begins a small rise in $\delta^{13}C$ values from 1.1‰ to 2.1‰ at the extinction level. Therefore, it is likely that some environmental changes preceded the extinction of biota. In a lower Hirnantian the rise of $\delta^{13}C$ continues, MgO and Mn contents decrease. The sulphur content in sediments increases rapidly, reaching 0.5 % at a depth of 423.0 m. In the upper Hirnantian, thin silt- and sandstone interbeds, also increased SiO_2/Al_2O_3 and K_2O/Al_2O_3 ratios, evidence that the shoreline approached to the Taagepera area and sea level was low. The distribution of elements at the transition from Hirnantian to Rhuddanian is symmetrical to that described above (Fig. 1.).

Low Sr contents (100–200 ppm) in limestones probably hint at low rates of early diagenetic recrystallization of carbonates. Freshwater diagenesis in deep shelf sediments seem improbable. Higher Sr values in the Hirnantian, roughly correlating with $\delta^{13}C$, probably point to higher bioproductivity accompanied by increased precipitation of aragonite. The second element suggesting higher bioproductivity in the Hirnantian is sulphur. A sulphur content of 0.2–0.5 % indicates that sediment contained originally some organic matter, which diagenetic decomposition enabled fixation of sulphur in sediments in the form of pyrite. Therefore high bioproductivity could be also a cause of a positive $\delta^{13}C$ excursion.

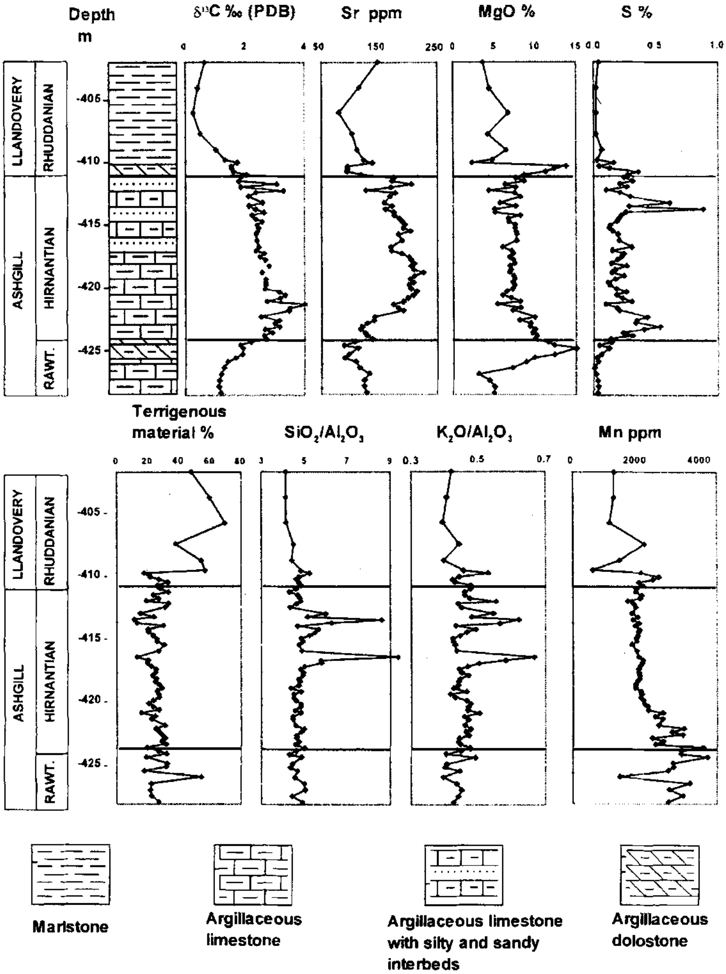

FIG. 1. Distribution of some chemical elements, element and isotopic ratios in O/S boundary beds in the Taagepera core.

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