

Lithium and its isotopes in Central European Rivers

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Lithium isotopes are a promising new means to study silicate weathering. To date most lithium isotope work on river systems has been done on ocean islands [1] or remote regions of, for example, the Himalayas [2] where human influence on rivers is minor. In this study we present lithium abundances and isotopic ratios for the central European rivers Danube, Elbe, and Rhine. The catchments of these rivers are highly populated, densely industrialised, and affected by a highly developed farming industry. The goal of this ongoing project is to identify major processes and anthropogenic sources which control lithium and its isotopes in central European rivers. The investigated waters show lithium concentrations (dissolved load) between ~2 and 22 µg/l and δ⁷Li from +4 to +22 ‰ relative to L-SVEC. Some Danubian and upper Rhine waters have lithium abundances close to 2 µg/l and high δ⁷Li up to +22 ‰. Similar concentrations (0.2-4.0 µg/l) and δ⁷Li ~+23 ‰ are reported for more pristine river systems worldwide [3] indicating that lithium in the upper Danube and upper Rhine is largely controlled by silicate weathering. The catchments of the lower Elbe, in particular waters of the river Saale, are characterized by high lithium concentrations and ⁷Li/⁶Li. These waters have also high sulfate concentrations and δ³⁴S up to +8.5 ‰ CDT indicating a contribution from Permian evaporites. This is reasonable because evaporites have been mined in the region for more than a century. Samples from the river Elbe near Dresden, all Rhine and Danube samples show a good correlation between lithium isotope ratios and silicon fraction in the dissolved load (r² = 0.7). The highest molar fractions of silicon are connected to low δ⁷Li ~5 ‰ and δ³⁴S ~3.4 ‰ in catchments of the river Elbe near Dresden. This is consistent with very intense weathering or a distinct style of weathering probably related to oxidation of sulfides and formation of highly acidic waters in old mining districts of the Erzgebirge.

[1] Pogge von Strandmann *et al.* (2008) *EPSL* **274**, 462-471; [2] Kisakurek *et al.* (2005) *EPSL* **237**, 384-401. [3] Huh *et al.* (1998) *GCA* **62**, 2039-2051.

Shale gas potential of the Upper Jurassic strata in the central part of the Polish Lowlands

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The Upper Jurassic strata, rich in organic matter, are regarded as the main source rock of the large hydrocarbon accumulations in the Nowegian sector of the North Sea [1]. Also in Poland the Kimmeridge and Tithonian strata were subject of a large-scale exploration. In numerous wells only oil and gas shows were recorded. [2]. Our present study shows a new point of view on the possibility of shale gas accumulation in these strata. The investigations were conducted in the central part of the Polish Lowlands where the analysed strata are covered by thick Cretaceous deposits.

In total, 126 samples (66 from the Kimmeridgian and 60 from the Tithonian strata, respectively) were collected. Rock-Eval pyrolysis indicates a large diversity in the total organic carbon (TOC) content, from 0.14 to 6.6 wt% (median 1.1 wt%) and from 0.19 to 10.2 wt% (median 1.6 wt%) in the Kimmeridgian and Tithonian strata, respectively. The total hydrocarbon content in the analysed rocks is not high and medians equal 1.32 and 4.2 mg HC/g rock, respectively. Hydrocarbon potential of the Kimmeridgian strata is usually low with the median value of 121 mg HC/g TOC indicating the presence of gas-prone kerogen, whereas for the Tithonian strata, the median of this index equals 272 mg HC/g TOC (mixed gas- and oil-prone kerogen). Maturity of organic matter corresponds with the initial phase of "oil window". The BasinMod® 1-D modelling revealed that the generation of hydrocarbons from the Upper Jurassic source rocks occurred in the Late Cretaceous time. This process was interrupted by inversion on the Polish Lowlands.

In the selected areas of the Polish Lowlands the Kimmeridgian and Tithonian strata have generated sufficient amount of hydrocarbons to saturate rock and can be considered as a potential shale gas source.

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[1] Justwan & Dahl (2005) *Proc. 6th Petrol. Geol. Conf.*, 1317-1329. [2] Karnkowski (1999) *Oil and gas deposits in Poland*, 380pp.