

Mobility of inorganic and organic compounds from black shales during unconventional gas production

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Taking into account the envisaged activities of shale gas exploitation and production from black shales in central Europe we see an increasing demand in a quantitative evaluation of possible environmental risks and impacts. For the development of a shale gas play, water is mixed with proppant material (e.g. sand grains) and 0.5 – 1% of additives. Additives, such as acids, biocides, corrosion inhibitors and friction reducers are used to optimize the fracturing job.

Besides of flow-back water a varying amounts of production water will appear at the surface containing various salt compounds, gases, heavy metals, radioactive elements and organics. In order to investigate the mobility of Ca, Fe, S and trace elements such as Co, Cr, Cu, Mn, Mo, Ni, Pb, U, V, Zn and selected organic compounds during hydrofracturing we performed sequential leaching tests with 12 black shales from five locations in Europe and the US. Using five different artificial fracking fluids 24h short-term experiments were carried out at ambient pressure and temperatures of up to 100°C. Two long-term experiments lasting, respectively, 6 and 3 months, respectively, at 100°C / 100bar were performed with selected black shales from Bornholm, Denmark and Lower Saxony, Germany, using a fracking fluid with additives provided by the industry.

We characterized the black shales by XRD, XRF and ICP-MS following HF-HClO₄ dissolution before and after the experiments. Fluids were analysed by ICP-MS, IC, LC-OCD and Gas MS and GC.

The amount of dissolved constituents after the experiment is independent from the pH of the fracking fluid but highly dependent from the element content in the black shale and the buffering capacity of specific components, namely pyrite and carbonates. Shales containing carbonates buffer the solution at pH 7-8. Sulphide minerals (pyrite) become oxidized and generate sulfuric acid (H₂SO₄) leading to a pH of 2-3. Shales containing pyrite but only traces of, or lacking, carbonates give rise to low pH fluids responsible for the much higher concentrations of most dissolved cations (except e.g. Mo, Sr). In each experiment, less than 15% of a certain element contained in the black shale was mobilised into the fluid.

Orogenic Eclogites, Rutile and Trace Element Flux in the Subduction Zone

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The geochemical evolution of the continental crust, oceanic crust and mantle is strongly influenced by complex geochemical processes occurring in the subduction zone. However, significant gaps exist in our understanding of these controls on the behaviour of important trace elements. Using orogenic eclogites from the Western Gneiss Region (WGR) of Norway as analogues for subducted oceanic crust, we quantitatively assess the behaviour of many of these elements.

Rare Earth Element (REE) and immobile High Field Strength Element (HFSE) compositions have shown that most Norwegian eclogites have E-MORB to N-MORB protoliths. Using elements thought to be highly immobile (e.g. Nb, Hf), we have estimated the likely total element flux for many more mobile trace elements.

We also assess the role of accessory rutile in controlling HFSE flux from the slab. Nb/Ta as well as Zr/Hf ratios in rutile vary from sub- to superchondritic, yet mean grain compositions appear essentially chondritic (19.9, 34.5 respectively). Whole rock samples reflect this variance on a much larger regional scale, since average ratios for eclogites across the whole WGR are also chondritic. We discuss possible explanations and consequences for heterogeneity in these processes.