**Evaluating fluid-rock interactions in black shales by using autoclave experiments**

Andrea Vieth-Hillebrand1, Franziska D.H. Wilke1, John P. Kaszuba2,

Axel Liebscher1, Brian Horsfield1

1 Helmholtz Centre Potsdam, GFZ, German Research Centre for Geosciences, Potsdam, 14473, Germany

2 University of Wyoming, Department of Geology & Geophysics & School of Energy Resources,

Laramie, WY 82071, USA

Black shales are a heterogeneous mixture of minerals, organic matter, and formation water and little is actually understood about the fluid-rock interactions that take place between the organic and inorganic fractions. A first insight into the composition, size and structure of the dissolved inorganic and organic compounds released from a variety of black shales under different environmental conditions will provide a better understanding of the fluid-rock interactions taking place in shale environments over both geological and human timescales. The release of organic and inorganic compounds from black shales into a variety of lab-made extraction fluids was studied over time and with different temperature and pressure conditions to provide a first insight into the interactions between the inorganic and organic fractions.

Autoclave experiments were performed simulating different p-T-conditions (100°C/100 bar; 115°C/350 bar). Samples from Posidonia, Alum and Niobrara Formations in Germany, Denmark and US were taken to reflect different thermal maturity of the organic matter but also a natural variety in mineral and elemental composition.

Our results show that the amount of dissolved inorganic constituents at the end of the experiment is independent of the pH of the extraction fluid but highly dependent on the composition of the black shale and the buffering capacity of specific shale components, namely pyrite and carbonates. The amount of elements released into the fluid is also dependent on the residence time in as half of the commonly measured elements (transition metals, earth- and alkali metals) show highest concentrations within four days.

We clearly demonstrate that the composition of the experimental fluid is effected by the natural organic matter composition and maturity of the shale and not just by the selected chemicals in the extraction fluid. Alum and Posidonia shale extracts tend to have their specific composition of DOC. These patterns in DOC composition are also released in presence of DOC-rich stimulation fluids. Due to this observation it can be assumed that even with the application of DOC-rich extraction fluids, the leachates tend to have very shale-specific compositions of DOC and these compositions were observed to change over time. The compositions of the extration fluids have the potential to change the mobilization of organic compounds from shales. The high yields of formate from Posidonia samples differ from earlier studies evaluating the potential of shales to release formate as being low (Olsson et al., 2013). It is not clear whether the release of formate from the natural organic matter of the shale may have been enhanced by the organic chemicals in the extraction fluid or whether the organic polymers in the extraction fluids may have been the subject of decarboxylation and generation of formate at the p-T-conditions of the autoclave experiments.

Reference:

Olsson, O., Weichgrebe, D., Rosenwinkel, K.-H. 2013. Hydraulic fracturing wastewater in Germany: Composition, treatment and concerns. Environmental Earth Sciences 70, 3895-3906.