

## GEOCHEMICAL COMPOSITION OF FLOWBACK AND PRODUCED WATER – INSIGHTS FROM LAB AND FIELD STUDIES

Andrea Vieth-Hillebrand<sup>1</sup>, Yaling Zhu<sup>1</sup>, Franziska D.H. Wilke<sup>1</sup>, Franziska E. Schmid<sup>1</sup>, Juraj Francu<sup>2</sup>, Olga Lipińska<sup>3</sup>, Monika Koniecznyńska<sup>3</sup>, Brian Horsfield<sup>1</sup>

<sup>1</sup> GFZ German Research Centre for Geosciences, Potsdam, Germany

<sup>2</sup> CGS Czech Geological Survey, Brno, Czech Republic

<sup>3</sup> PGI Polish Geological Institute - National Research Institute, Warszawa, Poland

The huge volumes and unknown composition of flowback and produced water cause major public concerns about the environmental and social compatibility of hydraulic fracturing and the exploitation of gas from unconventional reservoirs. Flowback and produced water contain not only residues of fracking additives but also chemical species that are dissolved from the target shales themselves. Shales are a heterogeneous mixture of minerals, organic matter, and formation water and little is actually understood about the fluid-rock interactions occurring during hydraulic fracturing of the shales and their effects on the chemical composition of flowback and produced water. To overcome this knowledge gap, interactions of different shales with different artificial stimulation fluids were studied in lab experiments under ambient and elevated temperature and pressure conditions.

Four shale samples were extracted with either distilled water or an artificial fracking fluid under ambient or elevated pressure and temperature conditions in an open or closed system, respectively. Three potential European shale gas systems (Alum, Posidonia, Mikulov) were selected. The Marcellus shale from the Elmsport quarry, in Pennsylvania (USA) was taken for comparison. The artificial fracking fluid contained choline chloride (clay stabilizer) and butyldiglycol (friction reducer). Water samples from these experiments were analysed for their concentrations of different inorganic and organic compounds by IC, ICP-MS, LC-OCD, and FT-ICR-MS. All samples show release of inorganic anions like low amounts of fluoride and nitrate. Phosphate concentrations are low in extracts from Mikulov and Posidonia shale samples but higher in Marcellus and Alum shale extracts. Release of sulfate is tremendously high in extracts of the Alum shale sample but still high in extracts of the Marcellus, Posidonia and Mikulov shale samples. The release of sulfate may be related to the presence of pyrite and pyrite oxidation. Contents of carbonate, as present e.g. in the Posidonia shale, may buffer pyrite oxidation (Wilke et al., 2015).

All water extracts indicate release of organic acids from the shales if being in contact with hot water for 48 hours, but quality and quantity of dissolved organic acid composition are different from sample to sample. In previous experiments it became obvious that thermal maturity of the shale organic matter has a strong control on the organic acid composition and concentration (Zhu et al., 2015). The overmature Alum shale sample only releases low amount of acetate (water extract), but higher amounts of formate and acetate if in contact with artificial fracking fluid for 6 days. Also extracts from the mature Posidonia shale show higher concentrations of acetate and formate if being in contact with artificial fracking fluid. The immature Mikulov shale sample shows high concentrations of organic acids in the water extract and slightly higher concentrations of acetate and formate in the autoclave samples after contact with artificial fracking fluid for 6 days.

These lab experiments showed clearly that fluid-rock interactions change the chemical composition of the fluid and this demonstrates that simulation/ modelling of flowback water composition in shale gas systems is not possible without consideration of the fractured shale geochemistry. In addition, flowback water samples were taken after hydraulic fracturing of one horizontal well in Pomeranian region, Poland and investigated for their chemical composition using the same analytical methods as in the lab experiments. With this presentation, results from lab and field studies will be presented and compared to decipher possible controls on chemical compositions of flowback and produced water.

### References:

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- Zhu, Y., Vieth-Hillebrand, A., Wilke, F.D.H., Horsfield, B., 2015. Characterization of water-soluble organic compounds released from black shales and coals. *International Journal of Coal Geology* 150–151, 265-275.