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Characterizing the variability in chemical composition of flowback water – results from laboratory studies

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Abstract

The large volumes and unknown composition of flowback and produced waters cause public concerns about the environmental and social compatibility of hydraulic fracturing and the exploitation of unconventional gas. Flowback and produced waters contain not only residues of fracking additives but also chemical species that are dissolved from the shales. Interactions of different shales with an artificial fracturing fluid were studied in lab experiments under ambient and elevated temperature and pressure conditions. Fluid-rock interactions change the chemical composition of the fracturing fluid and this indicates that geochemistry of the fractured shale needs to be considered to understand flowback water composition.

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1. Introduction

The growing importance of exploring gas and oil from unconventional reservoirs by hydraulic fracturing (HF) raises public concerns about the potential impacts on human health and the environment. Beside others, concerns are related to the high water demand for this technique as well as the application of tons of chemicals in the applied

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fracturing fluids and the composition of the resulting flowback and produced waters. On the one hand, provision of these huge amounts of water may provide problems to natural environments and drinking water supplies but on the other hand fracturing fluid and flowback water with unknown composition are feared to be contaminants and handling and proper treatment of these fluids are still under debate.

HF is a stimulation technique used to increase production of oil and gas and involves the injection of fluids under pressures great enough to fracture the oil- and gas-containing formations [1]. With HF, permeability in shales, tight sands, coal-beds, and other gas and oil-bearing strata is increased [2]. HF is used in conventional oil and gas reservoirs, but also to develop geothermal energy resources and unconventional oil and gas reservoirs. HF has been used since the late 1940s and wells stimulated by HF may be vertical, deviated, or horizontal in orientation, and they may be newly drilled or older at the time the fracturing is done [1]. The fracturing fluids generally consist of three parts: 1) the base fluid (i.e. water), 2) the additives and 3) the proppant. Each additive is a mixture of various chemicals with the main ingredient serving a specific purpose during HF (e.g. friction reducer, gelling agent, crosslinker, breakers, biocide, stabilizer) [3,4]. The particular composition of the fracturing fluid is selected by a design engineer based on empirical experience, the geological setting, reservoir geochemistry, economics, availability of chemicals and preference of the service company or operator [1]. The largest constituent of a typical fracturing fluid is water (>90%), followed by proppants (<10%) and additives (0.5 – 2%). After the formation has been fractured the pressure is released from the well which causes the fluid mixture to flowback to the surface. This fluid is generally classified as either flowback or produced water [2]. Flowback water is commonly defined as the water that is released within the initial two weeks following the completion of the HF process [5]. Produced water, however, is the naturally occurring water within the shale formation [2].

Composition of flowback is related to the composition of the initial fracturing fluid, the composition of the natural formation water of the shale and the possible interactions between fracturing fluid and shale system over time at the in-situ conditions. Initially this water is mostly fracturing fluid, but with time, it becomes more similar to the natural formation water, e.g. increase in salinity, and decrease in dissolved organic carbon (DOC) [6]. Concerning composition of flowback water, inorganic constituents (metals, salts), organic compounds (hydrocarbons, organic acids) and naturally occurring radioactive material (NORM) have to be considered. Therefore, to understand controls on the flowback water composition, composition of the initial fracturing fluids, natural formation waters and possible processes relevant in the reservoir need to be clarified.

To date, most publications on composition of flowback and produced water deal with samples from the Marcellus shale gas exploitation (see for summary [5]), only few publications exist from other shale gas sites in the US, Canada, China or Europe. Until now, the influence of the shale formation on the flowback water composition is quite often mentioned but not evaluated. Here, also experimental studies are necessary to assess the potential of the respective shale to release organic and inorganic constituents into the flowback water. Based on the extraction results of two European shale samples with an artificial fracturing fluid it became obvious that the flowback shows shale-specific characteristics in both, inorganic and organic composition [7]. In addition to this, it was shown that the thermal maturity of the individual shale sample has a strong influence on the extracted organic compounds [8]. Other laboratory experiments showed that the majority of reactions took place in the first 48 to 72 hours. Ca and Sr were released from the shale, indicating carbonate dissolution and the increase of metals such as Al, Cd, Co, Cr and Ni suggests the formation of secondary minerals [9]. Flowback was also reproduced and analyzed by Labus and coworkers [10]. The autoclave experiments implied that the composition of flowback water is more controlled by interactions of fracturing fluids and original pore water than by the properties of the reservoir rock. The fluid-rock interaction was based on carbonate and silicate dissolution and the oxidation of pyrite leading to an increase of sulfate. The initial high increase in the first 2 to 3 days was explained with a release of pore water.

The mobility of elements is strongly dependent on pH values, redox-conditions and only to a lower degree on temperature and solid:water ratios [7,9,11]. This was explored with batch experiments using core samples from the Bakken Formation (US). Similar experiments were done by Wang and coworkers using samples from the Eagle Ford Formation [12]. The pH value varies with the dissolution of carbonate and the oxidation of pyrite, therefore making it dependent on the chemistry of the reservoir rock. The interaction of reservoir rock and glutaraldehyde, a commonly used biocide additive in fracturing fluids, was investigated in lab experiments. Under high temperature and pressure conditions a rapid autopolymerisation of glutaraldehyde forming water-soluble dimers and trimers as well as precipitation at high temperatures were observed [13].

In this study, shale samples from Marcellus and Mikulov Formations have been used in two different experimental set-ups to investigate the effects of temperature, pressure and fluid composition on the composition of the resulting experimental flowback. The lab-derived flowback was analysed for its chemical composition. Two chemicals (choline chloride and butyldiglycol) were selected as additives for the artificial fracturing fluid. These chemicals have been presented as additives considered for future shale-gas hydraulic fracturing operations also by Gordalla and coworkers [14], choline chloride has been listed as one of the most often used additives in hydraulic fracturing by database FracFocus.

2. Study areas

2.1. Marcellus Formation

The Marcellus shale is a vast formation containing black organic rich shales, which are targeted for exploitation of shale gas. It is located in the US states Pennsylvania, New York, West Virginia, Ohio and Maryland and covers an area of approximately 152,000km². The Marcellus Formation is of Middle Devonian age and its sedimentation occurred in the Appalachian basin. The convergence of the continent Avalonia towards the continent Laurentia created an accumulation space for the Marcellus transgression. This was followed by the collision of the continents Gondwana and Laurentia, resulting in the Appalachian orogenesis [15].

The Marcellus Formation is the lowest unit of the Hamilton Group. The productive horizon lies at a depth of 1200 to 2590m and is of an average thickness of 15 to 60m [16]. The shale is of low permeability of 10^{-5} to 10^{-2}mD and of low porosity of 10% [17]. The average level of total organic carbon (TOC) lies between 3 and greater than 10% [15]. The investigated sample was taken at Elimsport Quarry in central Pennsylvania and represents the Eifelian Basal Union Springs of the Lower Marcellus Formation. The sample was taken as fresh outcrop and has been classified as argillaceous/siliceous mudstone (Table 1). TOC of the investigated sample lies at 3.82% (Table 1) and shows high maturity, equivalent to gas window (Tmax > 500).

Table 1. Basic characteristics of the investigated shale samples (courtesy of Czech Geological Survey).

	Marcellus	Mikulov
TOC (%)	3.82	1.08
Tmax	500+	434
HI	1.4	177
OI	17	57
TS (%)	1.9	0.3
Calcite (%)	5	35
Clays (%)	47	26
Quartz (%)	27	26
Dolomite-Ankerite-Siderite (%)	3	1
Feldspar + HM (%)	17	1.4
Pyrite (%)	0.6	0.6

2.2. Mikulov Formation

The Mikulov Formation is located in the South-East Bohemian Massif. It is believed to be the principal source rock formation in the Bohemian Massif, sealing off the Gresten Group sandstone underneath [18]. The Mikulov Formation is of Upper Jurassic age and was deposited in the Northern Tethys Ocean on the passive margin of the

European plate. The organic matter consists of mainly planktonic algae and some terrestrial debris. The Middle Jurassic fluvial deltaic environments evolved into carbonate platforms with anoxic-suboxic conditions. Therefore the matrix of the Mikulov shale is made up of fine carbonate grains [19].

The TOC varies between 0.2 and 10% with an average of 1.9% [17], the investigated sample has TOC of 1.08% (Table 1). The rock is brittle and covered with a network of microfractures, convenient characteristics for hydraulic fracturing. The results of the Rock-Eval Pyrolysis show that the material is immature with Tmax < 435. The gas window supposedly lies at 6 to 9 km depth and the oil window at 4 to 6 km depth. The sample was obtained at a depth of 2966 m and has been classified as mixed mudstone (Table 1).

3. Experimental set-up and analytical methods

3.1. Soxhlet extraction

Short-term water extractions were performed using a modified Soxhlet apparatus. 10 g of milled shale (<2 mm size) were extracted with 125 ml of destilled water at 100°C for 48 h. The pH of the fluid was measured instantaneously to avoid a change in pH. However, pH values should be seen as maximum values due to possible partial degassing upon sampling. Fluids were later analysed for DOC, DOC fractions, organic acids and inorganic anions (fluoride, chloride, sulfate, nitrate and phosphate).

3.2. Autoclave experiment

To study the fluid-rock interactions between the artificial fracturing fluid and the shale, both were placed into a 220 ml autoclave made of Hastelloy™ alloy and fully coated with PTFE for one week under elevated temperature and pressure conditions of 100 bar and 100 °C. The autoclave experiments were heated by a conventional heating plate to 100°C and stirred magnetically to enhance reactions during the whole run time. The pressure in the autoclave was adjusted to 100 bar by adding N_2 gas. It is important to note that the experimental set-up allowed exposure to air, fluids in the autoclave contained 1% O_2 at the start of the experiment [7]. All experiments were performed with a solid to liquid weight ratio of 1:12.5, i.e. 16 g of milled shale were eluted with 200 ml of artificial fracturing fluid. Fluids were sampled using a permanently installed PEEK capillary that ends in the middle of the autoclave. To protect the PEEK capillary, PTFE-filters are placed at the end of the capillary. About 5 - 10 ml fluid was sampled at each sampling time. The samples have been analysed in the same way as the samples from Soxhlet extractions.

3.3. Artifical fracturing fluid

To characterize the "water-mobile" constituents of the different shales, extractions with destilled water were performed using Soxhlet apparatus. Prior to extraction, the destilled water was treated via UV-photooxidation (Simplicity 185, Millipore) to remove organic compounds.

The artificial fracturing fluid used in the autoclave experiments consisted of choline chloride and 2-(2-butoxyethoxy) ethanol (trivial name: butyldiglycol), two chemicals which are frequently used as clay stabilizer and friction reducer in hydraulic fracturing of shales. The artificial fracturing fluid consisted of 0.15 % choline chloride and 0.062 % butyldiglycol in destilled water. The pH value of this artificial fracturing fluid was 5.8.

3.4. Analytical methods

The mineral content of the shales was obtained by X-ray diffraction (XRD) followed by Rietveld refinement for a quantitative evaluation as described by Wilke and coworkers [7]. Fluids were analysed by ion chromatography (IC) and liquid chromatography organic carbon detection (LC-OCD). IC analysis was done in replicate with conductivity detection (ICS 3000, Dionex) to determine the content of fluoride, chloride, sulfate, nitrate and phosphate and for

quantification of organic acids (formate, acetate, propionate, butyrate, oxalate). For chromatographic separation of the anions the analytical column AS 11 HC (Dionex Corp.) was used at a temperature of 35 °C. The sample was eluted by KOH solution of varying concentration over time [20]. Standards containing all of the investigated compounds were measured in different concentrations every day. Standard deviation of sample and standard quantification is below 10%.

The characterization and quantification of the DOC and its fractions were conducted by size exclusion-chromatography (SEC) with subsequent ultraviolet (UV; λ= 254 nm) and infrared (IR) detection by LC-OCD [21]. Phosphate buffer (pH 6.85; 2.5 g KH_2PO_4, 1.5 g Na_2HPO_4) was used as mobile phase with a flow of 1.1 ml/min [20]. The sample passed a 0.45 mm membrane syringe filter before entering the chromatographic column (250 mm x 20 mm, TSK HW 50S, 3000 theoretical plates, Toso, Japan). After chromatographic separation the organic compound fractions were characterized by UV detection. Quantification of DOC fractions by IR-detection of released CO_2 is possible after UV photooxidation (λ = 185 nm) in a Gräntzel thin-film reactor.

4. Composition of extracts

4.1. Marcellus

Water extract of the Marcellus shale sample had pH of 8.0 and contained low concentrations (<1 mg/L) of chloride, fluoride and nitrate; phosphate was about 7 mg/l and sulfate reached 916 mg/l. Also formate, acetate, butyrate and oxalate were detectable in this water extract (Fig. 1a and b).
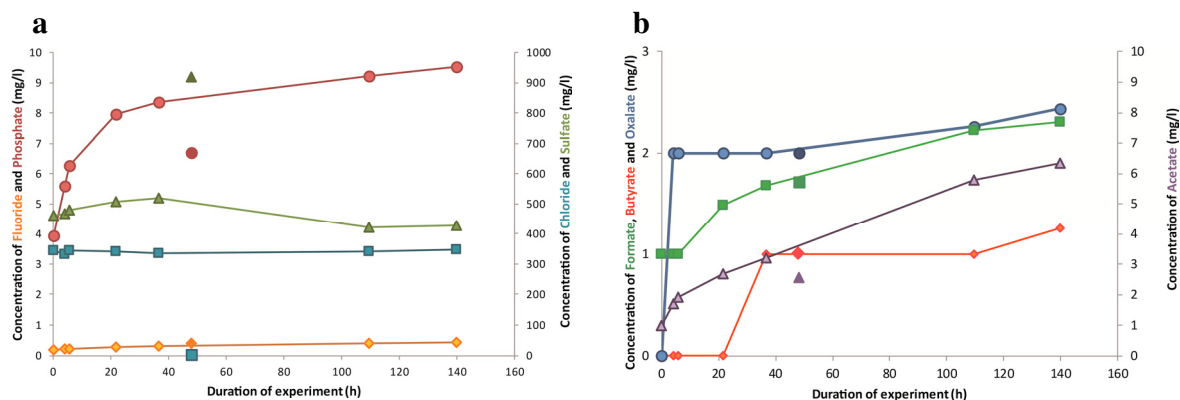

Fig. 1. (a) concentrations of inorganic anions (fluoride – diamonds; phosphate – circles; chloride – squares; sulfate – triangles) and (b) concentrations of organic acids (formate – squares; acetate – triangles; butyrate – diamonds; oxalate – circles) in fluids sampled from autoclave experiment with the Marcellus shale. Concentrations of anions in Soxhlet extract are given as single symbols.

The addition of chemical additives, increase in pressure and reaction time led to pH of 7.5 in the latest extract samples. Mobilization of fluoride and nitrate was comparable to the Soxhlet extract. The phosphate concentration was slightly higher (9 mg/l) and the sulfate concentration was much lower (430 mg/l). These lower concentrations of sulfate could be related to presence of lower amounts of oxygen in the autoclave experiment than during Soxhlet extraction. Organic acid concentrations increased with experimental run time, acetate had maximum concentration of 6.3 mg/l, formate concentration was 2.0 mg/l, oxalate reached 2.1 mg/l and butyrate 1.2 mg/l after 140 h of experiment run time. Interestingly, concentrations of organic acids in the water extract are comparable to concentrations of acids in autoclave experiment after the same run time of the experiment (Fig. 1a and b).
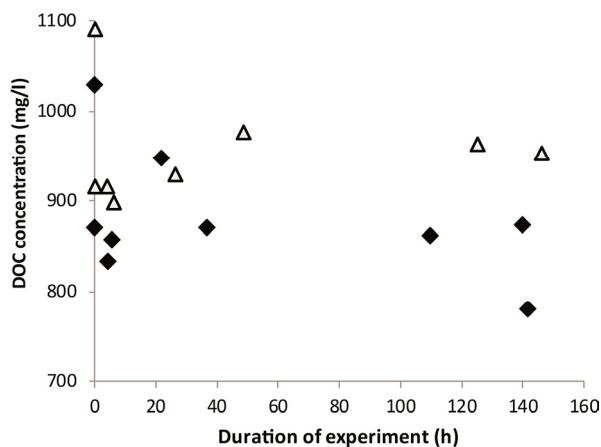
Fig. 2. DOC concentrations in samples from autoclave experiments with Marcellus (diamonds) and Mikulov (triangles) shales

The total load in DOC decreases from the initial concentration (1,029 mg C/l) of the artificial fracking fluid over time, reaching 780 mg C/l (75%) (Fig. 2). This loss in organic compounds may be related to sorption to the shale, as decrease is strongest directly after exposition of the artificial fracking fluid to the shale. LC-OCD chromatograms only consisted of two prominent peaks with retention times of 65 and 78 min. No other peaks were detectable. Based on comparison with chromatograms of pure solutions of choline chloride as well as butyldiglycol, it can be assumed that the first eluting peak consists of choline chloride, the second peak of butyldiglycol. Both peaks show decrease in peak areas over run time of the experiment, being consistent with decreasing DOC concentrations (Fig. 3). There was no UV-activity in any of the Marcellus shale extracts.
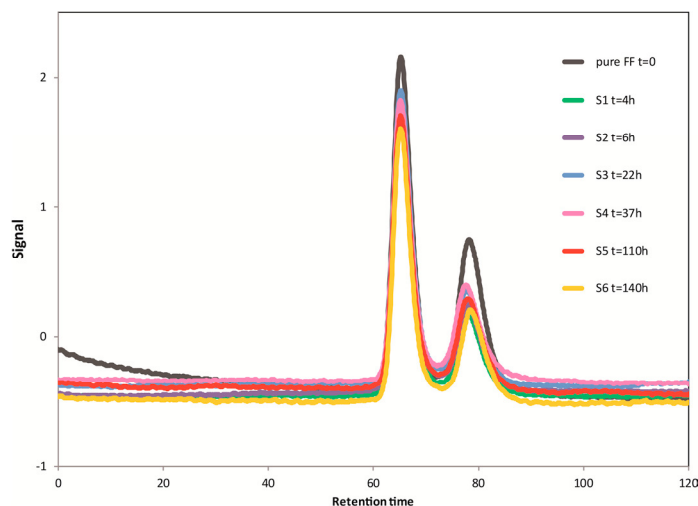

Fig. 3. IR chromatograms of the different samples taken from the autoclave experiment with Marcellus shale

4.2. Mikulov

Water extracts of the Mikulov sample had pH around 8.8 and contained low concentrations (<2 mg/L) of fluoride and nitrate; phosphate was not detectable, chloride was about 26.7 mg/l and sulfate reached 194.7 mg/l. Also formate, acetate, butyrate and oxalate were detectable in the water extract. Acetate had concentration of 6.9 mg/l, followed by oxalate (4.9 mg/l), formate (3.2 mg/l) and butyrate (1.0 mg/l) (Fig. 4a and b).

Fluid sample from autoclave experiment showed pH of 8.1. There was no change in mobilization of fluoride and nitrate; phosphate remained below detection limit. Sulfate concentration reached similar values (186 mg/l). Chloride (blank concentration of 331 mg/l) increased slightly over run time of the experiment. Organic acid concentrations increased with experimental run time, acetate had maximum concentration of 10 mg/l, formate concentration was 5.5 mg/l, oxalate reached 4.6 mg/l and butyrate 3.4 mg/l after 146 h of experiment run time. Concentrations of formate, acetate, and butyrate in water extract are lower than in autoclave experiment after the same run time. Only the oxalate concentration is higher in the water extract than in the sample from autoclave experiment (Fig. 4a and b).
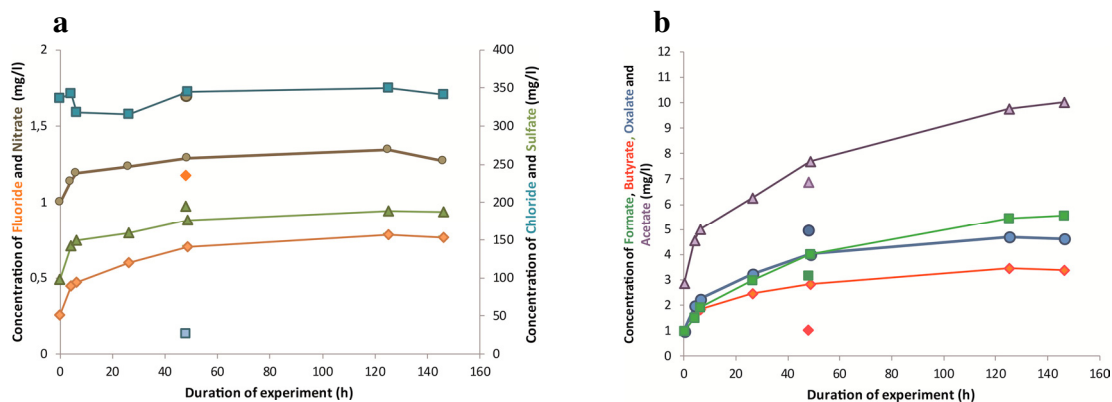

Fig. 4. (a) concentrations of inorganic anions (fluoride – diamonds; nitrate – circles; chloride – squares; sulfate – triangles) and (b) concentrations of organic acids (formate – squares; acetate – triangles; butyrate – diamonds; oxalate – circles) in fluids sampled from autoclave experiment with the Mikulov shale. Concentrations of anions in Soxhlet extract are given as single symbols.

The total load in DOC decreases to 82 % of the initial concentration of the artificial fracking fluid over the run time of the autoclave experiment. This loss in organic compounds may be related to sorption to the shale, as decrease is strongest directly after exposition of the artificial fracking fluid to the shale in both experiments. LC-OCD chromatograms show reduced peak area of both peaks over run time of the experiment, being consistent with decreasing DOC concentrations and the results of the Marcellus shale experiment. There was no UV-activity in any of the Mikulov extracts.

5. Discussion

All samples show release of inorganic anions like low amounts of fluoride. Phosphate was only detected in Marcellus extracts and in low concentrations, whereas nitrate was only present in low amounts in Mikulov extracts. Chloride concentration was very low in water extract from Marcellus but higher in Mikulov water extract. Release of sulfate is high in all extracts of the Marcellus and Mikulov shales. The release of sulfate may be related to the presence of pyrite and pyrite oxidation. Presence of carbonate may buffer pyrite oxidation and lead to relatively high pH values in the different extracts [7]. Therefore, higher carbonate content of the Mikulov samples is reflected in higher pH values of the Mikulov extracts in comparison to the Marcellus extracts.

In general, both shales show release of organic acids if being in contact with hot water for 48 hours, but quality and quantity of dissolved organic acid composition are different. In previous experiments it became obvious that thermal maturity of the shale organic matter has a strong control on acid composition and concentration in water extracts [8] and this is verified also in these experiments. The immature Mikulov shale sample shows higher concentrations of acetate, oxalate and formate in the water extract compared to the overmature Marcellus sample. Also in autoclave experiments, the concentrations of all detected organic acids, even butyrate, are nearly 2 times higher in the extracts of the immature Mikulov shale. The addition of chemicals may slightly favor the extraction of organic acids from immature organic matter, as was shown for the Mikulov shale extracts when comparing results of

water extraction with results of autoclave experiments after a run time of 2 days. This effect of chemical additives was also observed in autoclave experiments with mature Posidonia shale sample [7].

DOC concentration strongly decreases in all autoclave experiments directly at the start of the experiment. This may be related to sorption or binding of the applied chemicals to the shale organic matter. With reference to the change in IR-chromatograms it seems as if the second peak (probably derived from butyldiglycol) is much stronger reduced in peak area than the first peak (probably derived from choline chloride). When checking the physical and chemical properties of both compounds, it becomes obvious that butyldiglycol has a more lipophilic character, as indicated by the positive value for log Kow (0.56) in comparison to the negative value for log Kow (-5.16) for choline chloride. Over run time of the experiments, the peaks in the IR-chromatograms only decrease in size but there are no new peaks or strong changes in peak shape. This is surprising as the extraction of organic acids, as detected by IC, would be observable also in LC-OCD by a new peak at retention time of about 47 min. This may be due to the very high concentration of the two compounds in the artificial fracking fluid and the strong dilution of the samples that is necessary prior to measurements.

With the additional analytical data derived from these water extracts and autoclave fluids, more details on effects of fluid-rock interactions on elemental composition as well as organic compounds are available. These lab-derived results may be verified or falsified when "real" flowback samples will become available from shale gas systems that also have been studied in lab experiments.

Based on these and other lab experiments (see e.g. [7,8]) it is shown that fluid-rock interactions have influence on the chemical composition of the fluid and this clearly demonstrates that any simulation or modelling of flowback water composition in shale gas systems has to consider the interactions between the fracking fluid and the fractured gas shale system. This comprises e.g. organic and inorganic geochemistry of the shale, but also in-situ temperature and pressure conditions as well as the residence time of fracking chemicals.

6. Concluding remarks

In lab experiments, fluid-rock interactions have been shown to change the chemical composition of the fluid and this demonstrates that simulation and modelling of flowback water composition in shale gas systems is not possible without consideration of the fractured shale system. In future studies, additional analytical methods will be applied to these lab-derived shale extracts unveiling more details on the effects that fluid-rock interactions will have on the elemental composition as well as on high molecular weight polar organic compounds. Finally, examination of "real" flowback samples from shale gas systems that also have been studied in appropriate lab experiments will complete the preliminary assumptions on fluid-rock interactions in shale gas systems.

Acknowledgements

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