Induced mobility of inorganic and organic solutes from black shales using water extraction: Implications for shale gas exploitation

Franziska D.H. Wilke [a,b,*], Andrea Vieth-Hillebrand [a], Rudolf Naumann [a], Jörg Erzinger [a,b], Brian Horsfield [a]

[a] GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany
[b] University of Potsdam, Department of Earth and Environmental Sciences, Karl-Liebknecht Str. 24-25, 14467 Potsdam, Germany

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ABSTRACT

The study reported here evaluates the degree to which metals, salt anions and organic compounds are released from shales by exposure to water, either in its pure form or mixed with additives commonly employed during shale gas exploitation. The experimental conditions used here were not intended to simulate the exploitation process itself, but nevertheless provided important insights into the effects additives have on solute partition behaviour under oxic to sub-oxic redox conditions.

In order to investigate the mobility of major (e.g. Ca, Fe) and trace (e.g. As, Cd, Co, Mo, Pb, U) elements and selected organic compounds, we performed leaching tests with black shale samples from Bornholm, Denmark and Lower Saxony, Germany. Short-term experiments (24 h) were carried out at ambient pressure and temperatures of 100 °C using five different lab-made stimulation fluids. Two long-term experiments under elevated pressure and temperature conditions at 100 °C/100 bar were performed lasting 6 and 2 months, respectively, using a stimulation fluid containing commercially–available biocide, surfactant, friction reducer and clay stabilizer.

Our results show that the amount of dissolved constituents at the end of the experiment is independent of the pH of the stimulation fluid but highly dependent on the composition of 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 (e.g. pyrite) become oxidized and generate sulphuric acid leading to a pH of 2–3. This low pH is responsible for the overall much larger amount of cations dissolved from shales containing pyrite but little to no carbonate. The amount of elements released into the fluid is also dependent on the residence time, since as much as half of the measured 23 elements show highest concentrations within four days. Afterwards, the concentration of most of the elemental species decreased pointing to secondary precipitations. Generally, in our experiments less than 15% of each analysed element contained in the black shale was mobilised into the fluid.

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1. Introduction

The remarkable success with which gas could be produced from the Barnett Shale in Texas, especially over the last ten or fifteen years, has heralded intense exploration of other US basins, and inspired North American and European energy companies to consider opportunities abroad. Technologies that have greatly improved the economics of shale plays in the USA include horizontal drilling and hydraulic fracturing. Hydraulic fracturing creates minute cracks in the rock by the high-pressure injection of fluids, enabling hydrocarbons to flow to the wellbore (Wood et al., 2011). These injected fluids are typically a suspension made of 90% water (roughly 7000–18 000 m³ Gregory et al., 2011; SEAB, 2011), 9–9.5% proppant material (sand, ceramics) and 0.5–1% chemical additives (Arthur et al., 2008; King, 2012; Wood et al., 2011). Chemical additives are necessary to achieve a continuous and economically reasonable gas flow (e.g. Meiners et al., 2012; Waxman et al., 2011). The process of well stimulation is often initiated with small volumes (<10 m³) of acid mixtures to clean the perforation tunnels in the well. Corrosion inhibitors are added to the acid mixtures, while iron stabilizers prevent iron precipitation.

* Corresponding author. GFZ, Section 4.2, Telegrafenberg, 14473 Potsdam, Germany.
E-mail address: fwilke@gfz-potsdam.de (F.D.H. Wilke).

Following the acids, the fluid with proppant material that holds the fractures open is injected for the fracturing process. The fluid may contain friction reducers, surfactants, clay stabilizers, biocides and crosslinkers tailored for the specific application (e.g. Arthur et al., 2008). Approximately 10–80% of the injected fluid (Arthur et al., 2008; Wood et al., 2011), mixed with formation water to variable degrees depending on the formation characteristics, well design and operating parameters, returns to the surface as flowback. The highest rate of flowback occurs within the first day (Gregory et al., 2011) and will usually last up to two weeks.

Organic-rich shales are enriched in heavy elements like As, Cd, Co, Cr, Hg, Ni, Zn, V, Ba and radioactive elements (e.g. U, ^{226}Ra) because they have remained under reducing conditions since deposition (e.g. Raiswell and Berner, 1985 and references therein). If redox conditions were to be changed to an oxidising environment, e.g. by introduction of oxygen-containing water during hydraulic fracturing, tetravalent uranium U^{4+} is likely to be oxidised to the soluble and hence readily mobile hexavalent form (U^{6+}) and thereby enriched in the flow-back water. If acids are present in the applied stimulation fluids, U^{4+} would also be mobile, even under reducing conditions. It has already been reported that minerals and organic compounds that are present in reservoir formations will partly dissolve into the stimulation fluid, creating brines with high concentrations of metals and organic compounds (Gregory et al., 2011). Benzene, toluene, ethylbenzene, and the xylenes (BTEX) partition most readily into the water phase, as detected in tight gas drilling fluids from Germany (Gordalla et al., 2013). Approximately one thousand individual compounds belonging to the aliphatic, alicyclic, aromatic and PAH compound classes have been reported for flowback and produced waters from the Marcellus shale in the Appalachian Basin and the Bakken shale in North Dakota and Montana (Strong et al., 2013). Produced waters from the Marcellus, Eagle Ford (south Texas) and Barnett shales differ in their average total dissolved solids contents between 2.35 and 43.55 g/l as well as in the composition of the organic compounds (Maguire-Boyle and Barron, 2014). Polyethylene glycols and linear alkyl ethoxylates, used as surfactants, have been reported in flowback and produced water samples by Thurman et al. (2014). Low molecular weight (LMW) organic acids like formate and acetate have been detected in flowback water samples (Olsson et al., 2013; Lester et al., 2015). It has been proposed that the acetate and formate were probably degradation products of polymers contained in the stimulation fluid, meaning that they might serve as indicators of hydraulic stimulation fluid concentrations in flowback and tracers for calculating flowback efficiency (Olsson et al., 2013).

The study reported here evaluates the degree to which metals, salt anions and organic compounds are released from shales by exposure to water, either in its pure form or mixed with additives commonly employed during shale gas exploitation. The experimental conditions used here were not intended to simulate the exploitation process itself, but nevertheless provided important insights into the effects additives have on solute partition behaviour under oxic to sub-oxic redox conditions.

2. Materials and methods

2.1. Black shales

The Upper Cambrian Alum Shale of Scandinavia and the Lower Jurassic Posidonia Shale of Germany are potential targets for shale gas extraction (Horsfield et al., 2010). Five overmature black shale samples from the Alum Shale of Bornholm, Denmark (Schulz et al., 2015) and the Posidonia Shale of the Hils Syncline (Rullkötter et al., 1988), all taken from whole cores, were chosen for our experiments (Table 1). Drilling of both shales was performed with drinking water. The samples were completely milled to <2 mm grain size and the resulting different grain size fractions <2 mm were used for the experiments.

2.2. Set up of extraction experiments

Two experimental set-ups were designed consisting of A) 250 ml reaction vessels equipped with a reflux condenser for short-term experiments (24 h) under atmospheric pressure and 100 °C and B) 800 ml autoclave made of Hastelloy™ and fully coated with polytetrafluoroethylene (PTFE) to avoid chemical corrosion, for long-term studies under elevated temperature and pressure conditions of 100 bar and 100 °C. These conditions broadly reflect those of the target horizon in Damme 3 well (Lower Saxony), an industry site for studying hydraulic fracturing on shale, whose depth is ca. 1–1.5 km, hydrostatic pressure is 110–150 bar and temperature is 80 °C (Olsson et al., 2013). It is important to note that both experimental set-ups allowed exposure to air; short-term experiments took place under ambient conditions, whereas fluids in the autoclave contained 1% O_2 at the start of the experiment and 0.2% O_2 at the end.

Five different extraction fluids were prepared (Table 2) containing the type and amount of chemicals broadly reflecting the stepwise technical procedure during gas well development. An overview of ingredients in commercially used fluids, including the ones used here, were published in e.g. "Well record and completion reports" of various drill sites (www.rangeresources.com).

First, all samples were extracted for 24 h with distilled water to establish a baseline for each sample and, subsequently, for comparison with later extractions. Afterwards short-term extractions started for all shale samples using different stimulation fluids (SF1 – SF4, see Table 2 for details) containing acids, K_2CO_3 or four commercially–available additives typically applied during hydraulic fracturing (compare chemicals listed in Table 6 in Gordalla et al., 2013).

Two samples were selected for long-term experiments, lasting 2 months and 6 months, respectively, using the stimulation fluid SF4. The long-term experiments were stirred magnetically for 10 min/day to enhance reactions. All extraction experiments were performed with a solid to liquid weight ratio of 1:12.5. Fluids were sampled from the short-term experiments at the start and at the end of each 24 h extraction. The long-term experiments were sampled hourly during the 1st day of extraction, at least daily for 3–5 days and almost weekly afterwards. About 3 ml fluid was sampled at each sampling time. The pH 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 (Wilke et al., 2012). After sampling, the pressure in the autoclave was re-adjusted to 100 bar by adding N_2.

To evaluate reproducibility of the experimental set-up, we performed 6 parallel short-term experiments (24 h, 100 °C, 1 bar) of sample Posidonia 77. In addition, each stimulation fluid (Table 2) was blank extracted without any shale to detect impurities of the applied chemicals as well as possible side effects caused by heating of the stimulation fluids.

2.3. Analytical methods

The mineral content was obtained by X-ray diffraction (XRD) followed by Rietveld refinement for a quantitative evaluation. XRD analyses were performed using a PANalytical Empyrean. Data reduction was initially done using the software EVA (Bruker) to identify the minerals in the black shales. Subsequently, the program AutoQuant for Rietveld calculations was used to determine the amount of the identified minerals dependent of the height, width

Table 1
Description of black shale samples.

Name	Location	Stratigraphy	Age	Rock type	Depth [m]	CTOC
Alum 43	Bornholm (DK)	Alum shale	Upper Cambrian	black shale	36.9	7.3
Alum 18	Bornholm (DK)	Alum shale	Upper Cambrian	black shale	18.2	9.0
Posidonien 077	Haddessen (D)	Posidonia shale	Lower Jurassic	black shale	31.2	1.4
Posidonien 103	Haddessen (D)	Posidonia shale	Lower Jurassic	black shale	50.8	5.6
Posidonien 119	Haddessen (D)	Posidonia shale	Lower Jurassic	black shale	60.6	7.7

Table 2
Composition of applied fluids for extractions. The exact composition of SF4 cannot be provided due to a non-disclosure contract.

Extraction series name	Ingredients	Amount	pH
water	pure distilled water	100%	7
SF1	37% HCl	0.03 vol%	6.5
	Citric acid	0.01 wt%	
	K2CO3	0.01 wt%	
SF2	37% HCl	0.05 vol%	2.2
SF3	K_2CO_3	0.01 wt%	10.4
SF4	biocide	0.1 vol%	5.9
	surfactant	0.1 vol%	
	friction reducer	0.1 vol%	
	clay stabilizer	0.1 vol%	

and positions of their reflections. Rietveld uses a least squares approach to minimize the residue between the theoretical and the measured reflection. The method can also handle overlapping reflections but a complete match of measured vs. theoretical profiles will not be achieved (detection limit ~1wt%; Lin et al., 2014 and references therein). Original shales were analysed in the same way as the extraction residues (e.g. grain size <62 μm, measurement time 60sec/0.0131°2Theta) to track possible changes in the mineral paragenesis that have been taken place during the experiments with the stimulation fluid SF4 (Table 3).

Major shale element concentrations have been determined by X-ray fluorescence (XRF) using a PANalytical Axios. Shale trace and rare earth elemental concentrations are determined by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Thermo Element XR) following HF-aqua regia (1/1) digestion, fuming with $HClO_4$ and dilution by 1/1000 with 2% HNO_3. Hydrogen, carbon and sulphur were determined by the element analyzers Eltra CS 2000 and Elementar Vario ELIII.

Fluids were analysed by ICP-MS, ion chromatography (IC) and liquid chromatography organic carbon detection (LC-OCD). Reaction fluids were filtered using a 0.45 μm Nylon membrane filter and diluted by 1/10 with 2% HNO_3 before ICP-MS analyses. For all measurements, calibration solutions with concentrations of 0.25 and 10 μg/l were applied and at least three aliquots of the reaction fluids were analysed.

Extracts were analysed in replicate by IC with conductivity detection (ICS 3000, Dionex) to determine the content of F^-, PO_4^{3-}, NO_3^-, Cl^- and SO_4^{2-} 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. The initial KOH concentration was 0.5 mM, maintained for 8 min. After 10 min, 15 mM KOH solution was reached and kept constant for 10 min. After 3 min analysis time, 60 mM KOH concentration was reached, followed by a rapid increase to 100 mM after 30.2 min. At 32 min analysis time, KOH concentration was again at the initial level of 0.5 mM and kept there for additional 15 min to equilibrate the system. 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 dissolved organic compounds (DOC) and its fractions were conducted by size-exclusion-chromatography (SEC) with subsequent ultra-violet (UV; λ = 254 nm) and infrared (IR) detection by LC-OCD (Huber and Frimmel, 1996). 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 (Huber et al., 2011). The sample passed a 0.45 μm membrane syringe filter before entering the chromatographic column (250 mm × 20 mm, TSK HW 50S, 3000 theoretical plates, Toso, Japan). After chromatographic separation into individual fractions (biopolymers, humic substances, building blocks, low molecular weight acids and low molecular weight neutral compounds), these 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.

3. Results

3.1. Characteristics of different stimulation fluids and their blank extracts

Prior to the experiment, the stimulation fluids were characterized. The initial pH-values ranged from 2.2 to 10.4 (Table 2). SF1 contained citrate (105 mg/l), chloride (111 mg/l) and DOC (30 mg/l) as well as low concentrations of calcium (0.1 mg/l), copper (≤0.04 mg/l) and tin (≤0.05 mg/l). In SF2 chloride (202 mg/l), low DOC (0.3 mg/l), copper (≤0.04 mg/l) and tin (≤0.05 mg/l) were obtained. For SF1 and SF2 these impurities can be related to the used HCl. Anions of interest are below detection limit in SF3 and DOC was low (0.3 mg/l). In SF4, containing the commercially-available additives, formate (2.6 mg/l), acetate (1.0 mg/l), chloride (222 mg/l), nitrate (10 mg/l), and phosphate (1.7 mg/l) were detected. DOC was very high (900 mg/l) and low concentrations of calcium (0.1 mg/l), copper (≤0.04 mg/l) and tin (≤0.05 mg/l) were present. Short-term blank extractions of the stimulation fluids were performed without adding any shale. With blank extraction of these stimulation fluids only minor changes in concentrations occurred that are within the standard deviation of the applied analytical methods.

3.2. Testing the reproducibility of extractions with water

To evaluate reproducibility of the extractions six aliquots of Posidonia 77 sample were tested simultaneously with double distilled water and the extracts were analysed by ICP-MS and IC. The standard deviation (1σ) for Sr is 11.5 μg/l and for As is 0.12 μg/l for an average concentration of 255 μg/l and 1.26 μg/l, respectively. The average concentrations of acetate and formate are 12.7 and 0.8 mg/l with standard deviations of about 3% and 9%, respectively.

3.3. pH values of extracts

The initial pH-values of the stimulation fluids ranged from 2.2 (SF2) to 10.4 (SF3). Irrespective of these initial values, the pH of fluid

Table 3
XRD-results from experiments with SF4.

Sample	Original composition	Amount [%]	Uncertainty [%]	After short-term SF4 Amount [%]	Uncertainty [%]	After long-term SF4 Amount [%]	Uncertainty [%]
Posidonia 77	Carbonate	15.5	0.5	14.1	0.6		
	Kaolinite	30.3	0.8	29.9	0.8		
	Muscovite/Illite	25.5	0.8	26.0	0.8		
	Pyrite	3.0	0.3	3.6	0.3		
	Quartz	25.6	0.6	26.4	0.7		
Posidonia 103	Albite	4.0	0.5	3.7	0.5	3.7	0.5
	Carbonate	43.0	0.7	43.7	0.6	45.7	0.6
	Kaolinite	11.4	0.8	11.7	0.5	9.1	0.6
	Muscovite/Illite	16.0	0.6	15.1	0.6	16.1	0.6
	Pyrite	8.7	0.3	8.2	0.2	7.3	0.2
	Quartz	17.0	0.4	17.6	0.4	18.2	0.4
Posidonia 119	Albite	5.4	0.4	5.3	0.4		
	Carbonate	73.4	0.7	73.6	0.8		
	Kaolinite	2.8	0.6	3.3	0.5		
	Muscovite/Illite	7.0	0.5	6.2	0.5		
	Pyrite	2.5	0.1	2.7	0.1		
	Quartz	8.9	0.3	8.9	0.3		
Alum 18	Barite	5.1	0.2	4.9	0.2	5.1	0.3
	Muscovite/Illite	41.1	0.8	39.9	0.8	40.2	0.8
	Orthoclase	6.3	0.9	6.0	0.9	6.0	0.8
	Pyrite	11.4	0.6	12.5	0.6	13.0	0.3
	Quartz	36.1	0.8	36.7	0.7	35.7	0.7
Alum 43	Hexahydrite	–	–	1.1	0.9		
	Jarosite	4.2	0.4	3.5	0.3		
	Muscovite/Illite	43.7	0.8	43.3	0.9		
	Pyrite	10.7	0.3	10.6	0.3		
	Quartz	32.5	0.7	33.3	0.8		
	Sanidine	8.9	1.0	8.2	0.9		

Carbonate	–	–	15.5	43.0	73.4
Pyrite	10.7	11.4	3.0	8.7	2.5
ratio	–	–	5.2	4.9	29.4
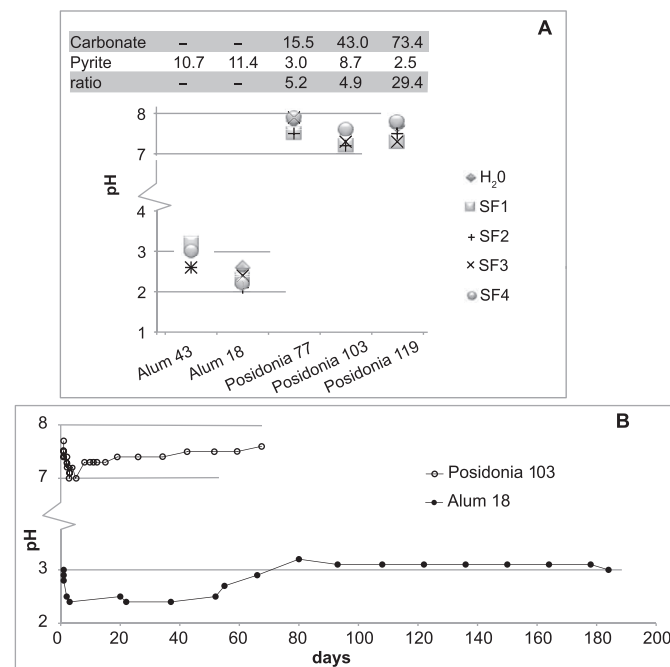
Fig. 1. pH trends during the courses of our short-term (A) and long-term experiments (B). The uncertainty is pH ± 0.1. The original pH of the used stimulation fluid is given in Table 2. Uppermost in (A): Rietveld results [in %; Table 3] for the carbonate and pyrite content of each shale is given for comparison to the pH.

samples after Posidonia shale exposure was between 7 and 8 (Fig. 1). These shale samples contain >10% carbonate in addition to pyrite (Table 3). In contrast, a pH ≤ 3.2 was obtained in fluid samples after Alum shale exposure. These shale samples contain no carbonate but >10% pyrite. This indicates that the occurrence of calcite and pyrite in the shale samples is directly reflected in the pH of the leachates.

3.4. Release of major and trace elements

Results of XRD analysis (Table 3) showed for some cases minor dissolution of carbonate (Posidonia 77) and/or sulphate (Alum 43) during the course of the short-term experiments. After the long-term experiment using the Alum 18 shale there is no visible change in the solid (Table 3), but drying-up the remaining extracted fluid from the experiment reveals traces (<1%) of sulphates such as gypsum and minerals of the hexahydrite group. Note that Rietveld calculations norm each result to 100%, which influences the quantities of the other minerals accordingly.

In the short-term experiments (100 °C, 1 bar) using five different black shales (Fig. 2), the extraction experiments with double distilled water resulted in a remarkably lower amounts of dissolved constituents in most cases than detectable in fluids from experiments with SF1 to SF4. Highest amounts of dissolved constituents were obtained when SF4 was used. In general, the shales released a steady high amount of iron and calcium into the fluids (Fig. 2) with the highest concentration obtained for iron being 782 mg/l released from the Alum 18 shale using SF4. Both Alum shales released the highest amounts of elemental species to the fluids in comparison to Posidonia, with the exception of molybdenum. The amount of uranium detected in the extracts was as high as 2.4 mg/l (Alum 18 shale with SF2).
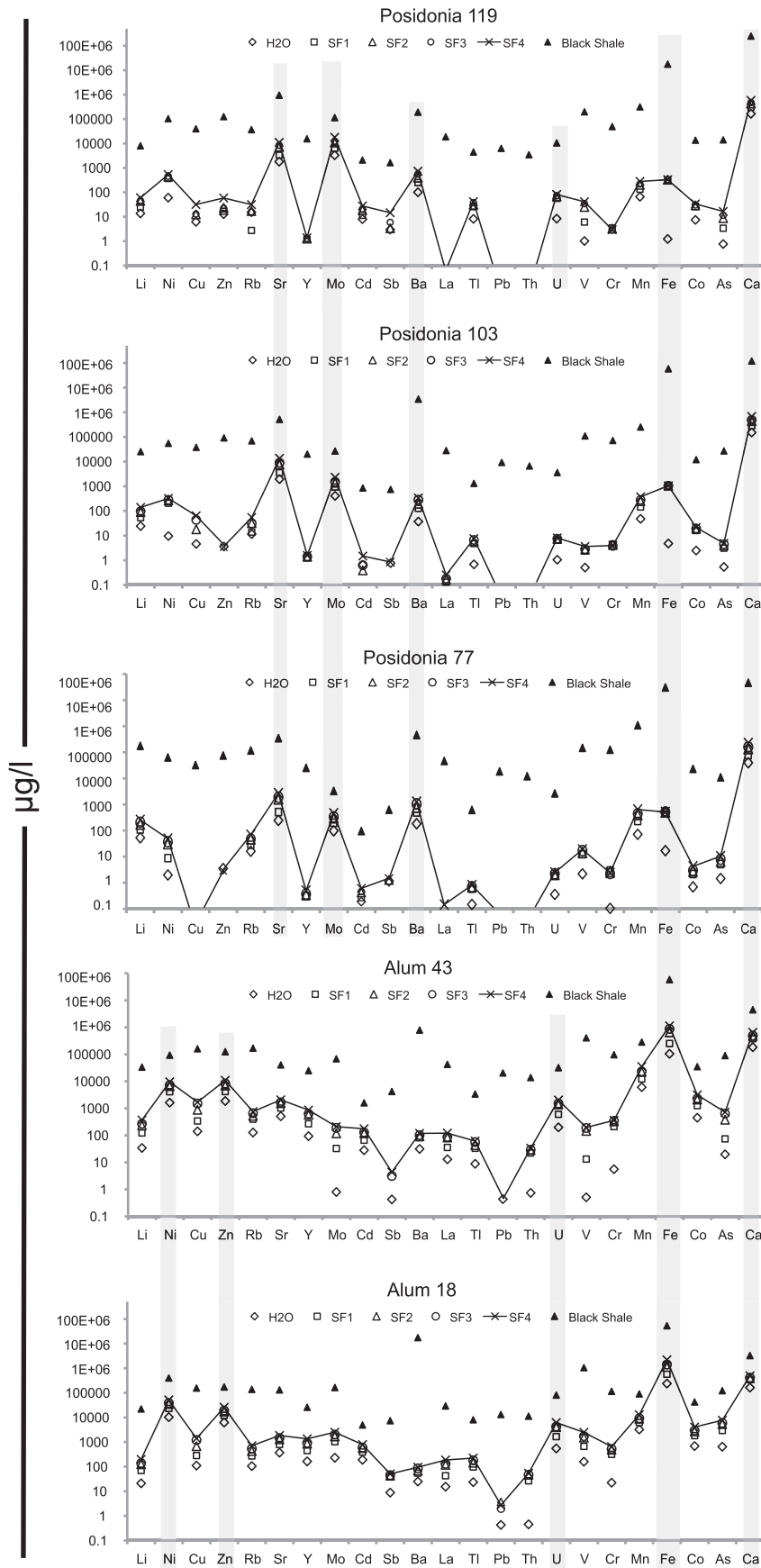
Fig. 2. Results of ICP-MS analyses of the extraction fluids after short-term experiments using water (H2O) and four different lab-made stimulation fluids (SF1–SF4; see Table 2 for details) to leach five black shales for 24 h at 100 °C and 1 bar. Swaths indicate similarities between different shales. The line connecting concentrations released during experiments with SF4 do also represent the always similar or highest amounts. The detection limit is 0.1 μg/l, the uncertainty at about 2–5%.

By comparison of both long-term experiments (100 °C, 100 bar) in which the Alum 18 and Posidonia 103 shales were extracted with SF4 one can observe that the amount of most elements released from Alum 18 shale is several times, but max. ~2000-times, higher (Fig. 3 and supplementary material to Fig. 3). This is in particular true for the transition metals like iron, cobalt, nickel, zinc but also for uranium. The concentrations of molybdenum and antimony were similar in the fluids of both experiments, and the concentration of strontium was twice as high after the experiment with Posidonia 103 compared to that with Alum 18. It is also shown (Fig. 4), that the Alum 18 shale released a higher percentage of its elements into the stimulation fluids, but no more than 15% of any particular element contained in the black shale was mobilised into the fluids in the long-term experiments.

## 3.5. Release of inorganic anions

In all extracts from short-term experiments, chloride and sulphate were detected (Fig. 5A, B) but fluoride, nitrate and phosphate were only found in minor amounts or in few samples. Using the different stimulation fluids, chloride concentrations released from Posidonia 119 were about 150 mg/l above blank level, with the exception of SF2 and SF3 (Fig. 5A). Posidonia 103 released about 73 mg/l chloride above blank level and just 8 and 29 mg/l in SF2 and SF3, respectively. Posidonia 77 showed chloride concentrations about 18 mg/l (blank corrected) using SF1 and SF4; in other extracts blank corrected chloride concentrations were near zero (water

extract) or below zero (−31 mg/l; SF2 extract). Both Alum samples released minor amounts of chloride in all short-term extraction experiments. Extraction with SF3 (basic fluid) resulted in a chloride concentration of 18−32 mg/l for all used black shales. Highest sulphate concentration had been detected in the SF4 extract from Alum 18 (2725 mg/l; Fig. 5B). Posidonia shales released fewer amounts of sulphate than Alum samples, where sulphate concentrations decreased in all extracts from Posidonia 103 to Posidonia 119 and to Posidonia 77. Sulphate concentrations in SF2 and SF4 extracts were relatively similar for each shale and lowest sulphate concentrations were measured in SF3 extracts. Highest fluoride concentrations were detected in extracts of Alum 18, fluoride concentrations in extracts of Alum 43 were lower, and all extracts of all Posidonia shales contain less than 0.8 mg/l fluoride.

When comparing the inorganic anions released from the two selected shales during long-term experiments, differences in sulphate concentrations of the leachates by one order of magnitude are evident, likely because of the pronounced presence of pyrite in the Alum shale (Fig. 6A). The concentration of sulphate increased to 3240 mg/l for the extract of the Alum shale, but only to 582 mg/l for the extracts of the Posidonia shale. Chloride release from Alum shale reached the maximum concentration of 133 mg/l in the extract (after 10 d, blank corrected) and Posidonia shale released up to 120 mg/l in the extract (after 136 d, blank corrected). Phosphate concentrations were up to a factor of 10 higher in extracts from the Alum shale than in Posidonia shale extracts at the beginning of the long-term experiments but were decreasing over time.
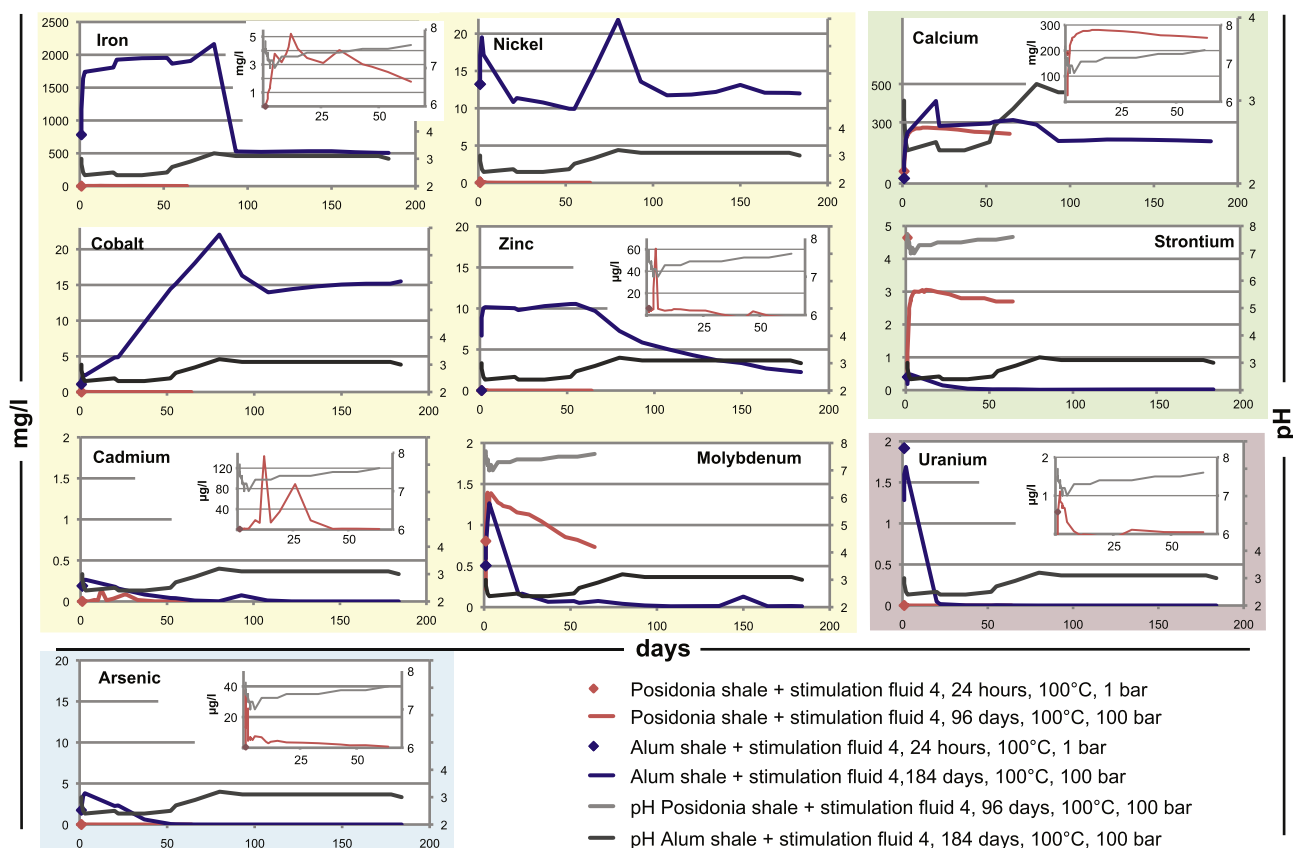
Fig. 3. ICP-MS analyses of sampled fluids during the course of long-term experiments (lines) using SF4 and the value of the short-term experiments (diamonds) to consider pressure and time dependencies. Diagrams are sorted by metals (yellow), metalloids (blue) and alkanine earth metals (green), and radioactive actinides (pink) and by their concentration for a better comparability. When necessary, pH is given along the secondary y-axis in the diagrams or in insets. Insets highlight the element concentration pattern for the experiment with the Posidonia 103 shale for comparison with concentration pattern from the Alum 18 shale. Please note the y-axis values. Further elements (Cu, V, Y, Ba, Li, Rb, Pb, Sb, La) are given in the supplementary material to Fig. 3. The uncertainty is 2−5% (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).
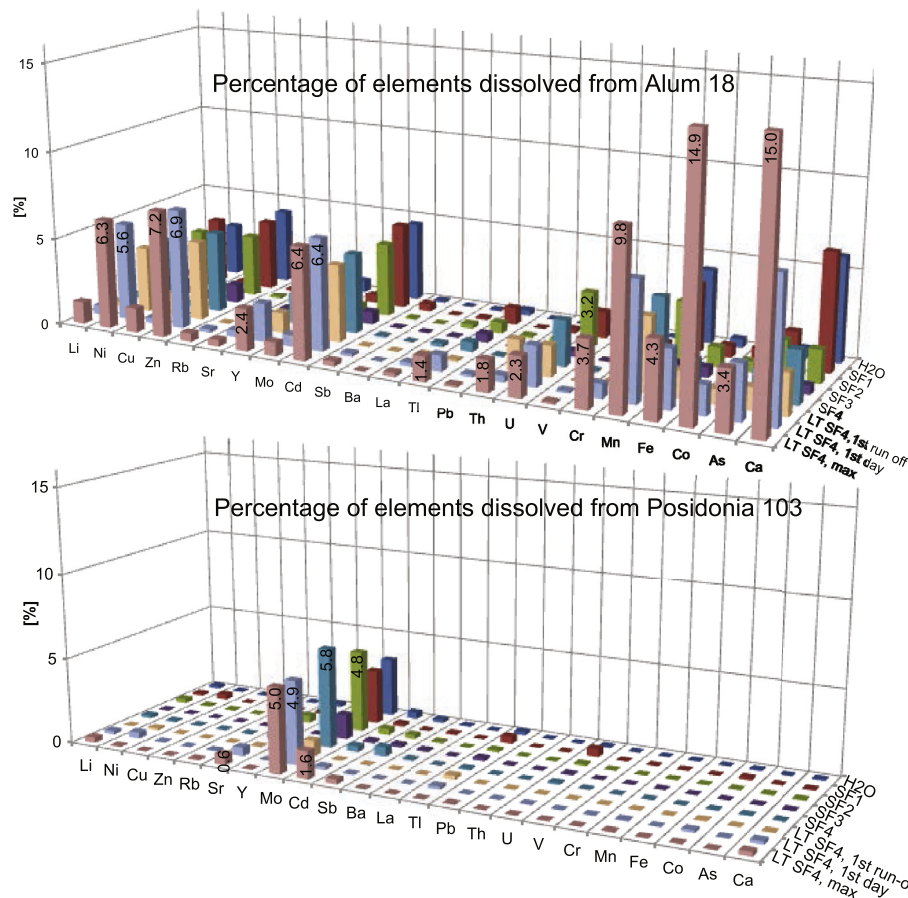
Fig. 4. Calculated percentage of elements released from the Alum and Posidonia shale into the stimulation fluids during and after experiments. Short-term experiments (24 h, 100 °C, 1 bar) are shown as "H_2O", SF1, SF2, SF3, SF4 (see Table 1 for details). Long-term experiments (experiments lasting 184 days with Alum and 64 days with Posidonia shales at 100 °C, 100 bar) are shown as: "LT SF4 1st run-off" representing the first sample taken after pressure was adjusted to 100 bar and temperature to 100 °C. The sample taken after 24 h is reflected in "LT SF4 1st day" and "LT SF4 max" is the highest concentration ever observed in the leachates from several samples throughout the running experiment.

3.6. Release of organic compounds

Extraction of the shales resulted in the release of LMW organic acids, mainly formate and acetate. When using the basic SF3, concentrations of acetate were below 1 mg/l in all samples. Concentrations of acetate were higher in extracts of Posidonia shales than of Alum shales (Fig. 5C). In general, differences in acetate concentrations were quite low for each sample irrespective of whether water, SF1, SF2 or SF4 was used for extraction. The concentrations of formate were very low in extracts of Posidonia and Alum shales using water, SF1, SF2 or SF3. But blank-corrected formate concentrations were two orders of magnitude higher in Posidonia extracts when using SF4. Formate release was also low from Alum shales when using SF4. SF1 contained 105 mg/l citrate but all SF1 extracts contained less citrate than the blank. In extracts of Alum samples only 2 mg/l citrate were detectable, citrate concentration in Posidonia samples ranged from 66 (Posidonia 119) to 33 (Posidonia 103) and 18 mg/l (Posidonia 77). No citrate was detectable in any of the other extracts.

During the long-term extraction experiments, formate, acetate, propionate, butyrate and oxalate were detected in the fluid samples (Fig. 6B). Comparing the results from Posidonia and Alum samples, the Posidonia sample released much more formate (up to 300 mg/l; Fig. 6B: 2nd vertical axis) than the Alum sample (up to 37 mg/l). Acetate concentrations were similar in both experiments (Fig. 6B). Low concentrations of propionate were detected in both experiments, but after a delay time of 2 days (Alum) or 5 days (Posidonia).

Butyrate was only detected in extracts of Alum shale in low concentrations (<1.5 mg/l) and is not given in Fig. 6B. Concentrations of oxalate reached 3 mg/l for Alum sample and up to 6.3 mg/l for the Posidonia sample.

3.7. Release of DOC and DOC fractions

From short-term experiments, only water extracts were analysed for DOC content and DOC composition by LC-OCD. DOC in water extracts of Alum 43 and Alum 18 was 3.3 and 8.3 mg C/l, respectively. Posidonia shales released comparable amounts of organic carbon; DOC in the water extracts was 5.5, 3.9 and 5.9 mg/l for Posidonia 119, Posidonia 113 and Posidonia 77, respectively. The DOC composition of both Alum shale extracts was comparable, but very different from the DOC composition of the Posidonia samples (Fig. 5D). In Alum samples, DOC consisted mainly of LMW neutral compounds, whereas water extracts of Posidonia samples were dominated by LMW acids.

DOC of the lab-made stimulation fluid SF4 was about 900 mg C/l. Due to this high background in DOC it is difficult to evaluate the much lower release of organic compounds from black shales correctly. Bulk DOC of the applied stimulation fluid SF4 mainly consisted of neutral compounds and minor percentages of biopolymers, building blocks and LMW organic acids. During the long-term extraction of the Alum shale, the percentage of neutral compounds increased very fast, the percentage of biopolymers decreased and the percentage of building blocks and LMW acids
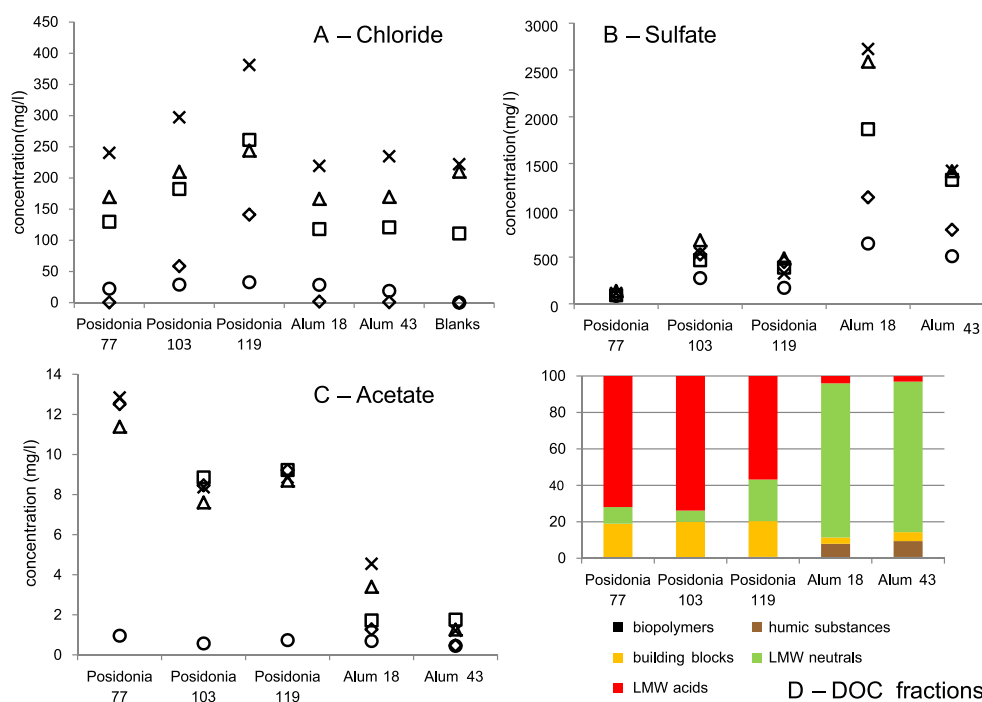
Fig. 5. A–C Results of different series of short-term extraction experiments; data from H₂O extracts are given as diamonds, SF1 extract data as rectangle, SF2 extract data as triangle, SF3 extract data as circle and SF4 extract data as cross. D) percentage of different DOC fractions in H₂O extracts.

tended to stay at the initial levels (Fig. 7). During the extraction of the Posidonia shale, the percentage of neutral compounds behaved inversely proportional to the percentage of LMW acids (Fig 7). Biopolymers became depleted during run time of the experiment but not as fast as during extraction of Alum sample.

4. Discussion

4.1. pH dependent reactions

The elemental species detected in the leachates are related to the elemental composition of the black shales but they are also highly dependent on the carbonate to pyrite ratio of the individual shale (Fig. 1A). This ratio has a pronounced influence on the pH of the leachates, while the pH of the stimulation fluid itself seems to be irrelevant (Fig. 1).

Exposed to air and moisture, sulphide minerals become oxidized and generate sulphuric acid, which causes rock disintegration and the release of elements contained therein (e.g. Jeng, 1991, 1992; Salomons, 1995). Sulphuric acid has probably been formed preferential to sulphurous acid because the experimental setup contains atmospheric oxygen, which is dissolved in the stimulation fluids. This process is very likely to occur during an initial stage of the hydraulic fracturing process because injected fluids used to contain oxygen, if not stripped with another gas (e.g. nitrogen) beforehand. By comparison of Fig. 6A with Fig. 1B one can observe that the amount of sulphate is inversely proportional to the pH in the fluids of the long term-experiments under elevated temperature and pressure. Pyrite was found in each black shale sample and is the driving force for acid generation and elemental release if only traces of or no carbonates are present. It can be assumed that the flowback may have a buffered pH of 7–8, which will result in low element loads as obtained for experiments with Posidonia shales, if the carbonate/pyrite ratio in a black shale is higher than 5. The effect of adding acids or carbonates on the total release of heavy metals was also seen in laboratory weathering

simulations with Norwegian Alum shale samples (Jeng, 1991, 1992). Therein, the milled shale was leached with distilled water for 100 days and with an acidic reaction fluid for 24 h. Lastly the solutions were treated with lime (CaCO₃) for 100 days. One shale sample with a high buffering capacity against acid, due to an elevated amount of carbonates in comparison to three other shales, was found to release much lower amounts of heavy metals like Fe, Cu, Zn, Ni and Cd. Recently, experiments with Eagle Ford shale samples (Texas, USA) from which the pH was seen to be primarily controlled by the oxidation of pyrite and the dissolution of carbonates showed the strong dependency on the release of major (Ca, Mg, Fe) and trace elements (As, U, Ba) with pH-values (Lin et al., 2014). Liming was effective and the mobility of metals ceased due to a pH > 7 (Jeng, 1992) and dissolved metals might have precipitated as hydroxides and/or carbonates (Lavergren et al., 2009). It should be noted that precipitations of sulphates or hydroxides could cover the surface of carbonates preventing further neutralization (e.g. Salomons, 1995).

During the short-term experiments under ambient pressure, the release of elements was always lower or equal to the release observed within the first day of the long-term experiments under elevated pressure, except for uranium. The highest amount of a cation was detected for iron (~2.2 g/l) during the long-term experiment with the Alum shale after 80 days. For nickel and cobalt the highest concentrations are also obtained at day 80 but the values are about 100-fold lower, reflecting the impurity status of both metals in pyrite. The dissolution patterns of iron and thallium (Fig. 3 and supplementary material) perfectly reflect the pH pattern until day 55, pointing to a comprehensive release of both elements from pyrite. The content of iron in the shale is ca. 5%, for calcium ca. 0.3%, for nickel 348 mg/l but only 148 mg/l for cobalt. With 22 mg/l of cobalt and 415 mg/l of calcium determined by ICP-MS in the fluid, nearly 15% of both elemental species were dissolved (Fig. 4). For comparison, a 9 month leaching test of non-weathered Alum shale from Öland, Sweden using distilled water adjusted to pH 4 by HNO₃ shows the pronounced release of cadmium, copper, nickel and zinc
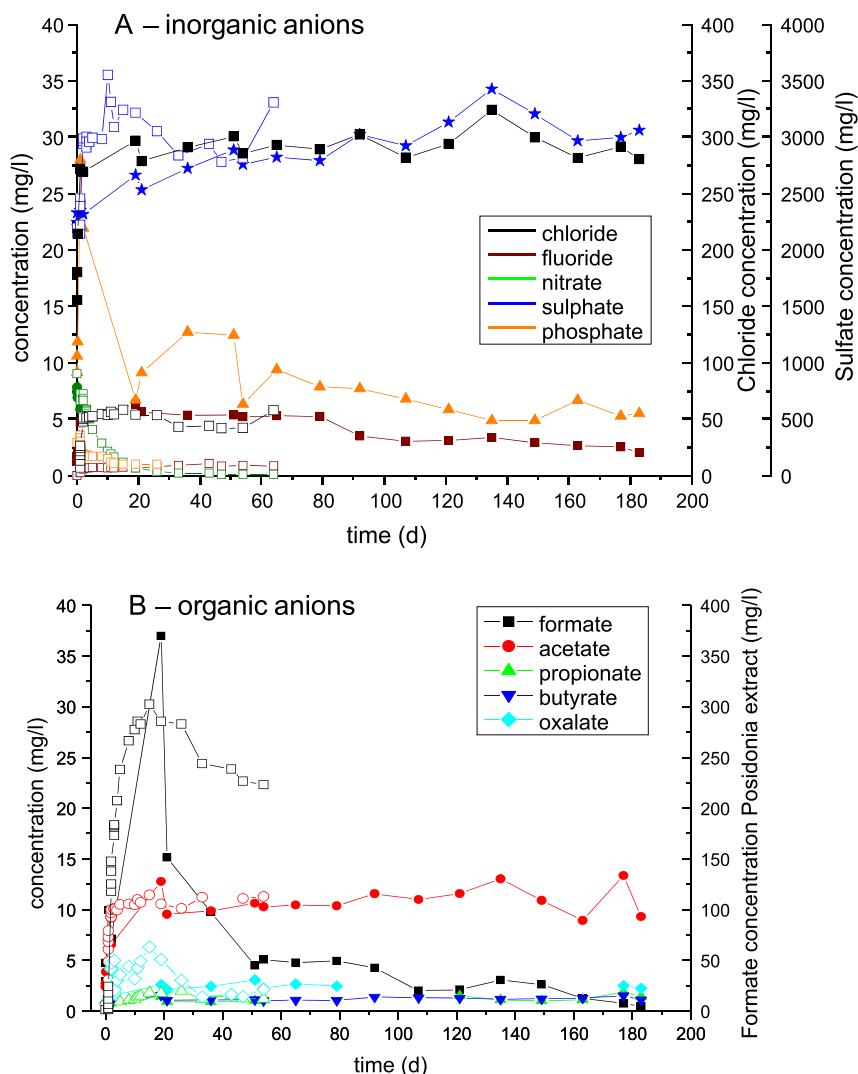
Fig. 6. Results of the two long-term extraction experiments over run time; data from Posidonia shale extracts are given with open symbols and data from Alum shale extracts with filled symbols.

(Falk et al., 2006) but with a proportion of the metal content leached out of always ≤ 17%. In contrast, with increased additions of HCl or HNO₃ towards pH 1, the Norwegian Alum shale released up to 62% Zn, 41% Ni and 26% Pb (Jeng, 1992).

4.2. Alteration products and precipitations

With the exceptions of lithium, rubidium and calcium for both long-term experiments and manganese for the experiment with the Alum shale (Fig. 3 and supplementary material), every cation shows a decreasing concentration in the reaction fluid over time. We have not changed the fluid throughout our experiment and therefore cations must be removed from the fluid by precipitation, an effect not detectable in the short-term experiments under ambient pressure. The reason for the abruptly decreasing element concentrations of iron, cobalt, nickel, zinc and thallium after day 80 remains open as there is no significant decrease in anions and pH. Using XRD, there is no detectable change in the Alum 18 solids taken before and after the experiment (Table 3). The high amount (3.2 g/l) of sulphate obtained from the fluid by IC (Fig. 6A) leads to the suggestion of possibly precipitated sulphate minerals. After drying the extracted fluid from the experiment and analyzing the residue by XRD we found traces of gypsum and minerals of the

hexahydrite group, namely moorhousite ((Cu, Ni, Mn^{2+})SO_4*6H₂O) and bianchite ((Zn, Fe^{2+}) (SO_4)*6H₂O). Both are alteration products or efflorescence of oxidizing sulphides. Nonetheless, we searched for hydroxides and found rare traces of Fe^{2+}, Mg and Zn- hydroxide. These findings were also described as artificial precipitants in deposits from heating elements in water heaters, the so-called lime-scale, so that their appearance could be foreseen in active shale gas sites. A study of progressive natural weathering of the New Albany Shale (USA) showed the precipitation of jarosite, gypsum, goethite, amorphous (Fe^{3+})-oxides and Fe^{2+}-Al sulphate salt by alteration of K-feldspar, plagioclase, calcite, pyrite and chlorite (Tuttle and Breit, 2009). Amorphous phases e.g. as thin films and nm-sized amorphous particles on mineral surfaces could also be present (e.g. Hellmann et al., 1989; Schepers and Milsch, 2013).

Regarding a directed and supported remediation via co-crystallisation with barite that is also present in the Alum 18 shale, there is the option for removing Cr (VI) and Ra^{2+} (Prieto et al., 2013 and references therein; Kondash et al., 2014). Cadmium as a highly toxic metal has similar ionic radii to calcium and the uptake of Cd^{2+} by co-precipitation on carbonate surfaces has traditionally been considered (e.g. Stipp et al., 1992). Practically, removing Cd^{2+} by calcite (Jeng, 1992) works only to a limited extend but it has been found that aragonite allows nucleation of (Cd, Ca)CO₃ crystals at the
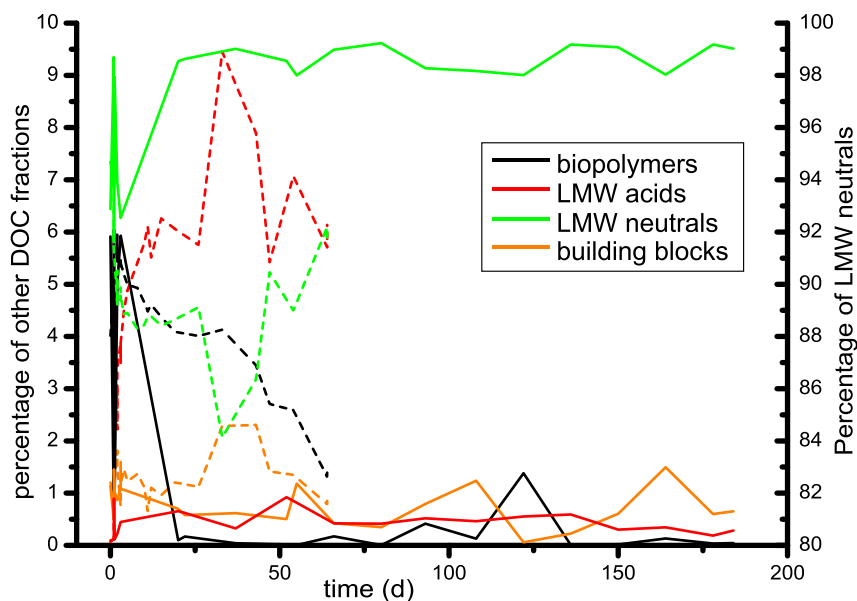
Fig. 7. Percentages of DOC fractions over run-time of the two long-term extraction experiments; data from Posidonia shale extracts are given with dashed lines and data from Alum shale extracts with solid lines. Fractions are indicated by colour (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

surface (Prieto et al., 2013). Comparing both long-term experiments, strontium was the only elemental specie found in a higher concentration in the reaction fluid using the Posidonia shale compared to the fluid from the Alum 18 experiment. Such a finding supports remediation aspects in as much as carbonate rich rocks that buffer fluids to a pH between 7 and 8 keep their heavy metals stored in the minerals and ores. Experiments with acid mine drainage fluids (AMD) reveal a maximum removal of e.g. Ra, Ba and Sr from hydraulic fracturing flowback fluids when AMD was previously treated with lime (Kondash et al., 2014). The higher concentration of strontium in the reaction fluid could be easily explained by its higher concentration in the Posidonia shale, probably due to impurities in albite, muscovite or in the carbonates. Carbonates are the most likely sources due to the comparable concentration pattern of calcium and strontium in the reaction fluid (Fig. 3) and the easier dissolution of carbonates in comparison to silicates. The high solubility of molybdenum might be due to thiomolybdates (Helz et al., 1996) and their binding to organic matter. Under oxidizing conditions, thiomolybdates will transform to mobile molybdate ions or molybdenum appears in the shale as water−soluble complexes because the organic matter became altered during diagenesis (Lavergren et al., 2009).

4.3. The behaviour of organic compounds

Black shales are known to have high TOC and the selected samples from Alum and Posidonia shales represent a high variability in TOC (Table 1). During water extraction DOC between 3.3 and 8.3 mg/l has been released from the shales. DOC of the stimulation fluid SF4 is about 900 mg/l which is three times as high as highly polluted domestic wastewaters that typically have DOC about 300 mg/l (Gordalla et al., 2013). Should DOC values be as high as these in real flowback waters, suitable disposal strategies would be required.

With our selection of shale samples from two different systems, we clearly demonstrate that the composition of the leachates, and therefore most likely also of real flowback waters, is effected by the natural organic matter composition and maturity of the shale and not only by the selected chemicals in the stimulation fluid. Based on the results of size-exclusion chromatography, the Alum and Posidonia shales tend to have their specific distribution of DOC fractions (Fig. 5D), which seem to reflect the different properties of the natural organic matter. These shale-specific patterns in DOC composition are also retained in presence of DOC-rich stimulation fluids like SF4. Due to this observation it can be assumed that even with the application of DOC-rich stimulation fluids, the resulting flowback waters tend to have very shale-specific compositions of DOC-fractions and these compositions also may change over time (Fig. 7). This variability in DOC composition makes it necessary to consider the highest concentrations with respect to exposure time when performing risk assessments for flowback waters.

The Posidonia Shale has abundant oxygen-contained species (Wilkes et al., 1998), some of which might break down to yield LMW acids on hydrolysis (e.g. Glombitza et al., 2009). Generally, the compositions of the stimulating fluids have the potential to change the mobilization of organic compounds from shales (e.g. SF4 tended to enhance the mobilization of formate). 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 formate released from the natural organic matter of the shale may have been enhanced by the chemical additives or whether the organic polymers within the stimulation fluids may have been the subject of decarboxylation and generation of formate at the environmental conditions of the shale formations. The release of formate in Posidonia leachates could be the results of subtle interactions between shale and chemical additives as no strong release of formate was observed in Alum leachates. These results may also complicate the application of formate and acetate concentration as tracers for stimulation fluids.

5. Conclusions

The long-term studies conducted under elevated temperature and pressure conditions reflect known naturally occurring p/T conditions in possible shale gas sites in Germany in a broad sense (e.g. Olsson et al., 2013). Furthermore, monitoring the mobility of inorganic and organic constituents over time allows for realistic insights into time-resolved processes that might occur in an active

shale site as it evolves during stimulation and production. Nonetheless, for evaluation of our results it must be stated that the surface area of the small grain size fractions used during the experiments is enormous, and not necessarily similar to the surface area that is available during hydraulic fracturing. However, the high water to rock ratio used during the experiments will influence the results in the opposite direction so that both effects could be compensated. As no flowback or production waters from active shale gas sites tapping these shale units were available for comparison our study can just give a first insight into possibly mobilized constituents.

Sulphide oxidation of black shales is sufficient to produce acidic waters (pH 2—3), which lead to alteration and disintegration of minerals and leachates with an elevated content of several metals like As, Cd, Co, Cr, Fe, Mo, Ni, U and Zn. The pH of the stimulation fluid used throughout our experiments was demonstrated to be irrelevant, even with a high solid to liquid ratio of 1:12.5. The use of the stimulation fluid with commercially—available additives lead to highest elemental load and to the formation of formate instead of acetate. Interestingly, the proportion of elements leached out is always less than 15%, which has only been obtained when the black shale contains pyrite but only traces of carbonates. If the black shale contains excess carbonate in comparison to pyrite the amount of elemental species released was remarkably lower and with dependent on impurities in the carbonates. It should be noted that pure water used as stimulation fluid lead to the lowest concentrations of cations and anions in the leachates.

Acknowledgements

Appendix A. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2015.07.008.

References

Arthur, J.D., Bohm, B., Layne, M., 2008. Hydraulic Fracturing Considerations for Natural Gas Wells of the Marcellus Shale. The Ground water protection council 2008 Annual Forum, Cincinnati, Ohio.

Falk, H., Lavergren, U., Bergbäck, B., 2006. Metal mobility in alum shale from Öland, Sweden. J. Geochem. Explor. 90, 157—165.

Glombitza, C., Mangelsdorf, K., Horsfield, B., 2009. Maturation related changes in the distribution of ester bound fatty acids and alcohols in a coal series from the New Zealand Coal Band covering diagenetic to catagenetic coalification levels. Org. Geochem. 40, 1063—1073.

Gordalla, B.C., Ewers, U., Frimmel, F.H., 2013. Hydraulic fracturing: a toxicological threat for groundwater and drinking-water? Environ. Earth Sci. 70, 3875—3893.

Gregory, K.B., Vidic, R.D., Dzombak, D.A., 2011. Water management challenges associated with the production of shale gas by hydraulic fracturing. Elements 7, 181—186.

Hellmann, R., Crerar, D.A., Zhang, R., 1989. Albite feldspar hydrolysis to 300°C. Solid State Ionics 32—33, 314—329.

Helz, G.R., Miller, C.V., Charnock, J.M., Mosselmans, J.F.W., Patrick, R.A.D., Garner, C.D., Vaughan, D.J., 1996. Mechanism of molybdenum removal from the sea and its concentration on black shales: EXAFS evidence. Geochim. Cosmochim. Acta 60, 3631—3642.

Horsfield, B., Schulz, H.-M., Aplin, A., Doornenbal, H., Moretti, I., Lorant, F., Thomas, R., 2010. Shale gas research: the way forward for Europe. Oilfield Technol. 3, 14—18.

Huber, S.A., Frimmel, F.H., 1996. Gelchromatographie mit Kohlenstoffdetektion (LC-OCD): ein rasches und aussagekräftiges Verfahren zur Charakterisierung hydrophoiler organischer Wasserinhaltsstoffe. Vom Wasser 86, 277—290.

Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography—organic carbon detection—organic nitrogen detection (LC-OCD-OND). Water Res. 45 (2), 879—885.

Jeng, A.S., 1991. Weathering of Norwegian Alum shales, I. Laboratory simulations to study acid generation and the release of sulphate and metal cations (Ca, Mg & K). Acta Agric. Scand. Sect. B — Soil Plant Sci. 41, 13—35.

Jeng, A.S., 1992. Weathering of Norwegian Alum shales, II. Laboratory simulations to study the influence of aging, acidification and liming on heavy metal release. Acta Agric. Scand. Sect. B — Soil Plant Sci. 42, 76—87.

King, G.E., 2012. Hydraulic fracturing 101: what every representative, environmentalist, regulator, reporter, investor, university researcher, neighbor and engineer should know about estimating frac risk and improving frac performance in unconventional gas and oil wells. In: SPE Hydraulic Fracturing Technology Conference. Society of Petroleum Engineers.

Kondash, A.J., Warner, N.R., Lahav, O., Vengosh, A., 2014. Radium and barium removal through blending hydraulic fracturing fluids with acid mine drainage. Environ. Sci. Technol. 48, 1334—1342.

Lavergren, U., Åström, M.E., Bergbäck, B., Holmström, H., 2009. Mobility of trace elements in black shale assessed by leaching tests and sequential chemical extraction. Geochem. Explor. Environ. Anal. 9, 71—79.

Lester, Y., Ferrer, I., Thurman, E.M., Sitterley, K.A., Korak, J.A., Aiken, G., Linden, K.G., 2015. Characterization of hydraulic fracturing flowback water in Colorado: implications for water treatment. Sci. Total Environ. 512—513, 637—644.

Lin, W., Fortner, J.D., Giammar, D.E., 2014. Impact of water chemistry on element mobilization from Eagle Ford Shale. Environ. Eng. Sci. 32, 310—320.

Maguire-Boyle, S.J., Barron, A.R., 2014. Organic compounds in produced waters from shale gas wells. Environ. Sci. Process. Impacts 16, 2237—2248.

Meiners, H.G., Denneborg, M., Müller, F., Bergmann, A., Weber, F.-A., Dopp, E., Hansen, C., Schüth, C., 2012. Umweltauswirkungen von Fracking bei der Aufsuchung und Gewinnung von Erdgas aus unkonventionellen Lagerstätten — Risikobewertung, Handlungsempfehlungen und Evaluierung bestehender rechtlicher Regelungen und Verwaltungsstrukturen. Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit.

Olsson, O., Weichgrebe, D., Rosenwinkel, K.-H., 2013. Hydraulic fracturing wastewater in Germany: composition, treatment, concerns. Environ. Earth Sci. 70, 3895—3906.

Prieto, M., Astilleros, J.M., Fernández-Díaz, L., 2013. Environmental remediation by crystallization of solid solutions. Elements 9, 195—201.

Raiswell, R., Berner, R.A., 1985. Pyrite formation in euxinic and semi-euxinic sediments. Am. J. Sci. 2858, 710—724.

Rullkötter, J., Leythaeuser, D., Horsfield, B., Littke, R., Mann, U., Müller, P.J., Radke, M., Schaefer, R.G., Schenk, H.-J., Schwochau, K., Witte, E.-G., Welte, D.H., 1988. Organic matter maturation under the influence of a deep intrusive heat source: a natural experiment for quantitation of hydrocarbon generation and expulsion from a petroleum source rock (Toarcian Shale, Northern Germany). Org. Geochem. 13, 847—856.

Salomons, W., 1995. Environmental impact of metals derived from mining activities: processes, predictions, prevention. J. Geochem. Explor. 52, 5—23.

Schepers, A., Milsch, H., 2013. Dissolution-precipitation reactions in hydrothermal experiments with quartz-feldspar aggregates. Contrib. Mineral. Petrol. 165, 83—101.

Schulz, H.-M., Biermann, S., van Berk, W., Krüger, M., Straaten, N., Bechtel, A., Wirth, R., Lüders, V., Schovsbo, N.H., Crabtree, S., 2015. From shale oil to biogenic shale gas: retracing organic—inorganic interactions in the Alum Shale (Furongian—Lower Ordovician) in southern Sweden. AAPG Bull. 99, 927—956.

SEAB, 2011. The SEAB Shale Gas Production Subcommittee. Ninety-Day Report.

Stipp, S.L., Hochella Jr., M.F., Parks, G.A., Leckie, J.O., 1992. Cd^{2+} uptake by calcite, solid-state diffusion, and the formation of solid-solution: interface processes observed with near-surface sensitive techniques (XPS, LEED, and AES). Geochim. Cosmochim. Acta 56 (5), 1941—1954.

Strong, L.C., Gould, T., Kasinkas, L., Sadowsky, M.J., Aksan, A., Wackett, L.P., 2013. Biodegradation in waters from hydraulic fracturing: chemistry, microbiology and engineering. J. Environ. Eng. 140.

Thurman, E.M., Ferrer, I., Blotevogel, J., Borch, T., 2014. Analysis of hydraulic fracturing flowback and produced waters using accurate mass: identification of ethoxylated surfactants. Anal. Chem. 86, 9653—9661.

Tuttle, M.L.W., Breit, G.N., 2009. Weathering of the New Albany Shale, Kentucky, USA: I. Weathering zones defined by mineralogy and major-element composition. Appl. Geochem. 24, 1549—1564.

Waxman, H.A., Markey, E.J., Degette, D., 2011. Chemicals Used in Hydraulic Fracturing. U.S. House of Representatives Committee on Energy and Commerce Minority Staff.

Wilke, F.D.H., Vásquez, M., Wiersberg, T., Naumann, R., Erzinger, J., 2012. On the interaction of pure and impure supercritical CO$_2$ with rock forming minerals in saline aquifers: an experimental geochemical approach. Appl. Geochem. 27, 1615—1622.

Wilkes, H., Disko, U., Horsfield, B., 1998. Aromatic aldehydes and ketones in the Posidonia Shale, Hils Syncline, Germany. Org. Geochem. 29, 107—117.

Wood, R., Gilbert, P., Sharmina, M., Anderson, K., 2011. Shale Gas: a Provisional Assessment of Climate Change and Environmental Impacts. The Tyndall Centre Manchester. Final draft.