

PS Probing the Influence of Reactions between Fracture Fluids and Marcellus Shale on the Composition of Major Ion and Trace Element Fluid Chemistry in Flowback Waters*

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Search and Discovery Article #80302 (2013)**

Posted July 29, 2013

*Adapted from poster presentation given at AAPG 2013 Annual Convention and Exhibition, Pittsburgh, Pennsylvania, May 19-22, 2013

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Abstract

Increased natural gas production from shales is due to the deployment of hydraulic fracturing technologies. Current practices employ large volumes of water with chemical additives, and result in the production of flowback waters that require treatment before reuse or disposal. An understanding of changes in fluid chemistry due to fracturing fluid-shale reactions provides direct input for reservoir design, and may guide development of strategies for managing and disposal of solid and liquid wastes.

In this study we investigated Marcellus Shale metal extractability and reactivity with fracturing fluids through bulk extractions, and fracture fluid-shale reactions in high pressure, high temperature autoclave systems. The primary goals for this study are to evaluate the role of shale-fluid reactions on controlling flowback water chemistry, and to evaluate the potential for metals to be extracted from organic-rich shales under various environmental conditions.

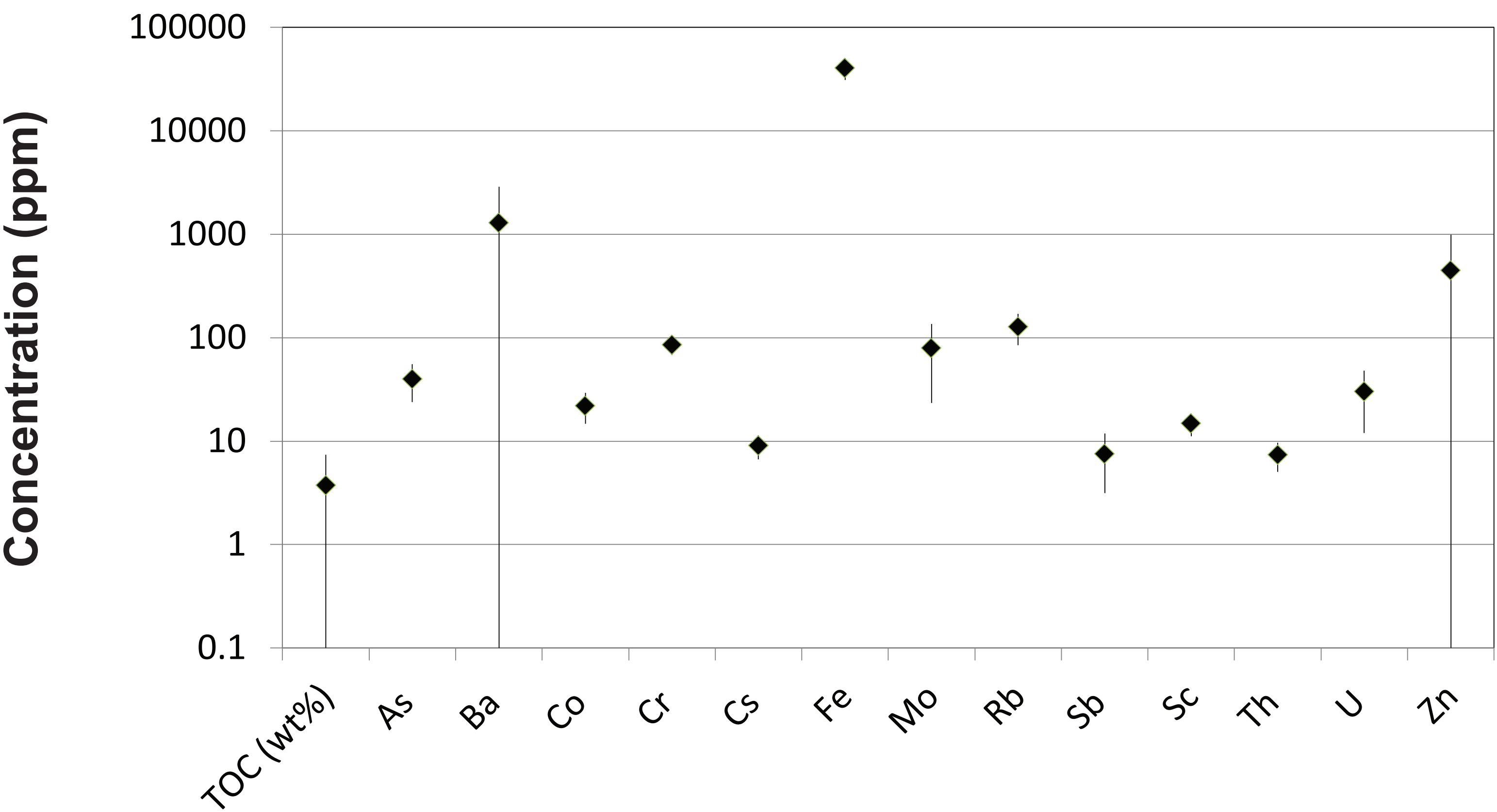
Metal extractability studies focused on Marcellus Shale core and outcrop powders and rock chips were performed under different temperature and pressure conditions with a variety of extractants. Reactions between synthetic fracturing fluids (designed based on information from FracFocus) and Marcellus Shale core are ongoing in high pressure, high temperature autoclave systems to evaluate changes to both trace element and total dissolved solids composition of the fluid, and changes to rock morphology and mineralogy, over time. Experimental results will be used to identify the primary solid phases controlling changes to fluid chemistry.

Our results to date show that, despite no statistical differences in trace metal concentrations in core and outcrop samples, extractability varies as a function of sample type and, generally, metal extractability is higher in outcrop samples. For example, in batch extractions using powdered

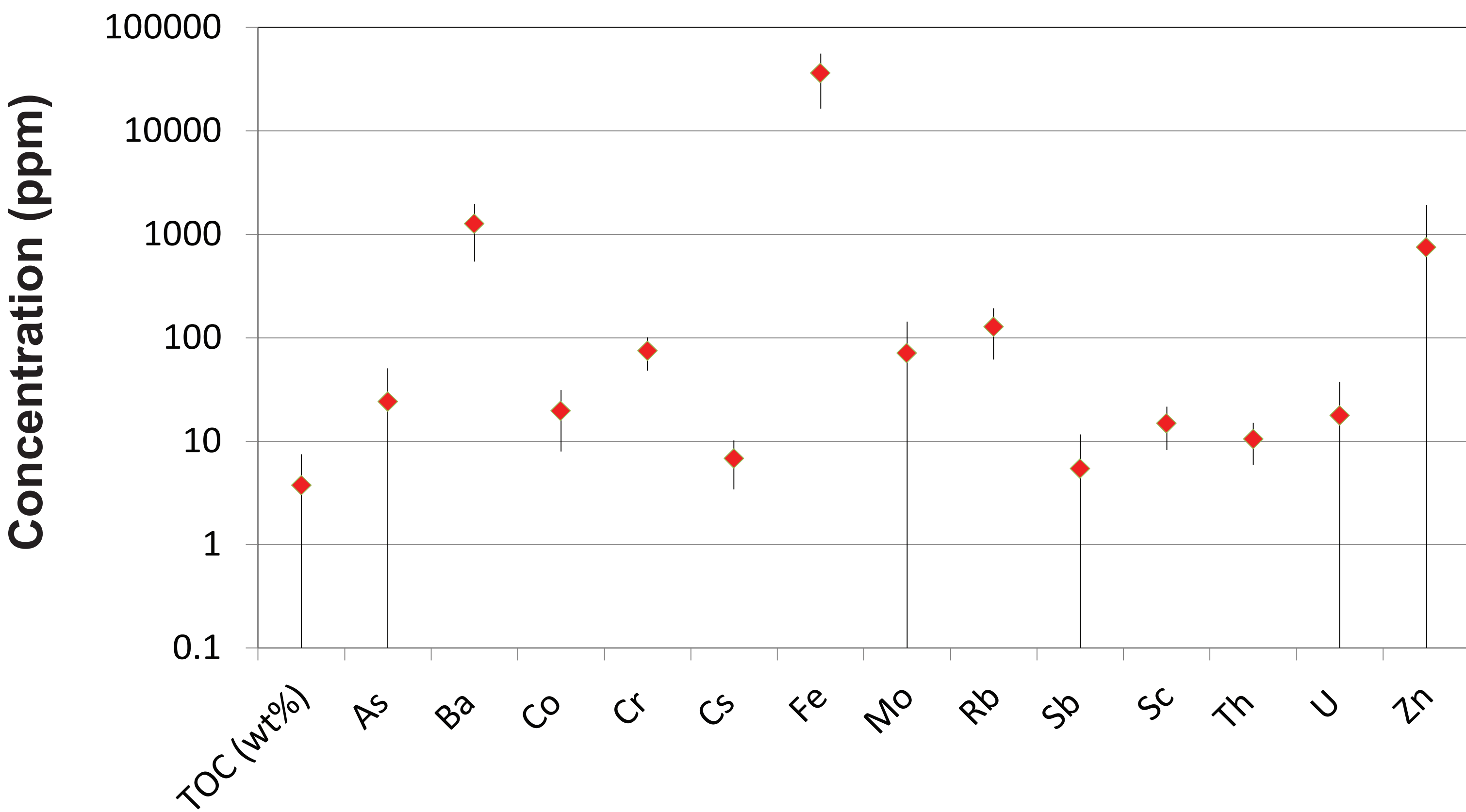
rock samples the extractability of U by oxidation of the organic matter with H_2O_2 is higher in outcrops (~10%) compared to cores (~0%) . For our rocking autoclave experiments, we anticipate that reactions between synthetic fracturing fluid and natural carbonate and clay minerals present in our samples will result in observable geochemical changes. Ongoing studies will 1) determine the rate of metal leaching and the influence of increased surface area on metal extractability, and 2) identify the primary reactions that occur between fracturing fluids and shales.

Total Trace Elements in Marcellus Shale Samples

Core

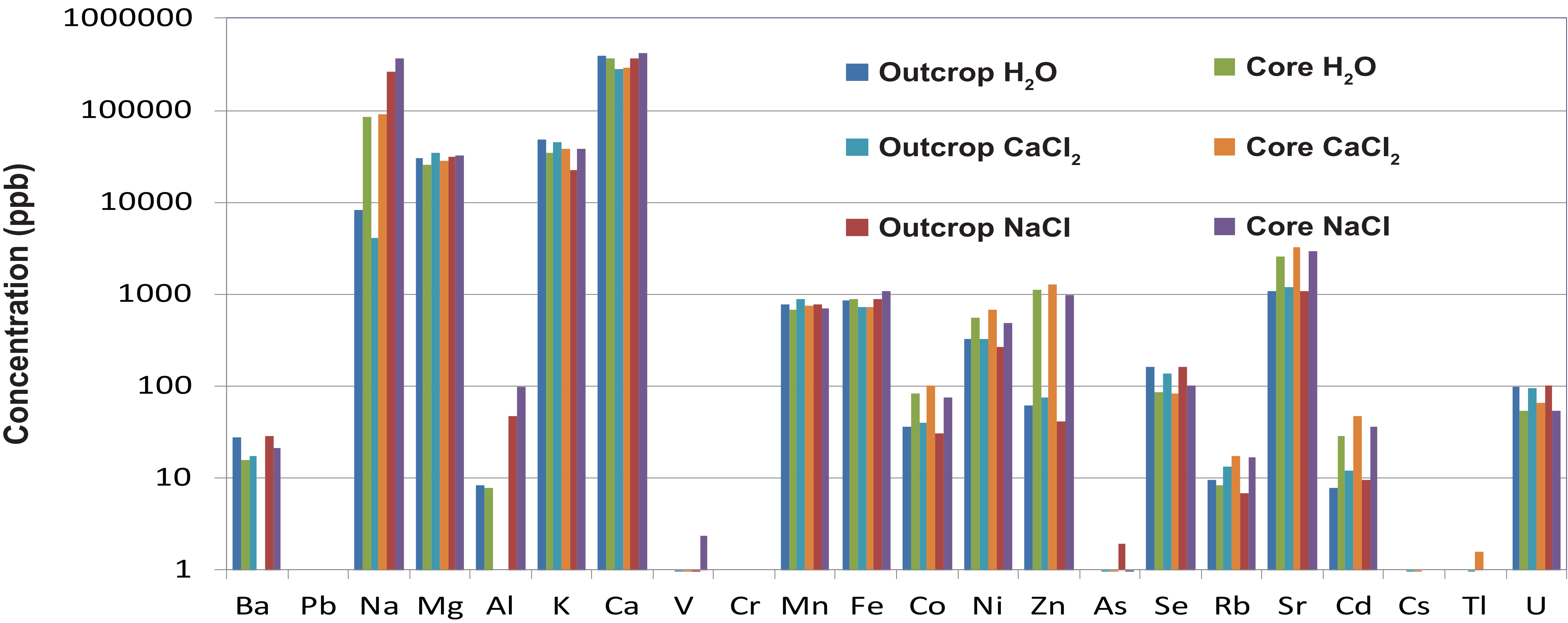


Outcrop



Metal concentrations for 24 core (left) and 14 outcrop (right) samples. Data points represent the average for each sample set, with value ranges representing the standard deviation for each set. Trace metal analyses were performed on samples ground to finer than 250 μ m. Samples were analyzed using Instrumental Neutron Activation Analyses (INAA) at Activation Laboratories in Ancaster, Ontario.

Trace Elements Extracted by Saline Solutions (Benchtop)



Metal concentrations in supernatant from extractions performed with one Marcellus Shale core sample ("Core") and one Marcellus Shale outcrop sample ("Outcrop").

Limited metal mobilization observed between weakly saline solutions and shales.

Low Ba concentrations measured due to formation of precipitates that settled.

Extraction solutions consisted of either: deionized water ("H₂O"); 10 mM CaCl₂; or 10 mM NaCl. Each batch extraction was performed at 25°C and 1 atm pressure for 2 months. Supernatant solutions were analyzed for elemental concentrations by ICP-MS.

Design of Autoclave Batch Experiments (Elevated P,T)

- Purpose:** Evaluate metal release and mineral reactions in Marcellus Shales at elevated pressures and temperatures to simulate geochemical reactions that may occur during hydraulic fracturing.
- Apparatus:** Dual-furnace rocking autoclave with flexible gold-titanium reaction cells within steel pressure vessels (Seyfried et al., 1987).
- Parameters:** 20:1 fluid:rock ratio, 275 bars (4000 psi), 130°C, 16 days. Geochemical models predicted the upper temperature limit for in situ mineral reactions, and experiments were performed at elevated temperature relative to formation conditions in order to drive reaction kinetics.
- Materials:** Synthetic brine (designed to mimic natural formation waters) and fracturing fluid (developed based on information collected from Frac Focus). Marcellus Shale cores from 7846 ft were ground to 147 μ m and combined with polished rock chips.



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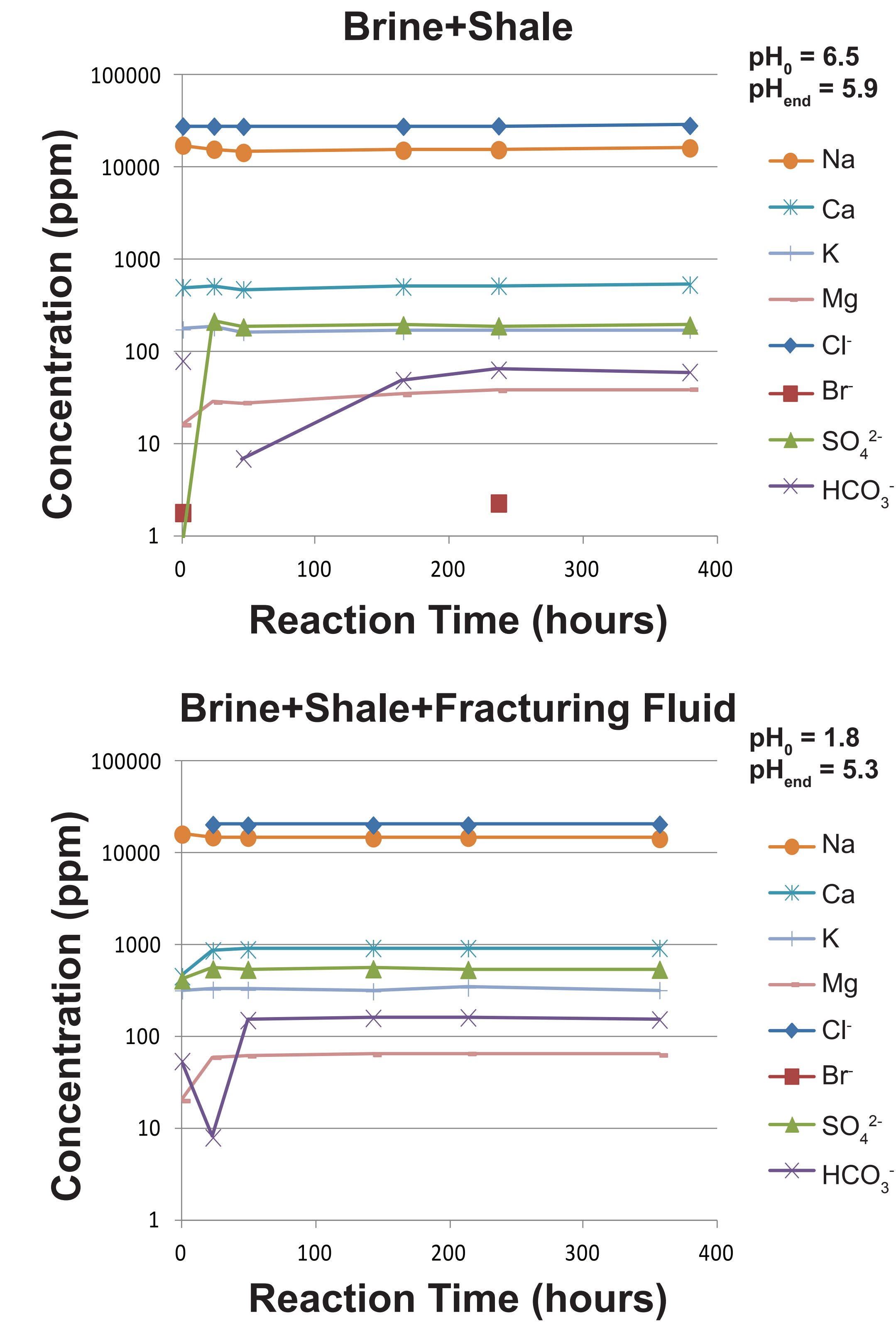
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Current hydraulic fracturing practices employ large volumes of water with some chemical additives, and also result in the production of produced waters that require treatment before reuse or disposal. An understanding of changes in fluid chemistry due to fluid-shale reactions provides direct input for reservoir design, and also may guide development of strategies for recycling, management and disposal of produced waters.

In this study we investigated Marcellus Shale metal extractability, and reactivity with fracturing fluids, through bulk extractions and experiments in high-pressure, high-temperature autoclave systems.

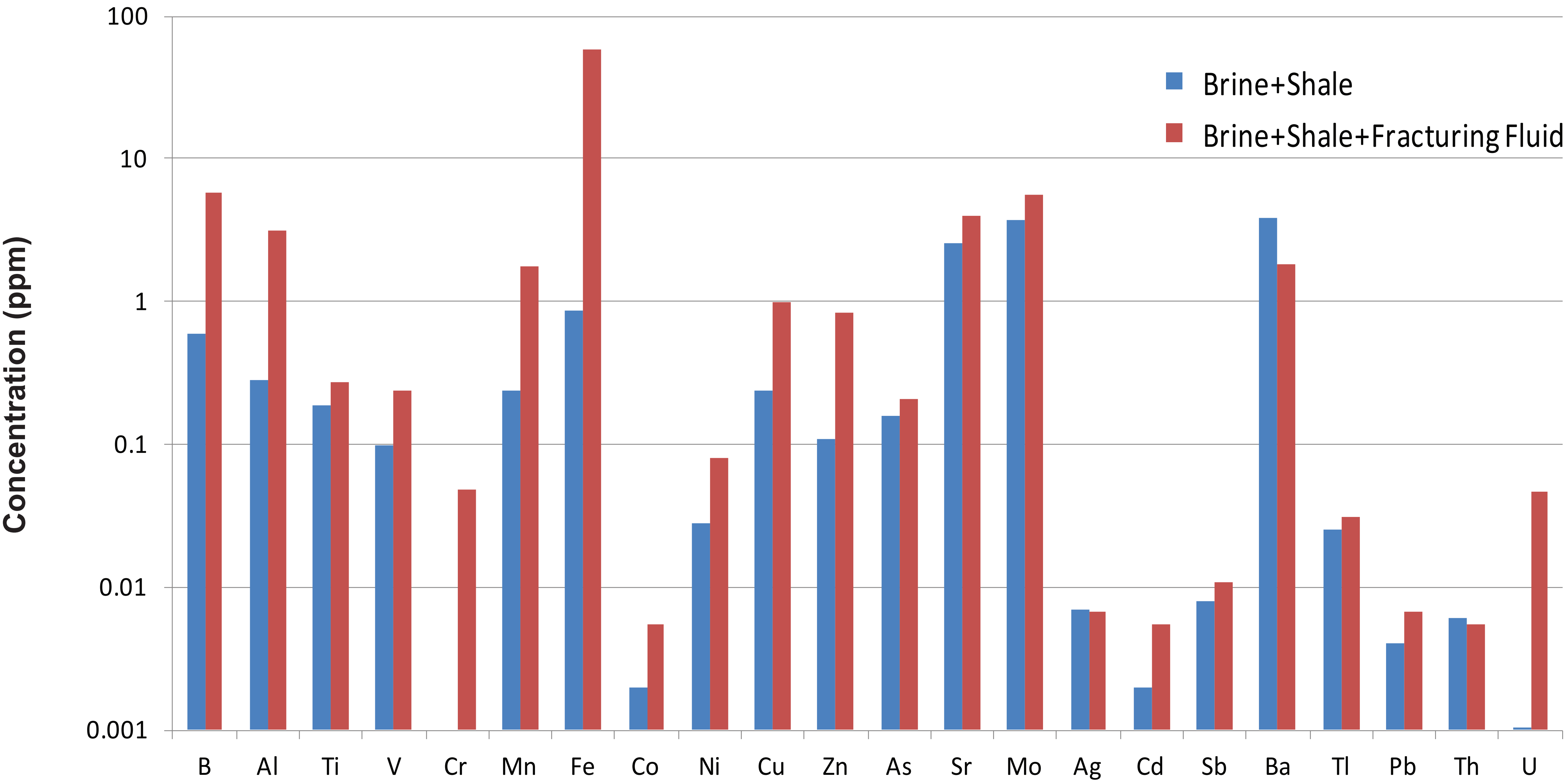
The primary goals for this study are to evaluate the role of shale-fluid reactions on controlling produced water chemistry, and to evaluate the potential for metals to be extracted from organic-rich shales under various environmental conditions.

Major Elements Released (Autoclave Experiments)



Major cations and anions released during experiments with fracturing fluid ("Brine+Shale+Fracturing Fluid") and a control ("Brine+Shale") at 275 bars and 130°C, measured by ICP-OES, ICP-MS, and ion chromatography. Lines are shown to illustrate trends and do not represent data fits. In situ pH values were calculated using pH and dissolved inorganic carbon measured at STP.

Trace Elements in Solution after ~ 15 Days of Reaction with Fracturing Fluids (Autoclave Experiments)

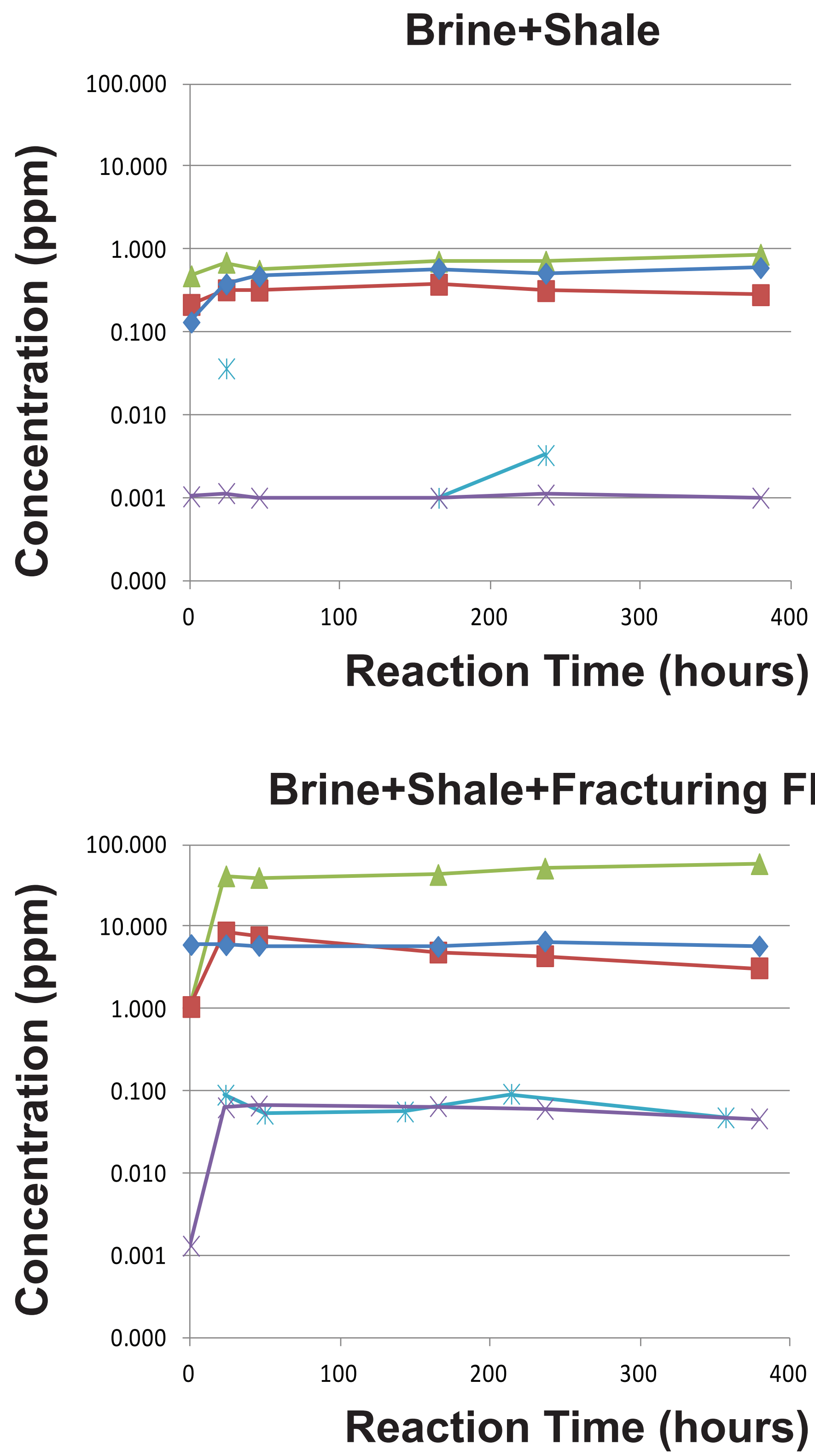


Trace element concentrations after 15 days of reaction in the rocking autoclave show enrichment of most elements in the experiment containing fracturing fluid ("Brine+Shale+Fracturing Fluid") relative to the control experiment ("Brine+Shale") (bar plot above; table below). Cr only was detected in the experiment with fracturing fluid. Ba and Th are elevated in the control experiments.

Values in the table represent the ratio of concentration in the experiment with fracturing fluid to concentration in the control at ~15 d. "FF-only" indicates that the element only was detected in the sample from the experiment with fracturing fluid. Concentrations were measured by ICP-MS.

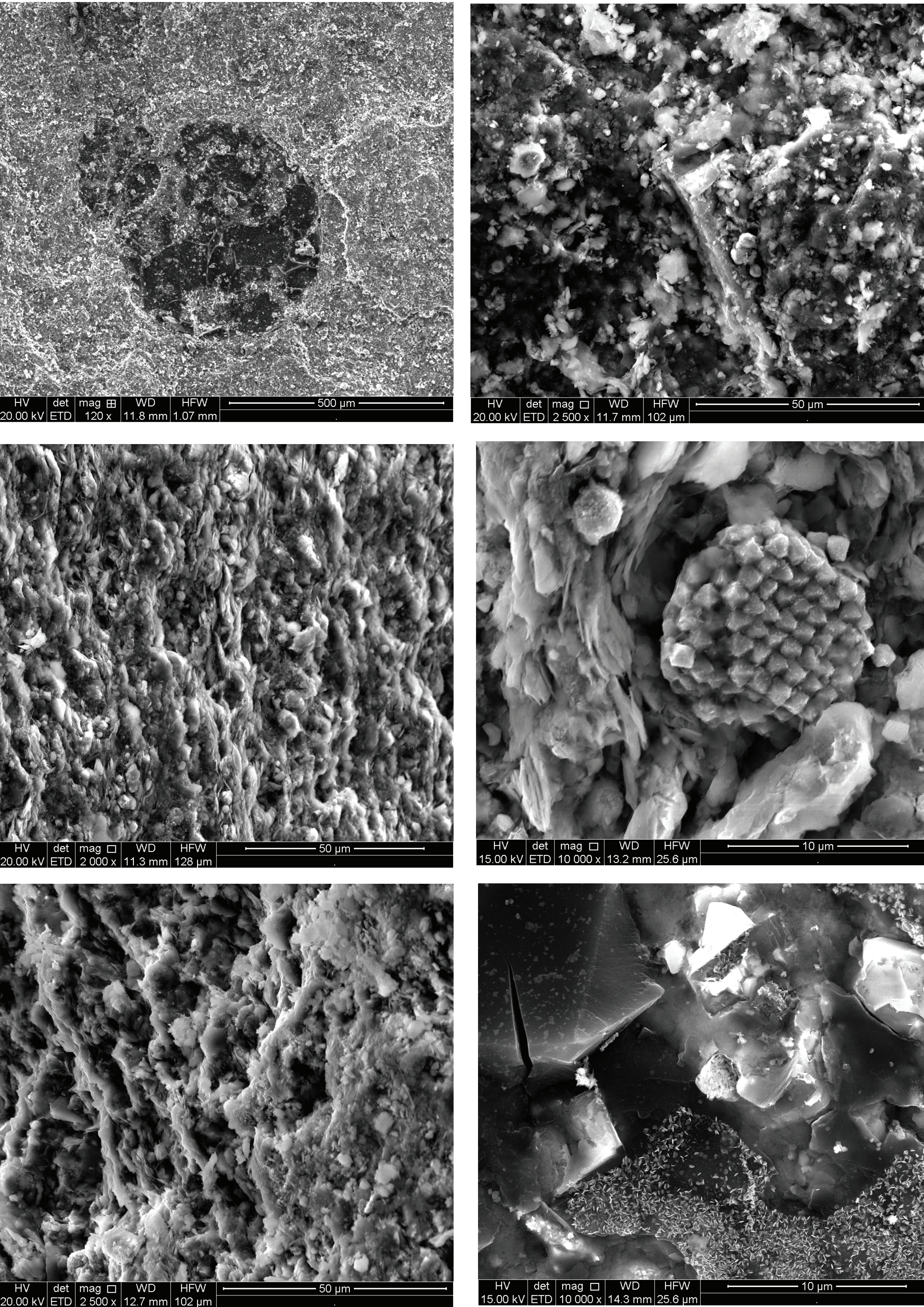
Element	Cr	Fe	U	Al	B	Zn	Mn	Cu	Ni	Co	Cd	V	Pb	Ti	Sr	Mo	Sb	As	Tl	Ag	Th	Ba
Enrichment in experiment with fracturing fluid relative to control	FF-only	67.0	46.2	11.1	9.7	7.6	7.4	4.2	2.9	2.7	2.7	2.4	1.7	1.5	1.5	1.5	1.4	1.3	1.3	1.0	0.9	0.5

Changes in Solid Phases (Autoclave Experiments)



Time series for both experiments show that trace elements with the greatest enrichment (> 10x) in experiments with fracturing fluids approach a steady state within 48 h of starting the experiment.

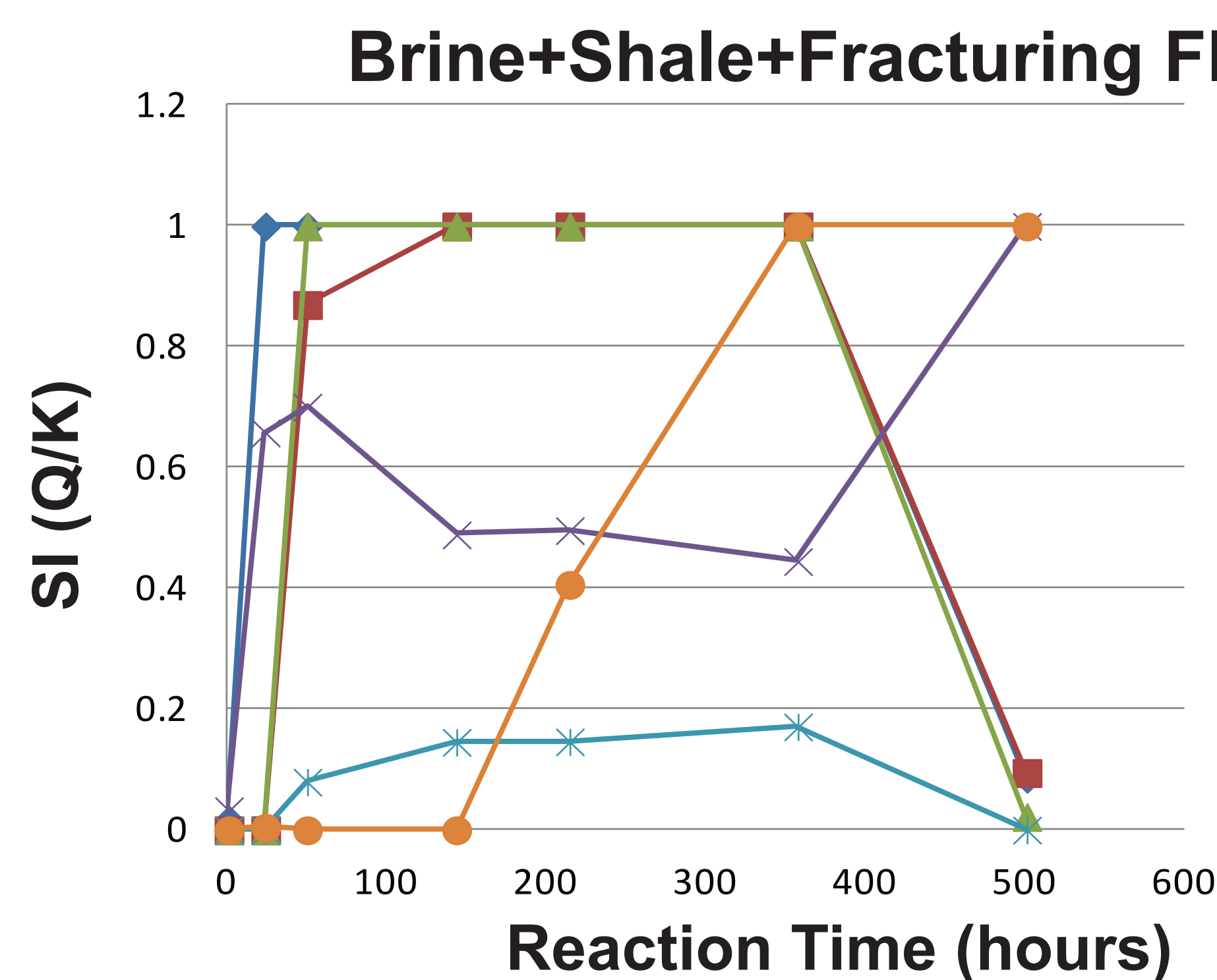
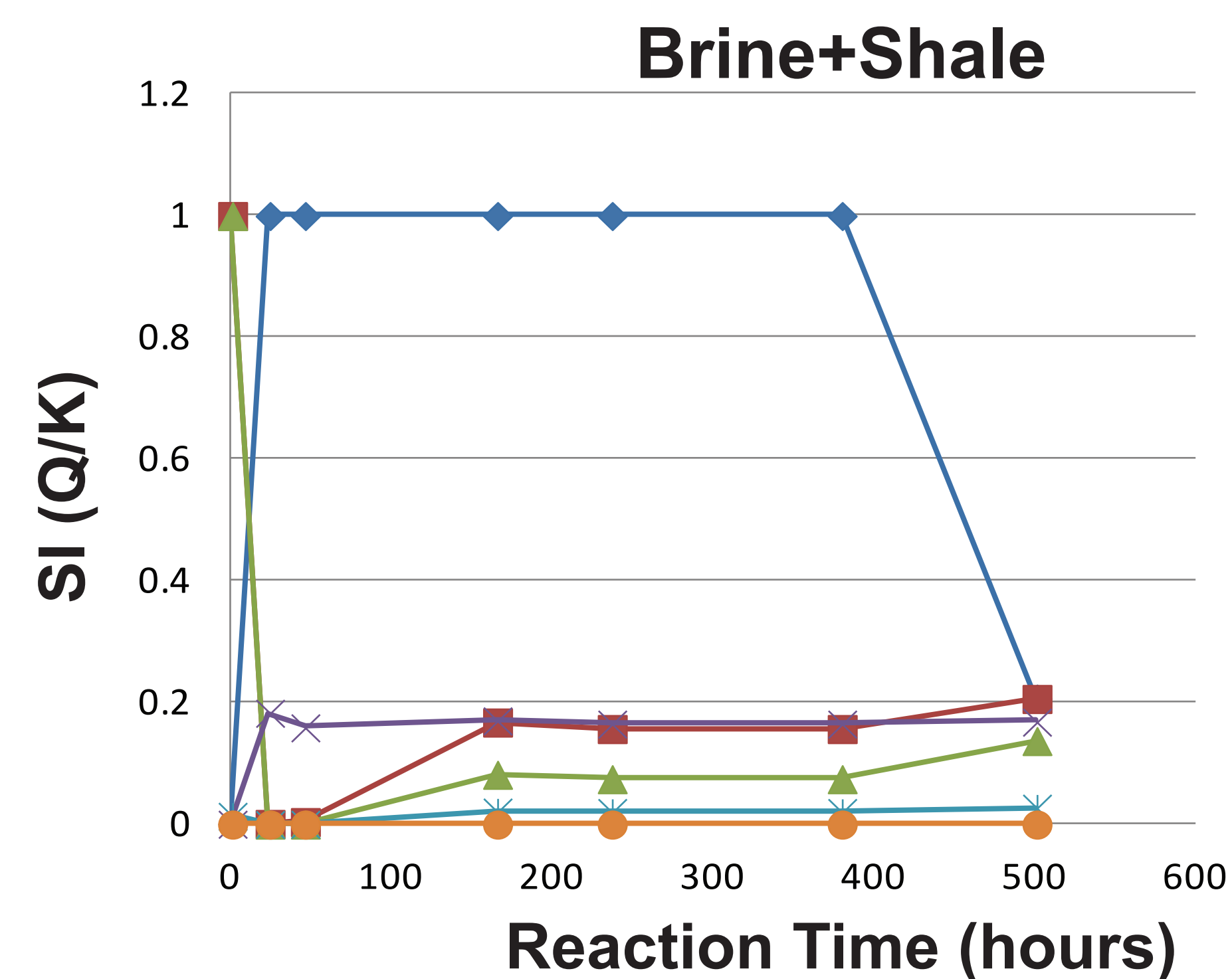
Lines are shown to illustrate trends and do not represent data fits. Concentrations were measured by ICP-MS.



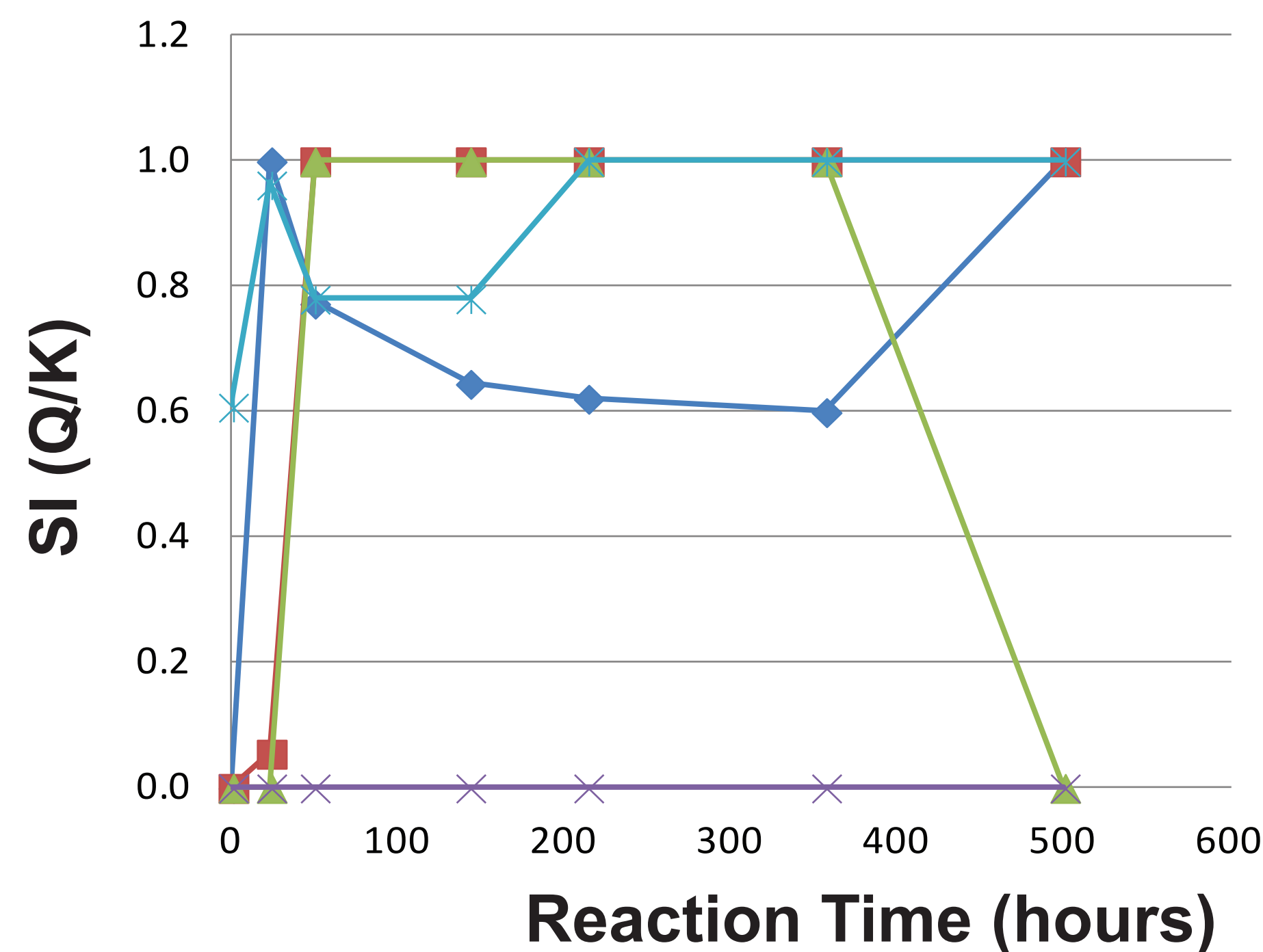
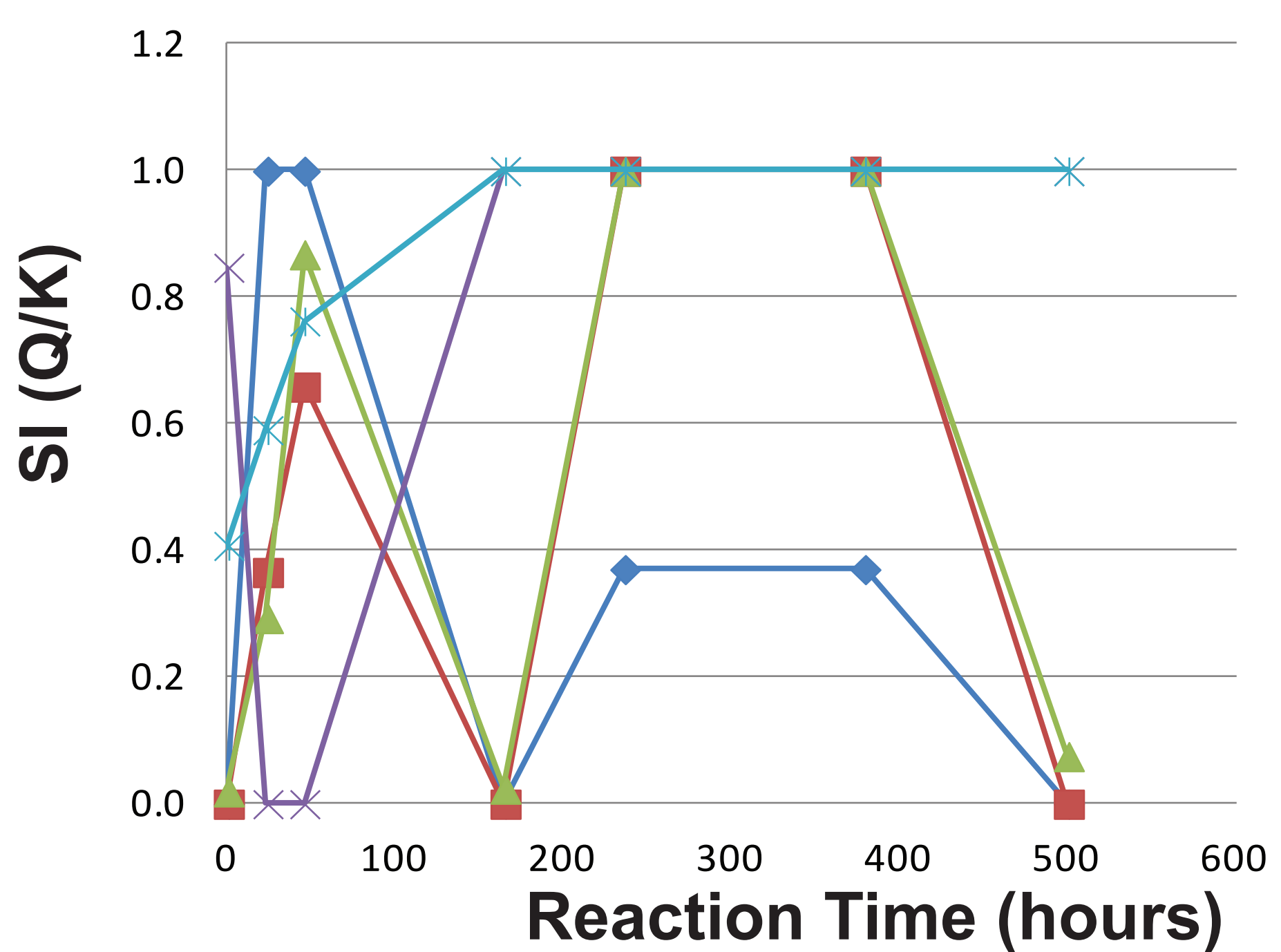
SEM images collected for Marcellus Shale samples used for the rocking autoclave experimental work.

The samples are clay-rich, and contain pyrite and organic matter. Total inorganic carbon concentrations (TIC) indicate dissolution of carbonate minerals during both experiments, with a greater magnitude in the experiment with fracturing fluid which also showed evidence of mineral precipitation.

Mineral Stability Evaluated by Geochemical Modeling (Autoclave Experiments)



Saturation indices calculated using experimental fluid data (Geochemist's Workbench v 9.0) show that after 16 days enough Ba, Fe and SO_4^{2-} are present in solution to allow for barite, pyrite and anhydrite precipitation in the autoclave experiment with fracturing fluid.

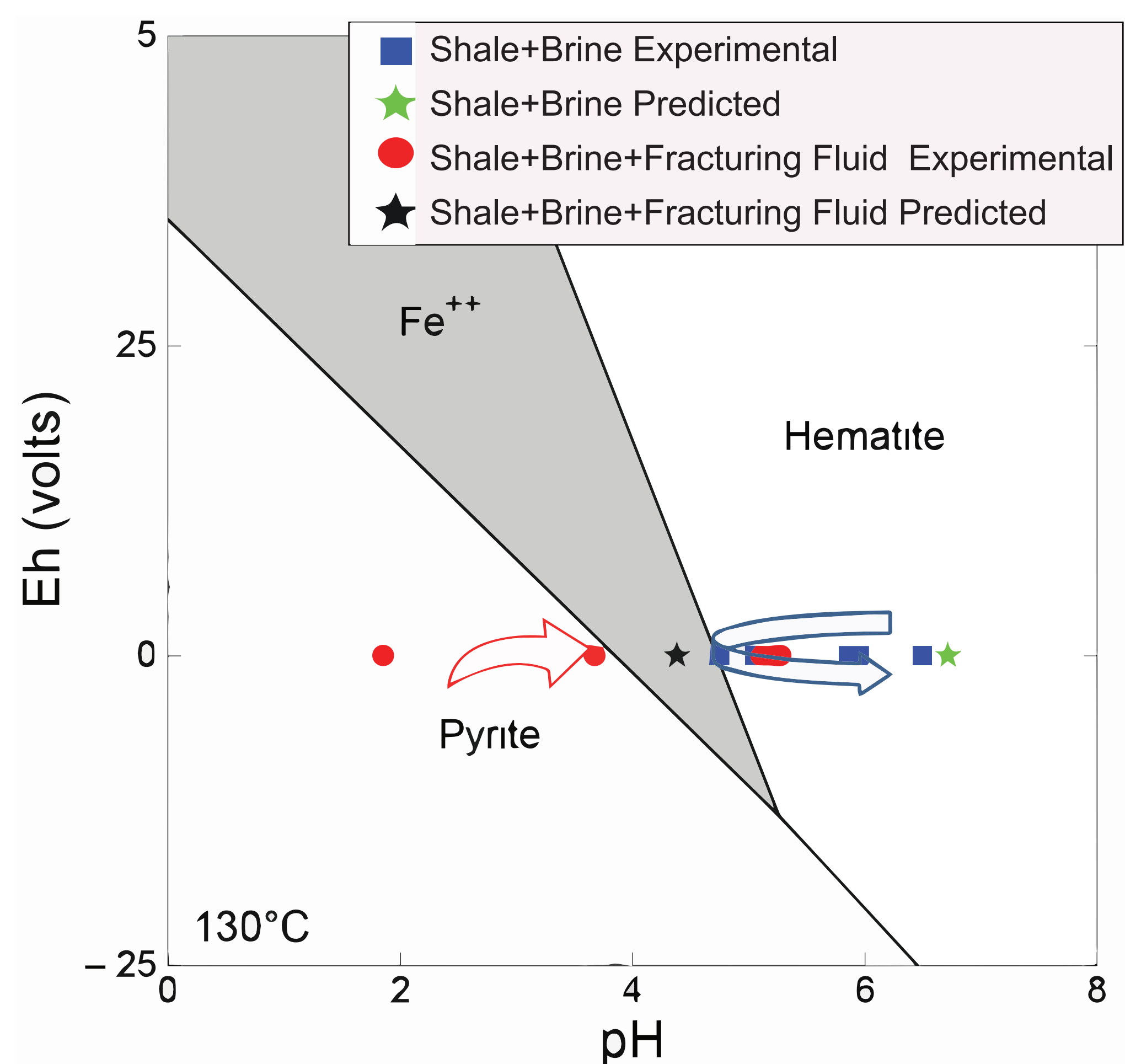
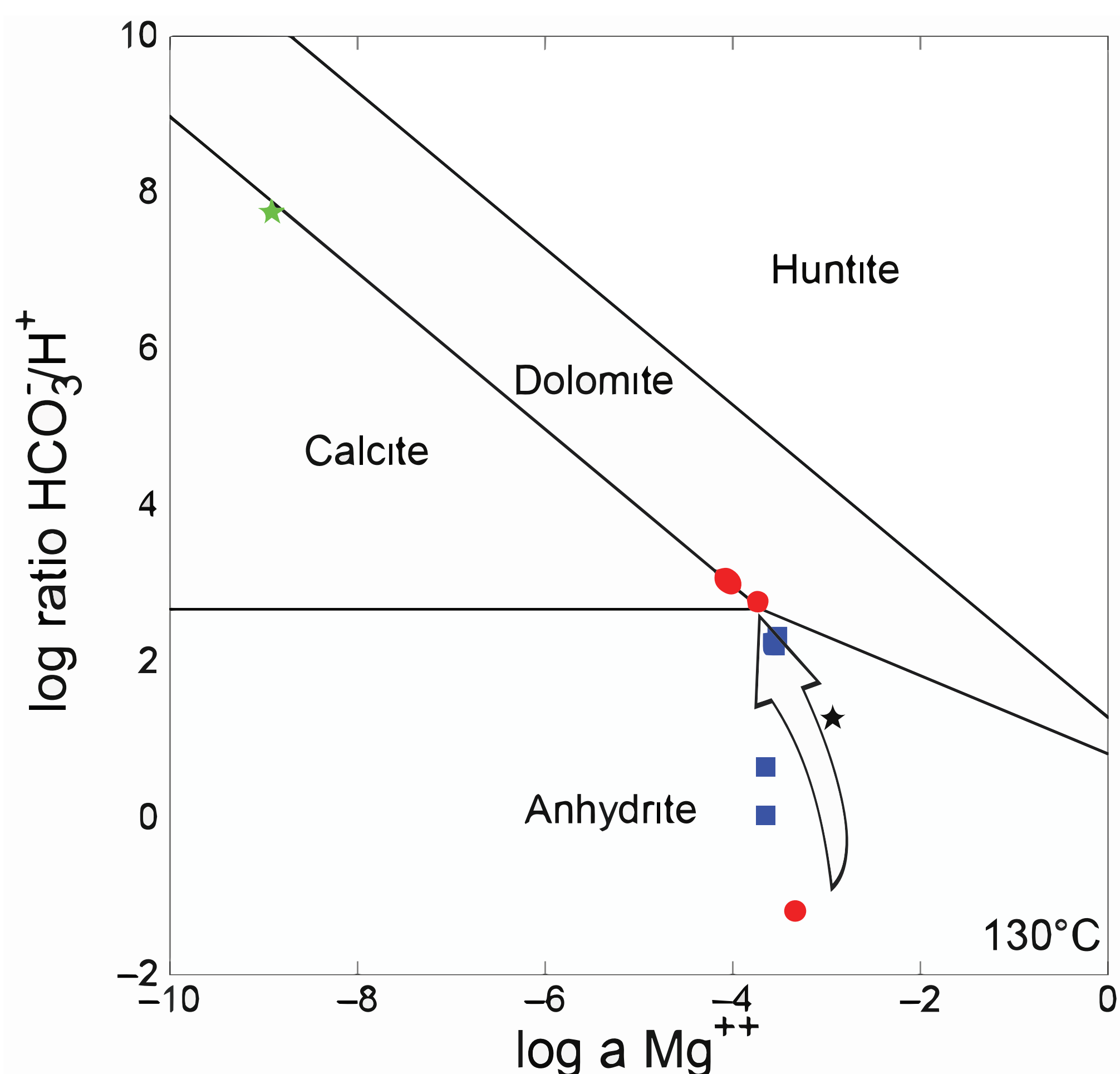


Saturation indices for clay minerals indicate that smectites (swelling clays) are stabilized during the Brine+Shale experiment, and are dissolved in the experiment with fracturing fluids.

The presence of sulfur is important for mineral stability during reactions between fracturing fluids and shale

Trend towards calcite-dolomite stability for carbonate minerals.

Stability relationship for CaO-MgO-CO_2 in the presence of SO_4^{2-} (activity = $10^{-3.5}$) at 130°C . The arrow indicates the general reaction path of the fluid. Experimental data are plotted.



Trend towards hematite stability for iron minerals, and no change in Eh occurs during the experiments.

Eh/pH diagram for $\text{Fe-SO}_4^{2-}\text{-H}_2\text{O}$ in the presence of CO_2 (activity $10^{-2.62}$) at 130°C . The arrows indicate the general reaction path of the fluid. Experimental data are plotted.

Acknowledgments

This work was performed through the Energy Policy Act 2005 Complementary Program, Office of Fossil Energy, U.S. Department of Energy. X-ray diffraction measurements were performed by Bret Howard (NETL). ICP analyses were performed by Neal Julien (URS/NETL). George Schlata, William Walker, and Richard Valdisera (URS/NETL) aided with preparation of the autoclave experimental apparatus. Reference to any specific commercial product or service does not constitute or imply endorsement by the U.S. Government.

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Frac Focus Chemical Disclosure Inventory, www.fracfocus.org

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