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Geochemical Modeling and Hydrothermal Experiments used to Constrain the Conditions of Illite Diagenesis in Sedimentary Basins

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GEOCHEMICAL MODELING
AND HYDROTHERMAL EXPERIMENTS USED TO CONSTRAIN
THE CONDITIONS OF ILLITE DIAGENESIS IN SEDIMENTARY BASINS

A Thesis

Presented to

The Faculty of the Department of Geology

San José State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Michael Joseph Murphy

December 2016

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The Designated Thesis Committee Approves the Thesis Titled

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ABSTRACT

GEOCHEMICAL MODELING
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by Michael Joseph Murphy

Two hydrothermal experiments were performed using sandstone core material from the Norwegian North Sea with synthetic brines reacted at approximately 150°C and 450 bars, temperature and pressure calculated to simulate a depth of burial of approximately 4 km. The results of the experiments were analyzed with geochemical modeling and with chemical and petrographic analyses. Geochemical modeling with several computer programs indicated that the experimental fluid was undersaturated with respect to K-feldspar, kaolinite, and illite, but supersaturated with respect to muscovite. Chemical analysis with inductively-coupled plasma mass spectrometry indicated that the fluid reached saturation with respect to K-feldspar. Petrographic analysis with scanning electron microscopy and energy-dispersive scanning indicated that changes took place over the course of the experiments in both the clay and non-clay mineral fractions, and this result was verified by X-ray diffraction analysis that indicated dissolution of both K-feldspar and illite and formation of muscovite. These converging lines of evidence indicate that significant changes took place in the clay mineral fraction of the experimental sandstone core material, reacted at realistic basin temperature, pressure and geochemical conditions, over the course of several weeks.

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INTRODUCTION

Illite overgrowth within hydrocarbon-bearing clastic sedimentary formations causes a large reduction in permeability, lowering of oil well production, and, consequently, significant economic loss (Bjørlykke and Brendsal, 1986; Bjørlykke, 1998). Illite was extensively studied in the 1970s through 1990s, especially in the European North Sea region, one of the largest petroleum provinces in the world. Researchers have made significant discoveries in regards to the diagenetic and authigenic processes controlling the growth of illite and other pore-blocking clay minerals in the North Sea and other sedimentary basins but have so far been unable to precisely constrain the geochemical conditions needed for illite to form. Precise constraints on formation water and mineral compositions, temperature, and pressure leading to the formation of illite would facilitate a more complete understanding of basin development outside of hydrocarbon emplacement.

In this investigation, I applied geochemical computer modeling with several geochemical modeling codes to characterize the thermodynamic states of minerals in both pre- and post-reaction experimental fluid chemistries. I carried out hydrothermal laboratory experiments using core samples from the studied North Sea basin combined with brines with representative formation water chemistries to simulate burial diagenetic processes, and I conducted detailed chemical and petrological analysis to examine changes in water chemistry and mineralogy over the course of the hydrothermal experiments. The study outlined below has led to an improved understanding of clay diagenesis in North Sea sandstone formations.

BACKGROUND

Illite is a 2:1 phyllosilicate clay mineral, with a base unit consisting of two silica tetrahedral layers sandwiching a single aluminum octahedral layer. The stable end-member composition of illite, commonly referred to as muscovite, is $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$. In naturally occurring illite, several cation substitutions occur: Na^+ and Ca^{++} may substitute for K^+ in inter-layer sites, Al^{3+} commonly substitutes for Si^{4+} in tetrahedral sites, and Fe^{++} , Fe^{3+} , Mg^{++} and, rarely, Ti^{4+} may substitute for Al^{3+} in octahedral sites (Gaudette et al., 1966; Warren and Curtis, 1989). Illite precipitates in several crystal habits, including thin plates, laths, and hairs, and in a variety of geologic settings, from shallow soils to deep sedimentary basins (Meunier and Velde, 2014); the latter were the setting of focus for the following study.

The primary geographic region selected for this study was the North Sea basin, selected due to its size, geology, and the numerous published studies on its sediment diagenesis. An example of a typical petroleum reservoir, the Brent Sandstone Formation in the northern portion of the North Sea, which spans from Great Britain to Norway, consists primarily of Middle-Jurassic sandstone interlayered with shale, coal, siltstone and mudstone. The sediments were primarily deposited in estuarine and deltaic environments. The mineralogy of the sandstone units consists of detrital quartz and feldspars, including orthoclase and microcline, along with some detrital muscovite. Cements consist of kaolinite, illite, quartz, and small amounts of calcite (Blanche and Whitaker, 1978; Bjørlykke and Brendsal, 1986). The core samples selected for the hydrothermal

experiments described below also contained numerous igneous and metamorphic rock fragments.

Bjørkum and Gjelsvik (1988) attributed the illitization of kaolinite in North Sea sandstone to the relative activities of aqueous silica and potassium in an aqueous system. They also suggested that illitization primarily takes place under isochemical (reaction 1), closed-system conditions that are slightly oversaturated with respect to quartz and at temperatures as low as 50°C.

Bjørlykke and Aagaard (1992) provided an overview of diagenetic processes that may have led to illitization during sediment burial. They concluded that illitization starts at or close to the surface with meteoric-water flushing leading to leaching of feldspars and, consequently, a supply of aluminum and silica needed to form authigenic kaolinite. As burial progresses, assuming a source of potassium from K-feldspar, illitization of existing kaolinite occurs isochemically with little to no mass transfer taking place. In later articles by Bjørlykke (1998, 2014), a depth of 3.5 – 4 km was noted for samples exhibiting a significant increase in illite, hypothesized to indicate that a threshold temperature between 130 and 140°C is needed for extensive illitization of kaolinite to occur in the presence of K-feldspar.

Bjørlykke et al. (1995) also investigated illite diagenesis in the North Sea. They concluded that formation of illite requires both a supply of aluminum from dissolving kaolinite and a supply of potassium from dissolving K-feldspar. This process can be

described by two reactions: at relatively shallow depths, dissolution of K-feldspar by groundwater produces kaolinite and K^+ :

followed by illitization of the kaolinite as burial progresses:

Bjørlykke et al. (1995) demonstrated that potassium is depleted in formation waters where illitization has taken place and enriched in formation waters that lack sufficient aluminum concentration for illitization to occur, implying that illite is a primary sink for potassium. A conceptual model of spatial and temporal variations in diagenesis was also presented that proposed that illitization occurs primarily during periods of burial and heating of sediments and shuts off during erosion and uplift, which leads to cooling.

Berger et al. (1997) concluded that, due to the high energy barrier of muscovite (as end-member illite) formation at near-equilibrium conditions, formation water must be slightly supersaturated with respect to K-feldspar in order for muscovite to form. Their model requires an open system in which potassium can migrate through pore water (reactions 2 and 3). Additionally, pH was not considered as a variable, because buffering to near-neutral pH by mineral dissolution/precipitation was assumed.

Thyne et al. (2001) created a reactive transport model of a system containing a sandstone-shale interface to test the effects of pore water residence time and potassium diffusion rates on illitization of kaolinite. By setting the dissolution of K-feldspar at a faster rate than diffusion, it was shown that a significant amount of potassium ended up in

the shale, and, consequently, less illite was formed in the sandstone. An interesting additional result of this modeling study was that the presence of hydrocarbons slowed down diffusion of potassium from the sandstone to the shale and, consequently, more illite was formed in the sandstone.

In their book on illite, Meunier and Velde (2014) presented a collection of studies with resultant data on illite mineralogy and diagenesis by themselves and other workers. They emphasized the important role that potassium activity in formation pore waters plays in the thermodynamics of illite formation. They hypothesized that there are multiple modes of illite formation or ‘ripening’; in closed, isochemical systems (reaction 1) such as shale and deeply-buried sandstone, illite formation is very slow due to a limited supply of potassium. In systems suddenly open to an influx of potassium from adjacent evaporite deposits, such as during basin-scale tectonic events, they hypothesized that illite formation is much more rapid (reactions 2 and 3), essentially instantaneous on the time scale of diagenesis.

Many of the above studies focused on the temperature and pressure of the pore fluid as the primary controls on illite diagenesis and somewhat ignored the effects of other controls on mineral saturation state. A significant factor that was examined in the following study is pH, as it acts as a primary control on both the dissolution and precipitation rate of clay mineral phases and on the mobility of ionic species, particularly aluminum (Hitchon et al., 1999; Kharaka and Hanor, 2014). The pH of formation water changes significantly with temperature. Although it may eventually buffer to near-neutral pH through mineral dissolution and precipitation as suggested by Berger et al.

(1997), it may be lowered significantly by rapid heating and introduction of organic acids during hydrocarbon emplacement, as well as by injection of CO₂ (Kharaka et al., 2013).

METHODS

Equilibrium Modeling with SOLMINEQ

Geochemical modeling was conducted prior to designing the hydrothermal experiments, using an updated version of the computer code SOLMINEQ.88 (Kharaka et al., 1988). SOLMINEQ.88 solves a system of equations utilizing an iterative approach to calculate ionic equilibrium speciation and mineral saturation states of simulated formation waters. The basis for the system of equations solved by the code is generated from inputs of ionic species (inorganic and organic), temperature, pressure, and pH, as well as input options for saturation with respect to specific minerals and thermodynamic data. Saturation states of mineral phases are represented by calculated values of the change in Gibbs free energy (ΔG , kcal mol⁻¹ (in SOLMINEQ) or kJ mol⁻¹). Values of change in Gibbs free energy indicate the direction in which a reaction will proceed to reach equilibrium and how far the reaction is from equilibrium. For any reaction, the magnitude of change in Gibbs free energy is given by

$$\Delta G = RT \ln \frac{Q}{K} \quad (4)$$

where R is the gas constant, T is temperature in Kelvin, Q is the reaction quotient, and K is the equilibrium constant. If $\Delta G = 0$, the system is at equilibrium and the mineral phases will neither dissolve nor precipitate. If $\Delta G < 0$, then the mineral phases present in the reservoir ('reactants') will dissolve to ultimately reach equilibrium; if $\Delta G > 0$, then the mineral phases will precipitate to reach equilibrium. The larger the departure of ΔG from 0, the more thermodynamic driving force there is for the reaction to proceed in the indicated direction (Kharaka et al., 1988).

Determination of Optimum pH and Aluminum Concentration for Formation of Muscovite/Illite in Closed Systems

The primary objective of this portion of the study was to find a region in which a representative formation water is undersaturated with respect to K-feldspar and kaolinite, and supersaturated with respect to muscovite (as a proxy for illite) in simulated formation water. The purpose of this exercise was to simulate formation of illite in isochemical, closed systems such as deeply buried sandstones and shale, once the system had reached a near-equilibrium state.

Several geochemical datasets were selected from North Sea studies by Barth (1991) and Egeberg and Aagaard (1989) as representative formation water chemistries. Data from selected samples were entered into a SOLMINEQ input file using the SOLINPUT user interface, and output files were generated using the SOLMIN executable (DeBraal and Kharaka, 1989).

Many data on formation waters lack values for aqueous silica and aluminum and require estimation of a value for modeling. In addition, values of pH measured at the surface after changes in temperature, pressure and gas exsolution must be corrected (Kharaka and Hanor, 2014). Because formation waters at temperatures above approximately 70°C are at equilibrium with quartz (Kharaka and Mariner, 1989; Kharaka and Hanor, 2014), that assumption was made to calculate aqueous silica concentrations for this exercise on deep sediments. Silica concentrations were set to equilibrium with quartz using the ‘dissolve/precipitate a mineral to saturation’ option under the ‘mass transfer’/‘dissolution/precipitation’ menus in SOLINPUT. If the modeled fluid was highly undersaturated with respect to calcite ($\Delta G \leq -1 \text{ kcal mol}^{-1}$) at the published pH

value, a new pH was calculated that resulted in saturation with respect to calcite at the modeled temperature and pressure, using an input file already at saturation with respect to quartz (generated from the previous output file using the ‘printout control’ menu in SOLINPUT).

Due to the inherent difficulty in analyzing the aluminum concentration in aqueous solutions, the aluminum concentration in modeling studies of formation waters is commonly set by equilibrating with kaolinite, illite, or K-feldspar (Hitchon et al., 1999). In this study, because these minerals (kaolinite, muscovite/illite, and K-feldspar) were the primary reactants and products of interest and equilibration with one of these minerals produces an unrealistically high aluminum concentration, aluminum was initially set to an arbitrary trace amount of 0.01 mg/L. The aluminum concentration was then titrated up or down between the range of values generally measured in formation waters, 0.01 to 0.1 mg/L (Kharaka and Hanor, 2014), in 0.005 mg/L increments to achieve the desired saturation states with respect to kaolinite, K-feldspar, and muscovite. After the above adjustments had been made, the resulting calculated charge balance was adjusted to within $\pm 1\%$ using either Cl^- or Na^+ , if necessary. Due to the high total dissolved solids (TDS) of 30,000 to 50,000 mg/L or more and the corresponding high ionic strength (0.5 to 1 M or more) of the waters used in the study (Barth, 1991; Egeberg and Aagaard, 1989), Pitzer ionic speciation equations (Nordstrom and Campbell, 2014) were used for thermodynamic calculations by setting the ‘use Pitzer equations’ option to ‘true’ in SOLINPUT. Pressure and temperature were held constant at the published values for the initial model runs. Where several temperatures were given in the published data set, an

average temperature was used. Where pressure was not given in the published data sets, values were calculated based on an AAPG standard depth/pressure equation using the fluid density calculated by SOLMINEQ (AAPG Wiki, 2015). Subsequent input files were then generated from the initial output using the method described above.

Simulation of Rapid Potassium Influx in an Open System

It was hypothesized by Meunier and Velde (2014), as well as by Berger et al. (1997), that rapid precipitation of illite in sandstone pores may be due to a sudden influx of potassium from an outside source, such as tectonic fracturing leading to rapid dissolution of evaporite salts such as sylvite, KCl, followed by illitization of kaolinite (reactions 2 and 3). To test this hypothesis, SOLMINEQ was used to simulate the dissolution of a small amount of sylvite (0.005 to 0.05 Mol) in order to ‘spike’ potassium concentrations and determine the possible changes in the saturation states with respect to the minerals of interest. Sylvite was added to one of the input files from the first SOLMINEQ study using the ‘dissolve/precipitate a specific amount of a mineral’ mass transfer option in SOLINPUT, and a new input file was run using the method described above. In order to compare saturation states with respect to K-feldspar, kaolinite, and muscovite calculated in this exercise with those of the initial SOLMINEQ study, pH was changed in 0.1 increments within the same range for subsequent model runs, and all other conditions were held constant.

Hydrothermal Experiments

Hydrothermal Experiments using North Sea Sandstone

Although geochemical modeling is a powerful tool that can be applied to many problems in geochemistry, modeling on its own can only be used to calculate and predict whether or not a mineral is likely to dissolve or precipitate. In the case of this study, it cannot be used alone to draw conclusions on whether or not illite will precipitate in a formation; these conclusions can be made more applicable to field situations and more acceptable by laboratory study of the water-rock systems of interest.

Two hydrothermal experiments to investigate diagenesis and illite formation in North Sea sandstone formations were designed and performed at the U.S. Geological Survey in Menlo Park, California. The primary goal of the experiments was to examine and quantify any changes in the mineralogy of illite or other clays formed during the simulated burial diagenesis of North Sea sandstone and formation waters.

Core samples were prepared by first grinding them down to a sand fraction using a mortar and pestle or mechanical grinders, if necessary, as described below in further detail. A portion of the ground sample was retained for X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis and for possible repeat experiments. An aliquot of the resulting material was then reacted in a flexible gold reaction vessel of approximately 250 ml volume with a prepared brine solution in approximately a 10 to 1 fluid-solid ratio (J. Bischoff, pers. comm., 2015). Hydrochloric acid was added to adjust the pH to approximately 5.5 at 150°C and 450 bars in order to duplicate as closely as possible the conditions at which the fluid showed the greatest saturation with respect to

muscovite in the results of the geochemical modeling study. The reaction vessels were secured within the fluid chamber of one of the oscillating furnaces in the hydrothermal lab, and the temperature and pressure were set using the appropriate procedure as described below (Bischoff and Dickson, 1975; Rosenbauer et al., 2005). Temperature was monitored throughout the course of the experiments and adjusted as necessary by proportional-integral-derivative (PID) controllers that continuously monitored output voltages from the thermocouples and adjusted input current to the heating elements accordingly. Pressure was adjusted using an external hydraulic pump system. After the experiments reached the specified temperature and pressure, fluid samples were withdrawn through the titanium outlet at regular intervals and processed as described below.

Sandstone Core Samples

Sandstone core material from North Sea wells, provided by Drs. P. Aagaard and H. Hellevang of the University of Oslo, Norway, was used in the hydrothermal experiments described below. Forty core samples were supplied, ranging in depth from 1787 to 4150 m. Individual samples ranged from 7 to 55 g in mass. The sample selected for experiment 15NS-101 was from Well 30/3-2 in the Vesselfrikk field at a depth of 2938.0 m (Fig. 1); the original mass of the core was 43 g. This sample was selected based on the depth of approximately 3 km, approximately 1 km shallower than the depth of 4 km simulated by the experimental conditions, and on X-ray fluorescence (XRF) analysis that showed an acceptably high aluminum and potassium weight percent (wt %). The core was described as very fine- to medium-grained sandstone, poorly sorted, light gray (10YR -7/2), very well cemented, and strong (Murphy, 2015).

Figure 1. Sandstone core from North Sea Well 30/3-2 at a depth of 2938.0 m.

The samples selected for 16NS-102 were from Well 31/3-3 at depths of 1865.2 m and 1869.2 m (Figs. 2 and 3, respectively); original masses of the cores were 12.0 g and 15.5 g, respectively.

Figure 2. Sandstone core from North Sea Well 31/3-3 at a depth of 1865.2 m.

Figure 3. Sandstone core from North Sea Well 31/3-3 at a depth of 1869.2 m.

The samples were selected based on depths of approximately 2 km, 50 percent of the depth of approximately 4 km simulated by the experimental conditions, geochemistry of the surrounding formation waters, and the results of the XRF analysis that indicated acceptably high aluminum and potassium wt %. The cores were described by the author as very fine- to coarse-grained sandstone, poorly sorted, light gray (10YR 7/1), well cemented, strong, and containing common rock fragments and mica flakes (1865.2 m), and as medium- to coarse-grained sandstone, moderately well sorted, sub-rounded to sub-angular grains, gray (10YR 6/1), moderately well cemented, and containing common rock fragments and mica flakes (1869.2 m) (Murphy, 2015). Because there was not a sufficient mass of either core sample to obtain a water/rock ratio of approximately 10/1 by mass and because the cores were similar in composition and appearance, in addition to having been taken from intervals separated by only 4 m, it was decided to use a mixture of both cores.

For experiment 15NS-101, a 23.5 g split of Well 30/3-2 2938.0 m core was carefully broken off, and initially pulverized using a mechanical ‘chipmunk’-type crusher. The sample was then further ground in a shatterbox apparatus using ceramic shatter plates. The chips were ground in the shatterbox for approximately 30 seconds, which produced complete disaggregation without powdering larger grains. Following homogenization of the ground core material with a splitter, approximately 3 g of the ground sample was retained for further analysis.

Small chips totaling approximately 4 g of Well 31/3-3 1865.2 m core, and approximately 5.5 g of Well 31/3-3 1869.2 m core, were carefully broken off and

retained separately for further analysis. For experiment 16NS-102, 7.8 g of the remaining Well 31/3-3 1865.2 m core and 9.4 g of the remaining 1869.2 m core were ground together using a ceramic mortar and pestle. This method was selected rather than the mechanical shatterbox method due to the very small (17.2 g) total sample prepared. Following grinding and homogenization using a splitter, a small aliquot of approximately 2 g was retained from the combined sample for further analysis.

Synthetic Brines

Synthetic brines were prepared using ultra-pure, deionized water and reagent-grade salts to simulate *in situ* formation water chemistry. Table 1 shows the composition of synthetic brines prepared for experiments 15NS-101 and 16NS-102.

For experiment 15NS-101, a synthetic brine was prepared using an average composition of three water chemistries sampled in the Veselfrikk Field, Etive Formation, taken from the North Sea Formation Waters Atlas (Warren and Smalley, 1994). Waters were modeled in PHREEQC and SOLMINEQ.88 to investigate mineral saturation indices and charge balances. Based on the results of the geochemical modeling studies described above, and because the only sample from Veselfrikk Field referenced in the North Sea Formation Waters Atlas was taken at a depth of 2200 m, while the other two were taken nearby at 2900 and 2950 m, closer to the core sample depth of 2938.0 m, it was decided to average the compositions of the three waters. This was accomplished using the 'MIX' command in PHREEQC. Brine composition was simplified to include only major cations (Ca, K, Mg, and Na) and anions (Cl, bicarbonate).

For experiment 16NS-102, a brine was prepared using the same methods as described above. The water selected was from Well 31/2-15 in the Troll Field, Sognefjord Formation, of the North Sea (Warren and Smalley, 1994). This water was selected based on geographic proximity to Well 31/3-3, depth, and potassium concentration. Geochemical modeling performed with SOLMINEQ.88 and PHREEQC indicated a high level of supersaturation with respect to muscovite at experimental conditions and saturation with respect to quartz.

The brines for both experiments were acidified immediately prior to the start of the experiment using Optima-grade HCl. The pH of the acidified brines was measured using a Hach portable pH probe for 15NS-101 and a Thermo-Fisher Orion flow-through probe for the 16NS-102 brine.

Table 1. Synthetic brines prepared for hydrothermal experiments using ultra-pure water and reagent-grade salts. Brine 15NS-101 was used in hydrothermal experiment 15NS-101. Brine 16NS-102 was used in hydrothermal experiment 16NS-102.

Brine ID	Na (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	HCO₃ (mg/L)	Cl (mg/L)	TDS (mg/L)
15NS-101	11722	606	400	84	244	19615	32671
16NS-102	18600	850	520	445	520	31655	52590

Hydrothermal Reactors

The primary equipment used to conduct the experiments consisted of ‘Dickson-type’ rocking batch reactors containing gold reaction vessels (Seyfried et al., 1979). The flexible gold reaction vessel, or ‘gold bag’, is secured to a titanium/steel head assembly equipped with a titanium tube to allow fluid sampling at experimental conditions, and the gold bag/titanium head assembly is placed inside a steel pressure vessel or ‘bomb’. The bomb is filled with deionized water that serves as the transfer medium for heat and pressure to the gold bag. The entire assembly is secured inside a ceramic furnace wrapped with electrical resistance heating coils and surrounded by fiberglass insulation, all of which is contained in a steel container or ‘can’. The bomb is pressurized both by an external hydraulic pump system and internal pressure at the vapor pressure of water. Heating is controlled by a system of four thermocouples cemented to the furnace, one thermocouple inside the transfer fluid, ‘Variac’ variable AC transformers, and analog PID controllers. A failsafe depressurization mechanism is provided by a rupture disc designed to rupture at 1000 bars. Rocking motion is provided by an electric motor powering a belt-and-gear-driven system that rotates the cans through 180°.

This type of reaction vessel allows the experiment to remain at constant temperature and pressure while reaction fluid is withdrawn through the titanium outlet. Additionally, the rocking motion of the vessel prevents flocculation of sediment and increases reaction rates by continually mixing the fluid.

Temperature and pressure were monitored and recorded daily throughout the course of the hydrothermal experiments, and adjustments were made as needed to

maintain the determined temperature and pressure. Upon termination of the hydrothermal experiments, the bombs were carefully removed from the furnace and immediately quenched in a bucket of cool lab tap water. Cool water was added to the bucket continuously until the water inside the bomb had cooled to approximately 30°C over a period of approximately 2 hours. The bomb and reaction vessel were then disassembled, and experimental sediment and fluids were saved for later analysis.

Hydrothermal Experiment 15NS-101

Experiment 15NS-101 was initiated on July 13, 2015 and terminated on November 6, 2015, for a total reaction time of 2785 hrs. Starting material consisted of 20.1 g of ground core material W 30/3-2 2938.0 m mixed with 201 g of brine 15NS-101 to produce a water/rock ratio of 10/1 (by mass). The pH of the brine was adjusted to ~5.5 using Optima-grade HCl immediately prior to assembling the experiment. The materials were placed in a gold reaction vessel that was secured inside a Dickson-type rocking furnace described above. Temperature was elevated to 140°C, and pressure was raised to approximately 450 bars, calculated to simulate a depth of burial of approximately 4 km. Upon reaching experimental conditions, a fluid sample was extracted through the titanium outlet tube. The fluid was filtered through a 0.1 µm Milipore filter, and aliquots were separated for cation, anion, and pH/alkalinity analysis. An additional, unfiltered aliquot was retained for immediate pH analysis. Throughout the course of the experiment, seven additional fluid samples were taken ranging in mass from 15 to 18 g. The masses of fluid withdrawn and the corresponding change in fluid/rock ratio are discussed in the Results section.

Hydrothermal Experiment 16NS-102

Experiment 16NS-102 was initiated on January 4, 2016 and terminated on February 17, 2016, for a total reaction time of 1032 hours. Starting material consisted of 15.3 g of core from Well 31/3-3 1869.2 m and 1865.2 m, mixed in a ratio of approximately 1.25:1. The ground core material was mixed with 213 g of the Troll 31/2-15 brine, which was acidified to a pH of 5.5 immediately prior to starting the experiment using Optima-grade HCl. The initial water/rock ratio was approximately 14/1 by mass. Temperature was elevated to 150° C, and pressure was elevated to 450 bars, calculated to simulate a depth of burial of approximately 4 km. Upon reaching experimental conditions, a fluid sample was extracted and divided into aliquots as described above. Five additional fluid samples were extracted throughout the course of the experiment.

Chemical and Petrographic Analysis

Chemical Analysis

Fluid samples taken during experiments 15NS-101 and 16NS-102 were analyzed using inductively-coupled mass spectrometry (ICP-MS) for cations. The purpose of the chemical analyses was to determine changes in fluid composition, particularly changes in relative concentrations of Si, K, Mg, and Al that could indicate precipitation or dissolution of illite, kaolinite, smectite or other clay minerals during the course of the experiments. Additionally, the pH of the brines was measured both before and during the hydrothermal experiments described above.

Inductively coupled plasma mass spectrometry analysis. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on fluid samples collected from hydrothermal experiments 15NS-101 and 16NS-102 using a Perkin Elmer NexION 300Q. Samples were withdrawn into a clean 10 mL syringe and filtered through a 0.1 μm syringe filter into 3 mL Nalgene bottles rinsed with ultra-pure water and 2% nitric acid. The samples were then acidified with one drop (~ 0.02 g) of Optima-grade nitric acid. The mass of the sample aliquots retained for ICP-MS analysis ranged from approximately 1.5 to 2.0 g each. Dilutions were prepared using 2% Optima nitric acid in nitric acid-rinsed Falcon sample tubes. Amounts of the sample and dilutant were measured using pipettes and verified gravimetrically to 0.001 g precision to calculate true dilutions. In order to avoid saturation of the cone detectors in the ICP-MS instrument, it was necessary to dilute the fluid samples by 1/100 for most of the major ions (Ca, K, Mg, and Si) and Al; for measurement of Na, it was necessary to dilute the samples by 1/1000 in order to obtain a concentration within the detection limits of the instrument. Analytical errors were calculated by multiplying the measured concentrations by the relative standard deviation (RSD) value calculated for each analysis.

pH measurement. Throughout the course of both hydrothermal experiments, pH was measured on fluid samples collected as described above. Samples collected for pH measurement were not filtered and were placed in a clean glass test tube and stoppered immediately after sampling. The pH was measured immediately following sampling to reduce cooling and equilibration with the atmosphere. For the first three samples measured for 15NS-101, a Hach Sension portable pH probe was used; a Thermo-Fisher Ross Orion flow-through probe was later obtained and was used for the remainder of the samples from 15NS-101 and all samples from 16NS-102. Both pH probes were calibrated using a two-point calibration with standard pH 4 and 7 buffers.

Petrographic Analysis

Petrographic analysis of the sandstone core material was performed using X-ray fluorescence (XRF), scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS), and X-ray diffraction (XRD) techniques. Samples were examined both before and after the hydrothermal experiments to determine qualitatively and quantitatively any changes in mineralogy that occurred during the course of the experiments. XRF and SEM/EDS analysis was performed at the USGS, Menlo Park, California; XRD was performed at the USGS in both Menlo Park, California, and in Denver, Colorado.

X-ray fluorescence analysis. X-ray fluorescence (XRF) analysis of the core samples was performed at the USGS, Menlo Park, using a Thermo-Fisher Niton hand held XRF unit mounted in a stand. Randomly sampled aliquots of approximately 1 g each were placed in plastic sample cups with X-ray film over one end to perform the

analyses. Following analysis, the aliquots were returned to the bulk sample. Analyses were performed on aliquots of the core sample used for experiment 15NS-101, and on separately ground aliquots of both Well 31/3-3 1865.2 m and 1869.2 m core samples used in the mixture for experiment 16NS-102, as well as an aliquot of the mixed sample, to obtain approximate weight percentages (wt %) of major elements.

X-ray diffraction analysis. Detailed X-ray diffraction (XRD) clay work was performed at the USGS in Denver, Colorado, by James Thordsen (USGS), under the guidance of Dennis Eberel and Kate Campbell on pre- and post-reaction aliquots of the sediment from experiments 15NS-101 and 16NS-102. XRD analysis was performed using a Rigaku XRD analyzer to measure the relative percentages of K-feldspar, kaolinite and illite present in both the reacted samples and the original sandstone core material pre-reaction. The results of post-reaction analyses were compared with XRD analysis of the initial ground sample and with either published XRD patterns for illite/muscovite or with patterns determined from in-house XRD analysis of pure illite.

Additional treatments, consisting of heating to 550°C, glycolation with ethylene glycol, or addition of hydrochloric acid to eliminate kaolinite, smectite and chlorite peaks, respectively, were undertaken to eliminate interference from these clay minerals (Moore and Reynolds, 1997).

Scanning electron microscope and energy-dispersive spectrometry analysis. Scanning electron microscope/energy-dispersive spectrometry (SEM/EDS) techniques were used to both image the structure and analyze the elements in clay cements from several North Sea cores both pre- and post-hydrothermal reaction. The samples were

prepared as described by Welton (2003), by mounting to an aluminum SEM stub and coating with carbon or with carbon and gold. SEM/EDS analysis of the prepared samples was performed at the USGS SEM lab in Menlo Park, California, under the technical guidance of Leslie Hayden.

SEM/EDS analysis was performed using a Tescan Vega 3 LMU VP-SEM scanning electron microscope on clay mounts prepared from both pre-reaction ground sandstone core material, small (approximately 1 cm²) chips of whole-rock core, and the post-reaction sediment collected from experiments 15NS-101 and 16NS-102. Following the dismantling and quenching of the reaction vessels, sediment contained in the remaining brine was decanted and left un-diluted. Residual sediment on the walls of the gold bags was rinsed out using deionized water, and the rinsate was decanted into separate bottles. The sediment-water mixture was then poured into 20 mL Falcon tubes, and a small amount of sodium hexametaphosphate was added to deflocculate clay particles. The resulting sediment-water mixture was shaken and allowed to settle based on the appearance of the water and calculated Stokes law settling velocities to separate clay- and silt-sized particles. A pipette was then used to draw off a small aliquot of fluid and suspended sediment (<1 mL) from several intervals, some including only clay-size particles, others including both clay and silt-size particles. The fluid and suspended sediment was then dropped onto 0.1 or 0.45 µm Millipore filters under vacuum and thoroughly rinsed with ultra-pure water to wash away any residual salts. The sediment-impregnated filters were then oven dried at 50° C for one hour, cut into small pieces (approximately 1 cm diameter) and affixed to an aluminum mounting stub with double-

sided carbon tape. The prepared sample tabs were then carbon- and gold-coated for conductivity.

For SEM and EDS analysis of pre-reaction whole-rock core material from Well 31/3-3 at 1865.2 and 1869.2 m depths used in experiment 16NS-102, small (approximately 1 cm²) chips were broken off, mounted to aluminum stubs using double-sided carbon tape, and coated with carbon and gold. To examine the pre- and post-reaction ground sediments, sediment recovered from the hydrothermal reaction vessel was prepared as described above; pieces of filter were affixed to aluminum stubs with double-sided carbon tape and coated with carbon and gold.

Additional Geochemical Modeling with PHREEQC and GWB

Following initial modeling studies with SOLMINEQ.88 to determine near-equilibrium conditions favoring illite formation, several additional modeling studies were undertaken to determine possible reaction pathways. The public-domain USGS computer code PHREEQC (Parkhurst and Appelo, 2013) was selected to perform post-experiment geochemical modeling, due to its extensive documentation, relative ease of running complex models with multiple data sets, and frequent updates to both the source code and thermodynamic databases. Data were entered either by directly typing in data blocks or by utilizing the user interface to create them. PHREEQC incorporates a Basic interpreter that allows programming of kinetic equations, generation of plots, and several other high-level functions. PHREEQC v.3 includes a Pitzer database (pitzer.dat) but may not be as robust as SOLMINEQ for calculating equilibrium states of highly saline (ionic strength > 1 M) solutions due to the lack of virial coefficients for aluminum species.

Reaction Path Modeling with PHREEQC

A simple reaction path model was used to study how the saturation indices of the minerals of interest in this study (illite, muscovite, K-feldspar, and kaolinite) may have changed over the course of the hydrothermal experiments described above. Water composition used for the model solution was an average of the ICP-MS concentrations measured for the respective experiments. Silicon and aluminum were both set at an arbitrary trace amount of 0.0001 mg/L or 0.1 µg/L in the initial solution. Temperature, pressure, and initial pH were set based on experimental values. An amount of K-feldspar corresponding to moles of K-feldspar dissolved during the experiment as measured by XRD was then dissolved in 50 incremental steps.

In order to examine the effect of changes in temperature on the saturation indices of the minerals of interest, PHREEQC was used to model saturation index vs. temperature for experiments 15NS-101 and 16NS-102. Compositions of the experimental fluids as measured by ICP-MS were used as the initial solutions. Starting at 20°C, the temperature was increased in increments of 10°C up to 150°C, using the ‘reaction_temp’ command. A plot was then generated of saturation index for the minerals of interest and of pH vs. temperature in degrees Celsius for both hydrothermal experiments.

Activity Diagrams with the Geochemist’s Workbench

The above modeling studies with PHREEQC were supplemented by similar studies using the Geochemist’s Workbench (GWB) (Bethke and Yeakel, 2014). GWB is a collection of codes, graphical user interfaces (GUIs), and databases designed to perform

a variety of geochemical modeling and data visualization functions including equilibrium state, reaction path and reactive transport modeling. In this study, the GWB program 'Act2' was used to create activity-activity diagrams of several activity ratios, calculated using ICP-MS concentrations measured for both experiments. By plotting a given activity ratio, such as K^+/H^+ , against another activity, such as SiO_2 , stability fields of minerals were calculated and displayed graphically. Points representing fluid sample compositions measured with ICP-MS were calculated using the geochemist's spreadsheet (GSS) application and projected onto the activity diagram.

RESULTS

Equilibrium Modeling with SOLMINEQ.88

Determination of Optimum pH and Aluminum Concentration

After appropriate adjustments were made to aluminum concentration and pH, and an initial input file was generated using the composition of formation water for Sample 2 from Table 1 of Barth (1991), new outputs were generated by adjusting the aqueous aluminum concentration in ± 0.005 mg/L increments at pH 5.5 until the values of change in Gibbs free energy difference (ΔG) were negative with respect to K-feldspar and kaolinite, indicating that dissolution is favored, and positive with respect to muscovite, indicating that precipitation is favored. At a pH value of approximately 5.5, at saturation with respect to quartz and with an aluminum concentration of 22.5 $\mu\text{g/L}$, the fluid was calculated to have been supersaturated with respect to muscovite, and undersaturated with respect to K-feldspar and kaolinite. The modeled fluid was calculated as undersaturated with respect to illite, with values of ΔG lower than -1 kcal/mol for all modeling runs. These values were not plotted because muscovite was being used as a proxy for illite. After the optimum aluminum concentration was determined, aluminum concentration was held constant while pH was varied in ± 0.05 increments, until values of ΔG with respect to kaolinite and K-feldspar were positive. Output values of ΔG with respect to kaolinite, K-feldspar, and muscovite were then plotted vs. pH (Fig. 4). It should be noted that average aluminum values measured in fluid samples from the experiments were approximately five times those used in this preliminary modeling study.

Figure 4. Plot of ΔG vs. pH with respect to kaolinite, K-feldspar, and muscovite, using Sample 2 from Table 1 of Barth (1991) modeled in SOLMINEQ at 134° C and 380 bars, with the addition of quartz to saturation and 22.5 $\mu\text{g/L}$ aluminum.

Simulation of Rapid Potassium Influx

To simulate a rapid influx of potassium, 0.05 moles of sylvite were added to the water from the above example at 134° C and 380 bars. The resulting scenario was then run at several values of pH, and calculated values of ΔG with respect to kaolinite, K-feldspar, and muscovite were plotted against pH (Fig. 5). The plots show that between a pH of 5.5 and 5.7, the modeled fluid is supersaturated with respect to both K-feldspar and muscovite, and slightly undersaturated with respect to kaolinite. The relatively large value of ΔG with respect to muscovite ($\sim 1.8 \text{ kcal mol}^{-1}$) in this plot demonstrates that, with rapid influx of potassium, muscovite/illite may precipitate rapidly.

Figure 5. Plot of ΔG vs. pH for the modeled fluid with respect to kaolinite, K-feldspar, and muscovite, using Sample 2 from Table 1 of Barth (1991) modeled in SOLMINEQ at 134° C and 380 bars, with the addition of quartz to saturation, 0.05 moles sylvite (KCl), and 22.5 $\mu\text{g/L}$ aluminum.

Chemical and Petrographic Analysis

Change in Fluid/Rock Mass Ratio

For hydrothermal experiments 15NS-101 and 16NS-102, the fluid/rock ratio by mass was measured and calculated throughout the course of the experiments as fluid samples were extracted. The results are presented in Tables 2 and 3.

Table 2. Mass ratio of fluid/solid for experiment 15NS-101. The change in mass of the fluid component was calculated by subtracting the cumulative mass of the fluid sampled from the initial mass.

Experiment-sample #	Mass fluid (g)	Mass sediment (g)	Mass fluid sampled (g)	Date	Elapsed time, hrs.	Mass ratio, fluid/rock
15NS-101-brine	201	20.1	0	07/13/15	0	10.0
15NS-101-1	186	20.1	15	07/14/15	24	9.3
15NS-101-2	170.7	20.1	15.3	07/24/15	264	8.5
15NS-101-3	153.5	20.1	17.2	08/04/15	528	7.6
15NS-101-4	137.3	20.1	16.2	08/24/15	1008	6.8
15NS-101-5	122.8	20.1	14.5	09/09/15	1392	6.1
15NS-101-6	105.2	20.1	17.6	09/30/15	1896	5.2
15NS-101-7	90.5	20.1	14.7	11/06/15	2784	4.5
15NS-101-8	72.9	20.1	17.6	11/06/15	2784	3.6

Table 3. Mass ratio of fluid/solid for experiment 16NS-102. The change in mass of the fluid component was calculated by subtracting the cumulative mass of the fluid sampled from the initial mass.

Experiment-sample #	Mass fluid (g)	Mass sediment (g)	Mass fluid sampled (g)	Date	Elapsed time, hrs.	Mass ratio, fluid/rock
16NS-102-brine	213	15.3	0	01/05/16	0	13.9
16NS-102-1	199.1	15.3	13.9	01/06/16	24	13.0
16NS-102-2	182.7	15.3	16.4	01/14/16	216	11.9
16NS-102-3	165.7	15.3	17	02/12/16	912	10.8
16NS-102-4	150.4	15.3	15.3	02/17/16	1032	9.8
16NS-102-5	134.2	15.3	16.2	02/17/16	1032	8.8

Chemical Analysis

ICP-MS analysis. ICP-MS analysis of fluid samples extracted over the course of experiment 15NS-101 showed changes in concentrations of several elements of interest (Figs. 6 and 7). Potassium (K) did not change within analytical error, silicon (Si) increased steadily throughout the experiment, asymptotically approaching calculated values for saturation with respect to quartz, and aluminum (Al) appears to have slightly decreased throughout the course of the experiment (Fig. 6). Sodium (Na) varied but did not show a significant net change over the course of the experiment, calcium (Ca) did not change within analytical error, and magnesium (Mg) showed a significant decrease over the course of the experiment (Fig. 7).

ICP-MS analysis of fluid samples extracted over the course of experiment 16NS-102 also showed changes in concentrations of several elements of interest (Figs. 8 and 9). Potassium did not change within analytical error, but silicon (Si) increased steadily throughout the experiment, approaching calculated values for saturation with respect to quartz, and aluminum (Al) concentration remained relatively constant throughout the course of the experiment (Fig. 8). Sodium (Na) did not show a significant change, calcium (Ca) increased, and magnesium (Mg) appears to have decreased over the course of the experiment, but the analytical error was greater than the change (Fig. 9).

Figure 6. Plots of concentrations of K, Si, and Al in ppm vs. elapsed time in hours for experiment 15NS-101. Uncertainties shown by error bars were calculated by multiplying analytical relative standard deviation values by dilution-corrected concentrations.

Figure 7. Plots of concentrations of Na, Ca, and Mg in ppm vs. elapsed time in hours for experiment 15NS-101. Uncertainties shown by error bars were calculated by multiplying analytical relative standard deviation values by dilution-corrected concentrations.

Figure 8. Plots of concentrations of K, Si, and Al in ppm vs. elapsed time in hours for experiment 16NS-102. Uncertainties shown by error bars were calculated by multiplying analytical relative standard deviation values by dilution-corrected concentrations.

Figure 9. Plots of concentrations of Na, Ca, and Mg in ppm vs. elapsed time in hours for experiment 16NS-102. Uncertainties shown by error bars were calculated by multiplying analytical relative standard deviation values by dilution-corrected concentrations.

pH measurement. The pH of fluid samples extracted from hydrothermal experiments 15NS-101 and 16NS-102 was measured as described above. The results of the pH measurements are presented in Table 4.

Table 4. Measured pH values for fluid samples from experiments 15NS-101 and 16NS-102.

Sample	Date	pH	Probe used
15NS-101 brine	7/13/2015	5.48	Hach
15NS-101-1	7/14/2015	6.11	Hach
15NS-102-2	7/24/2015	6.05	Hach
15NS-101-3	8/4/2015	6.03/ 6.63	Hach/ Orion
15NS-101-4	8/24/2015	6.28	Orion
15NS-101-5	9/9/2015	6.35	Orion
15NS-101-6	9/30/2015	6.21	Orion
15NS-101-7	11/6/2015	6.37	Orion
15NS-101-8	11/6/2015	6.65	Orion
16NS-102 brine	1/5/2016	5.54	Orion
16NS-102-1	1/6/2016	5.89	Orion
16NS-102-2	1/14/2016	5.90	Orion
16NS-102-3	2/12/2016	5.77	Orion
16NS-102-4	2/17/2016	5.74	Orion
16NS-102-5	2/17/2016	5.82	Orion

The results of the pH measurements indicate that, for experiment 15NS-101, the pH increased by approximately 1 pH unit over the course of the experiment. It should also be noted that the Hach probe originally used for pH measurements was found to have been converging within only ten iterations, leading to erroneously low values for the first three samples. Measured values of pH for samples extracted over the course of experiment 16NS-102 indicate that the pH increased by approximately 0.3 pH units.

Petrographic Analysis

XRF. The results of the XRF analysis to determine semi-quantitative elemental weight percentages in the sandstone core material as described above are presented in Table 5.

Table 5. X-Ray fluorescence (XRF) analysis of ground sediment samples used in experiments 15NS-101 and 16NS-102. For experiment 15NS-101, Well 30/3-2 core from 2938.0 m was used. For experiment 16NS-102, a mix of Well 31/3-3 core from 1865.2 and 1869.2 m was used. Individual rows represent averages of three analyses on randomly sampled aliquots of the ground sandstone core material.

SAMPLE	Fe wt %	Si wt %	Al wt %	K wt %	Ca wt %	Ti wt %
W 30 3-2 2938.0m	2.7	25.4	2.4	1.2	10.2	0.3
W 31 3-3 1865.2m	1.1	24.5	4.3	2.0	2.8	0.6
W 31 3-3 1869.2m	2.1	23.5	2.9	1.7	0.4	0.3
W 31 3-3 mix	2.0	26.2	4.4	2.0	1.6	0.5

The XRF analysis indicated that the mixture of the two ‘W 31/3-3’ core samples contained the highest weight percentage of aluminum and silicon, both indicated to be higher than either of the unmixed samples. This anomalous result was probably due to some drift or change in calibration of the XRF instrument, as the analyses of the individual samples were performed several weeks before the analysis of the mixed sample.

XRD. A summary of the results of the XRD analysis performed at the USGS in Denver, Colorado, by J. Thordsen, D. Eberl, and K. Campbell is presented in Table 6.

Table 6. Weight percentages of clay and non-clay minerals as analyzed by X-ray diffraction for pre- and post-reaction sediments from experiments 15NS-101 and 16NS-102. Analyses were performed by J. Thordsen, D. Eberl, and K. Campbell (USGS).

	15NS-101 (pre- reaction)	15NS-101 (post- reaction)^a	16NS-102 (pre- reaction)	16NS-102 (post- reaction)
Mineral	Weight %	Weight %	Weight %	Weight %
NON-CLAYS				
Quartz	52.7	59.5	62.3	65.7
K-spar	9.3	7.1	22.5	20.4
Plagioclase	2.3	2.6	3.6	3.4
Dolomite	0.5	0.2	2.0	1.0
Pyrite	0.4	0.2	0.7	1.2
Marcasite	5.4	4.4	0.2	0.2
<i>Total non-clays</i>	<i>89.7</i>	<i>96.8</i>	<i>91.6</i>	<i>92.0</i>
CLAYS				
Kaolinite (disordered)	5.3	3.2	4.4	4.5
Illite	3.1	1.8	3.2	1.2
Muscovite	2.7	0.0	0.2	1.7
<i>Total clays</i>	<i>11.2</i>	<i>5.0</i>	<i>7.8</i>	<i>7.3</i>

^a An aliquot of the post-reaction fluid and sediment mixture from experiment 15NS-101 was withdrawn from the bulk sample and was not remixed prior to XRD analysis.

The results presented in Table 6 indicate that, in experiment 15NS-101, the relative weight percent of the total non-clay minerals increased, while K-feldspar decreased. Total clay minerals decreased by approximately one-half, although it must be noted again that a fraction of the post-reaction water and sediment mixture containing fines was poured off previously, and was not remixed prior to the XRD analysis. Therefore, the analysis is severely limited in usefulness for interpreting changes in clay mineralogy over the course of the experiment.

For experiment 16NS-102, however, the XRD results clearly indicate that several important changes in the mineralogy of the sediment took place over the course of the experiment. A total decrease in K-feldspar of approximately 2 wt % was measured in the

non-clay fraction. In the clay fraction, kaolinite did not change significantly over the course of the experiment. The most interesting and important change measured was the change in the illite/muscovite fraction. In the pre-reaction sediment, approximately 3 wt% illite and no or very little muscovite was measured. In the post reaction analysis, the illite fraction has decreased to approximately 1 wt %, and the muscovite fraction has increased to nearly 2 wt%. An additional interesting result is the increased calculated smectite percentage in mixed-layer illite/smectite, from 8% in the pre-experiment core material to 30% in the post-experiment 16NS-102 sediment, corresponding to a decrease in illite percentage (of illite/smectite) from 92% to 70%. These results indicate a significant change in the crystallinity of the clay fraction.

SEM/EDS analysis. The results of the SEM and EDS analysis of experiment 15NS-101 are presented in Figures 10 and 11. SEM images and EDS spectra were compared with references in the *SEM Petrology Atlas* (Welton, 2003). Analysis performed on pre-reaction sediment from Well 30/3-2 2938.0 m indicated extensive K-feldspar (Fig. 10) and kaolinite, but few grains with illite-like EDS spectra. Analysis of sediment mounts prepared with post-reaction sediment from experiment 15NS-101 revealed extensive silt-size K-feldspar grains, as well as numerous clay-size grains (Fig. 11), many of which showed a kaolinite-like spectrum with approximately equal Si and Al peaks. Several clay-size grains also exhibited a small K peak, implying possible formation of ‘incipient’ or poorly-crystallized illite during the hydrothermal experiment.

Figure 10. SEM micrograph and example EDS spectrum of 15NS-101 sediment (from core W30/3-2 2938.0 m) pre-reaction. The EDS spectrum shows a typical K-feldspar trace, with similar Al and K peaks in addition to a larger Si peak.

Figure 11. SEM micrograph and example EDS spectrum of 15NS-101 sediment post-reaction. The EDS spectrum shows proportions of Al and Si typical of kaolinite, but with small K and Fe peaks.

SEM and EDS analysis of the pre-reaction core and sediment used in experiment 16NS-102 revealed extensive kaolinite (Fig. 12) in well formed ‘books’ present in many pore spaces, as well as extensive K-feldspar (Fig. 13); common plagioclase and quartz grains were also observed. The K-feldspar grains observed in the sandstone core samples were well formed and euhedral, indicating that no significant dissolution of the grains had taken place recently in the formation’s history.

SEM/EDS analysis of the post-reaction sediment from experiment 16NS-102, prepared on Milpore filters as described above, revealed a number of changes in overall morphology and composition of mineral grains, although a direct comparison with whole-rock core chips analyzed for the pre-reaction sediment is difficult to make due to the disaggregation of pore-filling material and likely fragmentation of larger grains during the grinding process.

Images mapping abundances of elements were produced with the Aztec® EDS imaging software in order to more easily identify the mineralogy of the post-reaction sediment from experiment 16NS-102. The EDS maps revealed common quartz, K-feldspar, and clay grains in the post-reaction sediment from experiment 16NS-102 (Fig. 14). Closer inspection of a K-feldspar grain approximately 10 μm in diameter from post-reaction sediment of experiment 16NS-102 revealed extensive erosion and surface dissolution features (Fig. 15) when compared to the well-formed, euhedral K-feldspar grains observed in the pre-reaction core material (Fig. 13).

EDS spectral traces from several points on this grain indicate a typical K-feldspar spectrum, along with peaks for iron (Fe), titanium (Ti), and chlorine (Cl) (Fig. 15). In

Figure 12. SEM micrograph and EDS spectral trace of kaolinite in 16NS-102 pre-experiment sediment from Well 31/3-3 1865.2 m core. Both the morphology and spectrum indicate authigenic kaolinite.

Figure 13. SEM micrograph and example EDS spectrum of K-feldspar in 16NS-102 pre-reaction sediment from Well 31/3-3 1869.2 m showing a K-feldspar grain surrounded by clay. Both K-feldspar and kaolinite are abundant in this sample.

Figure 14. SEM layered electron map of 16NS-102 post-reaction sediment showing relative elemental abundances and EDS spectrum of clay-sized grains. The spectrum shown is an average of the entire image, obtained by scanning the area shown in the image. Orange, blue, and red pixels indicate relative elemental abundance of Si, K, and Al, respectively.

Figure 15. SEM micrograph of eroded K-feldspar grain in 16NS-102 post-reaction sediment. Note strong Cl, Ti, and Fe peaks in addition to the K-feldspar background.

some of the traces, the Cl peak completely overshadows the other elements, indicating strong incorporation of Cl on the surface of the grain. The Cl signal is probably not from residual salts, because the sediment was well rinsed with DI water both during decanting and as part of the SEM sample preparation.

Close examination of the extensive clay-size grains revealed what appears to be well formed hexagonal plates with roughly turbostratic stacking and an EDS spectrum similar to illite, with strong Si, K, Al and Fe peaks, along with a strong Cl peak (Fig. 16). Based on the morphology and composition of these grains, it is possible that they are either detrital illite present in the pre-reaction sediment that have been altered by the hydrothermal experiments, or that they represent a transition from illite to a smectitic clay. A third possibility is that they are experimentally formed illite grains.

Additional Geochemical Modeling with PHREEQC and GWB

PHREEQC

Reaction path models were coded with PHREEQC for experiment 15NS-101, starting with the brine composition determined by ICP-MS with the addition of trace silicon (0.0001 mg/L) and trace aluminum (0.0001 mg/L). For the modeling run, 0.0007 moles of K-feldspar, calculated to correspond to the measured decrease in total weight percent of K-feldspar measured by XRD, was dissolved in 50 steps with the ‘incremental reactions’ option set as ‘true’. This causes the program to re-calculate saturation indices

Figure 16. SEM micrograph and example EDS trace of clay grains in 16NS-102 post-reaction sediment. This spectrum is typical of an illite or muscovite spectrum, with the exception of the Cl peak.

in incremental steps, based on the previous iteration, for each step. The resulting computed values for saturation indices (SI) with respect to muscovite, illite, kaolinite, K-feldspar, and quartz were plotted vs. dissolved Si to trace the reaction progress, using the 'user_graph' function (Fig. 17).

Results of the reaction modeling performed with PHREEQC using ICP-MS concentrations from experiment 15NS-101 indicated that the dissolution of the amount of K-feldspar calculated to have been dissolved during the experiment, approximately 0.7 millimoles based on the change in wt% measured by XRD, resulted in the fluid reaching saturation with respect to both quartz and K-feldspar. The fluid was calculated to have an increasing state of supersaturation with respect to muscovite. The fluid was initially undersaturated with respect to kaolinite and illite, reaching supersaturation with respect to illite when approximately one-third of the K-feldspar had dissolved, and with kaolinite when approximately one-eighth of the K-feldspar had dissolved.

A model was run for 16NS-102 using the same procedure as outlined above. The results were nearly identical, with the exception that the fluid was slightly higher in saturation with respect to all minerals (Fig. 18).

Stepwise increases in temperature from 20°C to 150°C were modeled as described above for experiments 15NS-101 and 16NS-102. Both model runs indicated a peak in saturation indices and a minimum in calculated pH at a temperature of approximately 70°C (Figs. 19 and 20). The calculated pH at experimental temperature showed a very close correlation with measured values for 16NS-102, but not for 15NS-101.

Figure 17. Plot of saturation indices (SI) for K-feldspar, kaolinite, muscovite, quartz and illite vs. dissolved silicon in mg/L for experiment 15NS-101. Values for major ion activities were calculated using measured ICP-MS concentrations for Ca, Mg, K, Na, Al, and Si. Experimental temperature of 150°C and pressure of 450 bars were used for this simulation.

Figure 18. Plot of SI for K-feldspar, kaolinite, muscovite, quartz and illite vs. dissolved Si in mg/L for experiment 16NS-102. Values for major ion activities were calculated using measured ICP-MS concentrations for Ca, Mg, K, Na, Al, and Si. Experimental temperature of 150°C and pressure of 450 bars were used for this simulation.

Figure 19. Plot of SI for muscovite, K-feldspar, kaolinite, and quartz and of pH vs. temperature for experiment 15NS-101.

Figure 20. Plot of SI for illite, muscovite, K-feldspar, kaolinite, and quartz and of pH vs. temperature for experiment 16NS-102.

Activity Diagrams with GWB

Activity-activity diagrams of $\log K^+/H^+$ vs. $\log SiO_2$ were generated using the ‘Act2’ application in the Geochemist’s Workbench (GWB) Student Edition software. The GWB spreadsheet application ‘GSS’ was used to calculate activity ratios, with ICP-MS concentrations as inputs. These were then projected onto the activity-activity diagram as points representing individual samples. The projected points indicate that all samples fall in the stability field of muscovite, moving towards ‘maximum microcline’ (K-feldspar) as SiO_2 activity approaches equilibrium with quartz (Figs. 21 and 22). For 15NS-101, all major elements were added to the calculation, hence the presence of

‘paragonite’, ‘albite-low’, ‘clinoptilolite-K’, and ‘clinoptilolite-Ca’ fields in the activity diagram; for modeling runs for 16NS-102, only Al, K, Si, and pH were considered to simplify the diagram.

Figure 21. Activity-activity diagram of $\log K^+/H^+$ vs. $\log \text{SiO}_2$ for experiment 15NS-101 generated with the Act2 application in The Geochemist's Workbench (GWB). Projected points were calculated with measured activities from samples 15NS-101-1 through 15NS-101-6 (Table 2).

Figure 22. Activity-activity diagram of $\log K^+/H^+$ vs. $\log SiO_2$ for experiment 16NS-102 generated with the Act2 application in The Geochemist's Workbench (GWB). Projected points were calculated with measured activities from samples 16NS-101-1 through 16NS-101-5 (Table 3).

DISCUSSION

Pre-Experiment Geochemical Modeling

Initial modeling results with SOLMINEQ showed that saturation states of all minerals of interest in this study are highly sensitive both to pH and to aluminum activity. The first modeling study indicated that the optimum pH for muscovite precipitation should be approximately 5.5, a pH value that was also predicted to cause the fluid to be undersaturated with respect to both kaolinite and K-feldspar for the given conditions. On either side of the local maximum calculated for saturation with respect to muscovite, the curve drops away, indicating that the fluid would be less supersaturated with respect to muscovite with a change in pH of ± 0.1 pH units (Fig. 4). Interestingly, the fluid was modeled to have been undersaturated by the same amount with respect to both kaolinite and K-feldspar at approximately the same point the maximum supersaturation with respect to muscovite was calculated, a pH of 5.5. The aluminum concentration in the model run that showed the maximum saturation with respect to muscovite and the minimum saturation with respect to K-feldspar and kaolinite was $22.5 \mu\text{g/L}$ (Fig. 4). Small changes in aluminum concentration, on the order of $\pm 10 \mu\text{g/L}$, were observed to cause a disproportionately large change in the saturation states of the minerals of interest.

As noted above, the mineral muscovite was used as a proxy for illite throughout this modeling study, due to both the variable composition of illite and the assumption that muscovite and illite should have similar thermodynamic properties. In the geochemical modeling, however, the fluid was consistently more supersaturated with respect to muscovite than illite, and a point was not observed where the fluid was more

supersaturated with respect to illite than muscovite. In the modeling results presented in Figure 4, ΔG values with respect to illite were below the scale of the plot of ΔG vs. pH. This result implies one of several possibilities: that muscovite is not a good proxy for illite, or that the model was not accurately simulating the geochemical conditions, given that the water chemistries, temperatures and pressures used are known to have led to the formation of illite. A third possibility is that the model was, in fact, accurately representing the fluid saturation states with respect to the minerals of interest.

Initially, it was thought that there were inaccuracies in the thermodynamic database of SOLMINEQ that led to illite and muscovite showing such a large difference in saturation states. Instead, it appears that the fluid in experiment 16NS-102 was supersaturated with respect to muscovite and undersaturated with respect to illite, and that the initial modeling study actually provided a good representation of the mineralogical changes that took place during the hydrothermal experiments.

Chemical Analysis

For experiment 15NS-101, ICP-MS analysis indicated no significant change in potassium concentrations throughout the course of the experiment. It was initially hypothesized that a decrease in potassium would indicate incorporation into clay minerals, including illite/muscovite, based on reactions 2 and 3. There are two fundamental flaws with this initial hypothesis. Firstly, in the overall reaction (reaction 1), potassium is conserved; therefore, any dissolution of K-feldspar that would produce K^+ ions is balanced by precipitation of muscovite/illite and other clay minerals such as smectite and chlorite that incorporate potassium, effecting a net change of zero in the

potassium activity of the fluid. Secondly, due to the relatively high initial concentrations of potassium in the brines used in the hydrothermal experiments (Table 1), a small change in potassium concentration would be difficult to measure within the analytical error of the method.

Experiment 15NS-101 did show a steady decrease in magnesium concentration over the course of the experiment, indicating possible uptake in smectite or another magnesium-incorporating mineral, possibly chlorite or dolomite. A steady increase in silicon dissolved in the fluid was also shown that was due to dissolution of K-feldspar, not quartz, as shown by XRD analysis.

ICP-MS analysis of fluid samples from experiment 16NS-102 did not show clear trends for most of the elements analyzed (Figs. 8 and 9). Silicon did show an increase corresponding to the fluid reaching equilibrium with SiO_2 and also corresponding to K-feldspar having dissolved to saturation. The lack of any clear trends for most of the elements of interest other than Si is likely due to both the short runtime of the experiment compared to that of 15NS-101 (1,000 vs. 2,800 hours) and to the limited number of fluid samples taken.

Petrographic Analysis

While analysis of the reaction fluids provided important information regarding the chemical changes that had taken place over the course of the experiments, in order to determine any changes in mineralogy it was necessary to analyze the rocks themselves. SEM/EDS analysis as described above indicated the presence of both K-feldspar and kaolinite in the pre-reaction core material for both hydrothermal experiments, in addition

to small amounts of illite/muscovite. Analysis of clay mounts prepared from the post-reaction sediments indicated both dissolution of K-feldspar grains and what appeared to be poorly-crystallized, possibly ‘incipient’ or neo-formed illite grains, not observed in clay mounts prepared with the pre-reaction sediment. Although this observation was encouraging, there are several reasons why it cannot be used alone to demonstrate whether formation of illite took place during the course of the hydrothermal experiments. It is difficult to determine whether the observed grains with illite-like EDS spectra were initially in the sandstone, or whether they formed during the experiment, based on SEM/EDS analysis alone.

Additionally, due to the nature of the clay mount preparation, it is possible that there were some inconsistencies in the grain size fraction that was placed on the filters. While steps were taken to homogenize the sediments, it is also possible that the aliquots extracted for the clay mounts were not representative of the bulk sediment. This could have caused illite to have appeared to be present in the post-reaction clay mounts and absent in the pre-reaction sediments.

In order to attempt to quantify precipitation or dissolution of clay minerals during the course of the experiments, XRD analysis was performed with bulk-rock samples pre- and post-reaction. The results of the XRD analysis outlined above indicate that there was a small decrease in K-feldspar wt % and no measurable change in kaolinite wt %, throughout the course of both experiments. Although the geochemical modeling studies described above did indicate supersaturation with respect to muscovite and undersaturation with respect to kaolinite and K-feldspar, these models represent possible

near-equilibrium conditions that could take thousands to hundreds of thousands or millions of years to reach at basin temperatures and pressures. While K-feldspar did decrease throughout the course of both experiments, especially poorly crystallized microcline, the relatively small change indicates that the fluid was not as understaturated with respect to this mineral as predicted by the geochemical modeling. This is possibly due to increases in the aluminum and silicon activities that could have pushed the fluid towards supersaturation with respect to K-feldspar after smaller, less well crystallized grains had dissolved and eroded. Post-reaction geochemical modeling indicated that the experimental fluid reached saturation with respect to K-feldspar.

Kaolinite did not change significantly over the course of either experiment. This may have been caused by the fluid reaching saturation with respect to kaolinite early in the experiment due to aluminum and silicon from dissolved K-feldspar. Additionally, a lower pH than that determined as optimum by the geochemical modeling was measured at *in situ* experimental conditions. This could have also pushed the fluid towards supersaturation with respect to kaolinite.

One very important result of the XRD analysis is that illite was present as a significant weight percentage of clays in pre-reaction sediment of both 15NS-101 and 16NS-102. This is critical to the interpretation of the results and a significant finding on its own, because it indicates that illite does form in significant weight percentages at much lower temperatures and depths (~60-100°C, 2-3 km) in North Sea sandstone formations than postulated by several prominent workers in the region including Bjørlykke and Aagaard (1992), Bjørlykke, et al. (1995) and Bjørlykke (1998, 2014), who

claimed that illite only forms extensively at temperatures between 135 and 150°C, corresponding to a depth of burial of around 3.5 to 4 km.

Illite showed a significant decrease over the course of experiment 15NS-101, but this cannot be quantified due to the post-experiment sediment/fluid mixture having been separated prior to XRD analysis. In experiment 16NS-102, well-crystallized illite did appear to decrease significantly over the course of the experiment, while muscovite increased. This may indicate dissolution of existing illite and recrystallization of muscovite, or, perhaps more likely on the timescale of the hydrothermal experiments, this indicated recrystallization or a change in crystallinity of the existing illite to one that was closer to muscovite.

It should be noted that it can be difficult to distinguish the illite spectrum from the muscovite spectrum (J. Thordsen, written comm., 2016); this implies that the observed change in diffraction could indicate a change in the stacking of existing illite/muscovite (D. Andersen, pers. comm., 2016). Regardless of the exact cause of the observed change in clay mineralogy, this result indicates a change in the crystallinity of the existing muscovite/illite fraction, and therefore cannot be ignored in the interpretation of the experimental results. Another interesting result of the XRD analysis is the increased calculated smectite percentage in mixed-layer illite/smectite, from 8% in the pre-experiment core material to 30% in the post-experiment 16NS-102 sediment, corresponding to a decrease in illite percentage from 92% to 70%. According to Wilson et al. (2014), illite in North Sea sandstone can often be mistaken for smectite in XRD analysis due to the similar peaks produced by very thin illite layers and smectite layers.

This result further supports the interpretation of illite crystallinity having changed in experiment 16NS-102.

Post-Experiment Geochemical Modeling

The results of geochemical modeling with PHREEQC indicate that illite and potassium feldspar were both initially dissolving, and that this illite dissolved and re-precipitated as muscovite, or that the illite did not completely dissolve and simply recrystallized as a phase that was analyzed as muscovite by XRD.

This interpretation correlates well with the results of the XRD analysis, which showed that, although the total amount of clay did not change significantly over the course of experiment 16NS-102, there was a significant change in the crystallinity of the illite/muscovite fraction. The results presented in Table 6 indicate that, over the course of experiment 16NS-102, the illite and muscovite fraction of the clays changed from almost entirely illite, to muscovite/illite, with the muscovite fraction increasing from close to zero to nearly 2 wt%, while the illite fraction decreased from approximately 3 wt% to 1 wt%.

Similar results were modeled for 15NS-101, but due to the separation of some of the fine material from the bulk post-reaction fluid sample, they cannot be directly correlated with the results of the XRD analysis.

The modeling of saturation indices and pH vs. temperature indicated that peak saturation with respect to both muscovite and illite would occur at around 60 – 100°C, corresponding to a minimum in pH. This temperature corresponds closely with measured

temperatures in North Sea wells at a depth of 2 – 3 km, very close to the depths of the sandstone core samples used in the experiments.

Activity diagrams generated with GWB indicated that each point measured by ICP-MS analysis was in the stability field of muscovite, a result that correlates well with XRD results showing muscovite increasing in experiment 16NS-102.

CONCLUSIONS

Several converging lines of evidence from chemical, computer modeling, and petrographic analyses indicate that illite crystallinity changed significantly over a short time (several weeks) under the pressures, temperatures and geochemical conditions utilized in the hydrothermal experiments.

Chemical analysis of fluid samples from hydrothermal experiments 15NS-101 and 16NS-102 indicated that Si concentration changed significantly over the course of both experiments, approaching saturation with respect to quartz. No quantifiable change in K concentration was observed in either experiment, likely indiscernible due to both the high TDS, and high initial K concentration.

Geochemical modeling exercises indicated that at a pH of 5.5, the experimental fluid would be supersaturated with respect to muscovite and slightly undersaturated with respect to kaolinite and K-feldspar. Dissolution of K-feldspar and of dolomitic cements was observed quantitatively and qualitatively in the petrographic analyses. The geochemical modeling exercises also indicated that the fluid would become supersaturated with respect to kaolinite at a pH < 5.4. Kaolinite percentages did not change significantly in either experiment, suggesting that either the *in-situ* pH of the experiment was lower than that calculated by the geochemical modeling exercises, that dissolved aluminum concentrations were higher than estimated, or both.

Petrographic analysis of pre- and post-hydrothermal experiment sandstone cores showed a decrease in the weight percentage of illite, but in 16NS-102, this was balanced by an increase in muscovite peaks as measured by XRD, indicating a change in the

crystallinity of the illite/muscovite clay fraction. These results neatly constrain geochemical modeling, both pre- and post-experiment, that indicated supersaturation with respect to muscovite, and undersaturation with respect to illite.

In experiment 16NS-102, an attempt was made to take the system further away from equilibrium by running the experiments at 150° C and 450 bars, more than doubling the *in situ* reservoir conditions of approximately 60°C and 200 bars, to simulate burial to a depth of approximately 4 km. However, XRD analysis of the post-reaction sediment from the hydrothermal experiments indicated that this produced no new illite, although a change in illite crystallinity was indicated by both SEM/EDS analysis and XRD analysis of the pre- and post-reaction sediments.

These results indicate that in order to precipitate extensive, well crystallized illite in hydrothermal experiments on a reasonable time scale (1-2 months), conditions may have to be taken very far from equilibrium. Future experiments could be performed that would produce more well constrained results. Several experimental parameters could be changed for future experiments, including temperature, pressure, core material, and fluid chemistry. Additionally, different types of reaction vessels, such as static vessels or flow-through cells with whole-rock core material, could be used. The results of these experiments could possibly provide reaction kinetics and reaction paths that could then be applied to more accurately interpret basin diagenesis.

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