SAND2016-8080C

Exceptional service in the national interest

Sandia National Laboratories

Photos placed in horizontal position with even amount of white space between photos and header

Mineralogical alteration of Mancos shale under conditions relevant to unconventional gas reservoirs

J. Kruichak, A. Ilgen, Y. Xiong, M. Rodriguez, J. Griego, Y. Wang

Jessica Kruichak
Fall 2016 ACS Meeting
August 20, 2016

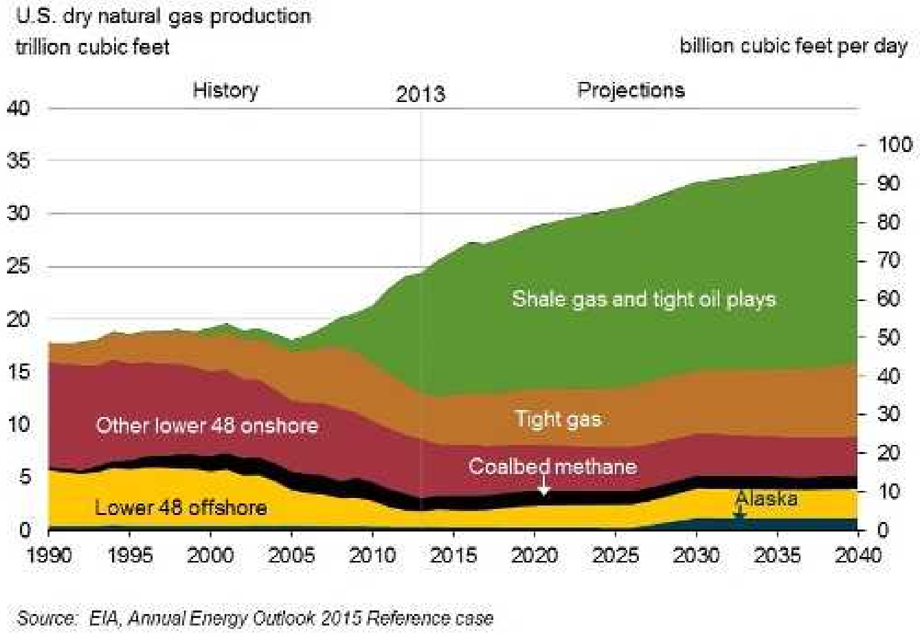
U.S. DEPARTMENT OF ENERGY

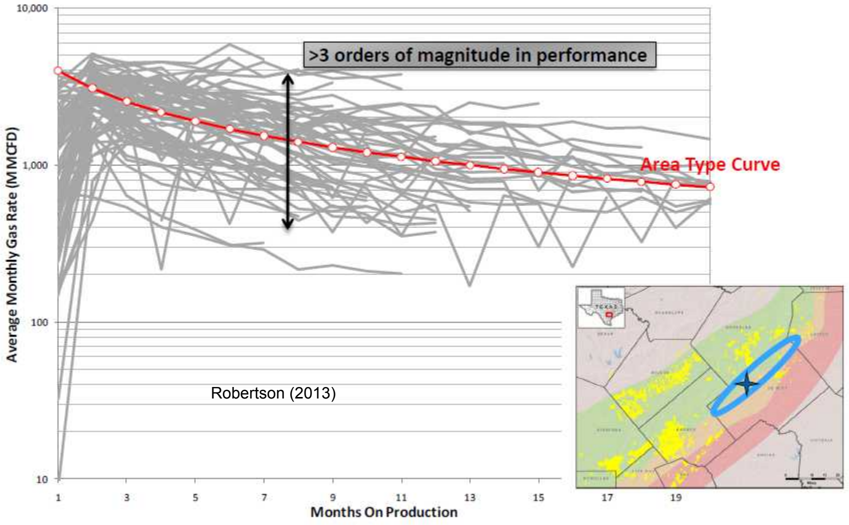
NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

Background

- Shale gas has changed the energy landscape in the US in the last decade; in 2013 is contributed to almost 50% for natural gas production in the US
- Despite the massive success there are still major concerns



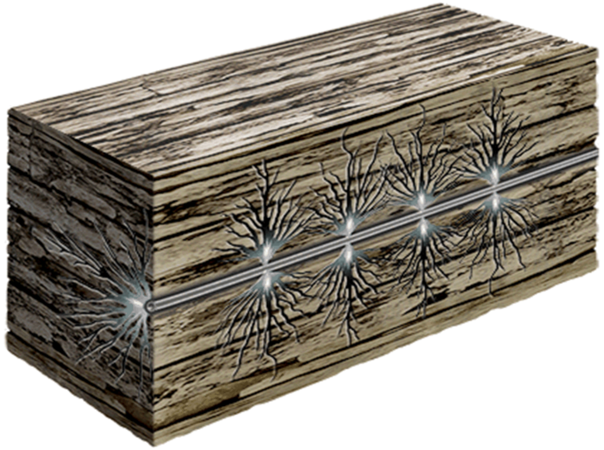


- Large variability and unexpected steep decline in well production (up to 95% reduction over first 3 years)
- Low recovery rates (<10%)

Research Focus

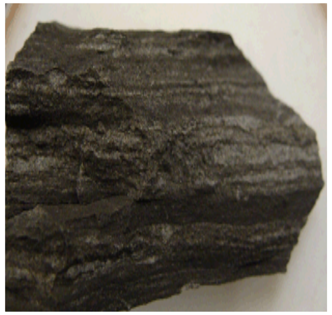
- We hypothesize the alteration of shale by hydrofracturing fluid affects the release of methane
- Proposed mechanisms responsible for production decline:

1. Thin water films, or imbibition of water
2. Swelling clays blocking porosity
3. Alteration of shale by hydrofracturing fluid affects methane adsorption affinity
    - Goal is to compare methane adsorption affinity for altered shale to unaltered shale



Methods

- Batch reactors:
  - Mancos shale powdered and chips, and model material; Illite clay <75um fraction
  - Manco shale and clay minerals were reacted with synthetic hydrofracturing fluid in Parr digestion vessels for 1-2 months at 90° C
    - Synthetic hydrofracturing fluid: 0.1% Polyacrylamide; 0.05% Sodium polyacrylate; 0.1% Sodium chloride; 0.02% Methanol; 0.01% Hydrochloric acid; 0.007% Tetrakis (hydromethyl) phosphonium sulfate



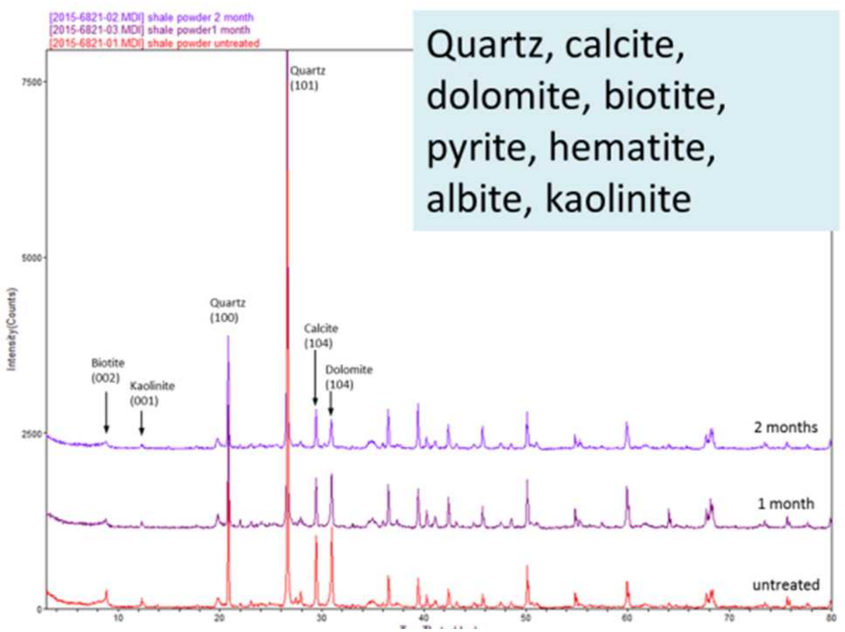
Methods

- Characterization:
  - X-ray diffraction (XRD)- powder micro-XRD, and micro-X-ray fluorescence mapping (micro-XRF).
  - Analysis of liquids for major anions and cations- ion chromatography (IC) and for trace metals by inductively coupled plasma mass spectrometry (ICP-MS).
- Geochemical modeling:
  - The Geochemist's Work Bench (GWB) Path of Reaction Modeling (Bethke, 1998) is used to interpret geochemical data. The initial aqueous composition is hydrofracturing fluid and reactants are the minerals detected in the Mancos shale.
- Methane Sorption:
  - We studied the adsorption kinetics by monitoring weight change as a function of time from the instant a dose of CO2 and CH4 gas mixture is adsorbed onto the sample, until the moment saturation equilibrium is reached. Using Netzsch STA 409 thermal gravimetric analyzer (TGA) with differential scanning calorimeter (DSC) and Differential temperature analyzer (DTA)
  - at reservoir relevant temperatures up to 125oC and constant pressures up to 1 bar.

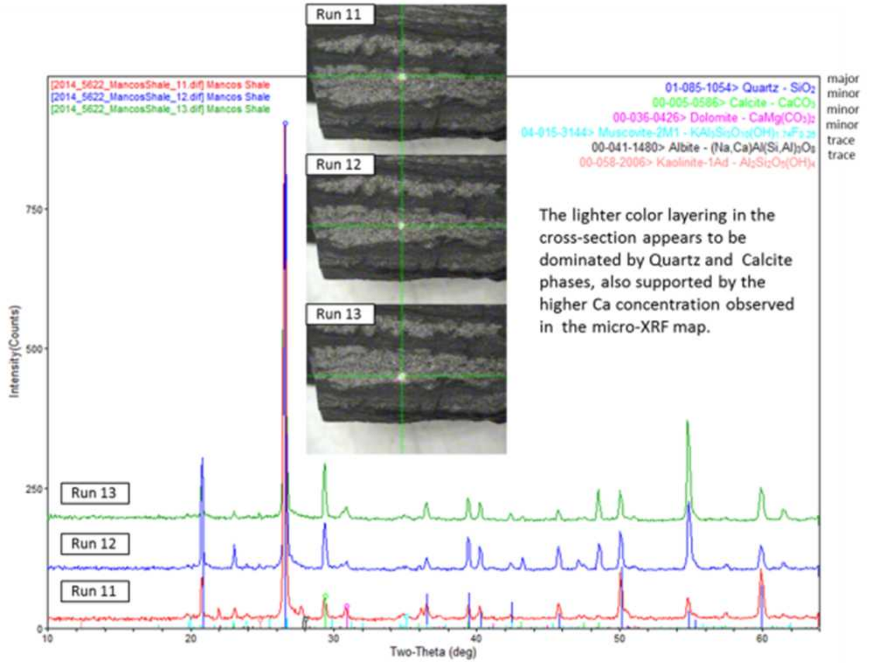
Results- Characterization

- Mancos shale characterization and mineralogical changes after reaction with hydrofracturing fluid:

Bulk XRD



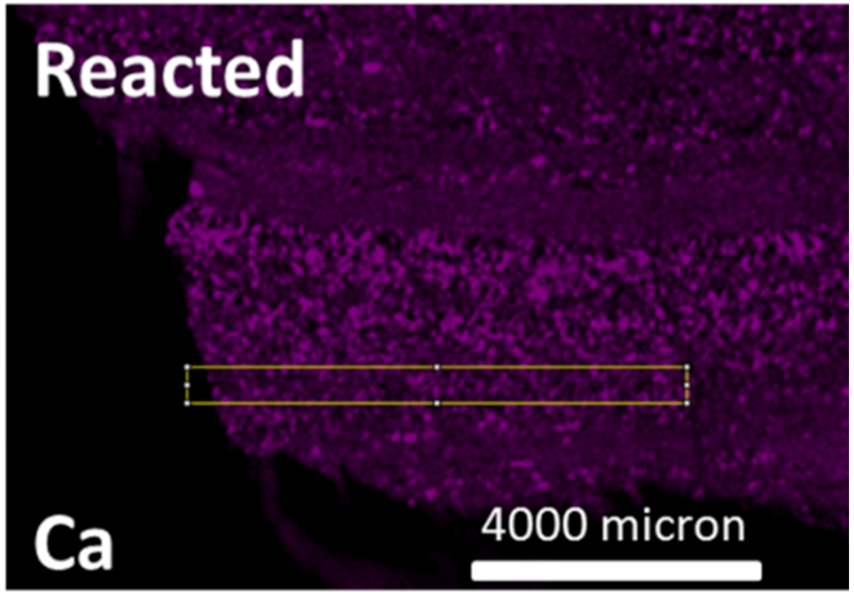
Micro-XRD

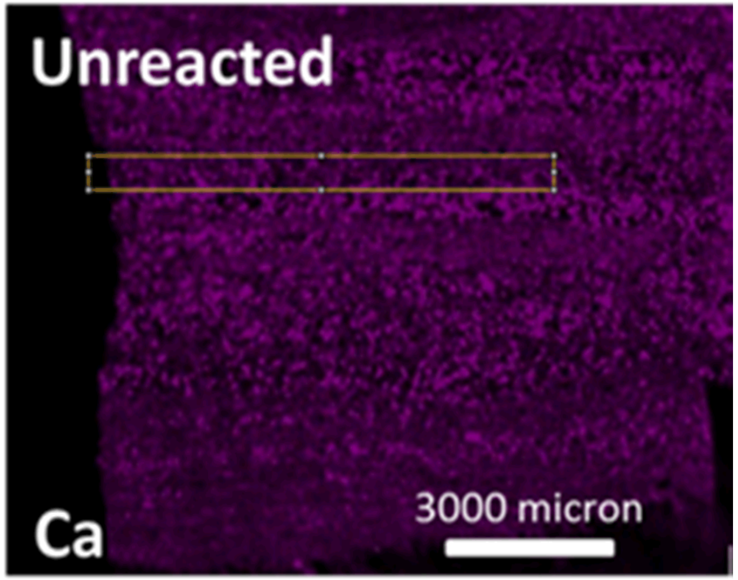


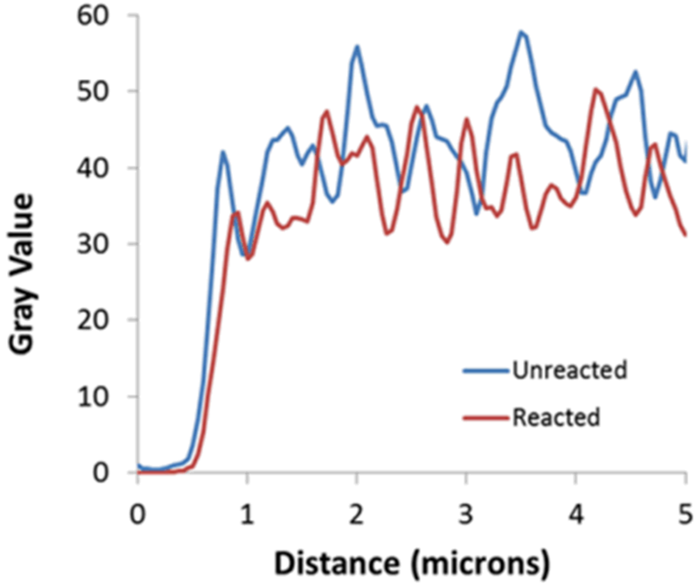
The XRD patterns normalized to the 100% peak for quartz indicate that the dolomite, calcite, biotite, and kaolinite peaks decrease in intensity relative to the quartz peaks with increased treatment time, indicating dissolution of these minerals.

Results- Characterization

- Surface alteration of Mancos shale by hydrofracturing fluid:



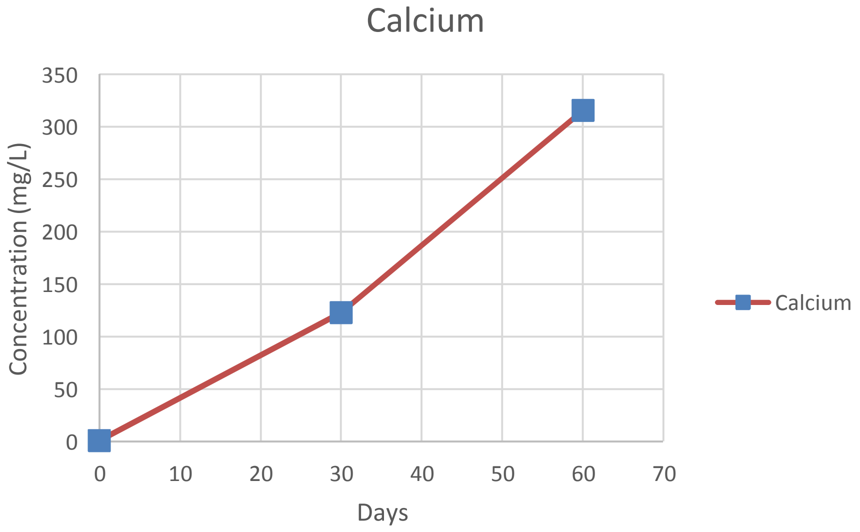


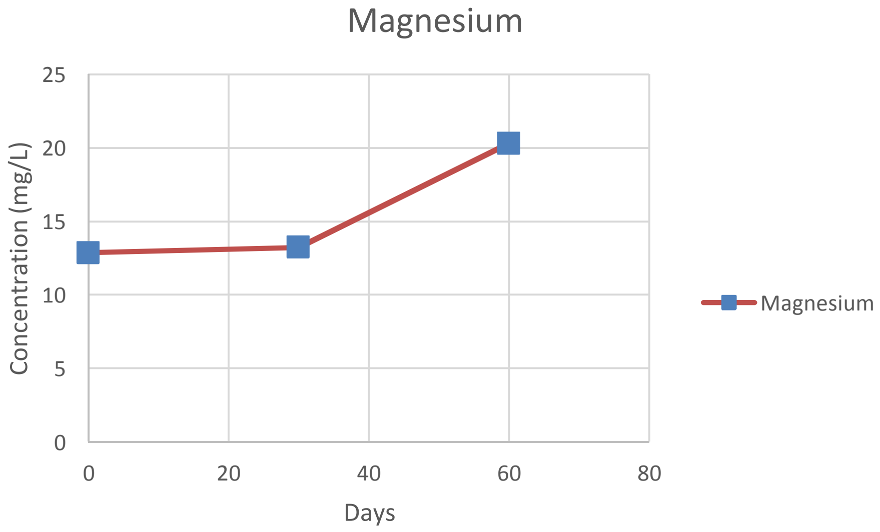


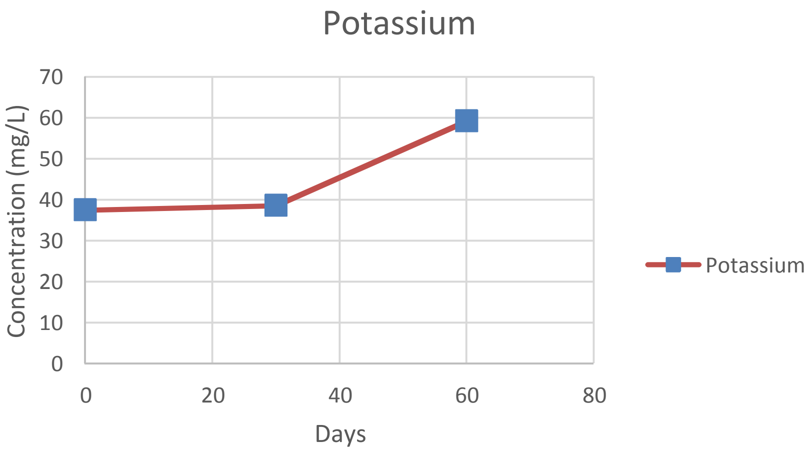
Micro-XRF mapping of the reacted “rind”. Altered zones on shale surface after 2 months of reaction are thin – likely, within a few microns. Hard to tell

Results- Characterization

- Aqueous concentration from powdered shale confirm- Dolomite, calcite, and biotite dissolution observed in XRD

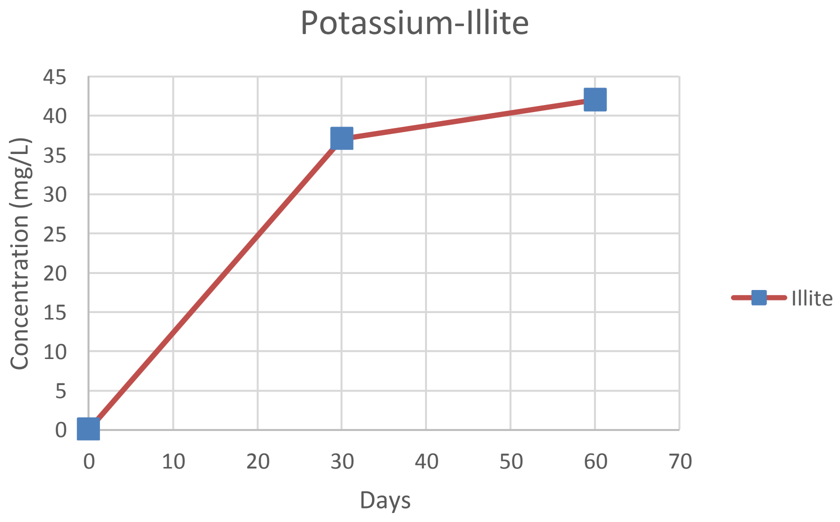


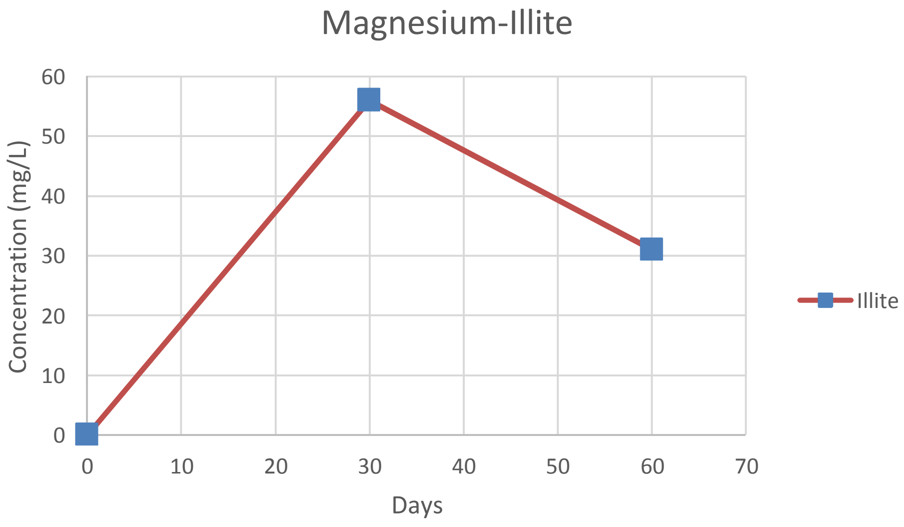


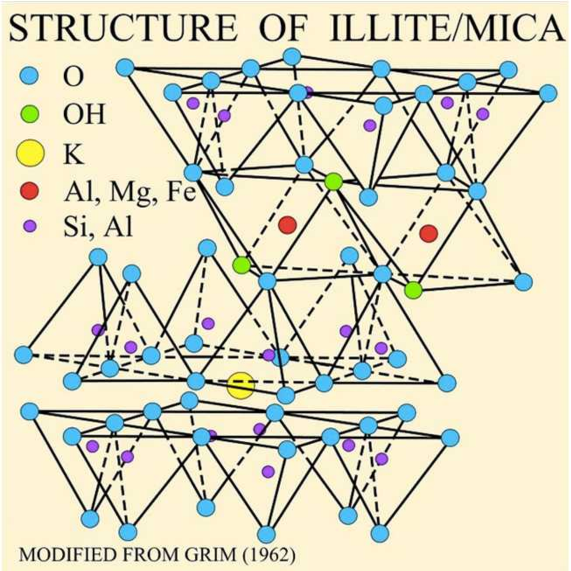


Results- Characterization

- Aqueous chemistry observations Clay minerals
- Clay is dissolving in hydrofracturing fluid







Results- Geochemical modeling

- Path of reaction modeling using Geochemists Work Bench (Bethke, 1998).

Initial aqueous composition

pH	4.14	
Cl^-	643	mg/L
SO_4^{2-}	15	mg/L
K^+	37.4	mg/L
Ca^{2+}	0.8	mg/L
Na^+	439	mg/L
Mg^{2+}	13	mg/L
Fe^{2+}	2	mg/L

Mineral	wt.%	k, mol cm^{-2} sec^{-1}
Quartz	80.5	1×10^{-17}
Albite	8.3	1×10^{-16}
Dolomite	7.6	1×10^{-12}
Calcite	4.9	1×10^{-8}
Muscovite	2	1×10^{-14}
Kaolinite	1	1×10^{-14}
Pyrite	1	2.5×10^{-15}
Hematite	1	2.5×10^{-14}

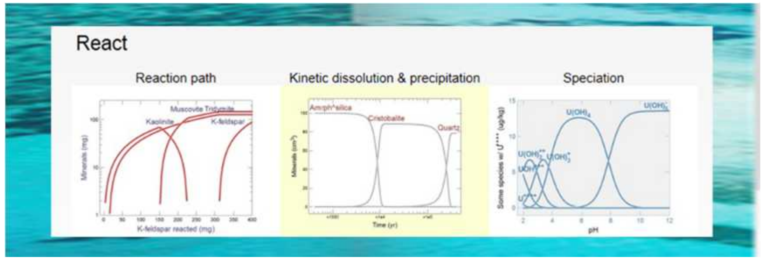
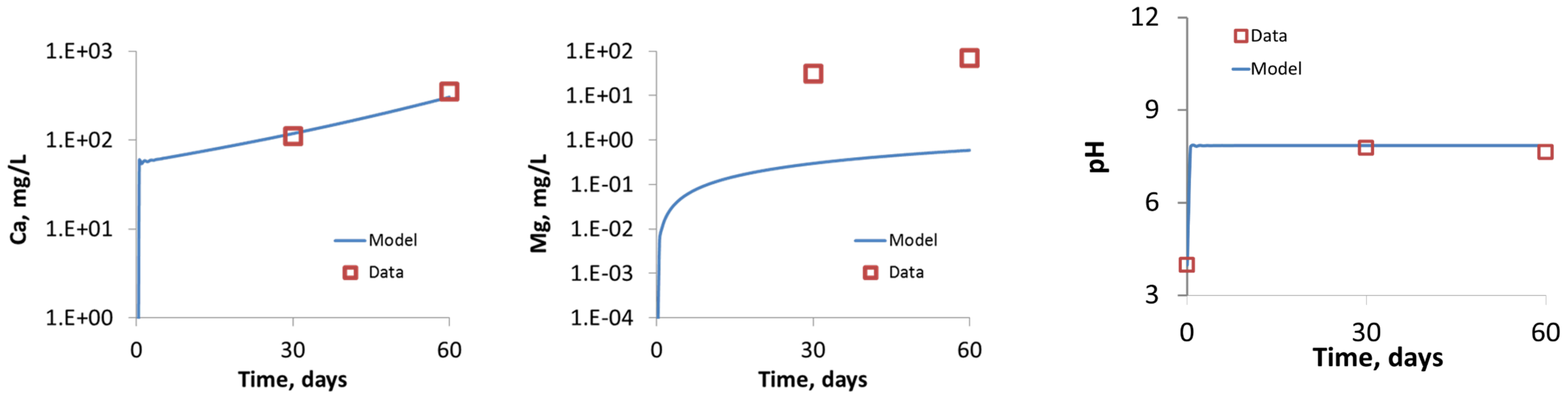


Image source: http://www.gwb.com/

Results- Geochemical Modeling

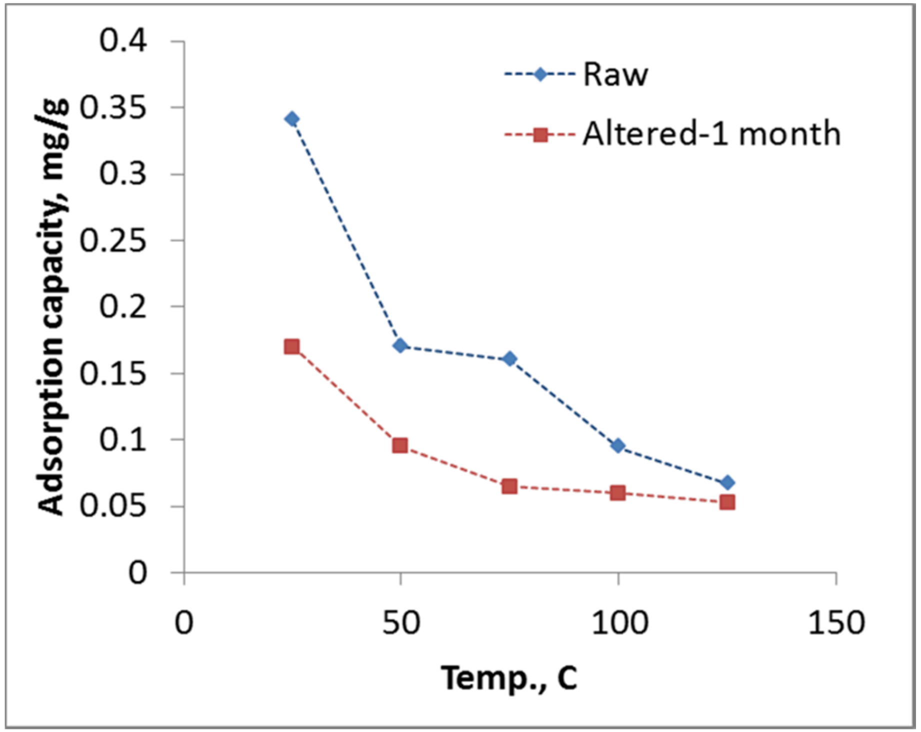
- **Aqueous chemistry observations and geochemical modeling**



Geochemical models capture some major elements and pH.

Results- Methane Sorption

- Sorption: methane adsorption on the altered and as is Mancos shale
- Between non altered and 1-month altered with hydrofracking fluid- the adsorption to methane decreased
- 2month data in the works



Sample ID	BET (m^2/g)
Unreacted Mancos shale	8.9
Mancos shale reacted for 1 month in fracking fluid	10.5
Mancos shale reacted for 2 months in fracking fluid	10.5

Conclusion

Sandia National Laboratories

- In carbonate rich Mancos shale we have observed dissolution of…. mineral alterations from reacting with fracking fluid

- The mineralogical changes cause a decrease in methane adsorption onto shale

References

- Ho,T.A. et al. Nanostructural control of methane release in kerogen and its implications to wellbore production decline. Sci. Rep. 6, 28053; doi: 10.1038/srep28053 (2016).
- Bethke C. (1998) The Geochemist's Workbench 8.0. University of Illinois at Urbana-Champaign, IL.
- Kaufman P., Penny, G.S. SPE 119900 . Presented at SPE Shale Gas Production Conference Irving, Texas 16-18 November 2008.
- Paktinat, J. et.al. SPE 144210. Presented at SPE North American Unconventional Gas Conference and Exhibition Woodlands, Texas 14-16 June 2011.
- Stefano, C., Gianguzza, A., Piazzese, D., Sammartano, S. Talanta 61. (2003) 181-194.
- EQT. Well Number: 590516

Acknowledgments

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Sandia National Laboratories

- Thank you for your time ☺