

## **Organic-Inorganic Interactions during Hydrocarbon Secondary Migration: Effects on Reservoir Quality**

Chen Zhu, Indiana University

### **Introduction**

Secondary migration transports hydrocarbon from source rocks to a reservoir through permeable carrier rocks. Organic catagenesis byproducts (e.g., CO<sub>2</sub>, H<sub>2</sub>S, and organic acids) and carbonic acid and carboxylic acids generated from oil degradation are corrosive to the carrier and reservoir rocks. The interactions between these acidic components and inorganic chemicals—solutes in brine and minerals in the solid matrix—can increase or redistribute the porosity and facilitate the creation of exploration “sweet spots.” However, controversy exists as to whether these interactions occur at a scale that is truly significant to reservoir quality and petroleum accumulation.

Much of this controversy centers on the plausibility of mass balance and thermodynamics. **Coupled Reactive Transport Modeling** (RTM) is effective to address these two key constraints, *quantitatively*. In this study, we use RTMs to simulate the multiphase flow of gas and water through a carrier bed and into a reservoir along temperature and pressure gradients at a time and spatial scales of up to 10<sup>6</sup> – 10<sup>7</sup> years and 10<sup>2</sup> kilometers, respectively, and test many concepts, arguments, and assumptions through scenarios analysis.

### **Progress to date**

#### ***Basin-scale coupled reactive transport modeling***

Numerical models for the charging of natural gas rich in acidic components (CO<sub>2</sub>) were developed for generic carbonate and sandstone reservoirs, respectively, to answer the following questions: (1) Can acidic matter redistribute/modify the local pores of reservoirs at a large scale? (2) How does the dissolved mass migrate? (3) What is the degree of local porosity change? (4) Dissolution/precipitation of which mineral(s) control porosity redistribution/modification?

For the carbonate reservoir, simulation results indicate (1) CO<sub>2</sub> can induce local mesogenetic dissolution, which occurs mainly in the vicinity of gas-water-contact (GWC) and, for the configuration in this study, results in the porosity increase limited in the trap. The dissolved minerals are transferred out by the groundwater flow. (2) Mesogenetic dissolution occurs on the localized area in the formation (e.g., the trap), not the entire formation. Therefore, it only requires a small amount of CO<sub>2</sub> and groundwater. The limited CO<sub>2</sub> from source rock and groundwater flow in the subsurface seem to be sufficient to support local secondary porosity generation.

#### ***A Mineral-Water-Gas Interaction Model of pCO<sub>2</sub> as a Function of Temperature in Sedimentary Basins***

Accurate prediction of CO<sub>2</sub> partial pressure (*p*CO<sub>2</sub>) in sedimentary basins is important for reducing the risks in natural gas exploration, improving reservoir quality prediction, optimizing production and reservoir management operations and understanding of geological storage of CO<sub>2</sub>. We developed a comprehensive model of CO<sub>2</sub>-water-rock interactions to interpret and predict *p*CO<sub>2</sub> in sedimentary basins. This improved model considers a gas phase explicitly, the gas composition through a Peng-Robinson equation of state, the pressure effects on thermodynamic properties of minerals and aqueous species, an expanded mineral assemblage, and the basin re-subsidence history. *p*CO<sub>2</sub> values under these conditions was then calculated via reaction path modeling.

The modeling results indicated that *p*CO<sub>2</sub> values in the sedimentary basin as a function of temperature are controlled not only by the thermodynamic equilibrium between water and aluminosilicate and carbonate minerals but also by the availability and composition of the co-existing initial gas (Fig 1). The effects of the addition of the same

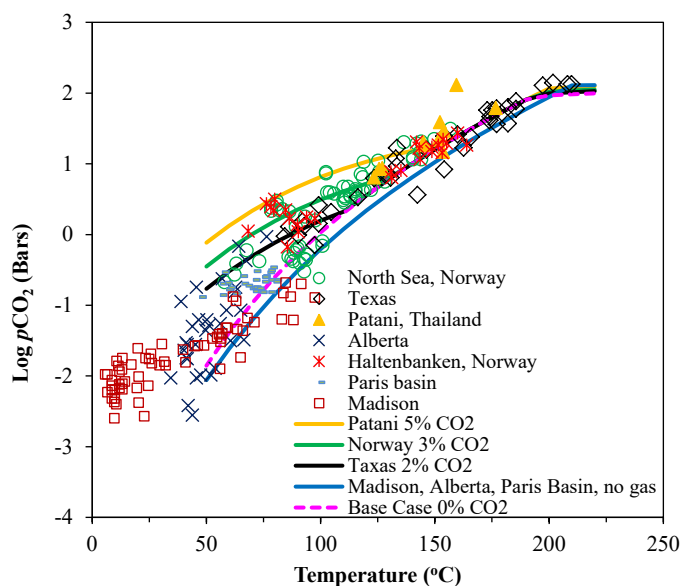


Figure 1.  $\log(p\text{CO}_2)$  as a function of temperature (and the corresponding pressure) in sedimentary basins with a simple burial history (monotonic subsidence). Symbols are field data and lines are simulation results.

### Timeline to completion

During Year 2, Tasks 4-5 were performed (Task 4: Influence of regional groundwater flow; Task 5: Influence of organic acids on the dissolution kinetics of aluminosilicate minerals). An abstract was submitted to national meetings (e.g. AAPG 2020 and AGU 2019, see below). One publication is accepted, and another is in review. A Ph.D. student is supported on the grant. The grant is on NCE 9/1/2019-8/31/2020. We expect two additional publications will be submitted during Year 3.

### Impact of Research

The research supported by this ACS-PRF New Direction grant represents a significant step forward in our understanding of the organic-inorganic interactions (water-gas-rock-hydrocarbon integrations) during hydrocarbon migration. The support provided to one graduate student has allowed him to continue his research into thermodynamics and kinetics of geochemical reactions.

### Publications

(‡student authors; \*corresponding authors)

‡Zhang GR, Lu P, \*Zhu C (accepted for publication) Effects of natural gas acidic components on local porosity generation in a carbonate reservoir: Insights from reactive transport modeling. AAPG Bulletin.

Lu P, Luo P, ‡Zhang GR, Zhang S, \*Zhu C. An Improved Model of  $p\text{CO}_2$  as a Function of Temperature in Sedimentary Basins. (Submitted to AAPG Bulletin)

‡Zhang GR, Lu P, ‡Zhang YL, \*Zhu C. SupPHREEQC: A program to generate customized PHREEQC thermodynamic database based on SUPCRTBL. (To be submitted to *Computers & Geosciences*)

### Abstracts and Presentations at National and International at Conferences

(‡student authors; \*corresponding authors)

Lu P, Zhang GR, Luo P, Zhu C (2020) Modeling effects of  $\text{CO}_2$  associated with natural gas generation on local mesogenetic dissolution in a carbonate formation. The 14th Middle East Geosciences Conference & Exhibition, 16 – 19 March 2020, Bahrain international exhibition & convention centre, Bahrain.

Zhang GR, Zhu C (2019) Reactive Transport Modeling to Study Local Mesogenetic Dissolution in Carbonates Induced by Natural Gas Acidic Components. *EOS Trans.* AGU fall meeting, Dec 9 – 13, 2019 San Francisco.

Lu P, Zhang GR, Zhu C (2019) Controls on  $\text{CO}_2$  Partial Pressure in Petroleum Reservoirs during Burial Diagenesis, Geoconvention, Calgary, Canada, May 13-17, 2019.

Lu P, Zhang GR, Zhu C (2019), Controls on  $\text{CO}_2$  Partial Pressure in Petroleum Reservoirs during Burial Diagenesis, International Petroleum Technology Conference, Beijing, China, March 26-28, 2019

Zhu C, Zhang GR, Zhang YL, Lu P (2018) Developing thermodynamic and kinetic databases for geochemical modeling, 2018 TOUGH Symposium, October 8-10, 2018, Lawrence Berkeley National Laboratory, Berkeley, CA

Lu P, Zhang GR, Sonnenthal E, Zhu C (2018) Impacts of  $\text{CO}_2$  on local mesogenetic dissolution in a carbonate reservoir: Insights from reactive transport modeling, 2018 TOUGH Symposium, October 8-10, 2018, Lawrence Berkeley National Laboratory, Berkeley, CA