



Controls on CO₂ Partial Pressure in Petroleum Reservoirs during Burial Diagenesis

Peng Lu¹, Guanru Zhang² and Chen Zhu¹

¹Department of Earth and Atmospheric Sciences, Indiana University, Bloomington, IN 47405, USA

² School of Earth Sciences, Chengdu University of Technology, Chengdu 610059, China

Summary

Accurate prediction of CO₂ partial pressure ($p\text{CO}_2$) in petroleum reservoirs is important for reducing the risk in natural gas exploration (high CO₂ abundance reduces the value of gas), improving reservoir quality prediction, assisting production and reservoir management operations and understanding of geological storage of CO₂. Previous models have provided significant insight into $p\text{CO}_2$ -Temperature relationships in sedimentary basins. However, most previous models neither considered a separate gas phase, nor the pressure effects on the minerals and aqueous species. In addition, the multi-component gas phase needs to be explicitly described and the effects of the presence of other gases on CO₂ need to be quantified to accurately calculate the partial pressure. In this study, we developed a mineral-water-gas Interaction model to provide a comprehensive view of $p\text{CO}_2$ as a function of temperature in petroleum reservoirs.

Our modeling results indicate that $p\text{CO}_2$ values in petroleum reservoirs as a function of temperature are controlled not only by thermodynamic equilibrium between water and aluminosilicate and carbonate minerals, but also by the availability and composition of the coexisting initial gas. The model highlights that ignoring the presence of gas; pressure effects on the minerals, aqueous species and gases; or the presence of other gases may result in relatively large errors in calculated $p\text{CO}_2$ values. Due to the irreversibility of aluminosilicate mineral reactions, carbonate-CO₂-water equilibrium is one of the primary controls on pH and $p\text{CO}_2$ in an uplift and re-subsidence scenario. The temperature versus $p\text{CO}_2$ relationship calculated by the model for sedimentary basins with uplift and re-subsidence events deviates from the trend for sedimentary basins with monotonic subsidence.

Method

Calculations on geochemical equilibrium systems and $p\text{CO}_2$ as a function of temperature in each system were aided with the computer codes PHREEQCI 3.4 (Parkhurst and Appelo, 2013) with an improved thermodynamic dataset for minerals. CH₄ is considered representative of all hydrocarbon gases. Chemical equilibrium was assumed among CO₂, water, aluminosilicates, and carbonate minerals at T >50 °C. The gas phase was modeled at fixed total P (Parkhurst and Appelo, 2013), which was hydrostatic pressure at the study depth. The volume and mass of the gases are allowed to change. Water/rock ratio changes due to variations of the gas volume during the course of burial diagenesis were ignored. The gas fugacity coefficient and its solubility were calculated with the Peng-Robinson approach (Parkhurst and Appelo, 2013).

In this study, the base case refers to a gas-water-mineral system of 2 moles of total initial gas with a composition of 0% CO₂ and 100% CH₄ in contact with 1000 cm³ water and 4000 cm³ rock. P of the systems was calculated as hydrostatic pressure corresponding to depth. Reservoir T was calculated using an average geothermal gradient of 27.5 °C/km assuming a surface T of 15 °C. We slightly modified the average abundances of minerals from North Sea, Frio, Haltenbanken, and Wilcox for the starting

mineralogy for our equilibrium model: quartz (76.5%), K-feldspar (8%), albite (4%), illite (0%), calcite (0.5%), kaolinite (9%), dolomite (1%), and siderite. For reservoirs with a complicated burial history, only forward reactions were considered and the backward reactions of some aluminosilicates were not allowed to proceed.

Results

Temperature (and corresponding Pressure) vs. $\log(p\text{CO}_2)$ data from the literature for sedimentary basins with a relatively simple burial history (monotonic subsidence) are shown in Figure 1. Different models with different percentages of CO_2 contents were constructed to model the observed $\log(p\text{CO}_2)$ in different fields: 5% CO_2 for Patani, Thailand; 3% for North Sea, Norway; and 2% for Texas, USA. The Madison, USA; Alberta, Canada; and Paris Basin, France data are from aquifers and therefore do not have a gas phase.

Field data provided constraints on the starting gas composition and gas-water ratio (Fig. 2). It was observed that the mole fraction of CO_2 increased with T (and P) without any external CO_2 source. The models successfully reproduced the sharp increase of CO_2 content around 140 to 190 °C and a slight decrease at 200 to 220 °C. Therefore, $p\text{CO}_2$ values in petroleum reservoirs as a function of temperature are controlled not only by thermodynamic equilibrium between water and aluminosilicate and carbonate minerals, but also by the availability and composition of the coexisting initial gas. The model highlights that ignoring the presence of gas; pressure effects on the minerals, aqueous species and gases; or the presence of other gases may result in relatively large errors in calculated $p\text{CO}_2$ values.

Due to the irreversibility of aluminosilicate mineral reactions (Helgeson, 1968; Helgeson et al., 1969), carbonate- CO_2 -water equilibrium is one of the primary controls on pH and $p\text{CO}_2$ in an uplift and re-subsidence scenario. The temperature versus $p\text{CO}_2$ relationship calculated by the model for sedimentary basins with uplift and re-subsidence events deviates from the trend for sedimentary basins with monotonic subsidence (Fig. 3).

Conclusions

In this study, we developed a mineral-water-gas interaction model to investigate the primary controls and provide a comprehensive understanding of $p\text{CO}_2$ as a function of T in sedimentary basins. The model also addressed pitfalls in the calculations and limitations of previous models. Our model considered a gas phase, P effects on the minerals and aqueous species, and the effects of the presence of other gases (compositions of the gas phases) on CO_2 on calculated $p\text{CO}_2$ values. The model facilitates the investigation of the primary controlling factors of $p\text{CO}_2$ in petroleum reservoirs. In addition, it addresses the pitfalls in the calculations and the limitations of previous models.

Acknowledgements

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research (PRF #57727-ND2 to CZ) and to Natural Science Foundation of China (#41702125 to GRZ) for partial support this research.

References

- Connolly, C. A., Walter, L. M., Baadsgaard, H., and Longstaffe, F. J., (1990). Origin and evolution of formation waters, Alberta Basin, western Canada sedimentary basin. I. chemistry. *Applied Geochemistry*, 5(4), 375-395.
- Coudrain-Ribstein, A., and Gouze, P., (1993). Quantitative study of geochemical processes in the Dogger aquifer, Paris Basin, France. *Applied Geochemistry*, 8(5), 495-506.
- Coudrain-Ribstein, A., Gouze, P., and de Marsily, G., (1998). Temperature-carbon dioxide partial pressure trends in confined aquifers: *Chemical Geology*, v. 145, no. 1-2, p. 73-89.

Franks, S. G., and Forester, R. W., (1984). Relationships among secondary porosity, pore-fluid chemistry and carbon dioxide, Texas Gulf Coast: Clastic Diagenesis, v. 59, p. 63-79.

Helgeson, H. C., (1968). Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions—I. Thermodynamic relations: *Geochimica et Cosmochimica Acta*, v. 32, no. 8, p. 853-877.

Helgeson, H. C., Garrels, R. M., and Mackenzie, F. T., (1969). Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions—II. Applications: *Geochimica et Cosmochimica Acta*, v. 33, no. 4, p. 455-481.

Imbus, S. W., Katz, B. J., and Urwongse, T., (1998). Predicting CO₂ occurrence on a regional scale: Southeast Asia example: *Organic Geochemistry*, v. 29, no. 1-3, p. 325-345.

Lundegard, P. D. and Trevena, A. S., (1990). Sandstone diagenesis in the Pattani Basin (Gulf of Thailand): history of water-rock interaction and comparison with the Gulf of Mexico. *Applied Geochemistry*, 5(5-6), 669-685.

Parkhurst, D. L., and Appelo, C. A. J., (2013). Description of input and examples for PHREEQC version 3-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey.

Plummer, L. N., Busby, J. F., Lee, R. W., and Hanshaw, B. B., (1990). Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota: *Water Resources Research*, v. 26, no. 9, p. 1981-2014.

Reaves, C., and Sulaeman, A., (1994). Empirical models for predicting CO₂ concentrations in North Sumatra, in *Proceedings 23rd Annual Convention, Volume 1, Indonesian Petroleum Association*, p. 33-43.

Smith, J., and Ehrenberg, S., (1989). Correlation of carbon dioxide abundance with temperature in clastic hydrocarbon reservoirs: relationship to inorganic chemical equilibrium: *Marine and Petroleum Geology*, v. 6, no. 2, p. 129-135.

Watson, M. N., Boreham, C. J., and Tingate, P. R., (2004). Carbon dioxide and carbonate cements in the Otway Basin: Implications for geological storage of carbon dioxide: *APPEA Journal*, v. 44, no. 1, p. 703-720.

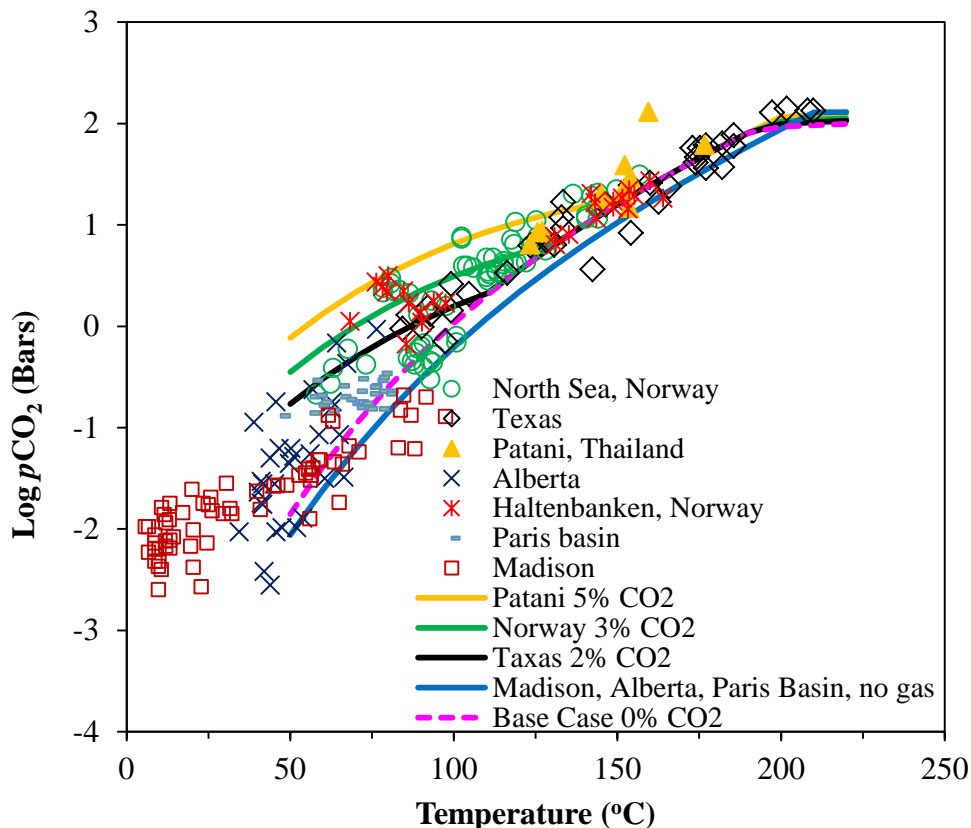


Figure 1. Log($p\text{CO}_2$) as a function of temperature (and corresponding pressure) in sedimentary basins with a simple burial history (monotonic subsidence). Symbols are field data and lines are simulation results. The purple dashed line shows the results from the base case (2 moles of total initial gas with a composition of 0% CO₂ and 100% CH₄), while orange, green, and black lines represents cases with 5% CO₂ and 95% CH₄, 3% CO₂ and 97% CH₄, and 2% CO₂ and 98% CH₄, respectively. The blue line represents saturation index of CO₂ defined as log(fugacity) of CO₂. Madison, Alberta and Paris Basin are confined aquifers without gas phase (Coudrain-Ribstein et al., 1998) and therefore the values are log(fugacity of CO₂) instead of log($p\text{CO}_2$). Data sources: Smith and Ehrenberg (1989) for North Sea and Haltenbanken, Norway; Franks and Forester (1984) and Smith and Ehrenberg (1989) for Texas, U.S.A.; Lundegard and Trevena, (1990) for Patani, Thailand; Connolly et al. (1990) for Alberta, Canada; Coudrain-Ribstein and Gouze (1993) for Paris Basin, France; Plummer et al. (1990) for Madison.

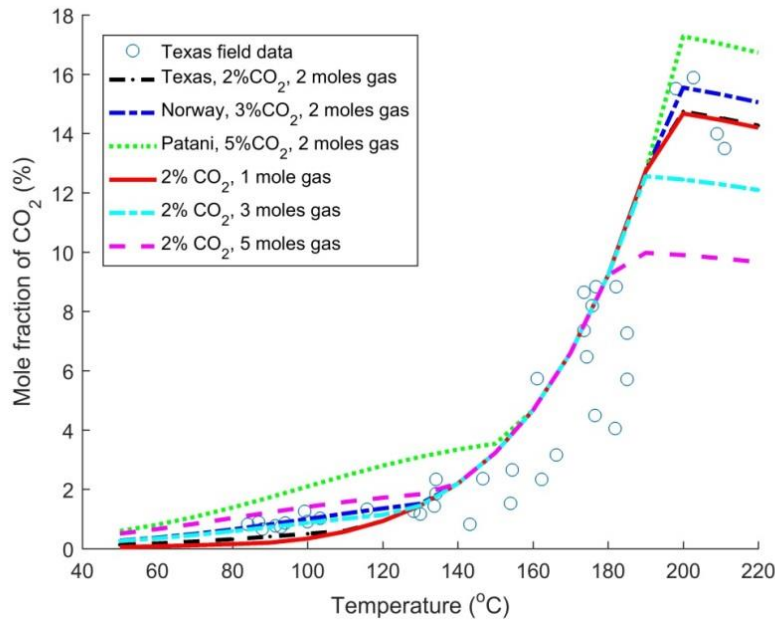


Figure 2. Mole fractions of CO₂ in the gas phase as a function of temperature (and corresponding pressure) for different starting gas compositions and total amounts of gas, compared with field data measured in Texas (Smith and Ehrenberg, 1989). Lines are simulation results.

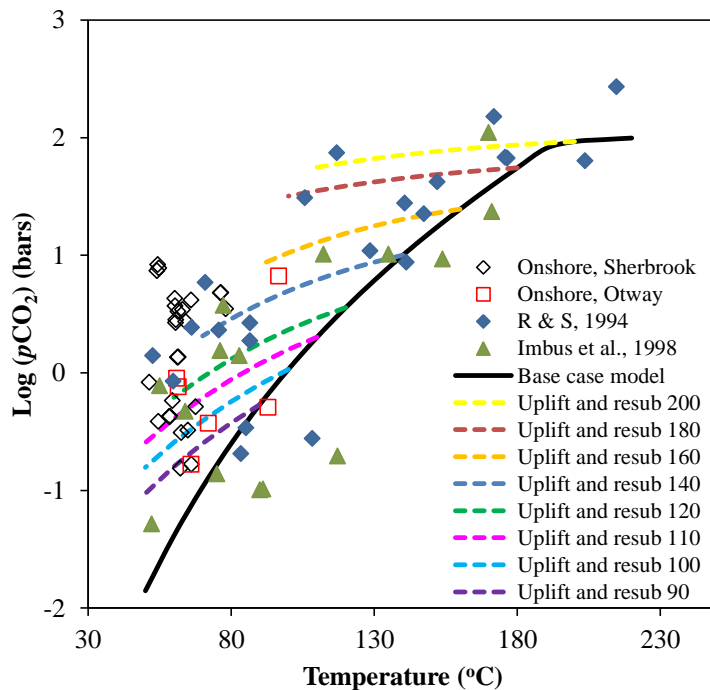


Figure 3. Log($p\text{CO}_2$) as a function of temperature (and corresponding pressure) in sedimentary basins with a complicated burial history (subsidence-uplift-resubsidence). Open symbols: Otway Basin, Australia; closed symbols: North Sumatra Basin. The solid line is the base case subsidence model. Dashed lines are a series of hypothetical pathways from different starting temperatures for the uplift-resubsidence events. Data sources: Watson et al. (2004), Reaves and Sulaeman (1994), and Imbus et al. (1998).