

**3.1.P10****Noble gases in natural CO<sub>2</sub> gas deposits: Identifying and quantifying natural CO<sub>2</sub> sequestration processes**

Z. ZHOU<sup>1</sup>, C.J. BALLENTINE<sup>2</sup>, M. SCHOELL<sup>3</sup>  
AND S. STEVENS<sup>4</sup>

<sup>1</sup> IGMR, ETH Zurich, Switzerland (zhou@erdw.ethz.ch)

<sup>2</sup> Department of Earth Sciences, The University of Manchester, UK (chris.ballentine@man.ac.uk)

<sup>3</sup> GasConsult International L.L.C., Danville, USA

<sup>4</sup> Advanced Resources International, USA

Natural CO<sub>2</sub> gas reservoirs provide an important analogue for studying sequestration systems. Noble gases are used here to identify CO<sub>2</sub> source and quantify interaction with groundwater in a naturally occurring CO<sub>2</sub> gas field. 10 samples were taken from a CO<sub>2</sub>-rich natural gas reservoir in Jackson Dome, Mississippi, USA.

We present compositional, stable isotope and noble gas results of Jackson Dome samples. <sup>3</sup>He/<sup>4</sup>He ratios are between 4.27 and 5.01Ra, indicating a strong mantle signature. Crustal radiogenic <sup>4</sup>He increases locally with water-derived <sup>20</sup>Ne, suggesting that <sup>4</sup>He is pre-mixed with the groundwater before contact with the CO<sub>2</sub> gas phase. N<sub>2</sub> concentrations also correlate with <sup>20</sup>Ne and appear to be sourced from the groundwater as well. <sup>40</sup>Ar/<sup>36</sup>Ar ratios are all above air ratio, ranging between 4071 and 6420. Air corrected <sup>40</sup>Ar\* vary between 92.7 and 95.4%, to give <sup>4</sup>He/<sup>40</sup>Ar\* ratios of between 1.26 and 2.52. This range is comparable with values estimated for the upper mantle. CO<sub>2</sub>/<sup>3</sup>He values are between 1.09×10<sup>9</sup> and 4.62×10<sup>9</sup>, and also fall in the mantle range, indicating that the CO<sub>2</sub> gas in Jackson Dome is also predominantly mantle in origin. A strong anti-correlation between <sup>20</sup>Ne and CO<sub>2</sub>/<sup>3</sup>He, is indicative that groundwater plays the principle control in changing the CO<sub>2</sub>/<sup>3</sup>He ratio. CO<sub>2</sub>/<sup>3</sup>He ratios also correlate with δ<sup>13</sup>C(CO<sub>2</sub>). Water seems responsible for 25% CO<sub>2</sub> loss and ~1‰ change in δ<sup>13</sup>C(CO<sub>2</sub>).

Our results show that the first charge of CO<sub>2</sub> migrates through the groundwater filled sedimentary rock and fills the crest of the trapping structure (CO<sub>2</sub>~98%, N<sub>2</sub>+CH<sub>4</sub>~2%, high <sup>20</sup>Ne and <sup>4</sup>He). Later charges of CO<sub>2</sub> migrate through the groundwater filled sedimentary rock to the trapping structure with pure CO<sub>2</sub> occupies the margins of the gas field (CO<sub>2</sub>~99.3%, N<sub>2</sub>+CH<sub>4</sub>~0.7%, low <sup>20</sup>Ne and <sup>4</sup>He). There is little transfer of low-solubility gases from the water to the new CO<sub>2</sub> gas as these have already been “stripped out” of the water phase. From <sup>20</sup>Ne we calculate the minimum volume of water responsible for removing CO<sub>2</sub> from the gas phase to be 1.05×10<sup>9</sup> m<sup>3</sup>. This quantifies for the first time the importance of the groundwater system in CO<sub>2</sub> gas sequestration.

**3.1.P11****Monte Carlo simulation of the hydration of Na-, Ca-, and K-montmorillonite at 353 K and 625 bar**

L. DE PABLO<sup>1</sup> AND M.L. CHAVEZ<sup>2</sup>

<sup>1</sup>Instituto de Geologia, Universidad Nacional A. de Mexico, Mexico D.F., Mexico (liberto@servidor.unam.mx)

<sup>2</sup>Facultad de Quimica, Universidad Nacional A. de Mexico, Mexico D. F., Mexico (marilu@servidor.unam.mx)

The hydration of Wyoming-type Na-, Ca-, and K-montmorillonite is studied at oil-reservoir conditions of 353 K and 625 bar and compared with hydration at the surface ambient conditions, by Monte Carlo simulations in the NP<sub>zz</sub>T and grand canonical μVT ensembles. Our results indicate that in the reservoir environment, Na-montmorillonite forms a stable one-layer hydrate of d<sub>001</sub> spacing 12.72 Å, 53 water molecules adsorbed, density 0.32 g/ml, internal energy -7.64 kcal/mol, six water molecules coordinated per sodium atom at a separation of 2.30-2.33 Å. Ca-montmorillonite develops a nearly stable one-layer hydrate of 12.50 Å spacing with 55 water molecules adsorbed, density 0.34 g/ml, energy -21.12 kcal/mol. K-montmorillonite could form a nearly stable one-layer hydrate of 12.75 Å spacing, 60 water molecules adsorbed, density 0.365 g/ml, energy -22.73 kcal/mol, coordination six. In the three cases, the water molecules cluster in a broad band about the interlayer mid-plane, with protons on both sides and on the mid-plane and the cations in positions intermediate to the water protons and oxygens, but in K-montmorillonite some K<sup>+</sup> ions remain in inner-sphere complexes with the siloxane oxygens. The two- and three-layer hydrates common under the surface environment of 1 bar and 300 K are not stable at the reservoir conditions of 625 bar and 353 K. Ca- and K-montmorillonite monolayer hydrates would only be stable at lower depths, in environments less stringent than 353 K and 625 bar; with increasing depth, the coordination of cations decreases and the displacement of water towards the bulk is favored. The force-field employed in this work has been shown to reproduce many of the experimental features of montmorillonite hydrates under ambient conditions; while predictions at higher temperatures and pressures are reasonable, it would be desirable to conduct proper experiments.