

## CO<sub>2</sub> Dissolution rates during CO<sub>2</sub> injection: a consequence and measure of reservoir heterogeneities

M.J. BICKLE<sup>1\*</sup>, K. DANIELS<sup>1</sup>, J. NEUFELD<sup>1</sup>,  
N. KAMPMAN<sup>1</sup>, A. GALY<sup>1</sup>, H.J. CHAPMAN<sup>1</sup>, Z. ZHOU<sup>2</sup>, B.  
DUBACQ<sup>1</sup>, M. WIGLEY<sup>1</sup>, O. WARR<sup>2</sup>  
AND C.J. BALLENTINE<sup>2</sup>

<sup>1</sup> Dept. Earth Sciences, University of Cambridge, Downing  
St., Cambridge CB2 3EQ, UK (correspondence:  
mb72@esc.cam.ac.uk)

<sup>2</sup> School of Earth, Atmosphere and Environmental Sciences,  
University of Manchester, M13 9PL, UK

CO<sub>2</sub> dissolution during and after injection into geological storage sites is potentially an important mechanism for stabilising and securing the storage but may lead to enhanced fluid-mineral reactions with both positive and negative consequences for the security of storage. Important questions are how does reservoir heterogeneity influence CO<sub>2</sub> dissolution rates and does the tendency of the low-viscosity CO<sub>2</sub> to finger during injection increase dissolution rates? Here we evaluate the rates of possible CO<sub>2</sub> dissolution in an injection setting by simple pseudo-1D flow modelling with diffusion in the orthogonal direction and compare this with numerical modelling of flow and diffusion in 2D. The results show that the magnitude of CO<sub>2</sub> dissolved is strongly controlled by the rapid flow of brines determined by reservoir heterogeneities. The consequences for fluid-mineral reactions are that these may be strongly localised and this could have important implications for feedbacks between flow and permeability changes in reservoirs.

The results are tested against an injection experiment which utilised CO<sub>2</sub> injection for enhanced oil recovery (EOR) in which we monitored sampled fluid chemistries for 6 months after initiation of CO<sub>2</sub> injection into a five-spot pattern. Interpreting the results required 1) identifying the various water masses present in the reservoir as a consequence of a long history of water injection and then 2) modelling changes in fluid chemistry in terms of CO<sub>2</sub> injection and fluid mineral reactions. The results show a surprisingly rapid increase of dissolved CO<sub>2</sub> in the extracted brines and that this rise was accompanied by initial rapid dissolution of carbonate minerals but longer term dissolution of silicate minerals. The rates of carbonate dissolution are sufficient to cause small increases in formation porosities but these would cause significant increases in the permeability of sandstones which exhibit power law permeability-porosity relations with an exponent of ~9.

## Fluid geochemistry of the deep CO<sub>2</sub>-rich Caprese Reservoir (Northern Apennines, Italy)

G. BIOCCHI<sup>1</sup>, F. TASSI<sup>1,2</sup>, M. BONINI<sup>2</sup>,  
F. CAPECCHIACCI<sup>2</sup>, G. RUGGIERI<sup>2</sup>, G. CHIODINI<sup>3</sup>,  
A. BUCCIANTI<sup>1</sup> AND O. VASELLI<sup>1,2</sup>

<sup>1</sup>Dipartimento di Scienze della Terra, Università di Firenze via  
La Pira 4, 50121 Firenze, Italy (\*correspondence:  
gabriele.biocchi@unifi.it)

<sup>2</sup>Istituto di Geoscienze e Georisorse, Consiglio Nazionale delle  
Ricerche, sezione di Firenze via La Pira 4, 50121 Firenze,  
Italy

<sup>3</sup>Istituto Nazionale di Geofisica e Vulcanologia, Sezione di  
Napoli, OV, via Diocleziano 328, 80124 Napoli, Italy

The chemical and isotopic composition of (i) CO<sub>2</sub>-rich fluids exploited from Caprese Reservoir (CR) by the ~5,000 m deep Pieve Santo Stefano 1 (PSS1) borehole located in the Upper Tiber Basin (Northern Apennines, Italy) and (ii) natural gas discharges located in the surrounding of the Mt. Fungai ophiolitic-bearing complex (Ligurian Units), are presented and discussed.

The CR fluids are hosted in fractured dolostones layers of Burano Fm. [1] and consist of CO<sub>2</sub>-, N<sub>2</sub>-rich gas phase and saline (~82 g/L) NaCl brine. The δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>15</sup>N-N<sub>2</sub> values are interpreted as produced by mixing of deep fluids originated by mantle degassing and thermometamorphic processes involving Mesozoic limestones. Water isotopes and <sup>3</sup>H values indicate that the CR brine is recharged by a long (>50 yr) hydrologic circuit fed by meteoric precipitations.

The naturally discharging gases from the study area are fed by CR, likely due to the fact that the steep Arbia Val Marecchia Line transverse tectonic elements provide preferential paths for these deep-seated fluids, favoring their uprising up to the surface gas vents [2]. The interaction of the ascending CR gas with ophiolite-bearing Ligurian Units and Cervarola-Falterona Unit produces secondary H<sub>2</sub>, H<sub>2</sub>S and light hydrocarbons in Mt. Fungai gases.

[1] Trippetta *et al.* (2013) *Int. J. Greenh. Gas Con.* **12**, 72-83.

[2] Bonini (2009) *J. Struct. Geol.* **31**, 44-54.