

## Carbon isotope fractionation of injected CO<sub>2</sub> in carbonate reservoirs: Comparison of results from the laboratory and enhanced oil recovery field sites in Alberta, Canada

M. NIGHTINGALE<sup>1\*</sup>, B. MAYER<sup>1</sup>, M. SHEVALIER<sup>1</sup>  
C. DALKHAA<sup>1</sup> AND V. BECKER<sup>1</sup>

<sup>1</sup>University of Calgary, Calgary, Canada, T2N 1N4.

(\*correspondance: night@earth.geo.ucalgary.ca)

Much of what can be surmised about the geochemical reaction of injected CO<sub>2</sub> when sequestered in geological formations has been gleaned from the chemical and isotopic analysis of produced fluids during CO<sub>2</sub> enhanced oil recovery (CO<sub>2</sub>-EOR). Carbon isotopes of produced CO<sub>2</sub> have been shown to be a valuable tool for tracing the fate of injected CO<sub>2</sub> [1]. When CO<sub>2</sub> is injected into water bearing carbonate rock, carbon from four distinct sources: 1) injected CO<sub>2</sub>, 2) in-situ CO<sub>2</sub>, 3) dissolved inorganic carbon (largely bicarbonate) and 4) dissolution of carbonate minerals in carbonic acid, can be expected to contribute to the overall “carbon pool” and may have an impact on the equilibrium carbon isotope ratios of both the produced CO<sub>2</sub> and dissolved inorganic carbon (DIC). We present the results of chemical and isotopic analyses of produced CO<sub>2</sub> and DIC before and after the initiation of CO<sub>2</sub> injection at two carbonate hosted CO<sub>2</sub> enhanced oil recovery projects in Alberta, Canada. Results suggest carbon isotope equilibrium is established in a fashion similar to open system carbonate dissolution in shallow environments [2]. In spite of large increases in dissolved bicarbonate attributed to carbonate mineral dissolution, the equilibrium carbon isotope values of the bicarbonate appear to be controlled largely by the injected CO<sub>2</sub> and system temperature. Field observations were verified via a series of laboratory experiments using artificial brines and isotopically distinct CO<sub>2</sub> ( $\delta^{13}\text{C} = -37.5\text{‰}$ ) and carbonate rock ( $\delta^{13}\text{C} = +1.2\text{‰}$ ). Observed increases in dissolved calcium up to 575 mg/l, and dissolved bicarbonate up to 1500 mg/l, can be attributed to the dissolution of added calcite. The  $\delta^{13}\text{C}_{\text{HCO}_3}$  of -28.1‰ at the end of the experiment demonstrates the dominance of the CO<sub>2</sub> and system temperature (20°C) in determining the  $\delta^{13}\text{C}$  values of DIC under equilibrium conditions and the “overprinting” of the isotopic signature of the carbon contributed through calcite dissolution.

[1] Johnson *et al.* (2011), IJGGC 5, 933-941. [2] Clark, I.D. & Fritz, P. (1997) *Environmental Isotopes in Hydrogeology*. Lewis Publishers, Boca Raton, FL.

## Magma sources within the Armenian territory since the Jurassic

I. NIKOGOSIAN<sup>1</sup>, KH. MELIKSETIAN<sup>2</sup>, M.J VAN BERGEN<sup>1</sup>,  
P.R.D. MASON<sup>1</sup> AND G. NAVASARDYAN<sup>2</sup>

<sup>1</sup>Department of Earth Sciences, Utrecht University,  
Budapestlaan 4, the Netherlands, (iniki@geo.uu.nl)

<sup>2</sup>Institute of Geological Sciences, ANA of Sciences, Yerevan,  
Armenia, (km@geology.am)

The Armenian Highland forms part of the intensely deformed central segment of the Alpine-Himalayan belt, where fragments of continental blocks of Gondwanaland origin, Mesozoic Tethian island arcs and Late Cretaceous ophiolite sequences constitute a complex geological mosaic. Extensive magmatic activity between the Early Jurassic and Holocene developed under a diversity of geological regimes, ranging between rift and post-collisional settings.

We undertook a detailed geochemical and petrological study of representative, MgO-rich igneous products to explore relationships between magmatism and geodynamics in key areas of the Lesser Caucasus. Samples cover the entire Jurassic-Quaternary time interval, and include picrites, ophiolites, subalkaline and alkaline basalts, dolerites, and shoshonitic-high-K calcalkaline basalts.

Early liquidus assemblages in most of the samples virtually always include high-Fo (>88) olivine that presumably crystallized from (near-)primary mantle-derived melts. Exceptions are low-Fo olivines from the Quaternary Aragats, Gegam and partially Syunik volcanoes that probably crystallized from crust-contaminated AFC melts and/or mixtures of mantle and crust-derived (adakite-type) melts. Spinel inclusions trapped in high-Fo olivines contain variable amounts of Ti, Al, and Cr, that enable us to distinguish the nature of mantle sources involved (MORB-type, OIB-type, subduction-type).

Geochemical signatures of the parental melts were obtained for all studied samples using LA-ICP-MS analysis of melt inclusions trapped in the high-Fo olivines. A wide diversity of (near-) primary melts was found within and between distinct magmatic systems. Where partial melting and secondary effects can be ruled out, much of this variation reflects the amalgam of different mantle-lithosphere domains, which were mobilized in response to the changing geodynamic conditions that have affected the region since Jurassic times.