Mafic and ultramafic rocks have been suggested as promising candidates to store anthropogenic CO$_2$ permanently due to their vast capacity, energetic favourability, and long-term stability (e.g., Seifritz 1990; Lackner et al. 1995; Matter and Kelemen, 2009; Kelemen et al., 2011). The field observations have confirmed the carbonation of mafic/ultramafic rocks at surface/subsurface conditions in human history, and open-system lab experiments show extremely fast carbonation rates for olivine and basalt powders (e.g., O'Connor et al., 2004; Giammar et al., 2005; Béarat et al., 2006; Dufaud et al., 2009; Garcia et al., 2010; King et al., 2010). Although these studies greatly improved our understanding of carbonation kinetics, a large degree of extrapolations under various modelling framework are needed to apply these results to real CO$_2$-sequestration practice in rock formations. In this study, we focus on understanding the kinetics of olivines (Fo$_{90}$) and high-Mg basalts (Hawaiian picrites) with CO$_2$-bearing fluid in a batch reactor, providing the direct measurement of the rate of carbonation reactions at various conditions and constraints on numerical modelling.

Gem-quality olivine grains, olivine powders (10-20 μm) and basalt powders of three different sizes (5-10, 10-40 and ~100μm) reacted with CO$_2$-containing solutions (e.g., 1M and 3M NaHCO$_3$ solution) in gold capsules placed in a hydrothermal autoclave at 200-400°C and 200-300 bar over the duration of 1-14 days. Dissolution experiments on these samples have also been carried out at three pH values (4.1, 6.9 and 9.3) to understand dissolution kinetics. After experiments, gold capsules were checked for leaks. Experimental run products were examined by SEM, Electron microscopes, XRD, and Raman/Infrared spectroscopy. The solution was analysed for alkalinity by titration. The major and trace element compositions were measured using ICP-MS at Yale University.

Our results show that carbonation rates of olivines and basalts are a function of chemistry of the solution, the grain size, the mineralogy of the solid, and the duration of the experiments. In general, the carbonation rates decrease with time, decreasing concentration of NaHCO$_3$, and the increasing size of olivine grains. Carbonation rates of olivines and basalts after the first day of experiment are significantly higher than that of the subsequent days and reach a plateau after 3-day reactions. An increase of NaHCO$_3$ concentration from 1M to 3M raises the carbonation rate for olivine grains by 4-10 times, and the carbonation rate for <30μm olivine powders with 1M NaHCO$_3$ solution is about two orders of magnitude higher than that for single olivine-grains after 3 days. However, at a similar condition, the carbonation rate for basalts is much slower than for olivines. An increase of NaHCO$_3$ concentration from 1M to 3M can raise the carbonation rate by a factor of 2 to 4, but a decrease in average grain size only increases the rate slightly. Secondary minerals could form during the reaction, which can slow down the carbonation reaction. A quantitative model is presented to interpret these results and make predictions about carbonation efficiencies in rock formations.

**Key Words:** carbonation kinetics, mafic/ultramafic rocks, CO$_2$ sequestration

**References**


Kelemen PB, Matter J, Streit EE, Rudge JF, Curry WB, Blusztajn J. 2011. Rates and mechanisms of mineral