Commentary: ex situ aqueous mineral carbonation

A commentary on

Ex Situ Aqueous Mineral Carbonation

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CO_2 conversion to calcium and magnesium carbonates has garnered
considerable attention since it is a thermodynamically downhill pathway to
safely and permanently sequester large quantities of CO_2 . This seminal
work performed at The National Energy Technology Laboratory in Albany
(NETL-Albany) reports the conversion of calcium- and magnesium-bearing
silicate minerals, such as olivine [$(Mg, Fe)_2 SiO_4$], wollastonite ($CaSiO_3$),
and serpentine [$Mg_3 Si_2 O_5 (OH)_4$], as they are reacted with CO_2 in an
aqueous environment to form magnesium or calcium carbonates. This paper
discusses various pretreatment methods of the starting materials, such as
grinding or heat treatment of hydroxylated Mg silicates, to enhance the
reaction kinetics. The effects of various chemical additives (e. g., NaCl and
$NaHCO_3$), and reaction parameters, such as temperature, pressure, and
reaction time, on the conversion are investigated. Feasibility assessments
and energy and economic analyses of the direct carbonation of calcium- and
magnesium-bearing minerals are presented.

The key contributions of this study are the identification of the optimal
conditions for the carbonation of olivine (185°C, $P_{CO_2} = 150$ atm , 1.
0M·NaCl + 0. 64M·$NaHCO_3$), wollastonite (100°C, $P_{CO_2} = 40$ atm ,
distilled water), and heat-treated serpentine (155°C, $P_{CO_2} = 150$ atm , 1.
0M·NaCl + 0. 64M·$NaHCO_3$). High extents of carbonation of 49. 5, 81. 8, and

73. 5% of olivine, wollastonite, and heat-treated serpentine, respectively, achieved within an hour of reacting with CO_2 in an aqueous environment are reported. The identification of the optimal reaction conditions to achieve the rapid conversion of calcium- and magnesium-bearing silicate minerals to carbonates has spurred a significant global scientific interest in mineral carbonation as a promising technology for CO_2 conversion and storage with the potential reuse of carbonates.

In particular, this work has found unique relevance for *ex situ* and *in situ* carbon mineralization. In *ex situ* mineral carbonation, CO_2 is converted to carbonates in engineered processes where there is considerable control over the reaction conditions. In *in situ* mineral carbonation, CO_2 is injected into geological formations containing calcium- and magnesium-bearing minerals and rocks with the aim toward natural carbon mineralization over time. Predicting the fate of CO_2 injected into geological formations containing these rocks and minerals and developing chemical processes for converting CO_2 to carbonates require a fundamental understanding of the kinetics of mineral carbonation and the corresponding morphological changes in materials. Thus, more recent studies have focused on understanding the carbon mineralization behavior *via* direct carbonation (Bonfils et al., 2012 ; Gadikota et al., 2014a ; Eikeland et al., 2015) and indirect carbonation, which involves the dissolution of minerals (Park et al., 2003 ; Park and Fan, 2004 ; Hänchen et al., 2006 ; Prigiobbe et al., 2009 ; Gadikota et al., 2014b), formation of carbonates (Ferrini et al., 2009 ; Saldi et al., 2009 , 2012 ; Cheng and Li, 2010 ; Bénézeth et al., 2011 ; Zhao et al., 2013 ; Fricker and Park, 2014 ; Swanson et al., 2014), and the corresponding morphological

changes in materials (Hövelmann et al., 2012 ; Olsson et al., 2012 ; Gadikota et al., 2014a). The effects of sodium and ammonium salts and Si-, Mg-, and Ca-targeting chelating agents on enhancing mineral carbonation behavior has been investigated (Bonfils et al., 2012 ; Highfield et al., 2012 ; Declercq et al., 2013 ; Zhao et al., 2013 ; Gadikota et al., 2014a , b ; Ghoorah et al., 2014).

These studies have formed the basis for understanding CO_2 interactions with calcium and magnesium silicates that extend beyond the laboratory to the demonstration scale (Reddy et al., 2010 ; Kelly et al., 2011 ; Zevenhoven et al., 2011 ; Hitch and Dipple, 2012 ; Brent, 2015) and toward geological carbon storage (Kelemen and Matter, 2008 ; Matter and Kelemen, 2009 ; Schaef and McGrail, 2009 ; Gislason et al., 2010 ; Rosenbauer et al., 2012). The studies performed at NETL-Albany have also been extensively cited in studies for the accelerated carbonation of industrial alkaline wastes [Pan et al. (2012) , Gadikota and Park (2014) , Sanna et al. (2012) , and references contained therein]. These materials are often fine, highly reactive, and have a high Ca and Mg content. Examples of these materials include coal fly ash, steel and stainless steel slags, cement and lime kiln dusts, and red mud. However, the availability of industrial alkaline wastes is much smaller compared to calcium- and magnesium-bearing silicate minerals. The global CO_2 storage potential of industrial alkaline wastes is about 200–300 Mt of CO_2 per year, while calcium- and magnesium-bearing silicates can store carbon to the order of thousands of Gt (Sanna et al., 2012). Regardless, the integration of carbon mineralization technologies with these carbon-intensive industries reduces the CO_2 footprint, the alkalinity of the wastes, and could

lead to the potential reuse of the carbonated materials as building, construction, or filler materials. Further development of carbon mineralization technologies requires a fundamental understanding of the formation of mass transfer limiting layers containing Si and Fe (Béarat et al., 2006 ; King et al., 2010 ; Daval et al., 2011 ; Saldi et al., 2013 , 2015 ; Sissmann et al., 2013 ; Harrison et al., 2015), linkages between the morphology with the chemistry (Hövelmann et al., 2012 ; Olsson et al., 2012 ; Gadikota et al., 2014a ; Eikeland et al., 2015), and the impact of impurities in the gas streams (e. g., SO $_2$) on the conversion of CO $_2$ to carbonates (Liu et al., 2010 ; Zevenhoven et al., 2014). While these findings are in the context of *ex situ* mineral carbonation, they are of relevance to *in situ* conversion of CO $_2$ to carbonates.

When CO $_2$ is directly injected into geological reservoirs with calcium- and magnesium-bearing silicates, carbonate formation is aided by the geothermal gradient, which provides reaction temperatures in excess of 80°C, P CO 2 $\sim 80 - 150$ bar available post-combustion and compression, and the presence of ground water. These conditions are analogous to the reaction conditions identified in this study. Of particular interest are the Oman peridotite (olivine-rich rock) (Kelemen and Matter, 2008 ; Matter and Kelemen, 2009) and the basalts in Iceland and Columbia River in the United States (Matter et al., 2009 ; McGrail et al., 2011). The chemomechanical effects due to extensive carbonate growth may induce microfractures, which in turn impact the permeability, fluid flow, and further reactivity of the rock (Kelemen et al., 2013). Regardless, the permanent *in situ* conversion of CO $_2$ to carbonates reduces the need to monitor mobile CO $_2$ over time.

While the experimental methodologies developed by the researchers at NETL-Albany have laid the foundation for a number of studies in this field, considerable uncertainties in the energy requirements for mineral carbonation exist. These uncertainties are attributed to some key parameters, such as the availability and cost of the feedstock, preprocessing of the materials, such as crushing and grinding, the conversion routes, and the use of heat vs. electricity. Regardless, the work performed at NETL-Albany has highlighted the need for a multi-scale understanding of the kinetics, mass transfer behaviors, competing reactions, and microstructural and chemical changes in heterogeneous materials, when reacted with CO_2. These insights can be used to tune the reactivity and morphology of the carbonated end-materials. Ultimately, a fundamental understanding of CO_2–reaction fluid–mineral/rock interactions is essential for developing large-scale chemical processes for converting CO_2 to carbonates, and for predicting the fate of CO_2 injected into geological formations containing calcium and magnesium silicate minerals and rocks.

Author Contributions

The author confirms being the sole contributor of this work and approved it for publication.

Conflict of Interest Statement

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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