COMMUNICATION
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Activation energy of magnesite (MgCO₃) precipitation: recent insights from olivine carbonation studies
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Quin R. S. Miller and H. Todd Schaefer

We present two new activation energies for magnesite precipitation during forsteritic olivine (Mg₂₋ₓFeₓSiO₄, 0.18 ≤ x ≤ 0.26) carbonation in high-pressure carbon dioxide. These new activation energies of 89 ± 6 and 85 ± 1 kJ mol⁻¹ are consistent with the literature for magnesite precipitation in aqueous media and extend the temperature range to encompass 90 °C to 50 °C. These insights will help improve understanding of mineral transformation kinetics in the subsurface, including carbon storage in mafic-ultramafic environments, and aid in the development of carbon dioxide removal (CDR) and net-negative-emissions technologies.

The concept of carbon dioxide removal (CDR) through carbon capture and sequestration is an integral component of current climate mitigation strategies and pursuit of net-negative emissions technologies. A promising CDR approach involves injection of carbon dioxide (CO₂) into reactive mafic and ultramafic rocks to form stable carbonate minerals, enabling rapid permanent carbon storage. In this context, understanding rates of mineral carbonation is crucial for predicting fate and transport of subsurface CO₂.

Olivine (Mg₂₋ₓFeₓSiO₄) is a key reactive component of mafic and ultramafic rocks, and its dissolution, hydration, and carbonation rates have received considerable scrutiny (c.f., ref. 9–13). The recent quantitative kinetics analyses and compilations of Miller et al. and Sendula et al. fit the Avrami model and shrinking particle model (SPM), respectively, to the broad olivine carbonation literature. The more recent and comprehensive study of Sendula et al. provided 35 new experiments, nearly doubling the amount of available datasets, and the SPM proved most flexible and adaptable for the diverse olivine carbonation literature. The goal of the present Communication is to extract carbonation activation energy parameters from recently compiled olivine carbonation studies. To do so we critically reviewed the datasets to identify two suitable internally-consistent collections of reaction rate vs. temperature data for magnesite precipitation during olivine carbonation. These datasets were suitable as they included reaction kinetics for at least three distinct temperatures.

The San Carlos olivine used in Sendula et al. has ~88–91% of the divalent metal sites occupied with Mg²⁺ [Fo₈₈–Fo₉₁; Mg₁.₇₆Fe₀.₂₄SiO₄ to Mg₁.₈₂Fe₀.₁₈SiO₄] and the composition of the Gadikota et al. olivine is Fo₉₇. The most rapid olivine carbonation occurs at ~185–200 °C (c.f., ref. 11 and 12) Indeed, the high-temperature datapoints of Sendula et al. (200 °C) and Gadikota et al. (185 °C) are lower than expected based on the calculated activation energies, consistent with this 185–200 °C temperature range being an inflection point for rate vs. temperature.

Plots of the Sendula et al. (Se21, 50–150 °C) and Gadikota et al. (Ga14, 90–150 °C) carbonation rates on Arrhenius plots (Fig. 1a and b) illustrate the linear relationships needed to calculate apparent activation energies. The linearity of the Arrhenius plots indicates that temperature is the dominant control, and other possible variations in chemical affinity and pressure (Fig. 1c) are negligible, at least for these far-from-equilibrium high-pressure carbonation studies. The olivine to magnesite activation energy values are “apparent” as they encompass contributions from all elementary reactions involved in the complex dissolution–precipitation processes. The calculations revealed the apparent activation energies of 89 ± 6 (Se21) and 85 ± 1 (Ga14) kJ mol⁻¹. These newly-determined
activation energies are consistent with the literature for magnesite precipitation in aqueous media (Table 1). This present analysis extended the temperature range of the Table 1 dataset down from 90 °C to 50 °C. Although the studies compiled in Table 1 span a range of aqueous-mediated processes, including olivine carbonation, hydromagnesite transformation, and step advancement on magnesite, all values are presented given the paucity of literature data. Our group at Pacific Northwest National Laboratory has also studied the influence of adsorbed water nanofilm thickness on the activation energy of forsterite to magnesite carbonation, demonstrating a linear relationship between reported monolayer H2O thickness and activation energy, from ~34 to ~130 kJ mol⁻¹. 24–26 Given the occurrence of multiphase CO₂–H₂O fluids, it is vital to understand the barriers to magnesite precipitation in aqueous media to predict and interpret experiments conducted in nonaqueous regimes (e.g., water films).

In summary, this Communication presents two new robust activation energies for the olivine to magnesite carbonation reaction. These types of monomineralic studies are important for delineating controlling reaction mechanisms and kinetic interpretation of mafic-ultramafic rock carbonation studies (e.g. ref. 22, 27–35). Further insights from dynamic kinetic model26 and reactive force-field27 development, along with additional carbonation kinetics studies12,16,38–40 are vital for clarifying the multiscale mechanisms and rates of silicate carbonation.

Table 1 Compiled apparent activation energies for magnesite precipitation in aqueous media

<table>
<thead>
<tr>
<th>Magnesite (MgCO₃) precipitation apparent activation energies</th>
<th>Temperature (°C)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td><strong>Present communication</strong></td>
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<tr>
<td>89 ± 6</td>
<td>50–150</td>
<td>This study, based on olivine carbonation kinetics reported by Sendula et al.12</td>
</tr>
<tr>
<td>85 ± 1</td>
<td>90–150</td>
<td>This study, based on Sendula et al.12 calculation of Gadikota et al.15 olivine to magnesite carbonation rates</td>
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<tr>
<th>Literature values</th>
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<tr>
<td>159 ± 17</td>
<td>90–100</td>
<td>Saldi et al. 2009 (ref. 41)</td>
</tr>
<tr>
<td>122.6 ± 20a</td>
<td>120–180</td>
<td>Di Lorenzo et al. 2014 (ref. 42)</td>
</tr>
<tr>
<td>100a</td>
<td>110–200</td>
<td>Zhang et al. 2000 (ref. 43)</td>
</tr>
<tr>
<td>93.3 ± 3.3a</td>
<td>120–180</td>
<td>Di Lorenzo et al. 2014 (ref. 42)</td>
</tr>
<tr>
<td>85.1 ± 7.7</td>
<td>100–146</td>
<td>Gautier et al. 2016 (ref. 44)</td>
</tr>
<tr>
<td>81a</td>
<td>110–200</td>
<td>Zhang et al. 2000 (ref. 43)</td>
</tr>
<tr>
<td>80.2</td>
<td>100–200</td>
<td>Saldi et al. 2012 (ref. 45)</td>
</tr>
<tr>
<td>92.9 ± 3.8a</td>
<td>15–35a</td>
<td>Arvidson and Mackenzie 2000 (ref. 46)</td>
</tr>
</tbody>
</table>

* Based on the solution-mediated transformation reaction of hydromagnesite [[(Mg₆(CO₃)₄(OH)₆·4H₂O)] to magnesite. Multiple Zhang et al.14 values are due to different fluid compositions, and multiple values for Di Lorenzo et al.43 were due to their use of two different kinetic models. Arvidson and Mackenzie46 used the approach of Lippmann7 in conjunction with the 39.3 kJ mol⁻¹ calcite (CaCO₃) activation energy of Kazmierczak et al.44 to calculate their magnesite precipitation activation energy.
transformations. Our analysis provides a basis for focusing future work on key mechanistic and kinetic unknowns that could improve understanding of mineral transformation kinetics in the subsurface, including carbon storage in mafic-ultramafic rocks, and aid in the development of carbon dioxide removal and net negative-emissions technologies.

**Conflicts of interest**

There are no conflicts of interest.

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