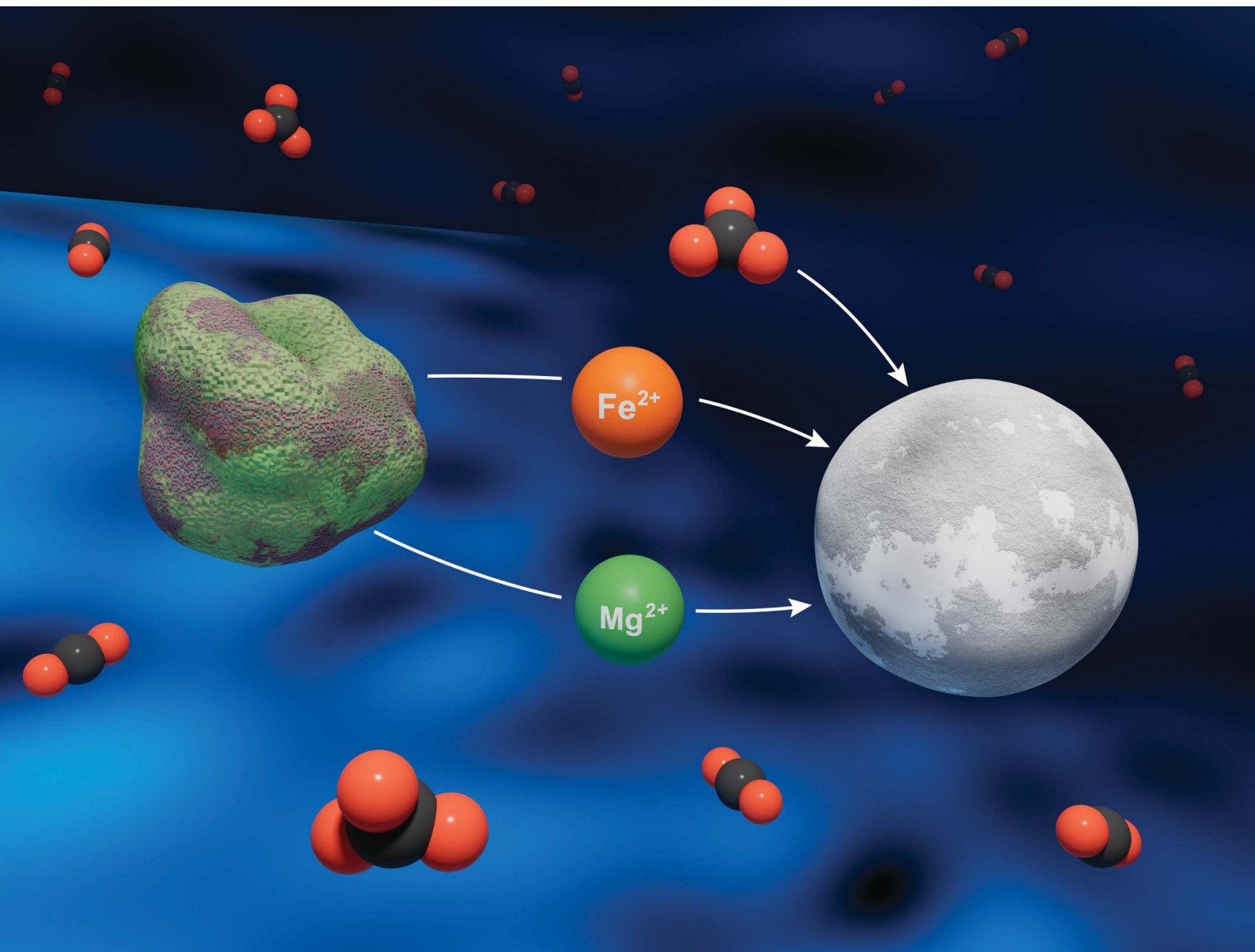


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## COMMUNICATION

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Activation energy of magnesite ( $\text{MgCO}_3$ ) precipitation:  
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## Activation energy of magnesite ( $\text{MgCO}_3$ ) precipitation: recent insights from olivine carbonation studies

Quin R. S. Miller \* and H. Todd Schaefer \*

We present two new activation energies for magnesite precipitation during forsteritic olivine ( $\text{Mg}_{2-x}\text{Fe}_x\text{SiO}_4$ ;  $0.18 \leq x \leq 0.26$ ) carbonation in high-pressure carbon dioxide. These new activation energies of  $89 \pm 6$  and  $85 \pm 1$   $\text{kJ mol}^{-1}$  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 ( $\text{CO}_2$ ) into reactive mafic and ultramafic rocks to form stable carbonate minerals, enabling rapid permanent carbon storage.<sup>1–8</sup> In this context, understanding rates of mineral carbonation is crucial for predicting fate and transport of subsurface  $\text{CO}_2$ .

Olivine ( $\text{Mg}_{2-x}\text{Fe}_x\text{SiO}_4$ ) 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.*<sup>11</sup> and Sendula *et al.*<sup>12</sup> fit the Avrami model<sup>14</sup> and shrinking particle model (SPM),<sup>12,15–17</sup> respectively, to the broad olivine carbonation literature. The more recent and comprehensive study of Sendula *et al.*<sup>12</sup> 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.<sup>11,12</sup> To do so we critically reviewed the datasets to identify two<sup>12,18</sup> suitable internally-consistent collections of

### Environmental significance

Olivine is a key constituent of reactive geologic formations and industrial wastes that are targets for permanent carbon storage *via* mineralization. The relative paucity of kinetic parameters for olivine transformation to magnesite *via* coupled dissolution and carbonate precipitation hinders efforts to predict rate and design efficient mineralization strategies. Our calculations of two new olivine carbonation activation energies help address these knowledge gaps relevant to natural and engineered environmental carbon-management processes.

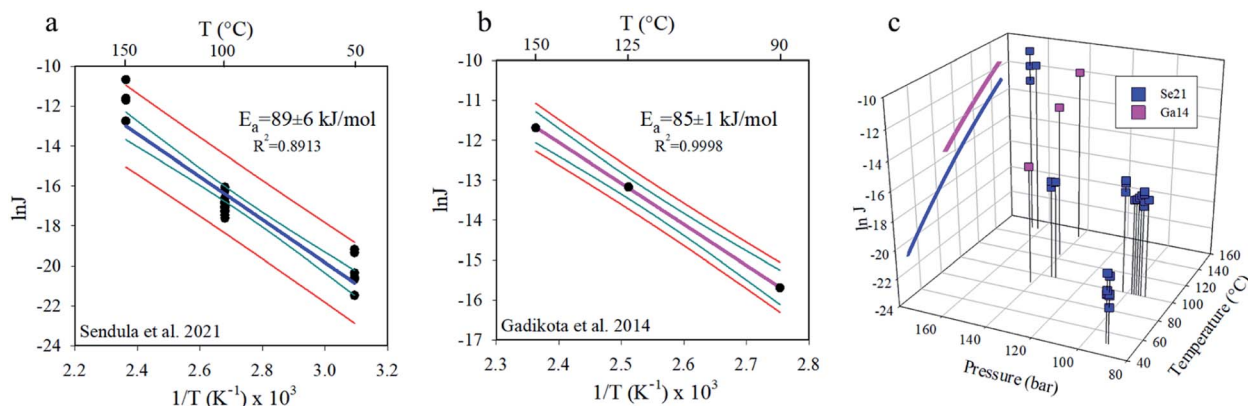
reaction rate *vs.* temperature data for magnesite precipitation during olivine carbonation. These datasets were suitable as they included reaction kinetics for at least three distinct temperatures.

The San Carlos olivine used in Sendula *et al.*<sup>12</sup> has ~88–91% of the divalent metal sites occupied with  $\text{Mg}^{2+}$  ( $\text{Fo}_{88}\text{–Fo}_{91}$ ;  $\text{Mg}_{1.76}\text{Fe}_{0.24}\text{SiO}_4$  to  $\text{Mg}_{1.82}\text{Fe}_{0.18}\text{SiO}_4$ ),<sup>19–23</sup> and the composition of the Gadikota *et al.*<sup>18</sup> olivine is  $\text{Fo}_{87}$ . 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.*<sup>12</sup> (200 °C) and Gadikota *et al.*<sup>18</sup> (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.*<sup>12</sup> (Se21, 50–150 °C) and Gadikota *et al.*<sup>18</sup> (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<sup>12</sup> (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  $89 \pm 6$  (Se21) and  $85 \pm 1$  (Ga14)  $\text{kJ mol}^{-1}$ . These newly-determined

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**Fig. 1** Arrhenius plots using the carbonation rate results of (a) Sendula *et al.*<sup>12</sup> (Se21) and (b) Gadikota *et al.*<sup>18</sup> (Ga14), showing the variation of the natural logarithm of the olivine to magnesite transformation rates ( $J$ ,  $\text{mol m}^{-2} \text{s}^{-1}$ ) as a function of 1000 times the reciprocal absolute temperature ( $T$ ) of the experiments. Temperature ( $^{\circ}\text{C}$ ) is labelled on the upper  $x$ -axis for reference. The calculated apparent activation energies, coefficient of determination, and uncertainties are given next to the linear best fits. Red and dark cyan curves denote 95% prediction band and 95% confidence bands, respectively. In panel (c), the Arrhenius trends have both been plotted on the  $^{\circ}\text{C}$  vs.  $\ln J$  plane, while the Sendula *et al.*<sup>12</sup> and Gadikota *et al.*<sup>18</sup> rates used to construct the Arrhenius plots are shown in the context of pressure and temperature conditions. The reference drop lines from the points to the  $P$ - $T$  plane help clarify the 3D perspective.

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  $90^{\circ}\text{C}$  to  $50^{\circ}\text{C}$ . 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  $\text{H}_2\text{O}$  thickness and activation energy, from  $\sim 34$  to  $\sim 130 \text{ kJ mol}^{-1}$ .<sup>24–26</sup>

Given the occurrence of multiphase  $\text{CO}_2$ - $\text{H}_2\text{O}$  fluids, it is vital to understand the barriers to magnesite precipitation in aqueous media to predict and interpret experiments conducted in non-aqueous 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 model<sup>36</sup> and reactive force-field<sup>37,49</sup> development, along with additional carbonation kinetics studies,<sup>12,16,38–40</sup> are vital for clarifying the multiscale mechanisms and rates of silicate carbonation

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

#### Magnesite ( $\text{MgCO}_3$ ) precipitation apparent activation energies

| Activation energy ( $\text{kJ mol}^{-1}$ ) | Temperature ( $^{\circ}\text{C}$ ) | Ref.  |
|--|------------------------------------|---|
| <b>Present communication</b>               |                                    |   |
| $89 \pm 6$                                 | 50–150                             | This study, based on olivine carbonation kinetics reported by Sendula <i>et al.</i> <sup>12</sup>   |
| $85 \pm 1$                                 | 90–150                             | This study, based on Sendula <i>et al.</i> <sup>12</sup> calculation of Gadikota <i>et al.</i> <sup>18</sup> olivine to magnesite carbonation rates |
| <b>Literature values</b>                   |                                    |   |
| $159 \pm 17$                               | 90–100                             | Saldi <i>et al.</i> 2009 (ref. 41)  |
| $122.6 \pm 20^a$                           | 120–180                            | Di Lorenzo <i>et al.</i> 2014 (ref. 42)   |
| $100^a$                                    | 110–200                            | Zhang <i>et al.</i> 2000 (ref. 43)  |
| $93.3 \pm 3.3^a$                           | 120–180                            | Di Lorenzo <i>et al.</i> 2014 (ref. 42)   |
| $85.1 \pm 7.7$                             | 100–146                            | Gautier <i>et al.</i> 2016 (ref. 44)  |
| $81^a$                                     | 110–200                            | Zhang <i>et al.</i> 2000 (ref. 43)  |
| 80.2                                       | 100–200                            | Saldi <i>et al.</i> 2012 (ref. 45)  |
| $92.9 \pm 3.8^b$                           | 15–35 <sup>b</sup>                 | Arvidson and Mackenzie 2000 (ref. 46)   |

<sup>a</sup> Based on the solution-mediated transformation reaction of hydromagnesite  $[(\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O})]$  to magnesite. Multiple Zhang *et al.*<sup>43</sup> values are due to different fluid compositions, and multiple values for Di Lorenzo *et al.*<sup>42</sup> were due to their use of two different kinetic models. <sup>b</sup> Arvidson and Mackenzie<sup>46</sup> used the approach of Lippmann<sup>47</sup> in conjunction with the  $39.3 \text{ kJ mol}^{-1}$  calcite ( $\text{CaCO}_3$ ) activation energy of Kazmierczak *et al.*<sup>48</sup> 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.

## Acknowledgements

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