

# Interfacial Hydrophilicity Controls Mineral Transformation Outcomes for Enstatite and Amorphous $\text{MgSiO}_3$

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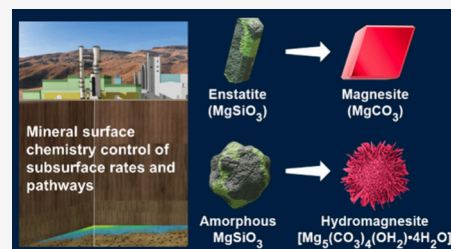
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Supporting Information

**ABSTRACT:** Subsurface injection of carbon dioxide ( $\text{CO}_2$ ) into mafic-ultramafic rocks for permanent storage via mineralization is being studied to reduce emissions. We investigated the carbonation products of enstatite ( $\text{MgSiO}_3$ ) to assess its efficiency in sequestering  $\text{CO}_2$  for safe and permanent storage as carbonate minerals. This was accomplished by conducting variable temperature carbonation reactions with samples of differing crystallinities and surface chemistries. Reaction progress was monitored utilizing in situ X-ray diffraction, and the presence of carbonate products was confirmed using additional techniques, such as thermogravimetric analysis coupled with mass spectrometry and scanning electron microscopy with energy dispersive spectrometry. Our results show that crystalline enstatite produces small amounts of the anhydrous form of  $\text{MgCO}_3$  (magnesite), while amorphous  $\text{MgSiO}_3$ , which was used to simulate mafic glass, more readily converts to the hydrated/hydroxylated hydromagnesite  $[\text{Mg}_3(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ . These results, supplemented with dynamic vapor sorption experiments, suggest that surface properties play a significant role in the pathway and degree of carbonation. These developments concerning the reactivity of  $\text{CO}_2$  with reactive mafic phases will help further our understanding of the reactivity of these mafic-ultramafic minerals with implications for permanent carbon storage and other subsurface engineering scenarios involving reactive reservoirs.

**KEYWORDS:** peridotite, pyroxene, hydromagnesite, glass dissolution, basalt, mafic-ultramafic, interfacial water film



## INTRODUCTION

Carbon capture and sequestration (CCS) of  $\text{CO}_2$  is a process that has the potential to reduce global  $\text{CO}_2$  emissions and often employs the storage mechanism of injecting captured  $\text{CO}_2$  deep into the subsurface. As opposed to conventional, sedimentary storage, in situ carbon mineralization promotes  $\text{CO}_2$ -water-rock reactions in mafic-ultramafic formations, which ultimately produces stable carbonate species.<sup>1–64</sup> Successful basalt carbonation following subsurface injection of  $\text{CO}_2$  has been demonstrated following field tests conducted at the Wallula Basalt Pilot Project<sup>17</sup> in Washington, USA, and the CarbFix project in Iceland.<sup>65</sup> The company 44.01, following successful mineralization pilot studies,<sup>66</sup> is currently planning to upscale their operation within the ultramafic Samail Ophiolite.<sup>48,57,67,68</sup> Additionally, studies have evaluated the potential for geologic carbon storage in ultramafic reservoirs for other global regions, including India, Africa, China, British Columbia, offshore, and beyond.<sup>26,69–82</sup> Carbonation of these reactive rock types also mobilizes critical minerals,<sup>11,63,83–105</sup> that if recovered, could provide the opportunity for revenue-generating carbon storage.<sup>11,63,83–104,106–108</sup>

Given that the amount and composition of mafic-ultramafic rocks differs greatly from region-to-region, research has been conducted on representative mafic and ultramafic minerals

(e.g., olivines, pyroxenes, and serpentines) to assess their efficacy for the formation of carbonates.<sup>32,51,109–112</sup> Olivine dissolution and carbonation<sup>40,53,113–146</sup> behavior, including reactivity in wet supercritical carbon dioxide ( $\text{scCO}_2$ ) fluids,<sup>4,14,125,129,147–159</sup> is well-documented, as is the dissolution<sup>160–180</sup> and carbonation<sup>14,131,133,181–189</sup> behavior of pyroxene. The Mg-endmember pyroxene, enstatite ( $\text{MgSiO}_3$ ), is the focus of this study due to the ubiquity of pyroxene in mafic-ultramafic rocks and the potential for exploring the role of structure and surface properties in determining mineral reactivity. Additionally, the amorphous form is a reasonable analogue for Mg-rich basaltic glass that is also reactive for carbonation. In this regard, nanosilicates are also of great interest in cosmochemistry.<sup>190–200</sup> Considering reaction conditions and variables, it is conceivable that subsurface injection of  $\text{CO}_2$  at depth can, at the toe of the injection well, sufficiently displace groundwater, flooding the pore space with a single phase wet supercritical  $\text{CO}_2$  fluid. For these conditions,

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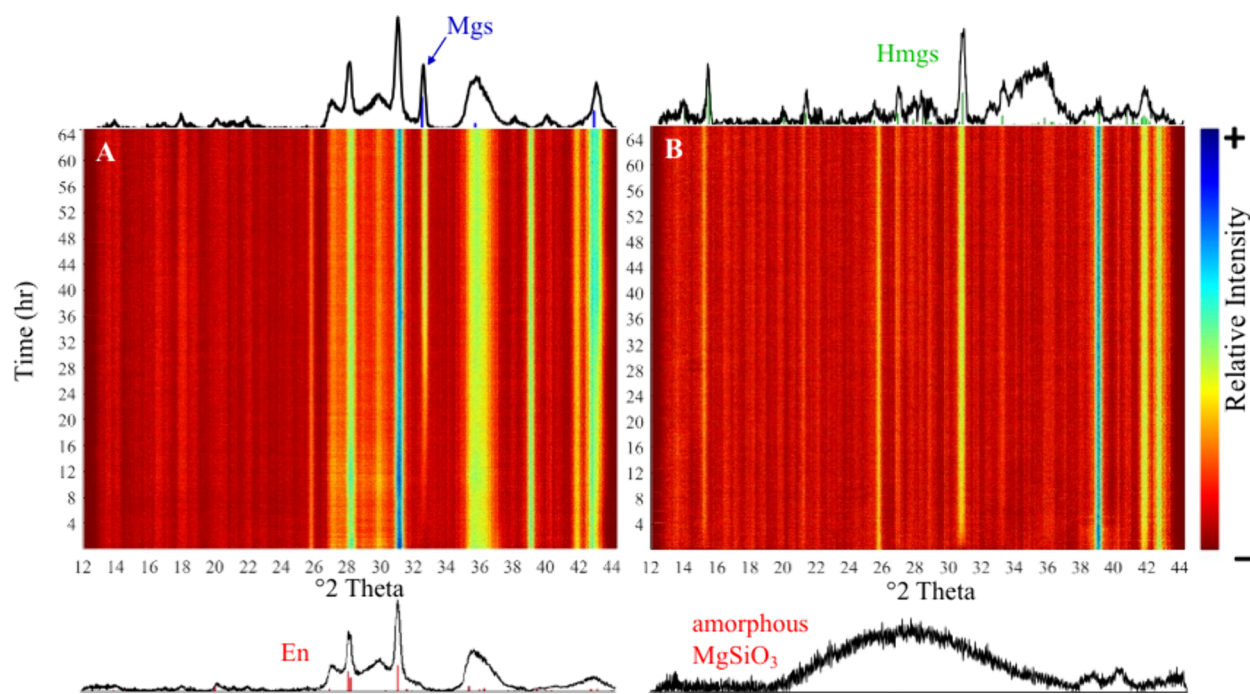


**Figure 1.** Direct comparison of crystalline (panel A, EXP 4) and amorphous (panel B, EXP 5)  $\text{MgSiO}_3$  through in situ time-resolved XRD conducted at 90 bar  $\text{scCO}_2$  and 110 °C with ex situ initial (bottom) and final (top) scans of the sample with corresponding PDF reference lines for enstatite (En, red), magnesite (Mgs, blue), and hydromagnesite (Hmgs, green).

previous laboratory experimental work has shown that the formation of molecularly thin water films on the rock interface enables carbonation reactions relative to the  $\text{CO}_2$ -saturated aqueous fluid regime.<sup>151,155,201</sup> Although sufficiently thick water films can enable reaction, information is still lacking on the varied effects from differing surface chemistries and their hydrophilicity.

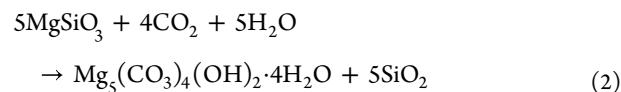
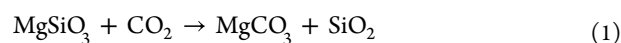
In this study, we directly compare the carbonation behavior of crystalline enstatite and amorphous  $\text{MgSiO}_3$  to investigate how surface hydrophilicity and structure influence reactivity and carbonate phase formation. We used laboratory-based in situ high pressure X-ray diffraction (XRD) to observe the carbonation of enstatite and amorphous  $\text{MgSiO}_3$  in water-saturated  $\text{scCO}_2$  at 90 bar and 50–110 °C, conditions relevant to geologic carbon mineralization. These experiments explored reaction pathway differences between crystalline and amorphous  $\text{MgSiO}_3$  and provided insight into how the degree of carbonation and kinetics were influenced by factors such as hydrophilicity and the formation of interfacial layers. These results will contribute to the knowledge-base and help in enabling the commercial-scale deployment of carbon storage.

## METHODS AND MATERIALS

**Crystalline and Amorphous  $\text{MgSiO}_3$ .** The synthesis and characterization of nanocrystalline enstatite [ $9.3 \text{ m}^2/\text{g}$  specific surface area (SSA)] used in this study has been previously detailed.<sup>202</sup> Synthetic amorphous nano- $\text{MgSiO}_3$ <sup>194</sup> ( $25.1 \text{ m}^2/\text{g}$  SSA) was recently described.<sup>193,200</sup>

**In Situ High-Pressure X-ray Diffraction Silicate Carbonation Experiments.** Time-resolved high-pressure XRD (HXRD) experiments were conducted to track  $\text{MgSiO}_3$  carbonation outcomes in water-saturated ( $\sim 0.35\text{--}2.5 \text{ mol } \%$   $\text{H}_2\text{O}$ )<sup>203</sup> 90 bar  $\text{scCO}_2$  at 50, 90, and 110 °C (Table S1). The relevant overall carbonation reactions that produce amorphous

silica and magnesite ( $\text{MgCO}_3$ ) and/or hydromagnesite [ $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ] are



The HXRD system and methods, are described in detail in the [Supporting Information](#) and our previous studies.<sup>152,153,157,182,201,204–207</sup> Pristine and reacted samples were analyzed with thermogravimetric analysis coupled with mass spectrometry (TGA-MS).<sup>153,182,204,208</sup> to identify reaction products and quantify carbonation extent.<sup>209,210</sup> Briefly, the samples were heated to 850 °C in the TGA to determine mass losses during thermal decomposition, while ion currents (mass/charge,  $m/z$ ) for evolved  $\text{CO}_2$  ( $m/z = 44$ ) and  $\text{H}_2\text{O}$  ( $m/z = 18$ ) were monitored with the MS. Unreacted enstatite TGA-MS results were used to account for any TGA-MS characteristics from residual organics leftover from synthesis<sup>202</sup> (Table S2 and Figure S 2f). Reacted samples recovered from HXRD experiments were also analyzed with scanning electron microscopy and energy dispersive spectrometry (SEM-EDS) was utilized to study the morphology and composition of the mineral assemblages. Full details of the TGA-MS and SEM-EDS methods are found in the [Supporting Information](#).

**Silicate Surface Characterization.** To better understand the surface chemistry of the two  $\text{MgSiO}_3$  reactants, gravimetric dynamic vapor sorption (DVS) characterization was conducted to determine water adsorption and condensation regimes in the context of a simplified form of the Do-Do model.<sup>211</sup> A similar form of the Do-Do model has also been used in studies of water interactions with mineral surfaces. Full details of the DVS procedure and Do-Do model analysis are reported in the [Supporting Information](#) (Table S3).

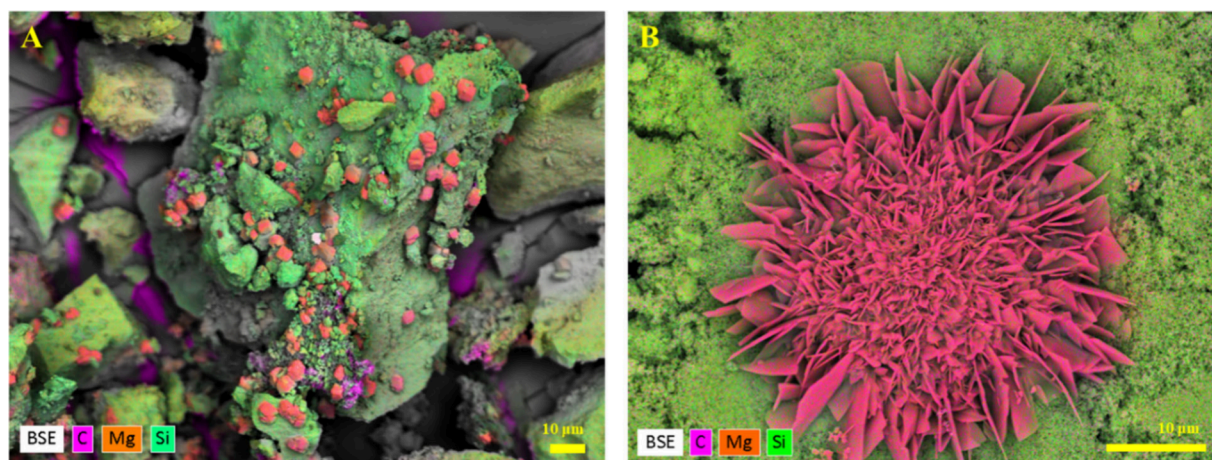


**Figure 2.** SEM-EDS composite images of reacted samples (110 °C and 90 bar hydrated  $\text{scCO}_2$ ) recovered from the high-pressure XRD reactor demonstrating reaction pathway differences providing distinct carbonation outcomes. Magnesite crystallites on reacted enstatite (panel A, EXP 4), and a hydromagnesite rosette formed during amorphous  $\text{MgSiO}_3$  carbonation (panel B, EXP 5, a wider field of view of Hmgs formation can be seen in Figure S11). The scale bars in both images are 10  $\mu\text{m}$ .

## RESULTS AND DISCUSSION

**Enstatite Carbonation.** Initial experiments were conducted at increasing temperatures and 90 bar to simulate subsurface injection conditions. EXP 1, performed at 50 °C, was reliant on ex situ XRD analysis due to the higher density of  $\text{CO}_2$  at lower temperatures, inhibiting in situ examination of low intensity carbonate peaks once pressurized.<sup>129,212</sup> The conditions and results for all experiments are summarized in Table S1. After reacting for 137.6 h the system was depressurized and high quality XRD scans were collected. Compared to the initial scans of enstatite there is evidence of a new peak beginning to form that aligns with the PDF reference lines for magnesite, a crystalline form of anhydrous  $\text{MgCO}_3$  (Figure S1). It is possible that weakly crystalline and/or nanosized magnesite<sup>153,213,214</sup> contributed to the magnesite peak being obscured by the enstatite peaks at  $\sim 32^\circ 2\theta$  and overall background of the XRD pattern. This identification was supplemented with TGA-MS (Figure S2a), and based on the sample mass loss the reaction extent was calculated to be 3%. This experiment represents the onset of magnesite precipitation with overall low reaction extent. The early release of  $\text{CO}_2$  at  $\sim 50^\circ\text{C}$  in the TGA-MS data likely corresponds to surface complexes,<sup>151,158</sup> as opposed to  $\geq 150^\circ\text{C}$  coincident releases of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  corresponding to amorphous magnesium carbonate.<sup>189,201</sup> Comparison of SEM images of unreacted enstatite (Figure S4a) and postreaction sample for EXP 1 (Figure S4b) indicates minor morphological differences with the presence of a granular product on the reacted surface.

Experiments conducted at 90 °C (EXP 2 and 3) revealed magnesite precipitation (Figure S5 and Figure S6). This identification was confirmed with ex situ scans postreaction with more pronounced magnesite peaks evident (Figure S7). Further examination of 2D XRD detector images collected from EXP 3 (Figure S8) show transient magnesite crystallites forming at 54.1 and 55.2 h into the reaction, highlighting the continual dissolution and precipitation of the carbonation process. This phenomenon is confirmed through examination of the SEM image for EXP 3 (Figure S4c) with prominent dissolution features that are not present in the unreacted sample image (Figure S4a). The TGA-MS peaks for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  showed similar positions and the TGA (Figure S2b and

c) indicated reaction extents of 4 and 2% for EXP 2 and EXP 3, respectively. What is interesting to note is that although at higher temperatures, the amount of total carbonate product did not significantly increase between EXP 1–3 even with extended reaction times, which suggests more complex surface interactions are at play causing an inhibitory effect on carbonation.

The temperature was then increased to 110 °C for EXP 4, with magnesite precipitation observed in situ beginning at  $\sim 8$  h with continual increase throughout the experiment (Figure 1a and Figure S9a). Ex situ examination of the postreacted sample provided the most intense magnesite peak of the carbonation experiments. TGA-MS confirmed the primary carbonate product, magnesite, and the sample mass loss was used to calculate the reaction extent to be 14% (Figure S2d), consistent with the intense magnesite XRD peak. SEM-EDS imaging of a sample from EXP 4 revealed a cluster of Mg-rich regions on the surface of the sample associated with magnesite crystallites of various product grains (Figure 2a and S4d).

**Kinetics and Pathway of Enstatite Carbonation.** The reaction extent results were plotted for each temperature vs time to better elucidate the kinetics of enstatite carbonation. As shown in Figure 3, forsterite ( $\text{Mg}_2\text{SiO}_4$ ) and diopside ( $\text{CaMgSi}_2\text{O}_6$ ) carbonation determined in our previous studies are substantially faster than that of enstatite for water-saturated  $\text{scCO}_2$  fluids, producing primarily magnesite and huntite [ $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$ ], respectively. This disparity in reaction rates, even though the specific surface area of the diopside is  $\sim 2.4$  times higher than that of the forsterite (63.5 vs 26.7  $\text{m}^2/\text{g}$ ), is likely due to the slower dissolution rate of diopside relative to that of olivine.<sup>116</sup> This discrepancy in reaction (dissolution and/or carbonation) rates between olivine and pyroxenes is also documented for enstatite and forsterite.<sup>183,215,216</sup> Pyroxenes have polymerized silica requiring more bond breakages, as opposed to the isolated silica tetrahedra of orthosilicate forsterite. Additionally, enstatite has a lower surface area (9.3  $\text{m}^2/\text{g}$ ) and, based on correlations<sup>217,218</sup> of inner sphere water exchange rates around metal cations and mineral dissolution rates, we expect that Ca-pyroxenes will dissolve faster than Mg-pyroxenes. Indeed, based on the mineral kinetics compilation of Palandri and Kharaka,<sup>116</sup> the dissolution of diopside in acidic conditions is nearly 3 orders of magnitude faster than

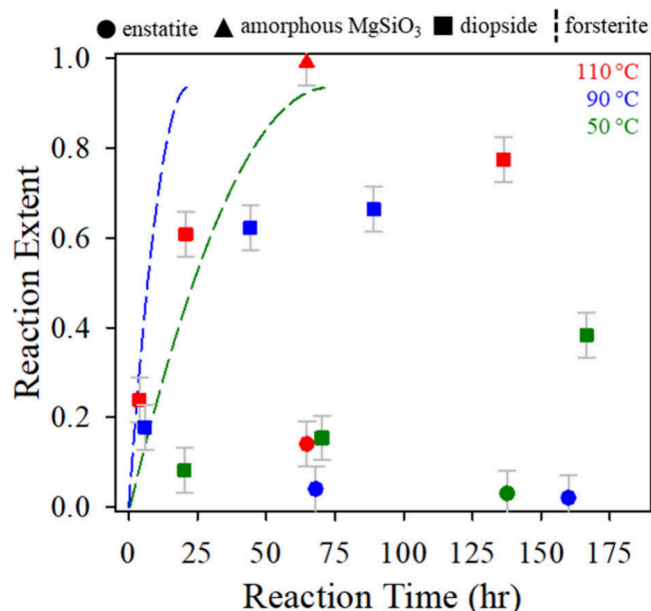


**Figure 3.** Reaction trend comparisons for synthetic silicate carbonation in water-saturated  $\text{scCO}_2$  from our previous studies. Time-dependent reaction extents for enstatite (circle) and amorphous  $\text{MgSiO}_3$  (triangle) carbonation experiments, with 50, 90, and 110 °C 90-bar experiments denoted by green, blue, and red symbols, respectively. The dashed curves correspond to forsterite carbonation trends determined in Miller et al.,<sup>204</sup> and the squares correspond to diopside carbonation experiments from Aguila et al.<sup>189</sup> Reaction extent calculations for silicate to Mg/Ca-carbonate transformations are based on TGA-MS results and further detailed in the Supporting Information and previous papers.<sup>189,204</sup>

that of enstatite. Also, the nucleation and growth of Ca-carbonates is more rapid than Mg-carbonates, including magnesite.

Looking more closely at SEM-EDS imaging of the reacted samples (Figure 2 and Figure S4), the Si-rich substrates potentially indicate the presence of amorphous silica-rich surface layers (ASSL, e.g.<sup>163,219,220</sup>), however, there is no morphological evidence present. The effect that ASSL has on the overall carbonation of minerals is likely dependent upon the structure and composition of the starting mineral and reaction environment.<sup>221</sup> The presence of ASSL has also been demonstrated to affect the amount of olivine dissolution whereby it inhibits further mineral dissolution by blocking water from interacting at the mineral surface.<sup>221,222</sup> As amorphous silica is less hydrophilic than simple silicate minerals,<sup>158,223</sup> it is conceivable that hydrophilicity may be impacted during carbon mineralization reactions that produce amorphous silica. However, this scenario seems to be more applicable in extreme water-limited conditions during the incipient stages of carbon mineralization.<sup>150</sup> Previous studies regarding enstatite dissolution rates as a function of temperature found that at lower temperatures less  $\text{Mg}^{2+}$  ions and Si were liberated compared to higher temperature experiments. Based solely on the reported<sup>171</sup> activation energy of enstatite dissolution, we would expect the reaction rates at 110 °C to be  $\sim 2.3\text{X}$  faster than at 90 °C and  $\sim 15.5\text{X}$  faster than at 50 °C, with 90 °C reaction rates  $\sim 6.9\text{X}$  faster than the 50 °C rates. Our results, however, show similar reaction extents at 50 and 90 °C, with a stark increase at 110 °C (Table S1). It is possible there are overlapping effects of the ASSL and the mechanistic

change in magnesite growth controls for temperatures  $>90$  °C. There is a temperature-dependent change in magnesite growth mechanism, with growth at  $>90$  °C controlled by step generation, and much slower growth at  $<90$  °C controlled by step advancement.<sup>224</sup> This discontinuity in kinetics as a function of temperature due to a change in reaction mechanism was also observed in our previous kinetics study<sup>225</sup> of olivine carbonation. These combined effects could explain the lower carbonation yields in the 50–90 °C experiments compared to the 110 °C experiment.

**Influence of Crystallinity and Surface Chemistry.** To further probe reactive outcomes for  $\text{MgSiO}_3$ , EXP 5 was conducted using amorphous  $\text{MgSiO}_3$  chosen to simulate mafic glass, at 110 °C and 90 bar (Table S1). In situ XRD monitoring of amorphous  $\text{MgSiO}_3$  revealed that the carbonate produced was hydromagnesite  $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ , with dissolution–precipitation rapidly occurring within  $\sim 2$  h (Figure 1b and Figure S9b). TGA-MS analysis (Figure S10b) showed that along with  $\text{CO}_2$ , there was an early release of  $\text{H}_2\text{O}$ , associated with the hydrated/hydroxylated carbonate product and a reaction extent of 99%. We conclude that amorphous  $\text{MgSiO}_3$  is more reactive than crystalline enstatite under the same reaction conditions, with faster reactivity and no plateau for amorphous  $\text{MgSiO}_3$  (Figure 3) indicative of different ASSL development and properties. SEM-EDS imaging of the reacted sample revealed the presence of hydromagnesite rosettes (Figure 2b and Figure S11c, d).

Additionally, the surface composition of amorphous  $\text{MgSiO}_3$  is likely more hydroxylated relative to its crystalline enstatite counterpart, based on the water sorption results. We propose that the increased affinity for water aides in the formation of a thin water film which influences product formation. DVS measurements (Figure 4) were used to confirm that amorphous  $\text{MgSiO}_3$  promotes a more hydrous interfacial environment, which would favor hydrated and/or hydroxylated Mg-carbonate precipitation, supporting our hypothesis. Similarly, Miller et al.<sup>153</sup> used water activity to control water film thicknesses, controlling the occurrences of anhydrous magnesite or hydrated nesquehonite ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ). Differ-

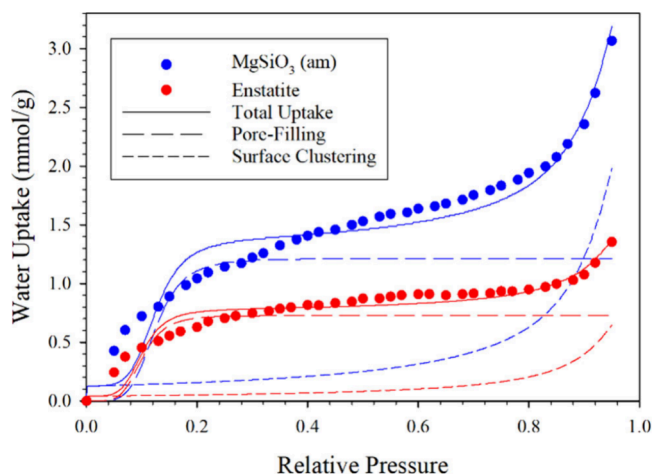


**Figure 4.** Dynamic vapor sorption (DVS) results for unreacted enstatite and amorphous  $\text{MgSiO}_3$ , from  $\sim 3$ –95% relative humidity (RH) at 25 °C after an initial 10-h sample exposure to dry  $\text{N}_2$  at 40 °C. Simplified Do-Do model<sup>211</sup> fits for total uptake, pore filling, and surface clustering are shown with solid, long dash, and short dash lines, respectively.

ent carbonation pathways are possible due to the more hydrous conditions for the amorphous  $\text{MgSiO}_3$  compared to enstatite, contributing to the greater degree of carbonation.

While we cannot completely disentangle the overlapping effects of mineral crystallinity, surface chemistry, solute species (e.g., silicic acid<sup>226,227</sup>), and water film thickness on carbon mineralization, this study is suggestive of a relationship between water film development and ASSL properties. We are currently pursuing a more targeted investigation focused on the relationship between metal silicate surface chemistry and carbon mineralization outcomes, including rates, reaction extents, and products.

## ENVIRONMENTAL IMPLICATIONS

Balancing environmental concerns and meeting modern energy requirements necessitates greater understanding of CCS technologies. Large-scale geologic carbon storage in the U.S. requires a Class VI well permit, which allows for subsurface injection of  $\text{CO}_2$ . A permit application is strengthened by reservoir simulations that are benchmarked and parametrized by relevant laboratory-derived data and field measurements, enabling accurate models for the transport and fate of injected  $\text{CO}_2$  fluids. This permitting process does not currently rely on reactive transport simulations that can accurately account for mineral dissolution–precipitation reactions taking place in wet  $\text{scCO}_2$  and  $\text{CO}_2$ -rich brine phases, but increasing interest in reactive reservoirs may drive implementation of these simulations in permit applications. In this work we have selected enstatite and an amorphous counterpart for in-depth study, extending on other Mg-silicate (e.g., forsterite) carbonation studies present in the literature. Our results show the differences in reaction rates and products formed depending on surface chemistry and crystallinity (Figure S12), highlighting that the proportion of glassy mesostasis and low crystallinity mineral species is a key property to consider for in situ mineralization in mafic-ultramafic reservoirs. Furthering our understanding of these complex phases will strengthen reactive transport models that predict the fate and transport of subsurface  $\text{CO}_2$  and are crucial components in the commercial-scale deployment of carbon storage, including that of a Class IV well permitting application. Additionally, these results have implications for  $\text{CO}_2$ -enhanced mineral recovery, where the dissolution of silicates in mafic-ultramafic can mobilize economically valuable critical minerals in the presence of an engineered  $\text{CO}_2$ -bearing fluid while also allowing for the permanent storage of  $\text{CO}_2$  via carbon mineralization. This in situ mining approach has potential to provide revenue generating carbon storage and reduction in emissions for the mining industry.<sup>94</sup> Overall, this work advances our knowledge of carbonation reactions in mafic-ultramafic rocks, with high implications for strengthening reactive transport modeling in mafic-ultramafic reservoirs, which ultimately facilitates commercial scale geologic carbon storage and the potential implementation of  $\text{CO}_2$ -based in situ mining technologies. More broadly, the differences in reaction pathways for crystalline or amorphous components of mafic-ultramafic rocks that our study is highlighting has interfacial reactivity implications for a broad range of environmental and technological systems. In the case of basalt, the modal abundance of the glass component varies widely, from <5% to upward of 70% in the Columbia River Basalt Group, and the glassy mesostasis of basalt has the fastest dissolution kinetics.<sup>177</sup> Understanding reaction mechanisms and pathways

of pyroxene and mafic glasses is critical as weathering and alteration of basalt in shallow crustal, subaerial, and suboceanic environments exerts first order controls on global water, nutrient, and climate cycles.<sup>228–232</sup>

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.5c00487>.

Tables S1–S3 and Figures S1–S13 with TGA-MS results, additional in situ and ex situ XRD characterization presented (stacked pattern and waterfall graphs), SEM imaging, and VANTEC-500 detector images (PDF)

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### Notes

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