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Accelerated carbon dioxide mineralization and polymorphic control facilitated by nonthermal plasma bubbles

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Mineralization of carbon dioxide is of interest for developing net-negative carbon technologies that mimic natural carbon cycles by removing and sequestering atmospheric carbon dioxide (CO₂). This study investigates plasma–liquid interactions (PLI) and the impact of modifying electron temperatures of nonthermal CO₂ plasmas to influence the nucleation and growth kinetics of calcium carbonate (CaCO₃). Through optimization of plasma discharge parameters, we show that plasma–liquid interactions can direct the formation of a pure vaterite phase of CaCO₃ over the more thermodynamically stable calcite phase under certain conditions. By varying the mole fraction of the discharge between a mixture of CO₂/Ar in the plasma bubbles, we show that increasing electron temperature enhances CO₂ capture, nucleation rate, and CaCO₃ yields. Increasing the electron temperature of the plasma by varying the Ar mole fraction in the flow increases CO₂ conversion nearly tenfold compared to pure CO₂ yet increases the competitive formation of carbon monoxide through CO₂ dissociation. When average electron energies were ~1 eV, the greatest selectivity toward CaCO₃ was observed. Our results support a mechanistic picture in which CO₂ mineralization is driven concurrently through gas-phase vibrational excitation of CO₂ and at the plasma–liquid interface by generating reactive hydroxyl species from plasma-activated water splitting. These plasma-generated species react to produce HCO₃⁻, which is the rate-determining step in CO₂ mineralization. By demonstrating accelerated mineralization kinetics and polymorphic control of solid carbonate formation at plasma–liquid interfaces, this study could have broader relevance for engineering net-negative carbon sequestration technologies into solid forms for long-duration storage.

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1. Introduction

Mitigating anthropogenic climate change is one of the grand challenges facing modern society. With increasing human populations and expanded industrialization across the globe, research efforts to capture carbon and lock it into solid forms are becoming increasingly important for climate resilience. To reach a net-zero carbon target, society must reduce greenhouse gas emissions by 40–70% by 2050 compared to 2010 levels and reach net-neutral or net-negative carbon emissions by the end of the century.¹ A promising net-negative emission technology inspired by Earth's natural carbon cycle is the sequestration of CO₂ into carbonate minerals.^{2,3} Carbonate minerals play a crucial role in marine sediments and impact ocean acidification by absorbing atmospheric CO₂ into calcium-enriched solutions.⁴ Beyond their potential in CO₂ sequestration, carbonate minerals, such as CaCO₃, are widely used in applications



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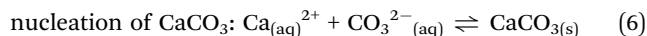
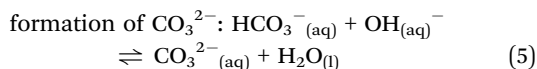
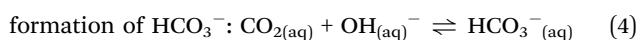
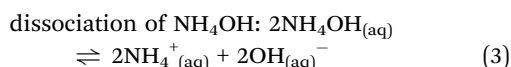
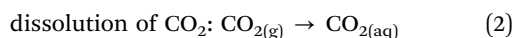


spanning construction,^{5–7} biomedical engineering,^{8,9} and gas storage.^{10–12}

Lab-scale mineralization of CaCO₃ commonly involves bubbling CO_{2(g)} into a supersaturated Ca_(aq)²⁺ solution with a buffer such as ammonium hydroxide (NH₄OH) to facilitate CO_{2(g)} absorption into the alkaline solution.^{13–16} The rate of CO_{2(g)} dissolution can be described as

$$r_{\text{CO}_2} = kC_{\text{B}}(C_{\text{CO}_2} - C_{\text{CO}_2,\text{eq}}) \quad (1)$$

where C_{B} is the concentration of OH_(aq)[−] ions in solution and k is the rate coefficient, which is dependent on the reaction temperature. The overall reaction proceeds as Ca_(aq)²⁺ + 2Cl_(aq)[−] + 2NH₄OH_(aq) + CO_{2(g)} → CaCO_{3(s)} + 2Cl[−] + 2NH₄⁺_(aq) + H₂O_(l) and the individual reaction steps for this process can be written as follows:



where the formation of bicarbonate (4) is a rate-limiting step for CaCO₃ formation.¹⁷ Numerous studies have explored pH ranges,^{15,18,19} additives,^{18–22} and temperature^{23–25} for CaCO₃ growth in gas–liquid systems. Some have employed bubble

reactors to demonstrate that the gas–liquid interface can significantly impact nucleation kinetics, particle formation, and the phase of the final CaCO₃ species.^{13,14,26} In these mineralization processes, CaCO₃ precipitation is limited by mass transfer of CO_{2(g)} into the solution and kinetic constraints resulting from CaCO₃ decomposition under increasingly acidic environments as a result of excess H₂CO₃ formation.²⁶

Plasma–liquid interactions (PLI) are a promising platform to explore novel methods of particle synthesis and CO₂ activation by coupling the aqueous environment with an energetic plasma state to exploit unique chemical pathways and overcome these mass transfer limitations.^{27–35} PLIs have been used for applications spanning nanomaterial synthesis,^{32,36,37} organic synthesis,^{37–39} wastewater treatment,^{40,41} and biotechnology.^{42,43} Nonthermal plasmas are characterized by electron temperatures greater than the temperature of heavier ionic and neutral species in the plasma, resulting in a deviation from the thermodynamic equilibrium. Like other states of matter, this plasma environment can interact with water, producing highly reactive radicals, UV photons, and free and solvated electrons.^{27,30,43–46} Among these species, the •OH radical is perhaps one of the most significant produced by plasma–liquid interactions in water due to its high oxidative potential and propensity to catalyse the generation of other reactive species (*e.g.*, H₂O₂), radical recombination, and other pathways.^{44,47–49}

Plasma–liquid interactions can affect various solution properties, notably pH, through the generation of OH_(aq)[−] and H_(aq)⁺, induce localized temperature increases due to electrical discharge, and alter solution conductivity.^{50–52} Plasma-activated water can also modify the surface energies of particles



Fig. 1 Experimental overview and pulse plasma discharge characteristics. (A) An experimental schematic of the plasma bubble reactor for CO₂ mineralization to CaCO₃. (B) and (C) Example of nanosecond pulse voltage–current waveforms taken for the carbonation experiment where the frequency is 500 Hz, the duty cycle is 83 μs, and the resonance frequency is 60.00 kHz (CO₂ flow rate: 200 sccm). Solution conditions: 0.500 M CaCl₂ and 0.750 M NH₄OH in deionized (D.I.) water.



and promote sites for heterogeneous nucleation.³² As a result, PLI can directly and indirectly influence particle growth and kinetics. The kinetics of PLI are complex and are affected by various solution properties—such as pH, concentration of reactive oxygen species, and conductivity of the solution—all of which depend on the plasma environment, making it challenging to gain mechanistic insights into particle growth.

This report demonstrates accelerated CO₂ mineralization *via* pulsed underwater electrical discharges within plasma bubbles (Fig. 1). This method has an advantage over discharging plasmas above the liquid surface, as plasma bubbles facilitate increased mass transfer between the gas and liquid phases and enhance the transport of reactive plasma intermediates in the aqueous environment through prolonged residence times, high internal pressures, and shockwave agitation from the bubble environment.^{27,29,53} Here, we explored the effect of the plasma-liquid interfaces on the solution-phase chemistry of CaCO₃ precipitation. We show that factors such as plasma composition and discharge voltage influence the production of important plasma species, such as OH_(aq)⁻ and vibrationally excited CO₂. These plasma-induced species directly impact the acid-base chemistry for CaCO₃ precipitation and enable control over CaCO₃ polymorph growth. Given the important role that net-negative carbon capture and utilization technologies must play in reaching global sustainability goals, this report on the pulsed discharge plasma bubble method provides a straightforward approach to tuning reaction dynamics crucial for solution-phase CO₂ mineralization. Furthermore, this demonstration that tailoring the plasma discharge characteristics controls the polymorphic phase presents evidence for carbon capture and utilization optimized toward applications in bioengineering and construction.^{54–58}

2. Results and discussion

CaCO₃ can crystallize into three phases of increasing thermodynamic stability depending on aqueous reaction conditions: vaterite < aragonite << calcite.^{15,18,23,59} The mechanism of calcite growth has been well-studied and can be summarized as three key steps.⁶⁰ First, amorphous calcium carbonate (ACC) growth occurs upon carbonation onset of a supersaturated Ca²⁺ solution. ACC then undergoes dissolution and reprecipitation into spherical vaterite, followed by Ostwald ripening of vaterite into thermodynamically stable aragonite and calcite particles under prolonged time scales (seconds to minutes) and elevated temperatures.^{15,19,60}

2.1 Voltage influence on the CaCO₃ phase and morphology

We first studied CaCO₃ nucleation as a function of plasma discharge on the resultant CaCO_{3(s)} polymorph phase. A plasma bubble reactor (Fig. 1A) was employed to discharge pure CO₂ plasma bubbles into a 50 mL saturated (0.500 M) CaCl_{2(aq)} solution under a constant flow rate. Experiments were repeated with fresh volumes of CaCl_{2(aq)} at increasing discharge voltages. Current and voltage waveforms were recorded with a Tektronix

2 Series Mixed Signal Oscilloscope (Fig. 1B and C). Plasma mineralization experiments ceased after 5 minutes of plasma exposure. All precipitated CaCO₃ was isolated by vacuum filtration and analysed *ex situ* using powder-X ray diffraction (pXRD; Fig. 2A). After each experiment, the final solution temperature and pH were measured, and the vaterite phase weight percent was determined using Rietveld refinements (Fig. 2B). Increasing the discharge voltage increased the final



Fig. 2 (A) Powder X-ray diffraction of precipitated CaCO₃ at different plasma discharge voltages. (B) Discharge voltage-dependent formation of vaterite (wt%) and the final temperature and pH of the bulk solution after 5 minutes of plasma exposure. (C) Induction time at various applied plasma voltages. The induction times observed occur at pH values ranging from 10.00 to 9.50.



solution temperatures and decreased the final solution pH after 5 minutes (Fig. 2B). The increase in temperature was expected because of Joule heating resulting from the electric current. The pH at the beginning of each trial is kept constant at 11, and a decrease in pH over the course of plasma-assisted carbonation indicates the production of HCO_3^- (aq), suggesting that mineralization occurs more rapidly at plasma-liquid interfaces. This result is hypothesized to be an outcome of PLI where the $\text{OH}_{(\text{aq})}^-$ species produced by water dissociation aid carbonation by increasing CO_2 dissolution and reacting with $\text{OH}_{(\text{aq})}^-$ produced *in situ* to create CO_3^{2-} (aq) while in basic solution (reaction (5)). Given that an increase in pH was not observed, $\text{OH}_{(\text{aq})}^-$ formation does not appreciably impact the reaction equilibrium in the presence of the buffer (reaction (3)).

From pXRD analysis, all reactions resulted in CaCO_3 in a mixture of calcite and vaterite phases (Fig. 2A). Applied discharge voltages up to 2.0 kV initially correspond to a decrease in vaterite wt%. With increasing voltages, a greater fraction of vaterite undergoes phase transformation to calcite within 5 minutes (Fig. 2B). This difference can be explained by an increase in voltage and an observed decrease in induction time (Fig. 2C), which allows for longer carbonation and aging times at lower pH values. Vaterite growth occurs faster, allowing for Ostwald ripening into the more thermodynamically stable calcite phase. This phase transformation will continue unless the solution conditions allow for the stabilization of the vaterite phase. Interestingly, between discharge voltages of 2.00 and 2.25 kV, pXRD analysis revealed CaCO_3 with 99% vaterite phase purity. This result can be explained by the pH and temperature of the reaction environment, which plays an important role in kinetically trapping metastable vaterite. In this region, a pH of 6–7 is optimal for producing high purity vaterite. However, across the CaCO_3 mineralization literature, the exact pH range favourable for vaterite formation remains disputed.^{13,15,19,61,62}

Temperature is also influential for vaterite stabilization, where elevated temperatures have been attributed to the transformation of thermodynamically stable calcite and aragonite. This has been reported to occur at temperatures above 30–35 °C,^{62,63} which is consistent with the results herein with decreasing vaterite wt% at the highest voltage and temperatures. It is also important to note the role of NH_4OH in stabilizing vaterite in this process. Previous work has suggested that NH_4^+ and NH_3 may facilitate kinetic trapping and inhibit phase transition by buffering the pH of the solution favourable for vaterite stabilization.^{15,64,65}

Precipitation begins once the supersaturation ratio, S , exceeds the solubility product, K_{sp} , of CaCO_3 and is influenced by the relative concentrations and activity of divalent ions, r (eqn (7)).

$$S = \sqrt{\frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{sp}}}} r^2 \quad (7)$$

It is generally observed that at a low pH, HCO_3^- (aq) formation (reaction (4)) is most favoured in solution, whereas CO_3^{2-} formation (reaction (5)) is favoured at higher pH

values.¹⁵ Thus, decreasing pH results in a decrease in the supersaturation ratio and nucleation rate, J , according to the classical nucleation theory:^{15,18–20}

$$J = A \exp \left[\frac{-16\pi\gamma^3\nu^2}{3(k_{\text{b}}T)^3} (\ln S)^{-2} \right] \quad (8)$$

In eqn (8), A is the pre-exponential factor, γ is the interfacial free energy between polymorphs, ν is the solid density, k_{b} is Boltzmann's constant, and T is the absolute temperature. This specific phase transformation proceeds *via* Ostwald's step rule of phases. At high supersaturation, the interfacial energy between polymorphs dominates, and metastable vaterite precipitates first, followed by more thermodynamically stable phases. As vaterite is thermodynamically unstable, it undergoes a phase transformation to calcite once these conditions are no longer favourable, *i.e.*, beyond a 2.25 kV discharge voltage of a pure CO_2 plasma. Extended times in solution will also favour the thermodynamic transformation of vaterite to calcite.

Scanning electron microscopy (SEM) was performed (Fig. 3) to track the morphology of calcite and vaterite. After 5 minutes of CO_2 bubbling without plasma (0 kV), CaCO_3 particles of primarily vaterite phase, characterized by uniform ellipsoidal particle morphologies, were precipitated. When plasma was introduced, the vaterite morphology was characterized mainly by spherical shapes, whereas calcite exhibited rhombohedral morphology. At 2.08 kV and 98% vaterite wt%, the morphology of CaCO_3 is primarily characterized by spherical/spheroidal vaterite with minor rhombohedral calcite. In contrast, at 2.24 kV with >99% vaterite, spherical vaterite dominated both in SEM and pXRD analyses. The ability to tailor nonthermal plasmas to produce vaterite-phase CaCO_3 selectively is particularly interesting, as this polymorph possesses enhanced porosity and solubility, along with distinct biochemical and optical



Fig. 3 Scanning electron micrographs of precipitated CaCO_3 at different discharge voltages showing the influence of phase purity on CaCO_3 morphology. (A) Ellipsoidal vaterite, (B) rhombohedral calcite, (C) spheroidal and rhombohedral vaterite and (D) spherical vaterite.



properties.^{54–58} These properties make CaCO₃ in the vaterite phase the most practical for important biomedical applications such as bone grafting and drug delivery.^{54–58}

2.2 The role of plasma-derived reactive species in nucleation

The rapid decrease in pH and resulting controlled nucleation of CaCO₃ polymorphs observed with CO₂ plasma bubbles at increasing discharge voltages motivated further investigation of how electron temperature affects nucleation and growth kinetics. The addition of argon (Ar) plasma into the CO₂ stream was investigated to understand the role of increasing electron temperature in nucleation. Under specific operating conditions, plasma discharge characteristics differ depending on the gas used due to their differences in electron energy distribution function (EEDF).⁶⁶ Although Ar has a larger first ionization energy, Ar has a smaller breakdown voltage than CO₂ because its electron energy is inefficiently distributed amongst rotational and vibrational degrees of freedom in CO₂ plasmas. In contrast, monatomic Ar is limited to excitations of translational degrees of freedom. The mean free path of Ar is also longer, such that electrons can accelerate under electric fields to larger collisional impact kinetic energies that ionize

and sustain plasma discharges.⁶⁷ Thus, Ar will produce more plasma-activated species with a longer average lifetime than pure CO₂, resulting in increased concentrations of solvated electrons and OH_(aq)⁻ at the plasma-liquid interface. Conversely, CO₂ plasmas can host unique reactive species at the PLI, such as HCO₂⁻, HCOOH, CO₂⁺, and C₂O₄²⁻, which can activate other pathways for nucleation.^{34,35,68–70}

To monitor the effect of the plasma environment on nucleation kinetics, the induction time, determined as the time between initial carbonation and the onset of the solution opaqueness, was monitored. A control experiment was first performed by bubbling pure Ar plasma into the saturated 0.500 M Ca²⁺ and 0.750 M NH₄OH solution. No precipitate was formed without a source of CO₂ after letting the reaction run for up to 1 hour. To isolate the contributions of specific plasma species produced at the PLI, we defined three sets of experiments performed using mixed-feed and co-feed CO₂ and Ar streams (Fig. 4A). For each experiment, flow rates of 100 standard cubic centimeters (sccm) per minute of CO₂ and Ar (totaling 200 sccm) were maintained to ensure similar bubble mass transport in the reactor. For the co-feed experiments, two bubble columns were placed in the reaction vessel where CO₂



Fig. 4 (A) Experimental schematics of plasma-bubble mineralization reactor configurations with CO₂ and/or Ar plasmas. Left: CO₂ plasma and Ar (no plasma) bubbling separately. Middle: Ar plasma and CO₂ (no plasma) bubbling separately. Right: 50:50 CO₂/Ar plasma bubbling together. (B) Lissajous plots for each condition described in (A) where the plasma power is within 23–25 W. (C) Induction times for CaCO₃ nucleation as a function of discharge voltage in the plasma bubble reactor configurations are defined in (A). (D) Isolated yields of CaCO₃ as a function of plasma voltage. Precipitated CaCO₃ was collected after 5 minutes of plasma exposure.



and Ar flowed separately. We tested each bubble column separately with plasma on or off. In a third set of experiments, a single bubble column was used with mixed CO₂/Ar plasma at varying voltages. In all experiments, the discharge tube consisted of a closed-end quartz tube with eight 200 micrometer holes evenly spaced with constant total flow rates so that the bubble sizes were kept mostly constant. At a given applied voltage, the bulk solution temperature remained within less than 2.0 °C deviation for each reaction configuration. The plasma capacity for each system is studied through Q-U Lissajous analysis (Fig. 4B). The breakdown voltage of the plasma, U_B , is deduced from eqn (9):

$$U_B = U_{\min} \times \frac{1}{1 + \frac{c_0}{c_p}} \quad (9)$$

where the plasma “off” capacitance, c_0 , plasma “on” capacitance, c_p , and minimum voltage, U_{\min} , are determined from fitting parameters from the Lissajous figure. The calculated breakdown voltage decreases with increasing Ar concentration ($U_{B,CO_2} = 0.044$ kV, $U_{B,CO_2/Ar} = 0.020$ kV, and $U_{B,Ar} = 0.013$ kV), which is expected given that Ar is easier to ionize than CO₂.

Induction occurs more rapidly in alkaline solutions where CO₂ can be absorbed and can react with OH_(aq)⁻ to produce HCO₃⁻_(aq), which results in rapid pH decreases. The direct production of OH_(aq)⁻ at the plasma-liquid interface is proposed to be the main cause of this observation, favouring HCO₃⁻_(aq) and lowering the pH to the point where the supersaturation begins to promote CaCO_{3(s)} nucleation. This is observed by the decreasing pH and induction times (Fig. 2B and C) at increasing voltages. This also suggests that despite continuous production of OH_(aq)⁻ at the local plasma-liquid interface, the bulk pH is governed by the competition of acidifying pathways in the reactor such as CaCO₃ mineralization. Across all voltage ranges studied, the condition where only CO₂ plasma bubbles were present with co-flow of Ar resulted in the slowest induction time (Fig. 4C). Mineralization with Ar plasma bubbles led to faster induction times, and experiments with mixed-feed CO₂/Ar plasma led to the quickest induction times. These trends of induction time as a function of voltage correlate to the isolated mass of precipitated CaCO_{3(s)}, where the equal volume of CO₂/Ar mixed-feed with plasma resulted in the greatest yield of CaCO_{3(s)} (Fig. 4D). The increased nucleation rate of CaCO_{3(s)} with experiments including a CO₂ plasma (Fig. 4D, teal and red markers) compared to when there is no plasma present (0.0 kV) is hypothesized to be due to increased activation of CO₂ to form HCO₃⁻_(aq) (reaction (4)). The faster induction time when Ar plasma was present is attributed to a greater presence of OH_(aq)⁻ formed in solution from plasma-assisted water splitting,^{48,71–73} which promotes the formation of HCO₃⁻_(aq) in accordance with Le Chatelier's Principle. As described above, Ar plasmas at the liquid interface generate more •OH_(aq) and OH_(aq)⁻ compared to pure CO₂ plasmas because of their greater average electron energies (see Fig. 5A and B). Under mixed-feed (CO₂/Ar)_{Plasma}, the reactivity of CO₂ is further enhanced through interaction with high-energy

metastable Ar species under Penning ionization.^{74,75} These contributions, in addition to the presence of more OH_(aq)⁻ formed from greater average electron energies, are synergistic toward promoting CO_{2(g)} dissolution and HCO₃⁻_(aq) formation. Under the most optimized conditions, mixed-feed (CO₂/Ar)_{Plasma} is more energy efficient than co-flow CO₂/Ar_{Plasma} and CO_{2Plasma}/Ar experiments with energy consumption of 0.017, 0.024, and 0.027 kWh per g-CaCO₃, respectively. For the former, this enhanced energy utilization is a result of a higher mass yield of CaCO₃ and more efficient plasma ionization, as shown by Lissajous analysis.

It is important to note that an increase in average solution temperature is observed with increasing plasma voltages (20–40 °C). According to Henry's Law, CO_{2(g)} solubility is expected to decrease with rising temperatures, resulting in a lower yield of CaCO_{3(s)}. Additionally, CaCO₃ formation is an exothermic process,¹⁴ so according to Le Chatelier's Principle, such an increase in solution temperature should generally decrease the formation of CaCO₃. However, we found the reverse to be true. With increasing voltages, the mass of precipitated CaCO_{3(s)} increased, suggesting that plasma activation of CO_{2(g)} at liquid interfaces is crucial in accelerating mineralization and overcoming the thermodynamic limit of CO_{2(aq)} in solution at elevated temperatures. We observed that the increasing yield of CaCO_{3(s)} between experimental setups corresponds to those with a faster nucleation rate and that the greatest amount of precipitate formed resulted in the mixed-feed (CO₂/Ar)_{Plasma} (Fig. 4D).

2.3 The role of electron temperature in reaction kinetics

Given that the mixture of CO₂ and Ar plasma best aided CO₂ mineralization to form precipitated CaCO_{3(s)}, we investigated the role of electron temperature at varying CO₂/Ar ratios. For these experiments, the output voltage was maintained at 2.0 kV, and the total flow rate was kept constant at 200 sccm. The electron Boltzmann equation solver, BOLSIG+, was used to calculate the electron temperature and simulate the EEDF at varying experimental CO₂/Ar fractions (Fig. 5A and B).⁷⁶ Simulations confirmed that the average electron temperature increased with decreasing CO₂ partial pressures. Average electron temperatures ranged between 0.95 eV and 3.19 eV at 100% and 10% CO₂ flows, respectively. These simulations were validated with optical emission spectroscopy (OES), which revealed Ca(II) H and K emission lines (393.4 nm and 396.9 nm, respectively) and Ca(I) emission at 422.7 nm that increased in relative intensity with increasing Ar fractions (Fig. 5C). As Ar has large ionization and excitation threshold energies (15.76 eV and 11.55 eV, respectively), inelastic collisions result in higher energy plasma electrons with longer average lifetimes, increasing the mean electron energy and relative intensity of the atomic Ca emission lines.⁷⁷ With increasing electron temperature, the •OH_(aq) (308.9 nm, A²Σ → B²Π) band intensity increased as well, indicative of increased rates of plasma-induced water dissociation.^{27,73,78} The •OH band is a key feature in describing the role of plasma-liquid interactions in accelerated mineralization, as it is a precursor to OH_(aq)⁻ formation.^{48,73} Subsequent increased



Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article are included in the text.

Acknowledgements

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