Experimental evidence for abiotic formation of low-temperature proto-dolomite facilitated by clay minerals

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ABSTRACT

The origin of sedimentary dolomite is a subject of long-standing enigma that still awaits resolution. Previous studies have shown that room temperature synthesis of abiotic dolomite is rarely achieved and primary (proto-)dolomite precipitation is closely associated with microbial activities. In this study, we demonstrate through laboratory carbonation experiments that highly negative-charged clay minerals (as indicated by the values of zetap potential) such as illite and montmorillonite can aid the precipitation of abiotic proto-dolomite under ambient conditions, whereas nearly-neutral charged kaolinite exerts negligible influence on such process. In comparison to montmorillonite, illite has higher surface-charge density, thus is more effective in catalyzing proto-dolomite precipitation. Furthermore, the signal of proto-dolomite in carbonate neoformations is enhanced with increasing concentrations of illite or montmorillonite. On the basis of these results, we suggest that clay minerals catalyze dolomite formation perhaps via electrostatic binding of Mg$^{2+}$ and Ca$^{2+}$ ions and simultaneously desolvating these strongly hydrated cations, a crucial step for dolomite crystallization. The resulting proto-dolomites display the morphologies, textures, and structures similar to those of biogenic dolomite reported before, which are considered precursors of ordered sedimentary dolomite. Therefore, our results offer a possible route to authigenic dolomite found in sedimentary environments.
1. INTRODUCTION

Dolomite [CaMg(CO$_3$)$_2$] is an important mineral component of sedimentary rocks (Warren, 2000). In pre-Holocene geological records, massive amount of dolomite formation could be commonly found in the carbonate platforms (Given and Wilkinson, 1987; Burns et al., 2000; Warren, 2000). Most ancient dolostone rocks which contain more than >75% dolomite by volume are even hundreds to thousands meter thick and cover areas of hundreds of kilometers wide (Warren, 2000; McKenzie and Vasconcelos, 2009). By contrast, the recent occurrences of dolomite are extremely rare in marine sediments, despite the fact that modern seawater is thermodynamically oversaturated with respect to this mineral (Burns et al., 2000). Such apparent discrepancy has stimulated intense studies and debates regarding the genesis of dolomite.

Most geologists contend that the majority of ancient dolomites (massive dolostone in particular) formed as a diagenetic replacement of limestone (i.e., dolomitization: 2CaCO$_3$ + Mg$^{2+}$ → CaMg(CO$_3$)$_2$ + Ca$^{2+}$ or CaCO$_3$ + Mg$^{2+}$ + CO$_3^{2-}$ → CaMg(CO$_3$)$_2$) (e.g., Land, 1985; Given and Wilkinson, 1987; Budd, 1997; Machel, 2004). This hypothesis has been supported by the geological observations (e.g., poor preservation of fossils, coarse dolomite grains with dissolution pores and cavities) in dolostone and reinforced by the fact that laboratory synthesis of dolomite is difficultly achieved at Earth surface temperatures (<60 °C), whereas it is relatively uncomplicated and proceeds at a rapid rate under higher temperature diagenetic conditions (Land, 1980, 1998; Morrow, 1982; Sibley et al., 1987; Arvidson and Mackenzie, 1999; Kaczmarek and Thornton, 2017). Furthermore, thermal dolomitization experiments have indicated
that metastable precursors exclusively occur at the expense of calcite (or aragonite) above 100 °C and finally convert to ordered-dolomite at temperature over 150 °C (e.g., Graf and Goldsmith, 1956; Baker and Kastner, 1981; Sibley et al., 1994; Kaczmarek and Sibley, 2011; Jonas et al., 2017). These metastable phases include proto-dolomite (sometimes referred to as “disordered-dolomite” or “very high-magnesium calcite, VHMC”) and calcian dolomite. Compared to their highly ordered counterpart (i.e., ordered-dolomite or stoichiometric dolomite), proto-dolomite displays none or very weak cation ordering and calcian dolomite exhibits partly ordered crystal structures, despite both of these Ca-Mg carbonates having compositions close to ordered-dolomite (Gregg et al., 2015).

In spite of their paucity, the Holocene dolomites have been repeatedly observed in evaporitic environments worldwide (Wells, 1962; Middelburg et al., 1990; Vasconcelos and McKenzie, 1997; Wright, 1999; van Lith et al., 2002; Wright and Wacey, 2005; Bontognali et al., 2010, 2012; Deng et al., 2010; Meister et al., 2011; Brauchli et al., 2016). Interestingly, these dolomites have been demonstrated to be low-temperature primary (or at least very early diagenetic) dolomite that directly precipitates from saturated solutions \((\text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-} \rightarrow \text{CaMg(CO}_3)_2)\) (McKenzie and Vasconcelos, 2009; Petrash et al., 2017). In addition, Holocene dolomites typically precipitate as proto-dolomite and calcian dolomite in the upper sediments, while they occur as more stoichiometric dolomite rhombs in the deeper layers, suggesting the recrystallization of dolomite upon burial diagenesis (Gregg et al., 1992; Vasconcelos and McKenzie, 1997; Wright, 1999; Petrash et al., 2017). Several dolomite-forming
environments, such as sabkhas of United Arab Emirates (UAE) and Coorong Lagoon of the South Australia, have been proposed as analogs for the origin of ancient dolomites (McKenzie and Vasconcelos, 2009). Besides the favorable abiotic geochemical parameters (e.g., oversaturated state, high Mg/Ca ratio and salinity), there may be natural catalysts overcoming the kinetic barriers to low-temperature dolomite formation. In fact, sulfate-reducing bacteria (Vasconcelos et al., 1995; Vasconcelos and McKenzie, 1997; Wright, 1999; Wright and Wacey, 2005; Deng et al., 2010; Bontognali et al., 2012; Krause et al., 2012), methanogenic archaea (Roberts et al., 2004; Kenward et al., 2009), fermenting bacteria (Zhang et al., 2015) and various aerobic halophiles (Rivadeneyra et al., 2000, 2006; Sánchez-Román et al., 2008, 2009, 2011a, 2011b; Deng et al., 2010; Balci and Demirel, 2016; Disi et al., 2017; Qiu et al., 2017) have been identified as effective catalysts that promote dolomite nucleation and growth. Proposed catalytic functions for microorganisms in dolomite formation include increasing dolomite saturation state and, providing cell walls and organic secretions (e.g., exopolymeric substances) serving as template for dolomite crystallization (McKenzie and Vasconcelos, 2009; Zhang et al., 2012a, 2015; Kenward et al., 2013; Roberts et al., 2013; Bontognali et al., 2014a; Qiu et al., 2017). Noticeably, an argument is recently proposed by Gregg and co-workers who reevaluated the published XRD data of biogenic dolomites and found that these precipitates are proto-dolomite (or VHMC) rather than presumably reported ordered-dolomite (Gregg et al., 2015). Nevertheless, as stated earlier, proto-dolomite is considered an important precursor for ordered-dolomite in sediments and sedimentary rocks. As such, a two-stage process, which
begins with proto-dolomite precipitation by means of nature catalysts (e.g., microbes) and is followed by diagenesis-controlled recrystallization of proto-dolomite towards ordered-dolomite, could account for the occurrence of Holocene dolomites and was probably involved in the formation of ancient dolomites.

In contrast to the growing body of research on microbe-catalyzed dolomite formation, the role of naturally-occurring abiotic mineral catalysts has been largely overlooked. Clay minerals are ubiquitous on the Earth’s surface and they are the important mineral constituents of aquatic sediments (Chamley, 1989). Although there are a few studies concerning the effect of clay minerals on abiotic dolomite formation, the interpretations are largely contradictory. Specifically, based on petrographic and mineralogic investigations, some suggest a close relationship between the clay minerals and abiotic dolomite formation in several depositional settings, such as dolostones (Kahle, 1965; Botha and Huges, 1992; Wanas and Sallam, 2016), cave speleothems (Pérez et al., 2015) and soils (Capo et al., 2000; Casado et al., 2014; Cuadros et al., 2016; Díaz-hernández et al., 2018). In these studies, clay minerals were proposed to be a source of magnesium for dolomite formation and/or function as nucleation centers for dolomite crystals (e.g., Kahle, 1965; Wanas and Sallam, 2016). However, no relationship between these two types of mineral has been detected in other sedimentary environments (Hatfield and Rohrbacker, 1966; Lumsden, 1974). Therefore, laboratory experiments are required to explicitly probe whether clay minerals can facilitate abiotic (proto-)dolomite precipitation. This interaction could arise from negative charges on the surface of clay minerals, which is analogous to that of microbes, and thus serve as
a template for (proto-)dolomite nucleation.

To test the aforementioned hypothesis, we performed a series of lab-bench carbonation experiments using different clay minerals at room temperature. Our results show that negatively-charged clay minerals can accelerate the abiotic precipitation of proto-dolomite under ambient conditions and this catalytic effect might depend on their charge densities.

2. MATERIALS AND METHODS

2.1. Clay mineral preparation and analyses

Illite (IMt-1), montmorillonite (SWy-2) and kaolinite (KGa-1b) were selected for the experiments. The criteria for the mineral selection are based on their ubiquitous occurrence in sediments and the various magnitude of charge density on their layer surface. Both illite and montmorillonite belong to the 2:1 layer-type clay mineral that consists of an octahedral sheet sandwiched between two tetrahedral sheets, whereas kaolinite possesses a 1:1 dioctahedral structure (Chamley, 1989). Specifically for most 2:1 layered clay minerals (e.g., illite and montmorillonite used in this study), their tetrahedrally-coordinated Si(IV) and octahedral Al(III) are partially replaced by lower valency cations, resulting in a net negative surface charge. By contrast, kaolinite is much less substituted by foreign cations, thus displaying negligible surface charge (Chamley, 1989).

All clay minerals used were purchased from the Source Clays Repository of the Clay Minerals Society (West Lafayette, Indiana, USA). Preparation of each clay sample
consisted in manual milling in a mortar followed by sieve through a 200-mesh stainless steel sieve (0.074 mm). The fraction with size less than 200-mesh was then washed three times with doubly distilled water (ddH$_2$O), collected, and then air-dried for all experiments. The detailed information regarding the physical and chemical properties is summarized in Table 1.

The surface electronic property of clay minerals was characterized by zeta potential ($\xi$) measurements. Briefly, the samples were suspended in ddH$_2$O (pH=7.0) at a concentration of 2 g/L. Upon homogeneous dispersion, clay suspensions were transferred into an electrophoretic cell, and the $\xi$ value of clay minerals was measured using a Zeta potential analyzer (ZetaSizer Nano ZS, Malvern Instruments, UK). It is well known that the negative electric charge of clay minerals is mainly attributed to their edge-surface hydroxyl groups (Chamley, 1989). As such, thermogravimetric analysis (TGA) was performed to determine the amount of surface-bound hydroxyl in used clay minerals. TGA analyses were made on a TGA system (Netzsch STA449F3, Germany). These analyses were performed on pre-weighted samples of about 20 mg heated in a corundum crucible from 30 to 1000 °C at a heating rate of 5 °C min$^{-1}$ under N$_2$ atmosphere.

2.2. Abiotic syntheses of carbonate minerals and chemical analyses

A precipitate solution with a Mg/Ca molar ratio of 8 was prepared for carbonation experiments. This Mg/Ca value is higher than that of present sweater (~5.2), but lies within the range of values measured in dolomite-forming environments (Deng et al., 2010). The precipitation system consisted of 10 mM CaCl$_2$, 80 mM MgCl$_2$·6H$_2$O, 20
mM Na$_2$CO$_3$, and different concentrations of clay minerals (0, 1, 2, 4 and 6 g/L; corresponding to different amounts of surface charge available for interacting with Ca$^{2+}$ and Mg$^{2+}$ ions).

In brief, aqueous solutions of CaCl$_2$/MgCl$_2$·6H$_2$O and of Na$_2$CO$_3$ were first prepared as stock solutions. Different amounts of clay minerals were added into aforementioned Ca$^{2+}$/Mg$^{2+}$ solution. After being stirred at room temperature overnight, the pH of mixture was adjusted to 7.0 by using 0.1 M NaOH. Then the solution of Na$_2$CO$_3$ was added dropwise into the clay suspension, leading to form gel-like precipitate. After about 30 min, the gel was placed in an incubator at 30 °C and all synthetic experiments reported are performed in duplicate.

Solution pH, aqueous Ca$^{2+}$ and Mg$^{2+}$ as well as dissolved inorganic carbon (DIC) were measured immediately after solutions were mixed (i.e., in the initial carbonation stage) and after 30-day ageing. The pH was determined using a Denver UB-7 meter (Denver, USA) with an uncertainty of ± 0.01 pH units. The concentrations of Ca$^{2+}$ and Mg$^{2+}$ were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermofisher ICAP6300, USA). Determination of DIC was performed by using Shimadzu SCN analyzer (TOC-V, Shimadzu, Japan). The concentrations of CO$_3^{2-}$ were further calculated from measured pH and DIC. On the basis of above analyses, the saturation indices (SI) with respect to common carbonates (calcite, aragonite, monohydrocalcite and proto-dolomite) could be calculated using PHREEQC (version 2; Parkhurst and Appelo, 1999).

2.3. Preparation of mineral standards
Hydromagnesite can easily be misidentified as dolomite (Zhang et al., 2012a), because the (310) peak of hydromagnesite appears at 30.818° (2θ, Cu Kα), very close to the strongest (104) reflection of (proto-)dolomite. To avoid this possible misidentification, a hydromagnesite, together with hydrothermally-synthesized proto- and ordered-dolomites, was prepared as a reliable standard for inferring the mineralogical composition of carbonate neoformations. Hydromagnesite, originally collected from hypersaline lakes on the Tibetan Plateau, was acquired from Xibeili mineral company (Jiangsu, China). Proto- and ordered-dolomite standards were prepared at 80 °C and 200 °C, respectively, based on the method of Rodriguez-Blanco et al. (2015).

2.4. Crystal characterization

After one month, the resulting precipitates were obtained by centrifugation, and subsequently rinsed three times with ddH2O, and then air-dried. Multiple methods were used for mineral analysis, including X-ray diffraction (XRD), Raman spectroscopy, and scanning and transmission electron microscopy (SEM and TEM).

The samples were analyzed with a Bruker D8 Advance XRD using Cu Kα radiation. The operation voltage and current maintained at 40 kV and 40 mA, respectively. The samples were scanned from 3 to 65° 2θ stepping at 0.02° with a count time of 1 s per step. The MgCO3 molar fraction in the crystal lattice of Ca-Mg carbonates was calculated from d-spacing of (104) peak using the empirical curve developed by Bischoff et al. (1983). Solids produced in the reactor with 6 g/L illite IMt-1, along with pristine IMt-1 and aforementioned mineral standards, were analyzed by
Raman spectroscopy. The Raman spectra were acquired using a Renishaw RM-1000 laser Raman microscope system in the range between 100 and 1200 cm\(^{-1}\) at an interval of 1 cm\(^{-1}\). A 514.5 nm Ar\(^+\) laser was used as the excitation source. Spectral peak positions were calibrated using the 520.5 cm\(^{-1}\) line of silicon as a standard. The dried solid samples were Pt-coated prior to observation using a Hitachi SU8010 SEM. In addition, a Horiba EX-350 energy-dispersive X-ray spectrometer (EDS) was employed in the SEM to determine the elemental composition of the solid experimental products. The SEM was operated at an accelerating voltage of 5-15 kV. TEM observations and EDS analyses were performed with an FEI Talos F200X TEM with an accelerating voltage of 200 kV. Samples for TEM analyses were first dispersed in ethanol and then pipetted onto 300 mesh copper TEM grids with a nitrocellulose membrane and carbon coating.

3. RESULTS

3.1. Characterization of clay samples

XRD results of pristine clay samples in the size range of less than 200 mesh reveal that both illite IMt-1 and montmorillonite SWy-2 also contain trace amounts of quartz, while kaolinite KGa-1b is highly pure (Table 1). The zeta potential of the clay minerals varies significantly. Specifically, the \(\xi\) value is \(-41.99\) mV for illite, \(-34.51\) mV for montmorillonite, and \(-3.93\) mV for kaolinite, which indicates that illite and montmorillonite have much higher layer-charge density than kaolinite. These results are consistent with the conventional view that illite and montmorillonite are 2:1 layer
clay minerals that carry a net negative electric charge that results from extensive isomorphous substitution of cations in their lattice structures, but 1:1 layer type kaolinite is nearly-neutral charged (Chamley, 1989). TGA results can also be used to compare the amount of surface hydroxyl between illite and montmorillonite. Two significant weight loss steps are observed in these clays: a dehydration first stage followed by a dehydroxylation second stage (Fig. S1). Results show that weight losses from dehydroxylation are 6.1% and 3.6% for illite and montmorillonite respectively, which confirms that illite has significantly more hydroxyl than montmorillonite (Fig. S1).

3.2. Changes of aqueous chemistry as a result of carbonation

As shown in Table 2, the ionic compositions of the reactors with 6 g/L clay minerals are selected as representatives to investigate the geochemical changes upon carbonation. In general, the pH of each solution decreases by ca. 0.7 pH units at the end of experiments, which is ascribed to the decline in CO$_3^{2-}$ concentrations. As a result of carbonate precipitation, Ca$^{2+}$ ions for each reactor are largely depleted. Even though the precipitation solutions are oversaturated with respect to Mg-bearing carbonates (e.g., proto-dolomite), a significant decrease of Mg$^{2+}$ is only observed in the systems with illite or montmorillonite, indicating that various carbonates occur in the clay-amended reactors.

3.3. Characterization of neoformed Ca-Mg carbonates

3.3.1. XRD results
As representatives, the XRD patterns of the particles grown in the presence of 6 g/L clay minerals are presented in Figs. 1 and 2. Without clay minerals, only aragonite is obtained (Figs. 1A). When clay minerals are introduced into the reactors, the solid products change greatly. Specifically, in the illite-amended system, dolomite-like material is the only carbonate phase detected (Fig. 1). In comparison, the characteristic peaks [(011), (100) and (-110)] of hydromagnesite are absent from our experiments (Fig. 1), which suggests that this carbonate phase is dolomite rather than hydromagnesite. The (104) reflection position of our produced dolomite is around 30.735° 2θ (d_{104}=0.2907 nm). This value reveals that its MgCO₃ content is ~46.2 mol% (Bischoff et al., 1983), much close to the stoichiometric composition. To assess the degree of cation ordering of low-temperature dolomite, the XRD patterns of illite-assisted dolomite, proto- and ordered-dolomite standards are further compared. It can be seen that the XRD pattern of illite-assisted carbonate precipitate is quite similar to that of proto-dolomite, as evidenced by the lack of superstructure ordering peaks [e.g., (101), (015) and (021)] and broad nature of the reflections (Fig. 1). It has been suggested that poor cation ordering and structural water could account for these characteristic appearances of the XRD pattern of proto-dolomite (Kelleher and Redfern, 2002). Not limited to the system with illite, proto-dolomite, accompanying with trace aragonite, is also observed in the montmorillonite-amended reactor (Fig. 2). However, its reflection intensity is significantly lower. By contrast, instead of proto-dolomite, only weak XRD signals characteristic of monohydrocalcite are detected in carbonate products from kaolinite-assisted experiments (Fig. 2). The XRD results show that low-temperature
formation of proto-dolomite can be catalyzed by clay minerals and thus suggest that this process may be mediated by negatively charged surfaces; that is, illite with highest charge density represents the most positive effective on proto-dolomite precipitation, and lower-charged montmorillonite contributes less to this reaction, while nearly-neutral charged kaolinite has a negligible impact.

In order to elucidate the relationship between the charge of clay minerals and the formation of proto-dolomite, the effect of clay concentration (i.e., charge magnitude in reactors) on proto-dolomite precipitation is also evaluated (Figs. S2 and S3). As expected, the peak intensity of the (104) plane of proto-dolomite also progressively increases with increasing concentrations of illite (Fig. S2) or montmorillonite (Fig. S3). In addition, aragonite and monohydrocalcite can also be precipitated in montmorillonite-amended experiments (Fig. S3) and when low concentration of illite is used (Fig. S2).

3.3.2. Raman data

As an independent characterization of the crystal structure of the experimentally-produced phase, the Raman spectra of carbonate precipitate with 6 g/L illite are directly compared to those of illite, and standards of proto-dolomite, ordered-dolomite, and hydromagnesite. Typically for dolomite, there four distinct vibrational modes can be observed in the range of 100-1200 cm\(^{-1}\) (Fig. 3). In general, compared to ordered-dolomite, proto-dolomite exhibits a broader peak width and band positions slightly shifted to lower wavenumbers, from 1097 to 1095 cm\(^{-1}\). Unlike dolomite, hydromagnesite only displays two characteristic modes (Fig. 3). After carbonation,
is one distinct band and three small humps emerged in illite samples (Fig. 3). In comparison to the standards, the position of these new peaks is similar to that of proto-dolomite, which independently confirms the existence of proto-dolomite in illite-amended carbonation experiments.

3.3.3. SEM observations

SEM images show that proto-dolomite crystals are exclusively distributed on the edge of platy illite particles, which suggests that the edges rather than basal surfaces are more effective catalytic sites for proto-dolomite crystallization (Fig. 4). These proto-dolomite crystals are 1-3 μm in size, and are either randomly dispersed on small illite particles (Fig. 4A) or in the form of aggregates covering the large illite crystals (Figs. 4B and C). High-magnification images of proto-dolomite crystals reveal a cauliflower-like (Fig. 4D) or dumbbell-shaped (Fig. 4E) structures. Nanoscale-resolution images show that the proto-dolomite has a granular texture comprised of many spherical crystallites around 10-20 nm in size (Fig. 4F). Elemental mapping by EDS reveals striking differences between illite and neoformed proto-dolomite (Figs. 4G-J). The proto-dolomite particles have high level of homogenously distributed Ca and Mg, but a trace amount of Si, while the signals of Ca and Mg are nearly invisible on the surface of Si-rich illite crystals (Figs. 4H-J). The chemical compositions of illite and proto-dolomite are further obtained by EDS spot scan, as shown in Figs. 4K-L. In comparison to illite, proto-dolomite particle is rich in C, O, Mg and Ca, and displays similar Mg and Ca contents (Mg-Kα and Ca-Kα). Proto-dolomite in the reactor with montmorillonite exhibits only spheroidal morphology (Figs. 5A and B), and is
surrounded by flaky-shaped montmorillonite (see Fig. 5B). The MgCO₃ content of these spheroids reaches approximately 47 mol% as determined by EDS (Fig. 5C). High magnification images show that dolomite spheroids are also composed of numerous nanoparticles (Fig. 5D), similar to those obtained in illite systems. Furthermore, SEM-EDS results indicate that dendritic-shaped aragonite is also produced in the presence of montmorillonite (Fig. S4).

### 3.3.4. TEM observations

The occurrence of proto-dolomite is also validated by TEM investigation. The TEM photographs of a representative sample from the 6 g/L illite system are presented in Fig. 6. In agreement with the SEM results, micron-sized proto-dolomites are primarily located on the illite external surfaces and have a spheroidal or fan (cauliflower)-like shape (Fig. 6A). The MgCO₃ content in the proto-dolomite is calculated to be ca. 46 mol% from the TEM-EDS data, again consistent with aforementioned SEM-EDS measurements. High-resolution TEM (HRTEM) images further confirm that the proto-dolomite crystals are made of numerous, randomly distributed, 10-30 nm sized nanoscopic crystals (Figs. 6B and C). The selected-area electron diffraction (SAED) pattern of these nanoparticles shows diffraction rings matching (hkl) indices of (012), (104), (006) and (113) of dolomite (Fig. 6C). However, the super-lattice reflections [e.g., (015), (101) and (021)] indicating the cation ordering are not found, which again independently confirms that proto-dolomite is synthesized in these experiments and agrees with our XRD and Raman spectra. The crystal lattice fringes also demonstrate the presence of proto-dolomite with a 2.906 Å d-spacing that
corresponds to the (104) plane of proto-dolomite and by its two sets of \{104\} face with angle of 75° (Fig. 6D).

4. DISCUSSION

4.1. The possible role of clay minerals in proto-dolomite crystallization

According to previous reports, the intrinsic difficulty to precipitate both proto- and ordered-dolomite is attributed to the Mg-hydration effect (e.g., Lippmann, 1982; de Leeuw and Parker, 2001; Romanek et al., 2009). In general and similarly to Ca\(^{2+}\) ions, Mg\(^{2+}\) ions are bound to water molecules, thus forming metal-H\(_2\)O association in aqueous solutions (Lippmann, 1973, 1982; Romanek et al., 2009; Hamm et al., 2010). Previous experimental and computational studies have demonstrated that the water coordination number for Mg\(^{2+}\) (6.0) is smaller than that for Ca\(^{2+}\) (6.0-9.2, with the mean number of 7.3) (Jalilehvand et al., 2001; Jiao et al., 2006; Hamm et al., 2010). However, as compared to Ca\(^{2+}\), much more energy is required to shed the water molecules around Mg\(^{2+}\) (1926 kJ/mole for Mg\(^{2+}\) vs. 1579 kJ/mole for Ca\(^{2+}\)), arising from the strong outer solvation shell of Mg\(^{2+}\) (Lippmann, 1973; Hamm et al., 2010). As a consequence, the persistent hydration shell of Mg\(^{2+}\) can poison the growth of Ca-Mg carbonates such that the formation of Mg-free aragonite is favored when Mg:Ca molar ratio exceeds 4:1 (Falini et al., 1996; Lenders et al., 2012; Zhang et al., 2012b; Shen et al., 2014, 2015).

As such, the predominance of aragonite over calcite and Ca-Mg carbonates takes place in modern seawater which has an average Mg/Ca molar ratio of ~5.2, and it is also observed in our clay-free systems with a Mg/Ca molar ratio of 8 (Fig. 1A).
However, it is generally considered that this Mg$^{2+}$-H$_2$O association can be destabilized by changing some physicochemical parameters. For instance, increase in salinity might reduce water activity and subsequently decrease the hydration energy of Mg (van Lith et al., 2002). Furthermore, dehydration of Mg$^{2+}$ and subsequent Mg incorporation into growing Ca-Mg carbonates can also take place in the presence of microorganisms, microbial exudates or other organo-molecules, leading to crystallization of magnesian calcite (e.g., Falini et al., 1996; De Yoreo and Dove, 2004; Rivadeneyra et al., 2004; Stephenson et al., 2008; González-Muñoz et al., 2010; Lenders et al., 2012; Han et al., 2013) and even (proto-)dolomite (e.g., Vasconcelos et al., 1995; Roberts et al., 2004, 2013; Sánchez-Román et al., 2008; Bontognali et al., 2012, 2014a; Zhang et al., 2012a, 2015). Moreover, carboxyl moiety (R-COO$^-$) associated with microbes and organo-molecules have been identified as the crucial functional group facilitating the loading of Ca$^{2+}$ and Mg$^{2+}$ during Ca-Mg carbonate growth (Kenward et al., 2013; Qiu et al., 2017).

There are at least two distinct hypotheses proposed to explain the positive role of microbes and organo-molecules in dewatering of Mg$^{2+}$-H$_2$O complexes: (1) a metal-chelation model (Mirsal and Zankl, 1985; Romanek et al., 2009; Wang et al., 2009; Kenward et al., 2013; Roberts et al., 2013) and (2) an adsorption-displacement mechanism (Zhang et al., 2015). In the first model, it has suggested that electronegative carboxyl functional groups can bind and partially dewater Mg$^{2+}$-H$_2$O complexes, generating Mg$^{2+}$-carboxyl group complexes. In doing so, Mg$^{2+}$-carboxyl complex requires much lower energy for carbonation than Mg$^{2+}$-H$_2$O complex (Kenward et al.,
In the adsorption-displacement mechanism, microbial exopolymers are preferentially adsorbed onto the growing Ca-Mg carbonate surface replacing the surface water molecules, which would otherwise be associated with Mg$^{2+}$, thereby benefiting the diffusion of Mg$^{2+}$ into crystal structure (Zhang et al., 2015).

Our experiments demonstrate that clay minerals can also facilitate and expedite proto-dolomite precipitation. Several lines of evidence suggest that clay mineral-mediated proto-dolomite formation might proceed through a metal-chelation mechanism. First as solid phases, clay minerals apparently cannot work in the same way as soluble microbial secretions (e.g., extracellular exopolymers, carboxylic acids and others), which could be easily adsorbed to growing carbonate as mentioned above. Second, it appears that only clay minerals with negative charges such as illite and montmorillonite promote proto-dolomite formation, which suggests that these clay minerals perhaps serve a function similar to that of negatively-charged microbial cells via binding Mg and Ca ions, thus facilitating the dehydration of Mg and Ca. Third, in comparison to montmorillonite, illite has a greater surface charge density (as evidenced by $\xi$ values), and therefore is shown to be more efficient at enhancing dolomite precipitation, further indicating that the magnitude of charge density plays a fundamental role in dolomite formation. Such hypothesis is reinforced by the observations that the proto-dolomite signal in XRD is enhanced with increasing concentrations of illite or montmorillonite (corresponding to elevated charge density in precipitation reactor). A similar finding has been reported by Kenward and co-workers who demonstrated that the formation of (proto-)dolomite can be achieved in the
presence of microorganisms with high charge density (Kenward et al., 2013).

Fourth, clay minerals are negatively charged primarily due to a large number of edge-bound hydroxyl groups. If clay minerals catalyze proto-dolomite crystallization via their surface binding, proto-dolomite should be preferably formed on the edge surface of clay particles. Since montmorillonite is irregular in shape, it is difficult to distinguish between its edge surface and basal surface under SEM. However, this is not a problem for illite. Our SEM results reveal that newly-formed proto-dolomite indeed precipitates on the edges of illite (Figs. 4A-C).

Therefore, we speculate that Ca and Mg ions are favorably adsorbed by electrostatic force onto clay surfaces, forming metal-hydroxyl complex and shedding partial water molecules simultaneously (Fig. 7). In a similar manner to metal-carboxyl, metal-hydroxyl might lower the energy required for carbonation, leaving illite or montmorillonite as a nucleation center for proto-dolomite crystallization, resulting in the formation of a thin dolomite layer (Fig. 7). Once this dolomite layer is created, it is generally thought that the homoepitactic growth of these pre-existing particles will continue when a supersaturated condition is maintained (Roberts et al., 2013).

4.2. Morphological features of low-temperature (proto-)dolomite

It has been repeatedly reported that dumbbell, cauliflower and spherical morphologies of non-stoichiometric dolomite form in microbial laboratory experiments (e.g., Warthmann et al., 2000; van Lith et al., 2003; Bontognali et al., 2008; Sánchez-Román et al., 2008; Qiu et al., 2017). These biogenic dolomites vary in size from several micrometers to a few hundred nanometers and normally consist of numerous
nanoglobules (Bontognali et al., 2008; Sánchez-Román et al., 2008). Such morphological and textural features are different from dolomite rhombs synthesized at high temperatures, and therefore have been proposed as potential biosignatures to trace microbial activities in the geological record (Warthmann et al., 2000; Sánchez-Román et al., 2008). However, the morphology and size of proto-dolomite precipitated with the aid of clay minerals are similar to those of microbially-mediated ones. These observations suggest that morphology criteria alone may not unambiguously unravel the biogenic origin of dolomite crystals in sedimentary samples, especially those intergrown with clay minerals. Instead of constituting evidence for its origin, such dumbbell-like or spherical dolomite might be an inherent feature of non-stoichiometric proto-dolomite. Indeed, the same observations were also found in abiotic synthesis of proto-dolomite at 60 °C (e.g., Malone et al., 1996; Rodriguez-Blanco et al., 2015).

Furthermore, Rodriguez-Blanco et al. (2015) demonstrated that amorphous Mg-Ca carbonate nanospheres first precipitated and then tended to be coalesced into micro-sized proto-dolomite spheroids, implying that proto-dolomite grows via oriented attachment of primary nanoparticles (De Yoreo et al., 2015) and thus exhibits a nanogranular texture.

### 4.3. Geological implications

Clay minerals are the most abundant minerals on the Earth’s surface (Chamley, 1989; Vorhies and Gaines, 2009), and they can be either formed authigenically or transported into marine waters or lakes by river, air or volcanic eruptions (Chamley, 1989). As such, clay minerals should be commonly found in modern dolomite-forming
environments. Indeed, it has been repeatedly reported that clay minerals commonly occur in sediments of coastal sabkhas and inland saline lakes in which primary dolomite deposits have emerged, such as the coastal sabkha in Abu Dhabi (UAE) (Sadooni et al., 2010) and highly alkaline playa lakes such as Deep Springs Lake in USA (Meister et al., 2011). Surveys of dolomite authigenesis in these settings also revealed that crystals of dolomite often grow in pore spaces around detrital clay particles (e.g., Sadooni et al., 2010). It is notable that in microbial mats of coastal sabkhas (UAE and Qatar), dolomite crystals were also found associated with authigenic clay minerals (Bontognali et al., 2010; Brauchli et al., 2016). These observations suggest that clay minerals might play a positive role in dolomite crystallization.

Our experiments show evidence that illite, montmorillonite and probable other negatively-charged clay minerals in an oversaturated solution could serve as nucleation centers for dolomite. Compared to modern seawater with ca. 0.27 mM CO$_3^{2-}$, higher concentrations of CO$_3^{2-}$ ions (20 mM) used in our precipitation experiments, which correspond to higher saturation state for dolomite. Nevertheless, these parameters are still within the range of values estimated in some environments showing ongoing dolomite authigenesis and perhaps in ancient sea. For instance, the concentration of CO$_3^{2-}$ of hypersaline dolomitic lakes in the Coorong region (Australia) fluctuates from 0.48 to 24.25 mM, depending on the stage of evaporation (Wacey, 2005). Moreover, apart from Carboniferous to Permian, it has been suggested that the saturation state of dolomite in ancient seas throughout the Phanerozoic was high compared to the present-day (Riding and Liang, 2005). Under aforementioned
highly oversaturated conditions, swelling clay minerals (e.g., montmorillonite) that can stay buoyant for longer than non-swelling clays (e.g., illite) can function as a template for the direct precipitation of proto-dolomites from solutions. Once deposited into sediments, negatively-charged clays including swelling and non-swelling phases still have such potential to facilitate dolomite formation. Specifically, it has been well documented that organic matter in marine sediments is tightly associated with clay minerals (Kennedy et al., 2002) and potentially promote the formation of authigenic clays (Bontognali et al., 2014b). Under decomposition of organic matter, NH₃ and CO₂ gas would be produced, which diffuse into porewaters and then significantly increase solution pH, carbonate alkalinity and saturation state with respect to dolomite. Clay minerals, together with other negatively-charged compounds (e.g., microorganisms and carboxyl-rich organic matters), could contribute to the crystallization of dolomites. Once these newly-formed dolomites are formed, they might be nuclei for later, more pervasive dolomite formation (Burns et al., 2000; Mazzullo, 2000). Such model might account for the occurrence of dolomite beds associated with organic carbon-rich deep-sea clayey sediments (Meister et al., 2007, 2008).

Upon burial diagenesis, proto-dolomite tends to transform into more stoichiometric dolomite through a dissolution-reprecipitation process (Malone et al., 1996; Warren, 2000; Vasconcelos and McKenzie, 1997; Rodriguez-Blanco et al., 2015). Therefore, the clay mineral-catalyzed dolomite precipitation model offers one possibility for interpreting the dolomite formation in certain geological environments,
in which a close relationship between clays and dolomite is observed (e.g., Wanas and Sallam, 2016).

5. CONCLUSIONS

We demonstrate that high negatively-charged clay minerals such as illite and montmorillonite are capable of mediating the formation of proto-dolomite through a metal-chelation mechanism. Cauliflower-like and dumbbell-shaped dolomite crystals are mainly distributed on the edge surface of illite particles, while spheroidal dolomites are observed in montmorillonite-amended systems. The proto-dolomite neoformations display granular textures that consist of nanoscopic particles, morphologically similar to those formed by biotic process. This new data provides laboratory evidence for the catalytic role of clay minerals in dolomite formation and suggests that morphology alone cannot be used as a criterion determining the origin for dolomite in the rock records.

ACKNOWLEDGMENTS

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REFERENCES


Graf D. L. and Goldsmith J. R. (1956) Some hydrothermal syntheses of dolomite and


Lumsden D. N. (1974) Relationships among insoluble residue, dolostone and limestone


Table 1

Types of clay minerals used in this study, their surface area, chemical composition and mineralogy.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>BET surface area (m²/g)</th>
<th>Chemical formula</th>
<th>Mineralogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite (IMt-1)</td>
<td>20.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>(Mg&lt;sub&gt;0.09&lt;/sub&gt;Ca&lt;sub&gt;0.06&lt;/sub&gt;K&lt;sub&gt;1.37&lt;/sub&gt;)(Al&lt;sub&gt;2.69&lt;/sub&gt;Fe&lt;sub&gt;0.82&lt;/sub&gt;Mg&lt;sub&gt;0.43&lt;/sub&gt;Ti&lt;sub&gt;0.06&lt;/sub&gt;)(Si&lt;sub&gt;6.77&lt;/sub&gt;Al&lt;sub&gt;1.23&lt;/sub&gt;)O&lt;sub&gt;20&lt;/sub&gt;(OH)&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Illite, trace quartz</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>22.7&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(Ca&lt;sub&gt;0.12&lt;/sub&gt;Na&lt;sub&gt;0.32&lt;/sub&gt;K&lt;sub&gt;0.05&lt;/sub&gt;)(Al&lt;sub&gt;3.01&lt;/sub&gt;Fe&lt;sub&gt;0.41&lt;/sub&gt;Mn&lt;sub&gt;0.01&lt;/sub&gt;Mg&lt;sub&gt;0.54&lt;/sub&gt;Ti&lt;sub&gt;0.02&lt;/sub&gt;)(Si&lt;sub&gt;7.98&lt;/sub&gt;Al&lt;sub&gt;0.02&lt;/sub&gt;)O&lt;sub&gt;20&lt;/sub&gt;(OH)&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Montmorillonite, trace quartz,</td>
</tr>
<tr>
<td>Kaolinite (KGa-1b)</td>
<td>13.1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(Mg&lt;sub&gt;0.02&lt;/sub&gt;Ca&lt;sub&gt;0.01&lt;/sub&gt;Na&lt;sub&gt;0.01&lt;/sub&gt;K&lt;sub&gt;0.01&lt;/sub&gt;)(Al&lt;sub&gt;3.86&lt;/sub&gt;Fe&lt;sub&gt;0.02&lt;/sub&gt;Ti&lt;sub&gt;0.11&lt;/sub&gt;)(Si&lt;sub&gt;3.83&lt;/sub&gt;Al&lt;sub&gt;0.17&lt;/sub&gt;)O&lt;sub&gt;10&lt;/sub&gt;(OH)&lt;sub&gt;8&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Kaolinite</td>
</tr>
</tbody>
</table>

<sup>a</sup> Dogan et al. (2007).  
<sup>b</sup> http://www.clays.org/Sourceclays.html.  
<sup>c</sup> Dogan et al. (2006).
Table 2

Geochemical changes in the carbonation reactors with and without clay mineral (6 g/L).

<table>
<thead>
<tr>
<th>Experimental set</th>
<th>Initial pH</th>
<th>Initial Ca$^{2+}$ (mM)</th>
<th>Initial Mg$^{2+}$ (mM)</th>
<th>Initial SI for carbonate phases</th>
<th>Final pH</th>
<th>Final Ca$^{2+}$ (mM)</th>
<th>Final Mg$^{2+}$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>calcite</td>
<td>aragonite</td>
<td>monohydrocalcite</td>
<td>proto-dolomite</td>
</tr>
<tr>
<td>Without clay mineral</td>
<td>9.74</td>
<td>9.91</td>
<td>81.03</td>
<td>4.77</td>
<td>4.65</td>
<td>3.44</td>
<td>10.02</td>
</tr>
<tr>
<td>With illite</td>
<td>9.78</td>
<td>9.95</td>
<td>80.47</td>
<td>4.78</td>
<td>4.66</td>
<td>3.45</td>
<td>10.03</td>
</tr>
<tr>
<td>With montmorillonite</td>
<td>9.79</td>
<td>10.07</td>
<td>80.26</td>
<td>4.79</td>
<td>4.67</td>
<td>3.46</td>
<td>10.03</td>
</tr>
<tr>
<td>With kaolinite</td>
<td>9.71</td>
<td>10.02</td>
<td>80.14</td>
<td>4.78</td>
<td>4.67</td>
<td>3.45</td>
<td>10.03</td>
</tr>
</tbody>
</table>
Figure caption:

Figure 1. XRD patterns of minerals obtained before and after carbonation experiments:
(A) mineral products without clay additives; (B) pristine illite IMt-1; (C) solid products
with IMt-1 as the additive; (D) standards of proto-dolomite, ordered-dolomite and
hydromagnesite (A, aragonite; I, illite; Q, quartz; D, dolomite).

Figure 2. XRD patterns for the solid samples collected before and after carbonation
experiments: (A) original montmorillonite SWy-2; (B) neoformed crystals with SWy-
2; (C) pristine kaolinite KGa-1b; (D) solid phases with KGa-1b (M, montmorillonite;
Q, quartz; D, dolomite; A, aragonite; K, kaolinite; MC, monohydrocalcite).

Figure 3. Raman spectra for the solids from the carbonation reactor with 6 g/L IMt-1,
pristine IMt-1, and standards of proto-dolomite, ordered-dolomite and hydromagnesite.
The arrows and dash lines highlight the characteristic bands of proto-dolomite
occurring in carbonation sample with IMt-1 as the additive.

Figure 4. SEM images of proto-dolomite synthesized in the solutions with illite. (A-C)
micron-sized dolomites (arrow) on the edge surface of illite; (D-E) the newly-formed
proto-dolomites appear as cauliflower and dumbbell grains, respectively; (F) a
magnified view that shows the details of neoformed proto-dolomite; (G-J) elemental
maps of the association between proto-dolomite and illite showing the distribution of
Ca, Mg and Si; (K-L) typical EDS compositions of illite and protodolomite shown in panel G (the Pt peaks correspond to sample coating).

Figure 5. SEM images of proto-dolomite synthesized in the reactors with montmorillonite. (A) montmorillonite samples after carbonation; (B) enlarged views show spheroidal proto-dolomites surrounded by flaky montmorillonite; (C) EDS spectra showing the elemental compositions of montmorillonite and proto-dolomite neoformation (the Pt signal is attributed to sample coating); (D) a high magnified image of proto-dolomite spheroid (the insert) displaying a granular-textured surface.

Figure 6. (A) TEM micrograph and EDS compositions showing the spatial association between proto-dolomite and illite particles; (B-C) high-magnification images of the inset views of dumbbell or cauliflower-like crystals indicating that nanocrystallites are at random orientations. The inset SAED pattern with indexation as dolomite does not show the super-lattice reflections; (D) HRTEM image showing the occurrence of 0.2906 nm lattice fringes, corresponding to d-spacing of (104).

Figure 7. Schematic diagram illustrating the catalytic role of negatively-charged clay minerals in proto-dolomite formation: (A) diagrammatic crystal structure of 2:1 layer clay minerals (e.g., illite and montmorillonite tested in this study); (B) the adsorption and dewatering of Mg and Ca ions by surface-bound hydroxyl groups; (C) the formation of Mg(Ca)-hydroxyl complexes favoring the carbonation reaction.
Figure 1
Figure 2

Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Supplementary material for

Experimental evidence for abiotic formation of low-temperature proto-dolomite facilitated by clay minerals

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Number of Figures: 4
Figure S1. TGA analyses of pristine illite and montmorillonite samples.
Figure S2. XRD patterns for the solid samples collected from the carbonation experiments using different concentrations of illite (I, illite; Q, quartz; D, dolomite; MC, monohydrocalcite; A, aragonite; H, hydromagnesite).
Figure S3. XRD patterns for the solid samples collected from the carbonation experiments using different concentrations of montmorillonite (M, montmorillonite; Q, quartz; D, dolomite; MC, monohydrocalcite; A, aragonite).
**Figure S4.** Result of the SEM-EDS analysis of newly-formed aragonite observed in the systems with montmorillonite. The Pt peak showing in EDS came from sampling coating.