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ORIGINAL ARTICLE

Unraveling dolomite dissolution stoichiometry in circumneutral to alkaline pH environments

Irshad Bibi[1,2] · **Aniqa Amin**[2] · **Ralf R. Haese**[1] · **Nabeel Khan Niazi**[2]

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Abstract Examining carbonate dissolution kinetics at mineral-water interface is crucial to understand numerous environmental and geochemical processes, including global carbon cycling, CO_2 sequestration in deep geological reservoirs, and trace elements release in terrestrial and aquatic environments. Here we explored the effect of circumneutral to alkaline pH solutions (pH 6–11) on dissolution kinetics of pure dolomite and Ca and Mg release stoichiometry in flow-through reactor experiments at 25 ± 1 °C. Results revealed that the dolomite dissolution rates obtained from effluent Ca and Mg concentrations (R_{Ca} and R_{Mg} in mol/cm^2/s) were dependent on input solution pH and HCO_3^- log activity. The pH dependence of dissolution rates showed two distinct trends, i.e., at circumneutral pH ranging between 6 and 8, the dissolution rate decreased with increasing pH, with minimum rate at pH 8. While in the highly alkaline pH range (pH 9–11), the dolomite dissolution rate increased with an increasing pH. Irrespective of the input pH, the dolomite dissolution rates indicated a reverse relationship with HCO_3^- log activity, with the lowest dissolution rate ($R_{Ca} = 3.80 \times 10^{-12}$ mol/cm^2/s) at pH 8 where HCO_3^- log activity attained the highest value (-3.957). The lower R_{Ca} and R_{Mg} obtained at pH 8 compared to all the other pH could possibly be attributed to an inhibition caused by high HCO_3^- log activity in solution at this pH. Dolomite dissolution rates were non-stoichiometric at all the experimental pH values, showing higher preferential Ca over Mg release ($R_{Ca} > R_{Mg}$) whereas an opposite trend was observed at pH 8, with $R_{Ca} < R_{Mg}$ at the steady state. Saturation index values calculated using geochemical speciation modelling were positive for Mg-bearing minerals (brucite, dolomite, artinite) at alkaline pH of 10–11, indicating favourable conditions for their precipitation under studied conditions. This study provides insights on the significance of log ion activities of HCO_3^- and Me-OH$^+$ under varying pH for elucidating the dissolution mechanism of dolomite in circumneutral to alkaline aqueous environments.

Keywords Alkaline waters · Carbonates · Mineral dissolution · Stoichiometry

1 Introduction

Over the past three decades, rigorous research has been carried out to attain fundamental understanding on the reactivity of carbonate minerals (e.g., calcite, dolomite) from various experimental dissolution studies to examine the dissolution kinetics and reaction mechanisms (Arvidson and Morse 2014; Bibi et al. 2018; Fischer and Luttge 2017; Pokrovsky et al. 2009; Ruiz-Agudo et al. 2011; Saldi et al. 2021). Although majority of these studies advanced scientific knowledge on the calcite dissolution and reaction kinetics pathways, there is a dearth of understanding required to shed light on the complexity of dolomite dissolution at surface and near-surface, low temperature environments. There is a multitude of processes that require a deep understanding of carbonate mineral dissolution reactions, including carbon capture and storage processes, cement hydration, nutrient and trace elements release and cycling in soil, natural carbon (C) cycle, and nuclear waste management.

Dolomite is the second most abundant carbonate mineral, which is commonly found in ancient platform carbonates,

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✉ Irshad Bibi
irshad.bibi@unimelb.edu.au; irshad.niazi81@gmail.com

[1] School of Geography, Earth and Atmospheric Sciences, University of Melbourne, Melbourne 3053, VIC, Australia

[2] Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad 38040, Pakistan

especially in Precambrian rocks (Wacey et al. 2007). Under natural environments, it may form through biogenic and abiogenic pathways (Arvidson and Morse 2014; Manche and Kaczmarek 2021). There is substantial evidence that bacteria and Archaea can initiate the formation of dolomite in both surface and sub-surface environments where the source of Mg is sea water and shallow continental subsurface environments (Arvidson and Morse 2014). Additionally, Manche and Kaczmarek (2021) reported a dataset on Phanerozoic dolomite mineralogy suggesting that restrictive conditions can drive dolomitization, which depends upon temperature, salinity, Mg concentration, and Mg/Ca ratio. However, it is rare in Holocene sediments and hardly forms in modern carbonate-bearing geo-environments (Arvidson and Morse 2014).

The uncertainty of its origin, occurrence and behaviour has gained interest among researchers over the last two centuries. As such, its origin remains a long-standing enigma in sedimentology that is often referred as the 'Dolomite Problem' (Gregg et al. 2015). The 'Dolomite Problem' is mainly about the inability of researchers to precipitate dolomite inorganically in the laboratory under Earth surface temperature and pressure, together with the mystery of the relative scarcity of modern occurrences of the mineral despite seawater being supersaturated with respect to dolomite. This has been linked to three main kinetic constraints on dolomite formation: (i) high hydration energy of Mg^{2+}; (ii) the low concentration and activity of CO_3^{2-}; and (iii) the presence of SO_4^{2-}, which increases the solubility of Mg^{2+} by making neutral ion pairs with it (Wacey et al. 2007). Although modern day formation of dolomite in Earth's environment is rare, there is clear evidence of its formation in restricted environments, e.g., in alkaline lakes of Coorong region of South Australia (Wacey et al. 2007), where sulfate reducing bacteria are reportedly playing an important role in dolomite precipitation.

In stark contrast to calcite, research to understand the dolomite dissolution reaction kinetics is limited; that is possibly due to its relatively slow reaction rate and limited relationship between cation order and reactivity (Saldi et al. 2021). In recently formed dolomite surface and subsurface sediments, the formation of dolomite is dependent upon reaction kinetics that are relatively slow even with high supersaturation of the reacting solution (Arvidson and Morse 2014). The rate of dissolution of dolomite is a complex function of several factors, including but not limited to ionic strength, total dissolved carbonate, temperature, saturation state, pH, the activity of hydrous Ca and Mg ions, hydrodynamic conditions and the concentration of organic and inorganic ligands (Urosevic et al. 2012). Previous studies on dolomite dissolution kinetics were conducted under a variety of solution conditions and were able to provide some major insight into the effects of geochemical factors, such as temperature, CO_2 pressure, solution pH and ionic strength (Pokrovsky et al. 2009; Zhang et al. 2007). The available data on the relationship between dolomite dissolution and pH is highly dispersive, possibly because these studies were conducted in diverse ionic strength, hydrodynamic environments and at variable CO_2 pressure. However, all of these studies agree that compared to other studies carbonates, such as calcite, aragonite, and magnesite the dissolution reaction of dolomite is complicated, and therefore, it needs further detailed investigation (Urosevic et al. 2012). In addition, the observed non-stoichiometry of dolomite dissolution in previous macroscopic and microscopic studies, rendering several interpretations of the reaction mechanism still remains unclear (Putnis et al. 2014; Saldi et al. 2021; Urosevic et al. 2012). To date the stoichiometry in the release of ions from dolomite dissolution under variable solution compositions remains an area of interest as it may be helpful in understanding the constraints on dolomite formation under current Earth's environment.

The overarching aim of this paper is to present data from flow-through study of dolomite dissolution over circumneutral to alkaline pH range of 6–11 at 25 °C and under far from equilibrium environments. The effect of experimental conditions on stoichemetry of dolomite dissolution was determined through monitoring of Mg/Ca ratio of effluent and its comparison with Mg/Ca ratio of the solid dolomite. The speciation control of dissolved ions on dissolution reaction at the steady state was determined by calculating saturation index values and log ion activities from geochemical speciation modelling using the effluent data (Creg et al. 2024).

2 Materials and methods

2.1 Flow-through dissolution experiments

All the flow-through dissolution experiments were carried out on pure dolomite mineral sample supplied by Excalibur Mineral Corporation, Charlottesville, the USA. Mineral purity was confirmed by random powder X-ray diffraction (XRD) analysis (GBC MMA diffractometer with monochromatic CoKα radiation). Mineral sample was comprised of 99% dolomite with minor impurities of Fe and Si. Based on XRD analysis, the d-spacing of dolomite sample for d-104 peak was 2.885 Å and the 015/110 peak intensity ratio was 1.05. There was no pre-treatment of the mineral involved in the dissolution experiments, except for a gentle grinding to attain a homogeneous fine powder of mineral sample prior to use in the flow-through dissolution kinetics experiments. The dissolution experiments were performed in flow-through reactors comprising of three chambers. The input solution entered the reactor through bottom chamber where it was filtered by a 2 µm pore size filtration membrane before reacting with dolomite mineral sample placed in the middle chamber. The output solution exited through the upper chamber by filtering through another (2 µm pore size) filtration membrane. The input solutions at a pH ranging between 6 and 11were prepared using either 0.1 M H_2SO_4 or 0.1 M NaOH depending on the solution pH to be attained. An ionic strength of 0.01 M was attained in all the input solutions using AR-grade sodium chloride (NaCl).

A fixed dolomite mineral mass of 0.5 g was used in all the flow-through dissolution experiments. The dissolution experiments were performed at 25 ± 1 °C, which was maintained through a thermostatic water bath. Dolomite mineral was ground using an agate pestle and mortar to fine powder with particle size ranging from 50 to 100 µm. The flow rate of the input solution was kept constant at 0.5 mL/min and it was maintained by a Gilson peristaltic pump. The flow rate and input solution composition were kept constant for the duration of dissolution experiments. The residence time of the input solution in the flow-through reactors ranged between 0.3 and 336 h depending on the sampling interval.

Output solutions were collected after fixed reaction intervals and analysed for pH, calcium (Ca) and magnesium (Mg) concentrations. Output solution pH was measured immediately after collecting the sample using a pre-calibrated pH meter. The concentration of Ca in samples was determined using a flame photometer and Mg concentration was analysed using an atomic absorption spectrometer (AAS). The experiments were continued until a steady state was attained, which was confirmed by $<6\%$ variation in the released Ca and Mg concentration for at least seven consecutive days (Bibi et al. 2014).

2.2 Mineral dissolution kinetics measurement and saturation state calculation

The dissolution reaction of dolomite can be expressed as (Eq. 1):

$$\mathrm{CaMg(CO_3)_2} \rightarrow \mathrm{Ca^{2+}} + \mathrm{Mg^{2+}} + 2\mathrm{CO_3^{2-}} \tag{1}$$

Dolomite dissolution rate, Rj (mmol/cm^2/s), was calculated using the concentration of Ca (R_{Ca}) and Mg (R_{Mg}) in output solutions (Eq. 2):

$$\mathrm{R_j} = -\frac{1}{\mathrm{V_j}} \cdot \frac{\mathrm{F}}{\mathrm{SM}}\left(\mathrm{C_j}\right) \tag{2}$$

where C_j is the concentration of Ca or Mg in mg/L in the output solution, V_j is the stoichiometric coefficient of the respective element in the dolomite dissolution reaction, F is flow rate of the fluid in L/s, M is mass of the sample in gram (g) and S is the specific surface area of the mineral in cm^2/g (Bibi et al. 2011).

The analytical uncertainty in the dissolution rate was calculated using Eq. 3 as described by Bibi et al. (2014):

$$\frac{\sigma R}{R} = \sqrt{\left(\frac{\sigma_C}{C}\right)^2 + \left(\frac{\sigma_F}{F}\right)^2 + \left(\frac{\sigma_M}{M}\right)^2} \tag{3}$$

where σR is the uncertainty in the calculated rate, σC is the uncertainty in the concentration of Mg or Ca in the output solutions and σF and σM are the uncertainties associated with the input flow rate and specific surface area, respectively.

Solution speciation calculations and mineral saturation indices (SI) were determined using the Geochemist's Workbench (Creg et al. 2024).

3 Results

The evolution of dolomite dissolution reaction kinetics was monitored through Ca and Mg concentrations in the output solutions (Fig. 1). The Ca and Mg concentrations obtained from each experiment were plotted against the reaction time (Fig. 1). The output Ca and Mg concentrations were relatively high at the onset of each experiment followed by a gradual decrease until the attainment of stable concentrations afterwards. The initial high release stage continued for at least first 50 h in most of the experiments. An initial preferential release of Mg over Ca was observed in most of the dissolution experiments at all pH values, with the highest release of Mg over Ca at pH 8 (Fig. 1c).

Stoichiometry of dolomite dissolution reaction was monitored through changes in Mg/Ca ratios in the output solution for the whole duration of experiments where Mg/Ca ratios were plotted against time (h) (Fig. 2). For a stoichiometric dissolution of dolomite, a Mg/Ca ratio of 1 is expected based on their concentration in the output solution. Therefore, Mg/Ca ratio above 1 indicate a preferential release of Mg over Ca and a Mg/Ca ratio less than 1 shows a preferential release of Ca over Mg. The Mg/Ca ratio values >1 were obtained at the initial stage of all the dissolution experiments and showed a decreasing trend with time, except at pH 8, where a preferential release of Mg over Ca was continued for the whole duration of the experiment (Fig. 2c).

The average Mg/Ca ratio at pH 8 was 1.64 that was greater than the average Mg/Ca ratios of all the other dissolution experiments. Data reveal that for the dissolution experiments at pH less than 8 the Mg/Ca ratios at the final stage of the experiment showed preferential release of Ca over Mg while a preferential release of Mg over Ca was observed at pH 8 (Mg/Ca = 1.27). Such as, at pH 7 high Mg/Ca ratio was observed at the start of the experiment that decreased with time and reached near to the stoichiometric ratio (Mg/Ca = 1.1) after 240 h (Fig. 2b) and ultimately

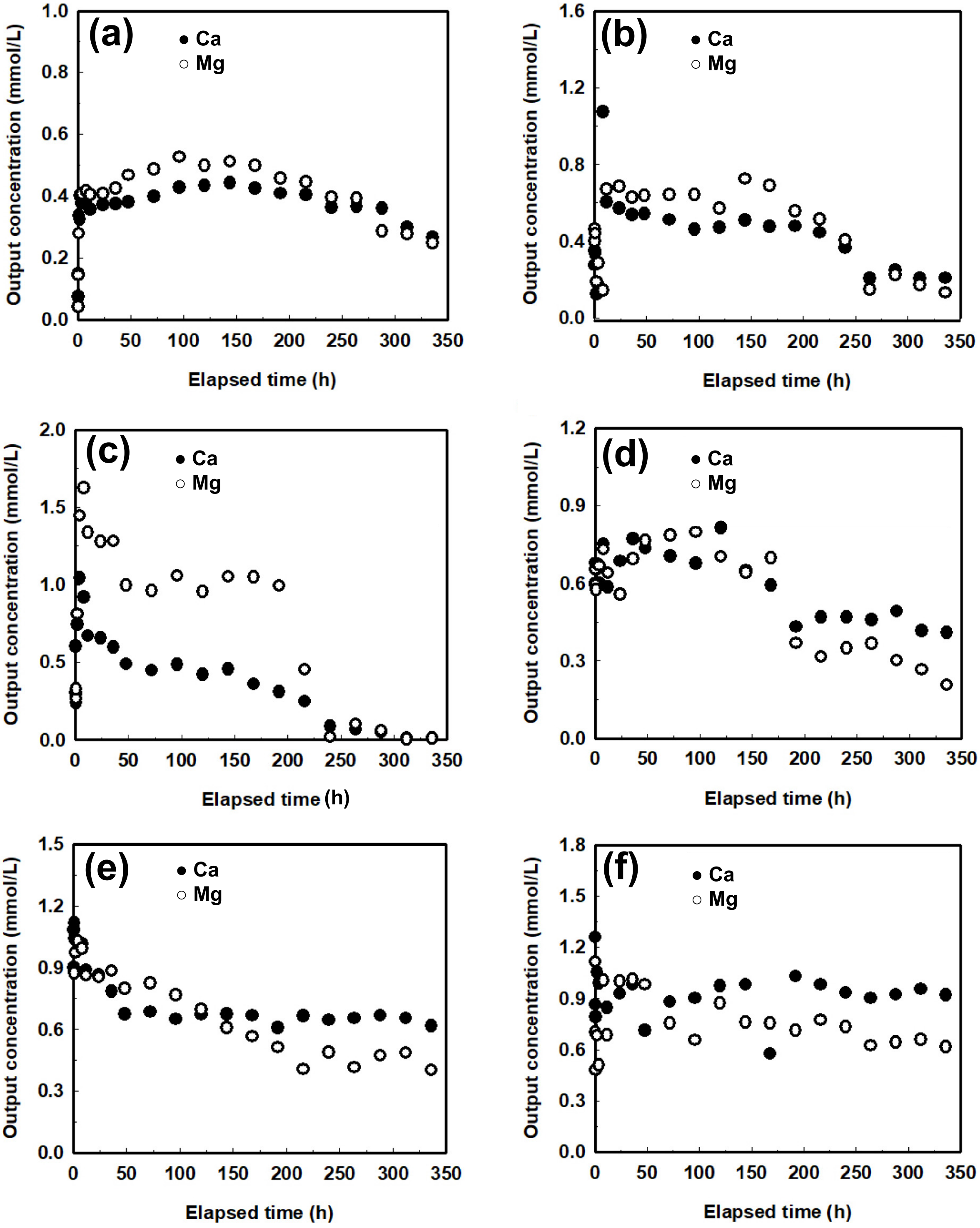

Fig. 1 Variation in Ca and Mg concentrations (mmol/L) in the effluent time lapsed samples in dolomite dissolution experiments conducted at pH 6–11 at 25 °C

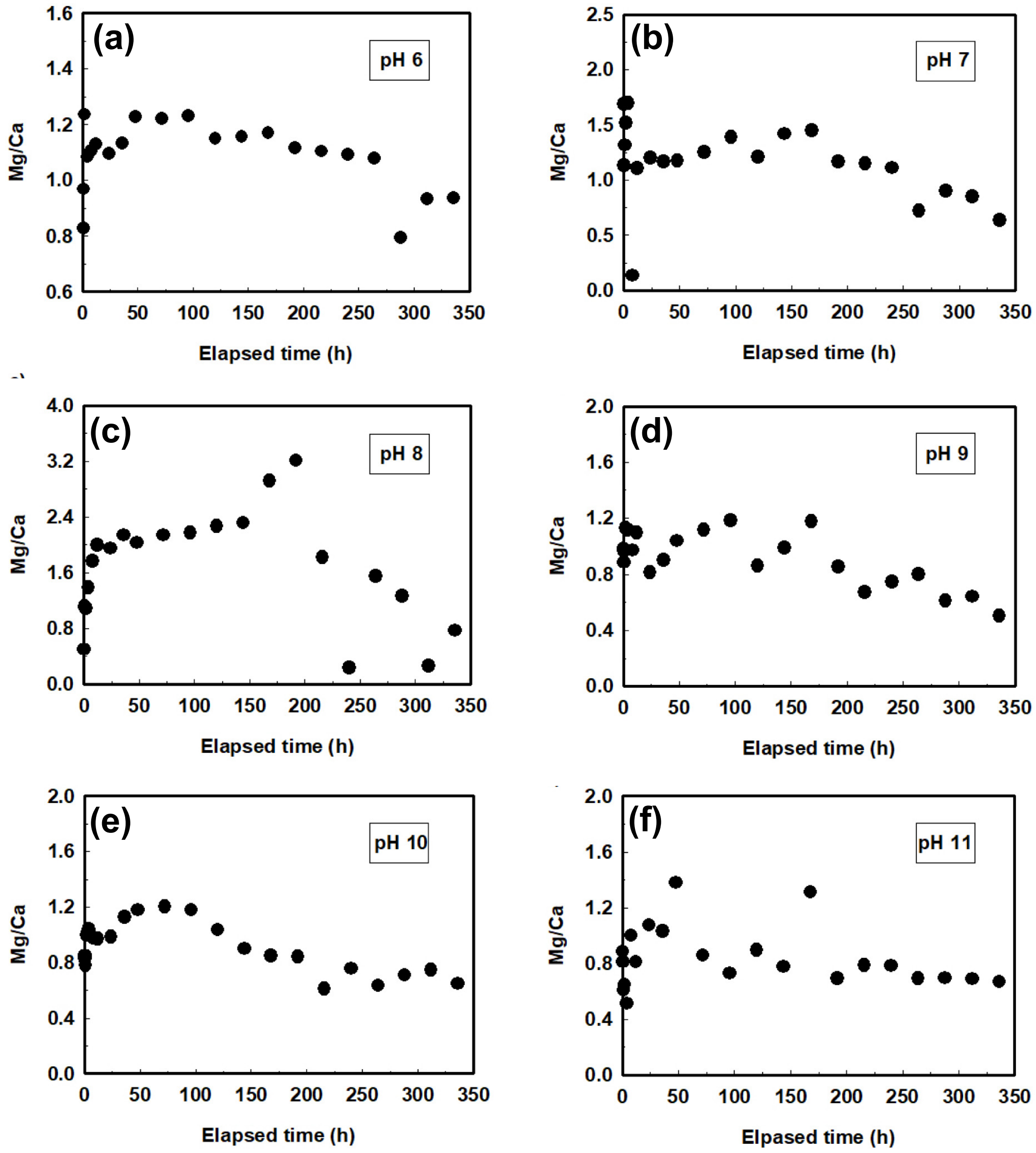

Fig. 2 Variation in Mg/Ca ratio of effluent solutions from time lapsed samples in dolomite dissolution experiments conducted at pH 6–11 and at a constant temperature of 25 °C

reduced to 0.64 indicating a higher release of Ca over Mg at the steady state.

Steady state experimental conditions, including experiment duration (h), Ca and Mg concentrations (mg/L), dolomite dissolution rates (mmol/cm^2/s) and Mg/Ca ratios calculated from dolomite dissolution experiments at pH 6–11 are given in Table 1. The dissolution experiments took between 48 and 312 h to reach the steady state, except at pH 9 and 10, which required minimum time to stable Ca and Mg release. Interestingly, the steady state Mg/Ca ratios increased with increasing pH from 6 to 8, while these decreased with a further increase in pH from 9 to 11 (Table 1). Steady state dolomite dissolution rates obtained from steady state Ca and Mg concentrations (R_{Ca}, R_{Mg}, respectively) are presented

Table 1 Input solution pH, experiment duration (h), Ca and Mg concentrations (mg/L), dissolution rates (R_{Ca} and R_{Mg}, mmol/cm^2/s) and Mg/Ca ratios calculated from dolomite dissolution at 0.01 M ionic strength (I), fluid flow rate of 0.5 mL/min, initial mineral mass of 0.5 g and at 25 °C

pH	Elapsed time (h)	Ca	R_{Ca}	Mg	R_{Mg}	Mg/Ca
6	336	10.4 ± 0.8	2.14E-11	6.1 ± 0.72	1.99E-11	0.94
7	312	8.0 ± 1.6	1.62E-11	4.1 ± 0.24	1.38E-11	0.85
8	288	2.0 ± 0.8	3.80E-12	1.46 ± 0.24	4.78E-12	1.27
9	240	18.8 ± 0.4	3.72E-11	8.5 ± 0.48	2.75E-11	0.74
10	264	26.1 ± 0.4	5.17E-11	10.2 ± 1.20	3.31E-11	0.64
11	312	38.1 ± 0.8	7.55E-11	16.0 ± 0.97	5.25E-11	0.69

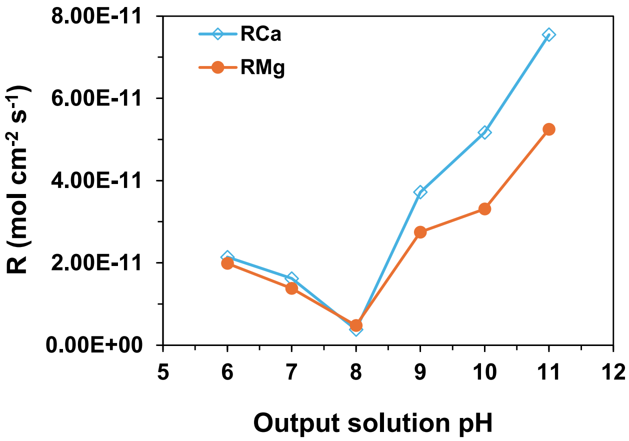

Fig. 3 The plot of dissolution rates based on Ca (R_{Ca}, mol/cm^2/s) and Mg (R_{Mg}, mol/cm^2/s) release against input solution pH in dolomite dissolution experiments conducted at pH 6–11 and 25 °C

in Table 1. Dolomite dissolution rates obtained at pH 6–11 were plotted against the reaction pH (Fig. 3). The dissolution rates of dolomite increased with pH from 6 to 8, with the minimum dissolution rate obtained at pH 8, whereas an increase in dissolution rate was observed at pH 9 to 11 (Fig. 3). A notable effect of solution pH on dissolution rates calculated using Ca and Mg, R_{Ca} and R_{Mg}, was observed at the alkaline pH range of 9–11. However, the dissolution rates of dolomite at circumneutral pH range (pH 6–8) calculated based on R_{Ca} and R_{Mg} were almost similar. Notably, the difference in dissolution rates of dolomite between R_{Ca} and R_{Mg} became high in alkaline solutions, with the greatest difference observed at pH 11. Overall, a higher steady state R_{Ca} was obtained over R_{Mg} for all the experiments (Table 1; Fig. 3), except at pH 8.

3.1 Saturation state of effluent solutions

The saturation state of the effluent solutions with respect to all the relevant minerals including dolomite at steady state was calculated using SpecE8 module within the Geochemist's Workbench (Creg et al. 2024). The saturation index (SI) values for seven Ca- and Mg-containing minerals from steady state solutions at pH 6 to 11 are presented in Table 2. The steady state solutions in experiments at pH 6–9 were undersaturated with respect to all the Ca and Mg bearing mineral phases. However, the solutions at pH 10 and pH 11 showed saturation with respect to calcite, dolomite and brucite (Table 2). The solution at pH 11 was saturated with respect to artinite, which is a hydrated Mg-carbonate mineral [$(Mg_2\ (CO_3)\ (OH)_2{\bullet}3H_2O)$]. The highest SI value of 2.12 was calculated for brucite at pH 11, thus showing highly favourable conditions for its precipitation at pH 11 (Table 2).

The changes in the log activities of species controlling the release of Ca and Mg in different dissolution experiments are plotted against pH (Fig. 4). Figure 4a shows changes in log activity of Ca containing species and the log activity of Mg species is presented in Fig. 4b. In the case of Ca, log activities of $CaHCO_3^+$ sharply decreased as solution pH

Table 2 Saturation indices calculated from the geochemical modelling using Geochemist's Workbench for various carbonate minerals in the steady state solutions at pH 6–11 and 25 °C

Mineral species	Input solution pH					
	6	7	8	9	10	11
Calcite	− 4.0769	− 2.6895	− 1.8143	− 0.5477	**0.0118**	**0.1139**
Aragonite	− 4.2418	− 2.8544	− 1.9792	− 0.7126	− 0.1531	− 0.0510
Magnesite	− 4.8012	− 3.5316	− 2.5541	− 1.4046	− 0.8619	− 0.7996
Monohydrocalcite	− 5.0709	− 3.6835	− 2.8083	− 1.5418	− 0.9823	− 0.8802
Dolomite	− 7.2493	− 4.5923	− 2.7395	− 0.3235	**0.7787**	**0.9430**
Brucite	− 8.1330	− 6.3345	− 4.5997	− 2.0937	**0.0275**	**2.1243**
Artinite	− 13.9944	− 10.9263	− 8.2140	− 4.5585	− 1.8946	0.2643

Bold: values indicate positive saturation indices for the predicted mineral species

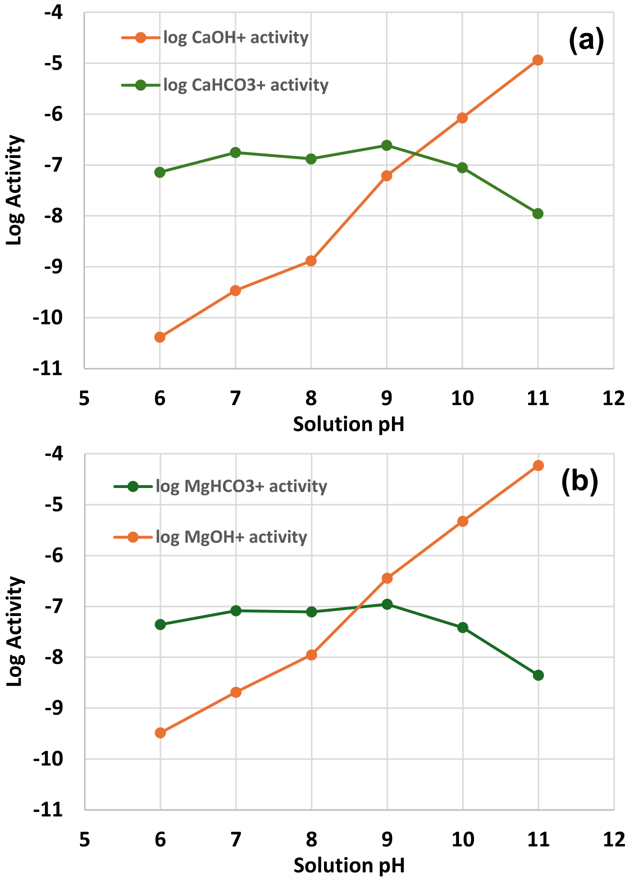

Fig. 4 The log activity of geochemical species involved in Ca and Mg release in the steady state solutions against input solution pH range of 6–12 in dolomite dissolution experiments. (a) log activities of Ca-species against pH; (b) log activities of Mg-species

increased in the alkaline range from pH 9 to 11 (Fig. 4a). In contrast to $CaHCO_3^+$, the log activity of $CaOH^+$ increased with pH showing the highest value at pH 11. Looking at the Mg speciation results, the log activity of $MgHCO_3^+$ sharply reduced with pH in the alkaline range (pH > 8 to 11) (Fig. 4b), whereas the activity of $MgOH^+$increased with pH throughout the pH range of pH 6–11 (Fig. 4b).

4 Discussion

An early rapid release of (Ca, Mg) elements during first few hour of the experiments was observed from dolomite dissolution in flow-through reactor experiments conducted at pH 6–11 and at 25 °C. A similar trend of rapid initial element release rates has been reported in several previous studies for carbonates and clay minerals (Bibi et al. 2014; Pokrovsky et al. 2005, 2009; Saldi et al. 2021). For instance, Pokrovsky and Schott (2002) reported an initial rapid dissolution of dolomite in mixed flow reactors. After almost 50 h of experimental duration, the high dissolution rate of dolomite was a time-independent stationary rate in their experiments. Pokrovsky et al. (2009) also reported a rapid dissolution rate of calcite, dolomite and magnesite at the beginning of the experiments where the structural cations (Ca, Mg) were rapidly released into the output solution. Such rapid release at the initial stage of dissolution experiments in previous studies has been attributed to certain factors, such as availability of highly reactive sites at the onset of experiments, leading to a rapid dissolution rate of the mineral under investigation (Bibi et al. 2011, 2014; Cama and Ganor 2006; Ganor et al. 2007). In addition, the presence of fine particles in the powdered mineral sample and the presence of cracked or strained surfaces that are formed during grinding could be other factors contributing to these rapid onset rates (Bibi 2012).

In this study, Ca and Mg release rates were highly non-stoichiometric during the initial rapid release stage. At pH 6–8, significantly higher initial Mg release was observed over Ca (Fig. 1a-c). However, at the alkaline pH (pH > 8) the initial release rates of Ca and Mg were close to stoichiometric rates (Fig. 2d–f). Interestingly, the greatest difference in the initial Ca and Mg release rate was observed at pH 8.

In contrast to the present study, many previous studies on dolomite dissolution reported an ease of Ca release at the initial stage of the experiments (Pokrovsky et al. 2005; Zhang et al. 2007) and attributed it to the lower hydration energy of Ca compared to Mg. As such, it leads to $CaCO_3$ component dissolving faster than $MgCO_3$, the latter being the rate limiting step for dolomite dissolution. Pokrovsky et al. (1999) also reported an initial preferrred release of Mg over Ca at pH 8 and ascribed it to the precipitation of $CaCO_3$ in a supersaturated solution as a single phase or to the formation of a $CaCO_3$-rich layer on the surface of dolomite that may change its reactivity and chemical attributes. In the current study, all the dissolution experiments except at pH 8 showed a steady state preferential Ca release over Mg (Table 1). The preferential release of Ca on dolomite dissolution could be due to the lower hydration energy of Ca than Mg, which favours its fast release to the fluid (Saldi et al. 2021; Zhang et al. 2007). Previously, some microscopic studies on dolomite dissolution have reported the formation of Mg-rich precipitates showing a lower Mg/Ca ratio calculated from fluid-phase than the solid-phase (Emmanuel 2014; Urosevic et al. 2012).

In the current study, the predominant mechanism controlling the dolomite dissolution throughout the pH range (pH 6–11) could possibly be hydrolysis of the surface metal sites ($>MeOH_2^+$) as described in earlier studies (Pokrovsky et al. 2009; Pokrovsky and Schott 2002). It is evident from the geochemical speciation data that the (log) activities of $CaOH^+$ and $MgOH^+$ in the solutions were minimum at the circumneutral pH (pH 6–7.5). This may indicate a slow reaction rate under these conditions, and therefore, the dissolution experiments took maximum time to attain a stable elemental (Ca, Mg) release rate. Under alkaline conditions (pH 9–11), the ease of hydrolysis reaction and the formation of $MeOH^+$ (Ca- and Mg-OH) surface complexes may be responsible for an accelerated dolomite dissolution (Pokrovsky et al. 2005, 2009; Pokrovsky and Schott 2002).

Both R_{Ca} and R_{Mg} showed a decrease with pH from 6 to 8, attaining a minimum value at pH 8, however, an increase in rates was observed with pH from pH 9 to 11. A close agreement between R_{Ca} and R_{Mg} was observed at pH 6–8 whereas the difference between them widened with increase in pH in alkaline range of pH 9–11 (see Fig. 3). At alkaline solution pH, ranging from pH 9–11, the R_{Ca} value was higher than the R_{Mg}. The rates obtained from Ca concentrations had the lowest value of 3.80×10^{-12} mol/cm^2/s at pH 8 and the highest value at pH 11 (7.55×10^{-11} mol/cm^2/s). The Mg derived rates ranged between 4.78×10^{-12} and 5.25×10^{-11} mol/cm^2/s at pH 8 and 11, respectively (Table 1; Fig. 3). Urosevic et al. (2012) reported dolomite dissolution rate of 4.7×10^{-12} mol/cm^2/s in deionized water using the AFM, which is an order of magnitude lower than the slowest rate obtained in the current study. However, their macroscopic rates ranged between 0.272×10^{-9} and 0.014×10^{-9} mol/cm^2/s at pH ranging from 7 to 10, which are much higher than the rates obtained in the current study.

In this study, particularly in the alkaline pH range ($pH > 8$–11), non-stoichiometric dissolution rates of dolomite were due to differences in the steady state Ca and Mg concentrations (Table 1). Relatively higher R_{Ca} compared to R_{Mg} in most of the dissolution experiments concurs with previous studies on dolomite dissolution. For example, Zhang et al. (2007) observed non-stoichiometric dissolution of dolomite in acidic and alkaline solutions at 25 °C and 250 °C, with Ca/Mg ratios in the output solution between 2 and 6.

A preferential Ca over Mg steady state release rate has been reported in some previous studies, possibly because of an ease of Ca detachment from dolomite due to its lower energy requirement compared to Mg (Pokrovsky et al. 2009; Pokrovsky and Schott 2002). Some earlier research on dolomite dissolution using AFM attributed such difference between preferential Ca over Mg release to the precipitation of a Mg-rich phase (Putnis et al. 2014; Urosevic et al. 2012). It is noteworthy that the steady state solutions with highly alkaline pH (pH 10–11) in the present study approached at equilibrium state with respect to Mg-rich mineral phases, such as brucite [$Mg(OH)_2$], dolomite [$Ca,Mg(CO_3)_2$] and artinite [$Mg_2(CO_3)(OH)_2 \bullet 3H_2O$], which is evident from the geochemical speciation data (Table 2).

Urosevic et al. (2012) reported non-dependence of dolomite dissolution rates in the pH range of 5–10, which is in contrast to our results as we observed dolomite rate dependence on pH, obtaining different trends in circumneutral and alkaline pH ranges. The macroscopic rates obtained by Urosevic et al. (2012) ranged between 0.272×10^{-9} and 0.014×10^{-9} mol/cm^2/s at pH ranging from 7 to 10, which are much higher than the rates obtained in the current study.

By looking at the geochemical speciation data in Fig. 4 for both Ca and Mg species distribution at the steady state, a peculiar trend was observed for the activity of $CaOH^+$; it showed a sharp increase in alkaline pH (pH 9–11), thus attaining the highest activity at pH 11. Similarly, the log activity of $MgOH^+$ showed a sharp increase with increasing pH from 9–11, with the maximim activity at pH 11. These trends are consistent with the findings by Pokrovsky and Schott (2002), who suggested metal centres hydrolysis as a dominant and rate controlling mechanism under alkaine pH ($pH > 8$ to 11) based on their surface complexation model data. In contast to Mg species, there was a sharp decline in the activity of $CaHCO_3^+$ with an increase in pH in alkaline range from 9 to 11, with the lowest activity value at pH 11. It is evident from results that two separete trends at circumneutral and alkaline pH conditions in dissolution rates were observed in this study. A decrease in R_{Ca} and R_{Mg} at circumneutral pH range from pH 6–8 and an increase in R_{Ca} and R_{Mg} at alkaline pH range (pH 9–11), thus suggesting the operation of two separate mechanisms controlling the dolomite reaction rates under each pH window.

5 Conclusions

The dissolution kinetics of dolomite was investigated at circumneutral (pH 6–8) to alkaline pH (9–11) conditions at 25 °C in a flow-through reactor experimental setup. An initial rapid release of both Ca and Mg was followed by a stable release stage, the attainment of which was dependent on the reaction rate. All the experiments exhibited initial, highly non-stoichiometric Ca and Mg release rates, showing higher Mg/Ca ratios at circumneutral pH conditions and lower Mg/Ca ratio under alkaline conditions than the Mg/Ca ratio of the dolomite sample. The steady state Mg/Si ratios were also non-stoichiometric (Mg/Ca ranged between 0.64 and 0.94) for all the pH range except at pH 8 where a Mg/Ca ratio of 1.27 was obtained.

For dolomite dissolution rate data, two separate trends were obtained at the circumneutral pH (6–8) and the alkaline pH range (pH 9–11). The dissolution rates (R_{Ca} and R_{Mg}) decreased with pH from pH 6–8, with the slowest rates obtained at pH 8 and increased with pH from pH 9–11. The experiment at pH 8 showed an inhibition caused by the release of HCO_3^- ions in solution, which showed maximum log activity at pH 8 (Fig. 5). The HCO_3^- activity seemed to be the controlling factor for dolomite dissolution under the experimental conditions as the dissolution

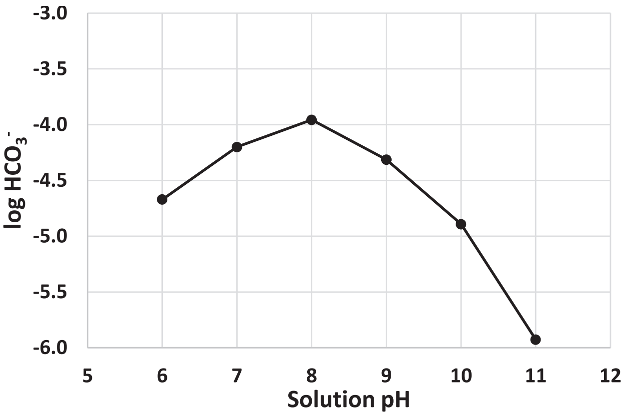

Fig. 5 The figure showing changes in log HCO_3^- activity of steady state solutions against input solution pH ranging from 6 to 11

rates increased as the activity of HCO_3^- ions in solution decreased. The release of Ca to solution was controlled by the formation of $CaHCO_3^+$ and $CaOH^+$ complexes in circumneutral and alkaline pH regions respectively. Likewise, the release of Mg^{2+} could be linked to the formation of $MgHCO_3^-$ and $MgOH^+$ complexes in circum-neutral and alkaline pH ranges, respectively. Geochemical speciation results also indicated the approach of equilibrium with respect to Mg containing minerals such as brucite and dolomite at highly alkaline pH of 10 and 11, which could be responsible for a significant decline in steady state R_{Mg} compared to R_{Ca}.

This study advances understanding on preferential Ca release over Mg from dolomite, notably under alkaline conditions, thus having broad geochemical implications. Such as, under alkaline aquifer environments where CO_2 is sequestered in deep settings; in alkaline surface and near-surface soils where an enhanced Ca release may affect the availability of other nutrients. such as phosphorous which is an important macronutrient.

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Author contributions Aniqa Amin and Irshad Bibi performed dissolution experiments; Irshad Bibi conceptualized, analysed data, provided resources and prepared paper, revised and finalized; Ralf R. Haese and Nabeel Khan Niazi provided conceptual and intellectual contribution, read, improved and edited paper.

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Data availability All data have been presented in this paper.

Declarations

Competing Interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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