

Sabkha dolomite as an archive for the magnesium isotope composition of seawater

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ABSTRACT

Recent studies have uncovered the potential of Mg isotopes ($\delta^{26}\text{Mg}$) for studying past ocean chemistry, but records of such data are still scarce. Dolomite has been suggested as a promising archive for $\delta^{26}\text{Mg}$ of seawater. However, its enigmatic formation mechanism and the difficulty in precipitating dolomite in the laboratory at surface temperatures decrease confidence in the interpretation of $\delta^{26}\text{Mg}$ values from the rock record. To evaluate factors determining the $\delta^{26}\text{Mg}$ of dolomite, we studied pore water and sediment from Dohat Faishakh Sabkha, Qatar—one of the rare environments where dolomite is currently forming. The $\delta^{26}\text{Mg}$ values of the dolomite (-2.56‰ to -1.46‰) are lower than that of seawater (-0.83‰), whereas $\delta^{26}\text{Mg}$ values of pore water (-0.71‰ to -0.14‰) are higher. The isotope fractionation accompanying dolomite formation is generally in accordance with an empirical fractionation from the literature, extrapolated to the sabkha's temperature (-1.84‰ to -1.51‰). The results suggest that evaporated seawater is the sole source of Mg, and isotopically light dolomite is the major sink, so that the $\delta^{26}\text{Mg}$ of the dolomite-forming pore water is equal to or greater than that of seawater. Thus, provided that the lowest $\delta^{26}\text{Mg}$ value among several dolomite samples is used, and the formation temperature is known, similar sabkha-type dolomites can be utilized as an archive for $\delta^{26}\text{Mg}$ values of ancient seawater.

INTRODUCTION

Reconstructions of the oceanic Mg budget are important to our understanding of Earth's history because important surface processes, such as weathering, mid-ocean-ridge volcanism, and carbonate precipitation, control oceanic Mg inputs and outputs (e.g., Elderfield, 2010). Recent studies have shown the potential of Mg isotopes to enhance our understanding of the Mg budget of past oceans (e.g., Tipper et al., 2006; Shalev et al., 2019). A few pioneer studies have produced Cenozoic seawater $\delta^{26}\text{Mg}$ records from Ca-carbonate archives (Pogge von Strandmann et al., 2014; Higgins and Schrag, 2015; Gothmann et al., 2017). However, the scarcity of such data records and differences between existing data sets currently limit this approach.

Dolomite, a common sedimentary rock constituted by the eponymous mineral $\text{CaMg}(\text{CO}_3)_2$, has been suggested as a promising archive for seawater $\delta^{26}\text{Mg}$ because Mg is a major element in dolomite, and, therefore, it is less sensitive to

postdepositional alteration than other substrates (e.g., Geske et al., 2012; Hu et al., 2017). However, the use of dolomite is more complicated than Ca-carbonate archives. For example, the $\delta^{26}\text{Mg}$ value of marine-derived dolomite-forming solutions may be altered by contributions of Mg from sources other than seawater (e.g., Azmy et al., 2013), or by a Rayleigh distillation effect due to dolomite or Mg-evaporite precipitation (e.g., Li et al., 2011; Blättler et al., 2015; Shalev et al., 2017). Furthermore, the mechanism of isotope fractionation between dolomite and its parent solution is not fully understood (e.g., Li et al., 2015). Many factors have been suggested to affect the isotope difference between dolomite and solution, $\Delta^{26}\text{Mg}_{\text{dol-aq}}$, including temperature, aqueous speciation, precursor mineral formation, precipitation rate, and others (e.g., Geske et al., 2015a, 2015b; Schott et al., 2016). In particular, because microbes and their extracellular polymeric substances (EPS) are considered to be an important catalyst for dolomite formation (Petrash et al., 2017), it is possible that the $\Delta^{26}\text{Mg}_{\text{dol-aq}}$ value may also be influenced by biological factors.

Previous studies aiming at quantifying $\Delta^{26}\text{Mg}_{\text{dol-aq}}$ values have yielded a wide and often inconsistent range of results (e.g., Li et al., 2015). Higgins and Schrag (2010) suggested that $\Delta^{26}\text{Mg}_{\text{dol-aq}}$ is between -2.7‰ and -2.0‰ for deep-marine dolomite. In contrast, higher values (-0.7‰ to $+0.1\text{‰}$) were reported for recent sabkha dolomite in Abu Dhabi (Geske et al., 2015b). Li et al. (2015) suggested a temperature-dependence equation for $\Delta^{26}\text{Mg}_{\text{dol-aq}}$, based on experiments at high temperatures:

$$\Delta^{26}\text{Mg}_{\text{dol-aq}} = -0.1554 (\pm 0.0096) \times 10^6/T^2, \quad (1)$$

where $\Delta^{26}\text{Mg}_{\text{dol-aq}}$ is the isotope difference between a dolomite and its forming solution, and T is the temperature in Kelvin. Extrapolation of this equation to low temperatures yields a $\Delta^{26}\text{Mg}_{\text{dol-aq}}$ value in accordance with that suggested for deep-sea dolomite (Higgins and Schrag, 2010) but different from a previous sabkha study (Geske et al., 2015b). Theoretical calculations predict fractionation factors that are different from each other and from the experimental and natural data (Rustad et al., 2010; Schauble, 2011).

To evaluate factors determining the Mg isotope signature of dolomite, we studied pore water and sediment from Dohat Faishakh Sabkha, Qatar. This coastal sabkha is among the very few environments in which dolomite is currently forming (e.g., Illing et al., 1965). This sabkha is an ideal natural laboratory because: (1) sediment contamination from eolian particles is minimal due to a location protected from the wind; (2) dolomite content in the sediment is high, up to 80%–90% (e.g., Illing and Taylor, 1993); and (3) dolomite occurs in association with evaporitic minerals (aragonite, gypsum), which are often found in ancient sedimentary dolomite sequences (Wells, 1962).

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GEOLOGICAL SETTING AND METHODS

Dohat Faishakh Sabkha is a marine evaporitic tidal flat on the western coast of the Qatar peninsula, and it includes a lagoon, an intertidal zone, and a supratidal zone (Fig. 1; Illing et al., 1965; Illing and Taylor, 1993; Al-Disi et al., 2017). Most of the sediment in the lagoon and the intertidal zone is composed of authigenic aragonite. The supratidal flats are the most saline zone, with authigenic dolomite and gypsum as the main sediments (e.g., Illing et al., 1965). The surface of the intertidal zone is fully colonized by microbial mats, which are also present, gradually degraded toward the land, below the surface of the supratidal zone (Brauchli et al., 2016). These mats have been suggested to play an important role in the formation of dolomite (Bontognali et al., 2010; Brauchli et al., 2016). Lagoon water occasionally floods the supratidal zone, partly evaporates, and infiltrates the sediment. Lateral flow back to the lagoon is likely to take place (Illing and Taylor, 1993). Sediment temperature is $32 \pm 6^\circ\text{C}$ (Müller et al., 2019).

We collected sediment cores, ~0.5 m each, at three sites: DFn1, DF_{BM}, and DFn3 (Fig. 1C;

Table S1 in the Supplemental Material¹). Pore water and lagoon water were extracted immediately after the collection of the cores in the field, using Rhizon devices. Cores and pore-water samples were then stored at -4°C . Site DFn1 was sampled during three trips to identify seasonal variations. The sediment cores were sampled in the laboratory (Table S3) and powdered. Then, ~20 mg aliquots of each sample were used for X-ray diffraction (XRD) analysis. Selected samples, in which dolomite comprises $\geq 58\%$ of the carbonates, were used for Mg isotope analysis. In such samples, the bulk $\delta^{26}\text{Mg}$ can be considered as the dolomite signature because the Mg contribution from other minerals is small. Solid samples were washed first with milli-Q water, to remove soluble salts, and then dissolved in HNO_3 . The methods used for chemical and isotope

¹Supplemental Material. Mg isotope measurements details, Supplemental Figures S1 and S2, and Supplemental Tables S1–S4. Please visit <https://doi.org/10.1130/GEOL.S.13020614> to access the supplemental material, and contact editing@geosociety.org with any questions.

analyses followed those described by Shalev et al. (2018a, 2019) and are summarized in the Supplemental Material.

RESULTS

Major cations, mineralogy, and Mg isotope results are presented in Tables S3 and S4. The lagoon water was about twice concentrated relative to seawater, and the pore water was more concentrated than the lagoon water (Figs. 2A and 2B). No significant seasonal change in concentration was observed at site DFn1. Lowest concentrations were observed at site DFn3, in the intertidal zone. Mg concentration, [Mg], was highest at site DF_{BM} (supratidal zone) and generally decreased with depth, whereas Na concentration, [Na], was highest at site DFn1 (supratidal zone) and was generally constant with depth (Figs. 2A and 2B). Mg isotopes were not fractionated in the lagoon, whereas all pore-water samples were enriched in ^{26}Mg , and all sediment samples were depleted in ^{26}Mg relative to the seawater source (Fig. 2C). A similar pore-water trend toward higher $\delta^{26}\text{Mg}$ values with depth was observed at sites DF_{BM} and DFn3, but not at DFn1, where the $\delta^{26}\text{Mg}$ values were generally constant. These trends are not reflected in the dolomite samples. No dolomite $\delta^{26}\text{Mg}$ values from DFn3 are reported in Figures 2 and 3 because the sediment at this site was mostly composed of aragonite and did not contain dolomite (Table S4).

DISCUSSION

The ^{26}Mg -enriched pore water (Fig. 2C) indicates that dolomite formation at the Dohat Faishakh Sabkha is ongoing over the residence time of the pore water. The contribution of isotopically heavy magnesium from silicate minerals (e.g., Teng, 2017) is expected to be negligible due to their low abundance in the sediment (Table S4). Mg-evaporites, which may form a ^{26}Mg -depleted sink (e.g., kainite; Shalev et al., 2017), are not expected to precipitate at such relatively low degrees of evaporation, within the gypsum facies (e.g., Shalev et al., 2018b). Indeed, they were not observed in XRD analyses. Aragonite and calcite may also form a ^{26}Mg -depleted sink (e.g., Wombacher et al., 2011; Mavromatis et al., 2013), but, due to their low Mg content, this Mg sink is relatively small. Furthermore, despite significant seasonality in rainfall, which is expected to dilute the pore water during the rainy season, no seasonal change in concentration was observed in the pore-water samples (Figs. 2A and 2B). This observation excludes potential contribution of Mg from runoff or shallow groundwater. The generally constant [Na] with depth (Fig. 2B) is also inconsistent with a groundwater contribution. Therefore, it is concluded that seawater is the major source of Mg to the pore water, and sedimentary dolomite is the major sink.

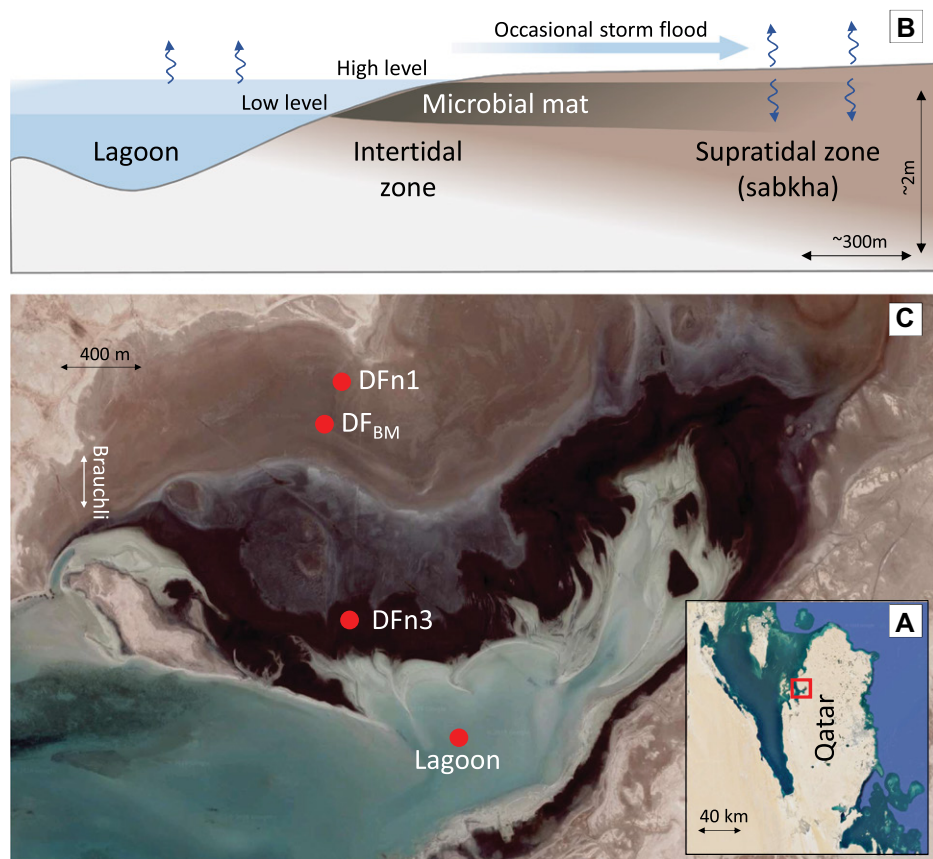


Figure 1. Geological setting of Dohat Faishakh Sabkha, Qatar. (A) Location map. Study site is at $25^\circ 38' \text{N}$, $50^\circ 57' \text{E}$ (see also Table S1 [see footnote 1]). (B) Schematic illustration of geological setting (after Illing and Taylor, 1993). (C) Sampling sites (red points) were distributed along the transect originally studied by Illing et al. (1965). Sites studied by Brauchli et al. (2016) are also shown (white arrow). Satellite images are from ©2019 Google (imagery ©2019 CNES/Airbus, Maxar Tech.; map data ©2019).

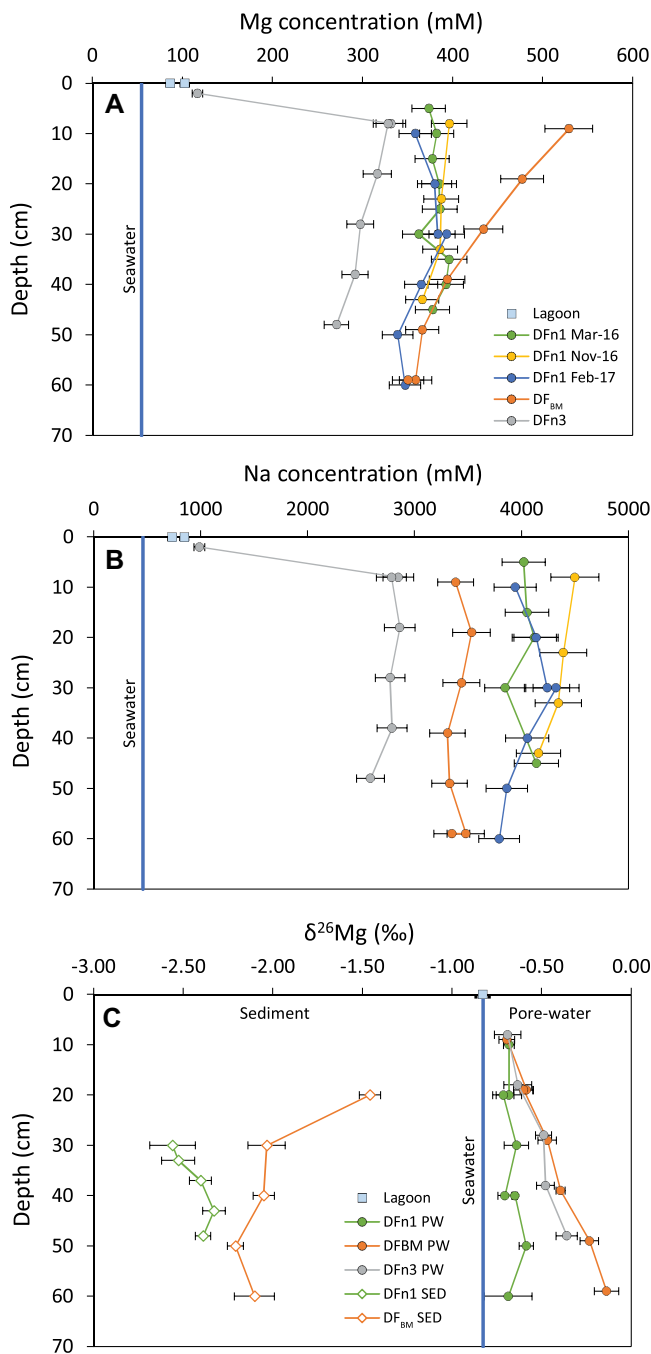


Figure 2. Depth profiles of pore water (PW) and sediment (SED). Colors: DF_{n1}—green, DF_{BM}—orange, DF_{n3}—gray, lagoon—cyan square, seawater—vertical blue line. DF_{n1} sampling trips: green (March 2016), yellow (November 2016), and blue (February 2017). (A,B) [Mg] and [Na] in water samples. Error bars are 5% analytical error. (C) $\delta^{26}\text{Mg}$ values of pore water (solid circles) and sediment (empty diamonds). Error bars are 2 standard deviation.

The isotopic difference between sediment and pore-water samples at the same depth, $\Delta^{26}\text{Mg}_{\text{sed-PW}}$, is between -1.97‰ and -1.57‰ (Fig. 3A, except for one sample: -0.86‰). For most samples, this isotopic difference is in accordance with $-1.84\text{‰} < \Delta^{26}\text{Mg}_{\text{dol-aq}} < -1.51\text{‰}$ (Equation 1; Li et al., 2015), as expected for dolomite precipitating in the temperature range for these sites, $32 \pm 6^\circ\text{C}$ (Müller et al., 2019). It should be noted, however, that the pore water is not necessarily the precipitating solution of the dolomite present at the same depth. Indeed, the formation of dolomite likely required hundreds of years, while the pore-water values represent a snapshot. Therefore, $\Delta^{26}\text{Mg}_{\text{sed-}}$

PW is not necessarily expected to be equal to $\Delta^{26}\text{Mg}_{\text{dol-aq}}$. Despite this caveat, the good agreement between the measured and the expected fractionations suggests that temperature is the major factor determining the Mg isotope fractionation in this sabkha system, and that any vital, rate, or other effects play a minor role. The microbial mediation process proposed for explaining sabkha-type dolomite formation is not expected to cause a metabolism-related Mg isotope fractionation (Brauchli et al., 2016). Magnesium is not assimilated by microbes, which catalyze the incorporation of Mg into the carbonate mineral by producing EPS that promote dehydration of aqueous Mg^{2+} (Bon-

tognali et al., 2014). It is, however, possible that the interactions between Mg^{2+} and the EPS cause an isotope fractionation that is in turn recorded in the dolomite. Our data suggest that such hypothetical EPS-related fractionation is limited or even absent.

The $\delta^{26}\text{Mg}$ values of pore water from each site are linearly correlated with both $\ln[\text{Mg}]$, where the slope gives $\Delta^{26}\text{Mg}_{\text{dol-aq}}$ for a Rayleigh model, and $1/[\text{Mg}]$, which simulates binary mixing (Figs. 3B and 3C). Thus, we suggest that the $\delta^{26}\text{Mg}$ of pore water evolved by Rayleigh distillation due to dolomite formation and/or by mixing of such dolomite-forming solutions from seawater that is evaporated to a different degree at each site. Since Mg is conservative during seawater evaporation (as long as there is no dolomite or Mg-evaporite formation), $[\text{Mg}]$ rises as evaporation progresses, while $\delta^{26}\text{Mg}$ does not change (blue arrow in Figs. 3B and 3C). Thus, for each site, the Mg concentration before the onset of dolomite formation can be calculated from the intersection between the correlation line and the marine $\delta^{26}\text{Mg}$ value (Figs. 3B and 3C). Then, a degree of evaporation of seawater (DE) can be calculated by

$$\text{DE} = [\text{Mg}]_i / [\text{Mg}]_{\text{sw}}, \quad (2)$$

where i and sw are intersection and seawater, respectively. The results suggest that the DE is 6.6–6.7 at DF_{n3}, 8.3–8.5 at DF_{n1}, and 10.5–10.9 at DF_{BM}. This further suggests that the pore water is evaporated to the gypsum facies, or beginning of the halite facies, supporting the lack of any Mg-evaporites.

At the DF_{BM} and DF_{n3} sites, the uppermost pore-water sample is the least evolved relative to the intersection, and $[\text{Mg}]$ decreases with depth, while the $\delta^{26}\text{Mg}$ value increases (Figs. 3B and 3C). Furthermore, the slope on the $\ln[\text{Mg}]$ diagram ($-1.69 \pm 0.35\text{‰}$ for DF_{n3} and $-1.35 \pm 0.32\text{‰}$ for DF_{BM}; Fig. 3B) is within the range expected from Rayleigh distillation, with an isotope fractionation as derived from Equation 1 (Li et al., 2015), i.e., -1.84‰ to -1.51‰ . This suggests progressive Mg loss to dolomite with downward percolation of evaporated seawater. However, it is also possible that the deep dolomite-forming pore water mixes back with the pore water from the upper parts of the sediment at each site. Unlike sites DF_{BM} and DF_{n3}, $[\text{Mg}]$ and $\delta^{26}\text{Mg}$ values at DF_{n1} show no specific trend with depth, and the slope in Figure 3B is much less negative ($-0.85\text{‰} \pm 0.22\text{‰}$). This might suggest that the uppermost pore water at this site mixes with dolomite-forming pore water from a different place in the sabkha, such as the DF_{n3} site (Fig. 3C). This further implies that there is no ongoing dolomite formation at DF_{n1} and, consistent with its landward location in the regressive sedimentary system, that the dolomite at this site is older.

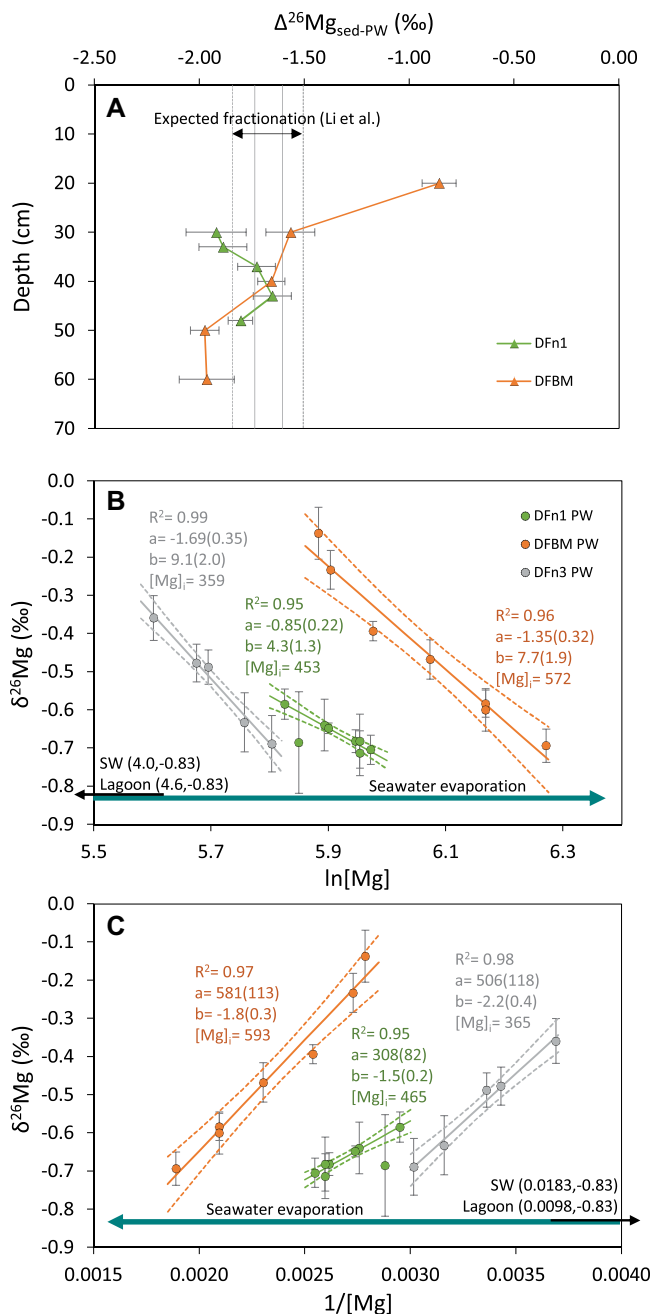


Figure 3. $\delta^{26}\text{Mg}$ values in Dohat Faishakh Sabkha, Qatar. (A) Isotopic difference between dolomite and pore-water samples at same depth, $\Delta^{26}\text{Mg}_{\text{sed-PW}}$. Error bars are propagated 2 standard deviation (SD). Black lines show expected fractionation for $32 \pm 6^\circ\text{C}$ (Equation 1; Li et al., 2015), with uncertainty (dotted lines). (B) Pore-water $\delta^{26}\text{Mg}$ versus $\ln[\text{Mg}]$. (C) Pore-water $\delta^{26}\text{Mg}$ versus $1/[\text{Mg}]$. Green—DFn1, orange—DFBM, gray—DFn3. Error bars are 2 SD. Linear correlation (colored solid line; $\pm\text{SE}$ shown as dashed lines), $Y = aX + b$, is shown for each site (a and b are indicated with 95% confidence limits in parentheses). One outlier, with the largest error, was not considered in the correlation for site DFn1. Seawater (SW) and lagoon water results are shown by black arrow. Seawater evaporation trend, without any dolomite formation, is shown by blue arrow. $[\text{Mg}]$ is Mg concentration (in mM) at intersection of correlation and evaporation lines.

It can be concluded, then, that the $\delta^{26}\text{Mg}$ values of dolomites in the Dohat Faishakh Sabkha are determined by three factors: (1) the formation temperature of the dolomite, which determines the isotope fractionation factor (though minor vital, rate, or other effects cannot be ruled out); (2) the extent of prior Mg removal into dolomite from pore water, which enriches the pore water in ^{26}Mg via a “Rayleigh effect”; and (3) the extent of mixing with less-evolved evaporated seawater, which lowers the $\delta^{26}\text{Mg}$ values of the pore water back toward the seawater value. Thus, the dolomite with the lowest $\delta^{26}\text{Mg}$, which was precipitated from pore water with the least Rayleigh-evolved $\delta^{26}\text{Mg}$, can be used for seawater reconstructions (though it will

always be a maximum limit for seawater $\delta^{26}\text{Mg}$). Indeed, application of this approach to the Dohat Faishakh Sabkha dolomite results in retrieval of the modern seawater value (Fig. S2).

CONCLUSIONS

The dolomite in the Dohat Faishakh Sabkha, Qatar, derives its Mg from evaporated modern seawater. An isotope fractionation, $\Delta^{26}\text{Mg}_{\text{dol-aq}}$, of -1.84‰ to -1.51‰ , as calculated by Equation 1 (Li et al., 2015) for the local temperature, is in accordance with the pore-water and sediment data. Mg loss into dolomite is shown to alter the $[\text{Mg}]$ and $\delta^{26}\text{Mg}$ values of the pore water, enriching it with ^{26}Mg through a “Rayleigh effect.” Mixing of such altered pore water with

unaltered evaporated seawater may reduce this ^{26}Mg enrichment, but $\delta^{26}\text{Mg}$ values never go below the value of the original seawater (-0.83‰). Thus, it is concluded that, provided the lowest $\delta^{26}\text{Mg}$ value among several dolomite samples from the same system is used, and the formation temperature is known, dolomite can be utilized as an archive for $\delta^{26}\text{Mg}$ values of ancient seawater. Also, tools such as Ca isotopes (e.g., Higgins et al., 2018) can be used to trace the extent of Rayleigh distillation. Last, to use this approach, some preliminary conditions, which are met in the Dohat Faishakh Sabkha, should apply: (1) seawater is the major source of Mg to the system; (2) no Mg-evaporites are present; and (3) dolomite is the major carbonate phase in the samples used.

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