Evaluating reflux dolomitization using a novel high-resolution record of dolomite stoichiometry: A case study from the Cretaceous of central Texas, USA

Cameron J. Manche and Stephen E. Kaczmarek
Department of Geological and Environmental Sciences, Western Michigan University, Kalamazoo, Michigan 49008-5241, USA

ABSTRACT

Reflexing brines are routinely invoked to explain dolomitization in peritidal settings. One such example is the Cretaceous Upper Glen Rose Formation (UGR) of central Texas, United States. The UGR is characterized by high-frequency cycles of variably dolomitized limestones interpreted to reflect periodic deepening and shallowing in a peritidal setting. Previous work suggests that reflux commenced near the top of each depositional cycle when evaporative brines seeped downward, causing dolomitization of the underlying sediments. To test this model, a novel high-resolution lithological, mineralogical, and geochemical data set is presented. These data show that transgressive facies successions exhibit a pattern of decreasing dolomite abundance, dolomite stoichiometry, and δ18O (relative to Vienna PeeDee belemnite [VPDB]), and increasing dolomite crystal size. In contrast, regressive facies successions are characterized by a pattern of increasing dolomite abundance, dolomite stoichiometry, and δ18O (VPDB), and decreasing dolomite crystal size. No such variability is observed laterally. The patterns suggest that fluids did not migrate and evolve downward or basinward during reflux, which would have produced a systematic decrease in dolomite abundance and dolomite stoichiometry within each cycle. The data instead support a model of syndepositional dolomitization whereby each facies was dolomitized before deposition of the overlying sediments. The mineralogical and geochemical trends thus reflect temporal changes in water depth as well as a combination of the Mg/Ca, temperature, and salinity of the formative solutions. These results suggest that syndepositional dolomitization in peritidal environments may be a more common and widespread occurrence than previously recognized, particularly during greenhouse conditions.

INTRODUCTION

Dolomite [CaMg(CO3)2] is abundant in the sedimentary rock record (Warren, 2000), yet debate continues about where and how it forms (e.g., Gregg et al., 2015; Kaczmarek et al., 2017; Petrash et al., 2017). Most Phanerozoic dolomites formed diagenetically when a sedimentary carbonate was replaced by dolomite (Machel, 2004). It is generally understood that dolomitization requires a large reservoir of Mg2+ and a hydrological mechanism to deliver Mg2+ to the precursor carbonate (Morrow, 1982). Although numerous hydrological models meet these criteria, some are more popular than others (Machel, 2004). The reflux model (e.g., Adams and Rhodes, 1960; Deffeyes et al., 1964), for instance, is commonly invoked to explain dolomitization in shallow-marine carbonates. This model describes a process whereby evaporated seawater (the Mg source) from an overlying intertidal/supratidal setting seeps downward through underlying carbonate sediments. Dolomitization in turn is promoted by elevated Mg/Ca of the fluids caused by evaporation past gypsum saturation, and hydrological flow driven by the dense, evaporative brine (Machel, 2004).

The current study evaluated the reflux model in the Upper Glen Rose Formation (UGR), central Texas, United States, a classic example of peritidal carbonate depositional cycles interpreted to have been dolomitized by downward refluxing brines (Fullmer and Lucia, 2010). To test the model, we evaluated mineralogical and geochemical data, including mineral abundances, stable isotopes, and crystal size data, including a novel, high-resolution record of dolomite stoichiometry.

The rationale for our approach was based on the recognition that environmental conditions play a critical role in dolomitization (Land, 1985). Peritidal carbonates, for example, are likely to be more dolomitized and more stoichiometric than their subtidal counterparts (Sass and Bein, 1988). This is consistent with data from modern supratidal settings, where dolomite typically forms in waters with elevated Mg/Ca and salinity (McKenzie et al., 1980), and higher temperatures (Bontognali et al., 2010). Field observations also agree with high-temperature laboratory experiments, which have shown that the rate of dolomitization and dolomite stoichiometry are strongly influenced by the Mg/Ca (Kaczmarek and Sibley, 2011), temperature (Gaines, 1968; Kaczmarek and Thornton, 2017), salinity (Medlin, 1959; Glover and Sippel, 1967; Cohen and Kaczmarek, 2017), sulfate (Baker and Kastner, 1981), dioxane (Oomori and Kitano, 1987), polysaccharides (Zhang et al., 2012), and pCO2 (Sibley, 1990) of the fluid. Taken together, field and laboratory observations suggest that dolomite stoichiometry may reflect the chemistry of the dolomitizing fluids. Therefore, dolomite stoichiometry may be a useful proxy for recording changes in the composition of the dolomitizing fluids along a flow path (Lumsden and Chimauskas, 1980; Kaczmarek and Sibley, 2011; Ren and Jones, 2017).

GEOLOGICAL SETTING

The peritidal carbonates of the UGR (early Alban) accumulated during greenhouse conditions (O’Brien et al., 2017) on a low-angle shelf (Phelp et al., 2014) called the Comanche Platform (Fig. 1). In the updip portions of the shelf, the focus of the current study, the UGR is composed of variably dolomitized subtidal mililod wackestones, intertidal packstones, and supratidal mudstones (details in Fullmer [2005] and Fullmer and Lucia [2010]). Previous work by Hoffman (2000) showed that these facies occur in 1–3-m-thick, 5th-order, high-frequency cycles (HFCs) that reflect oscillations between subtidal and supratidal conditions (Fullmer and Lucia, 2010).
METHODS

We collected data and samples for this study along a road cut near the Wild Basin Preserve (WBP) in Austin, Texas (Fig. 1). Vertical samples (N = 217) were taken every 8 cm (Fig. DR1 in the GSA Data Repository\(^1\)) over a height of ~8 m. Lateral samples (N = 102) were taken every 30 cm over a distance of ~33 m within a single bed located near the top of one HFC. Facies analysis, which integrated observations from outcrop, hand samples, and thin sections, documented lithology, fossil content, rock fabric, sedimentary structures, and stratigraphic surfaces. The percent dolomite (relative to calcite) was calculated following the approach of Goldsmith and Graf (1958). Dolomite stoichiometry (mol% MgCO\(_3\)) was calculated using the position of the corrected (104) dolomite reflection (Lumsden, 1979). Cation ordering, which describes the proportions of Ca and Mg correctly positioned within alternating cations layers, was calculated following Goldsmith and Graf (1958). Bulk \(\delta^{18}O\) and \(\delta^{13}C\) data are reported in standard delta (\(\delta\)) notation in per mil (‰) relative to Vienna Peedee belemnite (VPDB). Dolomite crystal diameters (N = 2400) were measured using a scanning electron micro-

RESULTS

Seven HFCs were identified at the WBP outcrop. HFC boundaries are marked by mud cracks, rip-up clasts, gypsum molds, and terra rossa staining. Above each HFC top, there is a gradual change from restricted maldic packstones to subtidal miliolid packstones and wackestones, followed by a gradational transition back to more restricted dolomudstones, maldic packstones, and intraclastic wackestone with evaporites and desiccation features (Fig. 2). Detailed facies descriptions are provided in the supplementary materials. Although the exact type and number of facies vary between HFCs, they generally exhibit symmetrical facies successions characterized by lower transgressive and upper regressive portions of roughly equal thickness.

Mineralogically, UGR dolomites are moderately ordered and nonstoichiometric. Dolomite abundance, stoichiometry, cation ordering, and average crystal size fluctuate vertically, however (Fig. 2). Dolomites are finely crystalline to micritic and lack compositional zoning (Fig. 3). As shown in Figure 2, there is a strong association between the facies and the various mineralogical and geochemical parameters. For example, supratidal/intertidal facies are generally >95% dolomite, whereas subtidal facies are ~74% dol-

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\(^1\)GSA Data Repository item 2019208, sample acquisition, analytical procedures, and facies analysis, Tables DR1–DR3, and Figures DR1–DR3, is available online at http://www.geosociety.org/daterepository/2019/, or on request from editing@geosociety.org.
mide, with the least-dolomitized rocks found in the deepest subtidal facies in five of seven cycles (Fig. DR3). In general, the lower portions of the HFCs are marked by an upward trend of increasing crystal sizes and decreasing stoichiometry, percent dolomite, and $\delta^{18}O$. The upper portions of the HFCs show an upward trend of decreasing crystal size and increasing percent dolomite, dolomite stoichiometry, and $\delta^{18}O$ (for samples >60% dolomite; Figs. 2 and 3). The lateral transect, in contrast, lacks variability with respect to dolomite stoichiometry (46.7 ± 0.2 mol% MgCO$_3$), percent dolomite (99.5% ± 0.2%), and $\delta^{18}O$ (1.99% ± 0.2%; Fig. DR2; Table DR2).

**DISCUSSION**

In general, both the facies and the boundaries between HFCs observed here are consistent with those reported by Fullmer (2005). The main difference is that vertical facies changes were mapped at a higher resolution, and so the facies successions within HFCs differ slightly from Fullmer (2005). Despite these differences, both studies agree that HFCs are characterized by roughly symmetrical cycles composed of a lower transgressive and an upper regressive facies succession (Fig. 2). Consistent with previous studies, these symmetrical HFCs are interpreted to reflect gradual changes in accommodation and fluid chemistry between subtidal and supratidal conditions.

Mineralogical and geochemical patterns (Fig. 2) also reflect gradual changes in water depth and fluid chemistry during UGR deposition. Accurate interpretation of these patterns, however, relies on the premise that UGR dolomites have not undergone significant recrystallization (sensu Machel, 1997). Although most sedimentary dolomites are susceptible to recrystallization (e.g., Woronick and Land, 1985; Kupeck et al., 1994), the data indicate that UGR dolomites were not recrystallized. Multiple lines of evidence, including incomplete dolomitization, nonstoichiometric (Ca-rich) compositions, moderate cation ordering (Kaczmarek and Sibley, 2014), fine crystal sizes, mimetic textures, lack of crystal zoning, and normal $\delta^{18}O$ and $\delta^{13}C$ (Machel, 1997), suggest that UGR dolomites retained their original mineralogical and geochemical signatures.

Prior work suggested that the UGR was dolomitized by hypersaline reflux where evaporated marine fluids migrated downward from the top of each cycle into the underlying limestones (Fullmer and Lucia, 2010). This particular model was tested by Garcia-Fresca and Jones (2011) using reactive transport models. They showed that reflux dolomitization in the UGR was feasible, but only if evaporative fluids percolated downward through multiple depositional cycles. The patterns in Figure 2 are inconsistent, however, with reflux through a single cycle (Fullmer and Lucia, 2010) and reflux though multiple cycles (Garcia-Fresca and Jones, 2011). Both scenarios should produce different dolomitization patterns than what is observed. Mass balance calculations (Kaczmarek and Sibley, 2011) and reactive transport models (Jones and Xiao, 2005) suggest that the Mg/Ca in downward refluxing brines will decrease during dolomitization. Thus, it was expected at the start of this study that dolomite stoichiometry and abundance would decrease downward from the top of each HFC. The data show, however, that dolomite stoichiometry decreases upward in the lower, transgressive portion of the HFC and increases in the upper, regressive portion (Fig. 2). The cyclical oscillations observed cannot be explained by downward refluxing fluids.

The absence of any mineralogical and geochemical trends in the lateral transect (Fig. DR2) also suggests that the dolomitizing fluids did not evolve laterally during reflux as has been suggested in other studies (Adams and Rhodes,
of syndepositional dolomitization where each facies was dolomitized prior to deposition of the overlying facies. This interpretation is consistent with Montañez and Read (1992) and Mutti and Simo (1994), who also interpreted correlations between dolomite abundance and facies as evidence for syndepositional dolomitization.

The lack of glacial ice, the elevated atmospheric pCO$_2$, warm ocean waters, and high eustatic sea level (Spicer and Corfield, 1992; Timofeeff et al., 2006) during the Cretaceous greenhouse provided favorable conditions for syndepositional dolomitization (Sibley, 1991; Sun, 1994). Global average temperatures were 6–12°C higher (Barron, 1983) and pCO$_2$ levels were 2–10 times greater (Cerling, 1991; Berner, 1994; Ekart et al., 1999), both of which have been shown to increase the rate of dolomitization (Sibley, 1990; Kaczmarek and Thornton, 2017).

CONCLUSIONS

Scrutiny of this novel, high-resolution data set reveals patterns inconsistent with reflux dolomitization, the most commonly invoked mechanism in peritidal carbonates. Instead, the mineralogical and geochemical patterns suggest that temporal fluctuations in the environmental conditions occurred during syndepositional dolomitization. This study offers two principal findings: (1) Syndepositional dolomitization may be a more widespread process than previously recognized, particularly in peritidal environments during greenhouse times; and (2) dolomite stoichiometry may provide a valuable new proxy resource with which to constrain paleoenvironmental conditions and hydrogeological processes responsible for dolomitization.

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