Dologrus: The impact of meteoric-water-controlled diagenesis following early-marine dolomitization

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Associate Editor – Alexander Brasier

ABSTRACT

Carbonate rocks that have suffered early near-surface dolomitization followed by extended meteoric exposure commonly undergo partial delithification, a process that results in the formation of dolomitic silts and sands, herein termed dologrus. Dologrus is interpreted to form as a result of diffuse dissolution in porous and permeable dolostones prior to burial and compaction. Such dissolution occurs at the crystal–pore-water interface, causing individual crystals to corrode along interfacial boundaries, eventually leading to delithification and the formation of sediment composed of corroded crystals. The resulting sediment grain size is likely controlled in part by the crystal size of the precursor dolostone. Loss of rock competency through the process of dologrus formation in the shallow subsurface can lead to collapse of overlying bedrock and the formation of dolines common to karstic carbonate landscapes.

Keywords Dissolution, doline, dolomite, karst, sand.

INTRODUCTION

The impact of near-surface dolomitization on carbonate sediments and rocks by reaction with marine waters of variable evaporative concentration has long been appreciated (not limited to; Adams & Rhodes, 1960; Illing et al., 1965; Land et al., 1975; Morrow, 1982, 1990; Patterson & Kinsman, 1982; Machel & Mountjoy, 1987; Budd, 1997; Warren, 2000; Machel, 2004; Gregg et al., 2015; Kaczmarek et al., 2017; Petrash et al., 2017; Manche & Kaczmarek, 2019). Dolomitization can overwrite primary pore-system development, and control flow and storage capability of affected rocks (Lucia & Major, 1994). Owing to the near-surface nature of the marine diagenetic environment in which such dolomitization is understood to occur, exposure of these early dolomites to meteoric waters following a relative sea-level fall is undoubtedly common. The impact of early meteoric diagenesis on matrix-scale pore systems of primary marine deposits comprised of aragonite and calcite has received considerable attention over several decades (Bricker, 1971; Bathurst, 1975; Budd, 1988; James & Choquette, 1990; McClain et al., 1992). Meteoric diagenesis is also important to the evolution of matrix-scale pore-systems in rocks that have undergone dolomitization. Examples include ‘dedolomitization’ or the replacement of dolomite by calcite (Frank, 1981; Kupecz et al., 1993; Nader et al., 2008; Rameil, 2008; Vandeginste & John, 2012) commonly in the presence of calcium sulphate dissolution (Von Morlot, 1847; Bischoff et al., 1994; Arenas et al., 1999; Hauck et al., 2018) and the formation of hollow dolomite rhombs (Jones et al., 1989; Youssef, 1997; Ryan et al., 2019). Dolomite dissolution in the meteoric realm has also been implicated in the formation of dolomitic sediment variably referred to as ‘pulverulent chalk’ (Blank & Tynes, 1965),
‘pulverulite’ (Rose, 1972; Chafetz & Butler, 1980; Kahle, 2012), ‘crushed dolomite’ (Zogović, 1966), ‘flour dolomite’ (Ji et al., 2004), ‘dolomite powder’ (Machel et al., 2012), ‘dolomite sand’ (James et al., 1993; Richter et al., 2018) and ‘disintegrated dolomite’ (Richter et al., 2018) and ‘disintegrated dolomite’ (Richter et al., 2018). At the platform scale, dolomite dissolution by meteoric waters has long been recognized to cause karstification (Kerans, 1988; Rubin & Lemiszki, 1992; Nader et al., 2003; Hartmann et al., 2010). In spite of its prevalence, the specific process by which such dolomitic sediment forms has remained uncertain. This study examines the mineralogy, fabric and geochemistry of such dolomitic sediments from dolines of the Qatar Peninsula, and compares them with similar deposits from other settings, in order to understand the genesis of this common karst deposit.

BOREHOLE LOCATIONS AND GEOLOGICAL BACKGROUND

The Qatar Peninsula protrudes into the southern Arabian Gulf (Fig. 1). Surface rocks and shallow subsurface rocks (upper 150 m of bedrock) are predominantly of Palaeogene age (Umm Er Radhum, Rus and Dammam formations) and mostly composed of dolomitized marine carbonates, with thinner intervals of calcitic rocks and evaporites (Rivers et al., 2019a). Dolomitization is interpreted to have occurred in marine waters soon after deposition (Holail et al., 2005; Rivers et al., 2019a). Since that time these rocks have remained in the near-surface environment and predominantly subjected to subaerial exposure (Van Buchem et al., 2014), with only localized fault-controlled deposition of shallow-marine carbonates (the Miocene Dam Formation) in narrow subsiding seaways (Rivers & Larson, 2018). The lengthy exposure of the Eocene strata has led to karstification and the formation of both open caves (Sadiq & Nasir, 2002) and more commonly dolines associated with cavern collapse, with some caverns interpreted to have formed through dissolution of stratified gypsum observed at depths of greater than 30 m (Eccleston et al., 1981). Two rock cores were taken from within large dolines (Fig. 1) to greater than 100 m depth (Fig. 2). Multiple intervals of dolomitic sediment were observed in these cores (Rivers et al., 2019a) and are the subject of the current investigation.

METHODS

Ten-centimetre-diameter rock cores were recovered from boreholes located in central Qatar (core E2) to a depth of 120 m, and northern Qatar (core E3) to a depth of 122 m (Fig. 1). Core recovery at both locations was >95% of rocks penetrated, although sections of both of the cored intervals suffered from poor rock competency. After rinsing in potable water, a variety of sediment, partially disaggregated rock and intact bedrock were analyzed. Mineralogical, sedimentological and stratigraphic attributes of the cores were reported in detail by Rivers et al. (2019a; cores 2 and 3). For comparison, sediment samples were also taken from karstified intervals of the Devonian Grosmont Formation (Canada) (Well-06-36-085-19 W4; #443093) from depths of 328.81 m, 334.52 m and 346.90 m. Bitumen was removed from these samples by reaction with an organic solvent, leaving pure lithic material for characterization.

Mineralogy of the solid products was determined using standard powder X-ray diffraction (XRD) techniques. Solids were pulverized by hand using an agate mortar and pestle. Powders were mounted on boron-doped silicon P-type zero background diffraction plates and analyzed with a Bruker D2 Phaser diffractometer using CuKα radiation (λ = 1.54184 A) at 300.0 watts (30 kV, 10.0 mA) using a fixed linear (position sensitive) LYNXEYE 1D strip detector (Bruker, Billerica, MA, USA). An incident beam axial soller slit (2.5°), divergence slit (1.0 mm) and an air scatter screen (3 mm) were used. A diffracted beam axial soller slit (2.5°) and a Ni Kβ filter were also used to ensure monochromatic radiation. Scans were acquired over 20 to 60 °2θ scan range, using a step size of 0.0060682 °2θ (6596 steps), and a count time of 2.0 s per step. The XRD patterns were analyzed using Bruker’s Eva software with the Crystallography Open Database (http://www.crystallography.net/cod/). Dolomite stoichiometry (mole % MgCO3) was calculated according to the relative corrected position of the d(104) dolomite reflection, consistent with the methods of Lumsden (1979). The degree of dolomite cation ordering was qualified by the presence of the three dolomite ordering reflections d(101), d(015) and d(021). Cation ordering was quantified with the ratio of the d(015) and d(110) reflection intensities (Goldsmith & Graf, 1958; Kaczmarek & Sibley, 2014).
Rock and sediment characterization for both sample sets was undertaken using binocular microscopy as well as plane-polarized light and cross-polarized light microscopy of both standard petrographic and ultra-polished thin sections cut from both core plugs and grains set in blue epoxy. Detailed characterization was also undertaken using a JEOL JSM-IT100 scanning electron microscope (SEM) (JEOL, Tokyo, Japan). Bulk samples were mounted on aluminum stubs with double-sided carbon tape and coated with approximately 20 nm of carbon to ensure electrical conductivity for imaging in high vacuum mode. Thin sections were not coated and were analyzed in low vacuum mode. All samples were analyzed at an accelerating voltage of 15 to 20 kV. Working distance (8 to 12 mm) and probe current (50 to 70 eV) were varied as needed to optimize imaging and geochemical data collection. Elemental data were collected using a JEOL JED-2300 energy dispersive microanalysis system (EDS) with a Peltier cooled silicon drift detector (KETEK GmbH, Munich, Germany) that was interfaced with the SEM. All crystals imaged with SEM were also analyzed with EDS to confirm composition. Magnesium/calcium molar ratios reported herein were measured on polished thin sections following the methods described by Ryan et al. (2019). In total, 375 EDS points were measured. Three of these were omitted from the dataset because the recorded Mg/Ca ratios fell below 0.85 and were therefore considered erroneous. Additionally, dozens of EDS area scans were also acquired to further characterize the major and trace element concentrations of the samples. Each area scan was performed for a minimum of 8 minutes.
Magnetic susceptibility was measured on both of the Qatar cores (Fig. 2). Measurements were made using a ZH Instruments SM30 magnetic susceptibility meter (ZH Instruments, Brno, Czech Republic) on contact with flat rock (split core) or flat sediment surfaces. Measurements were taken at a laboratory station away from strongly magnetic materials, and with the instrument in ‘drift correction’ mode. All measurements were reported in units of $10^{-5}$ SI. Repeated measurements ($n > 50$) using an internal rock standard show a standard deviation of $\pm 0.002 \times 10^{-5}$ SI.

RESULTS

In both of the Qatar cores, sections of incompetent rock and sediment were encountered, all within dolomitic intervals. In core E2, numerous intervals of incompetent rock were identified and found within both the Rus Formation (Traina Member) and the Umm Er Radhuma Formation, including between 101 to 87 mbs (metres below surface), 70 to 63 mbs and more variably between 60 to 45 mbs (Fig. 2). In core E3 only one such interval was encountered,
being in the Umm Er Radhuma Formation (91 to 74 mbs). The nature of the incompetent material differs between the two cores. Along incompetent intervals of core E2, both rocks and sediments were observed, with loose sediments varying in grain size from silt to cobble (Fig. 3A). Some intervals were typified by loosely-aggregated breccias (Fig. 3B), whereas in other intervals rocks retained horizontal bedding and appeared in-place (Fig. 3C) despite being extremely friable and highly corroded. Magnetic susceptibility measurements across the corroded intervals of core E2 showed no deflection relative to less-altered intact dolomitic rocks above and below the intervals (Fig. 2). Horizontally-bedded chert was observed at a depth of 88.3 mbs (Fig. 3D) in one corroded dolomitic interval, again indicating that a significant portion of the altered rocks were still in-place. Offset fractures were also noted, but uncommon. In thin section, lithified rocks from corroded intervals were composed entirely of non-mimetic planar-euhedral dolomite rhombs (Fig. 3E), with crystals typically \(<100 \mu m\) in diameter. In contrast, accompanying fine sediment was composed of disaggregated dolomite crystals of similar shape and size, although showed a greater degree of corrosion (Fig. 3F).

In core E3, the interval of incompetent material was predominantly composed of loose, well-sorted fine sand-sized and silt-sized sediment (Fig. 4A) comprised almost entirely of dolomite crystals (Fig. 4B). Intact bedrock above and below the sediment was composed of intergrown dolomite crystals of similar size. These rocks displayed dissolution vugs and moulds (Fig. 4C). Dark reddish-brown grains made up a small fraction of the sediment within the incompetent interval. Such brown grains commonly displayed surficial lineations with an earthy lustre (Fig. 4D). Bulk XRD showed that they were composed of clay (80%) with quartz (15%), the remainder being dolomite and calcite. The EDS spectra from SEM showed that these grains also contained variable but significant levels of Fe (up to 9% by weight; Fig. 5); however the precise mineralogy of this phase was uncertain. The dolomitic sediments had significantly higher magnetic susceptibility values (as high as \( +2.0 \times 10^{-5} \)) when compared to surrounding core, which were typically slightly negative (Fig. 2B).

The SEM imaging of both bedrock and sediment from corroded intervals in both cores showed that dolomite crystal textures ranged from euhedral to anhedral, but the outer crystal boundaries were universally corroded. Dolomite crystals generally measured 50 to 100 \( \mu m \) in diameter and lacked well-formed, flat euhedral crystal faces. Instead, crystal corners, edges and faces appeared abraded and/or corroded with irregular surfaces (Fig. 6). The boundaries between dolomite crystals were also irregular and corroded and in many instances were poorly-defined, yielding rounded crystal shapes. The main difference between the loose sediment (Fig. 7A and C) and the bedrock (Fig. 7B and D) was that dolomite crystals in the bedrock were weakly indurated, whereas in the loose sediment they were completely disaggregated. The degree to which the dolomite crystals were corroded is highly variable. At one end of the spectrum, dolomite crystals generally maintained their rhombic (planar-e) shapes but did display irregular edges (Fig. 8A). At the other end of the spectrum, dolomite crystals were rounded, and so corroded that it is difficult to confidently identify them as dolomite in SEM without EDS elemental data (Fig. 8B). In some instances, the dolomite crystals were characterized petrographically as having cloudy cores with clearer rims, with selective dissolution occurring along the boundary between the core and rim parallel with the principal cleavage plane. Under SEM, such dolomite crystal cores were partially to completely dissolved (Fig. 8C). In some cases, the partially dissolved cores were pitted or contain interlaced palygorskite clay fibres (Fig. 8D).

The XRD results showed that Eocene dolomites in both wells were stoichiometric and well-ordered (Table 1; Fig. 9). The SEM-EDS confirmed near-equal proportions of Mg and Ca in the dolomite crystals with no trace elements, such as Fe or Mn, detectable (Fig. 6). The EDS elemental chemistry revealed that some dolomite rims were slightly more Mg-rich than the associated cores. The differences were minor, however, because they fall within a single standard deviation (Fig. 10).

To compare with the Qatar study, samples of karstified dolomitic rocks and associated dolomite sediment from the Grosmont Formation were selected for petrographic and mineralogical analysis. The results showed that both sediments and rock samples were composed of 100% well-ordered stoichiometric dolomite (Table 1). Thin section images of dolomite sediment showed that it consisted of large (>200 \( \mu m \)) angular grains of coarse (20 to 100 \( \mu m \)) dolomite crystal aggregates floating in a
Fig. 3. Images for core E2. (A) Photograph of poorly-sorted dolomitic sediment (depth 99 mbs). (B) Photograph of breccia from karstified interval (depth 88.2 mbs). (C) Photograph of intact rock showing example of unrotated (horizontal) bedding within a karstified interval (depth 85.9 mbs). (D) An unrotated band of silicified rock (depth 88.3 mbs). (E) Photomicrograph of a thin section from a lithified interval immediately adjacent to dolomitic sediment (depth 87 mbs). (F) Photomicrograph of a thin section of dolomite sediment (depth 89.0 mbs). Thin section images are in plane polarized light.

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The differences between the subsurface karst features represented in the two cores is interpreted to reflect differences in the source of karst fill. In core E2, the presence of corroded in-place rocks, and the general poor sorting of associated sediment both point to in-place dissolution and collapse of bedrock. In core E3, the fine-grained and well-sorted nature of the karst fill indicates sorting by transport, although the similarity between the wall-rock dolomite crystals and sedimentary dolomite crystals is striking, and likely points to very locally sourced karst fill. The interpretation of transported material forming karst fill in core E3 is supported by presence of clay-bearing brown grains with surficial lineations (Fig. 4D), which are interpreted to be clay-coated soil pedds (argillans) with slickenside structures (Retallack, 1997) that have been translocated from the surface.

The MS of the rocks depends on their mineralogical content. Most minerals display one of three magnetic behaviours: (i) diamagnetic, with weakly negative susceptibilities (for example, carbonates and quartz); (ii) paramagnetic, with weakly positive susceptibilities (for example, clay minerals, ferromagnesian silicates and Fe-bearing carbonates; and (iii) ferromagnetic, with highly-positive susceptibilities (for example, magnetite or maghemite) (Walden et al., 1999). For carbonate rocks, MS typically reflects the amount of detrital siliciclastic material, which is commonly composed of a mixture of paramagnetic or ferromagnetic minerals (Ellwood et al., 2000). Changes in MS through carbonate rock successions can therefore be reflective of changes in parameters such as depositional sea level or climate (Da Silva & Boulvain, 2006). Most rocks in which the karst features reside show weakly negative MS, reflecting carbonate mineralogy effectively uncontaminated by detrital material (Fig. 2). In core E2 there is no MS deflection across karst features, supporting the interpretation that the karst fill is directly derived from surrounding country rock. In core E3, however, there is a significant positive deflection across the karstified interval (Fig. 3). This deflection likely reflects the presence of the brown clay-bearing grains, and perhaps is associated with trace quantities of magnetic Fe-oxides that can form within terra rossa soils overlying karstified limestones (Merino & Banerjee, 2008). Whereas magnetic phases were not identified in the brown grains, they bear elevated levels of Fe relative to the dolomite host sediment (Fig. 5).
Fig. 4. Images for core E3. (A) Photograph of well-sorted dolomitic sediment (depth 79 mbs). (B) Photomicrograph of dolomitic sediment (depth 90.1 mbs). (C) Photomicrograph of thin-section of dolomitized rock adjacent to interval containing dolomite sediment (depth 102.1 mbs). (D) Photograph of clay-bearing brown grains with slickensides (red arrow) (depth 90.2 mbs). Thin section image is in plane-polarized light.
The interpretation of in situ delithification of dolomitic rocks in core E2 helps to constrain the process by which the dolomite sediment formed. Eccleston et al. (1981) interpreted doline formation associated with subsurface collapse, in part as a result of sulphate dissolution. Rivers et al. (2019a,b), however, concluded that sulphate (mostly gypsum) deposits in the Umm Er Radhuma and Rus formations of Qatar were limited in extent to rocks located south of boreholes E2 and E3, forming in a separate fault-bounded basin. There was no evidence in either core of sulphate minerals having ever been present, and in the case of the area from which core E3 was extracted, Eccleston et al. (1981) concluded the same. Since these rocks were never deeply buried (Van Buchem et al., 2014), and there is no evidence in the cores of hydrothermal influence such as fracture-focused alteration, exotic mineral assemblages or anomalous isotopic measurements indicative of hot waters (Rivers et al., 2019a), alteration is inferred to have occurred in waters of the near-surface environment. The SEM images indicate that the transition from bedrock to neighbouring sediment involves dissolution of dolomite on the crystal-scale (Figs 6 to 8), causing the separation of interlocking crystals that form the bedrock. Such dissolution would not be expected to occur in normal marine waters, because they are greater than ten times supersaturated with respect to stoichiometric dolomite (Morse & Mackenzie, 1990; Rivers et al., 2019b). Therefore, meteoric waters, or potentially mixed meteoric-marine waters, are implicated in the dissolution of the dolomite and the formation of the dolomite sediment.
Commonly, dissolution of dolomite in meteoric waters is incongruent, resulting in calcite precipitation (Von Morlot, 1847; Frank, 1981; Kupecz et al., 1993; Bischoff et al., 1994; Arenas et al., 1999; Nader et al., 2008; Rameil, 2008; Vandeginste & John, 2012; Hauck et al., 2018). The formation of hollow dolomite rhombs has also been observed in Eocene rocks of Qatar (Ryan et al., 2019) and elsewhere (Jones et al., 1989; Youssef, 1997), likely driven by small differences in the chemistry and stability of dolomite cores versus rims (for example, Fig. 10). These are examples of mineral-controlled selective-dissolution or precipitation reactions (James & Choquette, 1990), which typically occur after pore waters have reacted to some degree with the host carbonate. However, dissolution processes associated with near-surface karstification, are the result of water-controlled congruent dissolution, whereby meteoric waters undersaturated with respect to the major carbonate phases dissolve indiscriminately.

Fig. 7. Scanning electron microscope (SEM) images of: (A) loose sediment from core E2; (B) bedrock from core E2; (C) loose sediment from core E3; and (D) bedrock from core E3.

Fig. 8. Scanning electron microscope (SEM) images of: (A) less-altered rhombs from the core E3 (depth 81.0 mbs); (B) corroded rhombs from core E2 (depth 91.6 mbs); (C) rhombs with dissolved cores from core E3 (depth 85.5 mbs); and (D) rhombs with palygorskite from core E3 (depth 85.5 mbs).
(James & Choquette, 1990), with greater dissolution occurring along higher permeability pathways. In many cases, such dissolution is focused along near-surface fractures that widen over time, becoming the features that define the karstic landscape (dolines, shafts, caves, etc.). This is particularly true for telogenetic karst, whereby carbonate rocks undergo stabilization, burial and compaction causing matrix porosity loss prior to uplift and exposure (Mylroie & Mylroie, 2013).

In the case of near-surface Qatar rocks, burial and compaction has not occurred, and early-dolomitized rocks retain high matrix porosity and permeability values, averaging 32% and 264 mD, respectively (n = 215), and reaching as high as 54% and 7.5 D, based on core plugs from three cores through the interval (Rivers et al., 2019a). Therefore, meteoric waters might be expected to move more diffusely through these rocks than they would through ancient dolomitic rocks that have undergone significant burial. In near-surface settings, such as the vadose and perhaps shallow phreatic zones, meteoric dissolution of matrix dolomite can be envisioned to occur congruently on the crystal scale prior to reaching saturation with respect to dolomite. This type of dissolution is interpreted to have occurred from the outside of the dolomite crystal inward along the crystal–water interface, eventually unlocking the crystals and so removing the material by which the rock is lithified. The final products of this process are the dolomite silts and sands encountered in the subsurface of the Qatar dolines.

**Table 1.** Compiled X-ray diffraction (XRD) data for rocks and sediments from Qatar cores (E2 and E3) as well as Grossmont Formation sediments (G1, G2 and G3).

| Core | Depth (m) | Induration | MgCO₃ mol% | Cation ordering |
|------|-----------|------------|------------|----------------|
| E3   | 81.00     | Consolidated | 52.19      | 0.74           |
| E3   | 85.50     | Consolidated | 51.96      | 0.56           |
| E3   | 89.55     | Loose       | 52.51      | 0.79           |
| E3   | 89.60     | Consolidated | 52.55      | 0.87           |
| E3   | 91.60     | Loose       | 51.49      | 0.67           |
| E3   | 96.00     | Loose       | 51.39      | 0.63           |
| E2   | 80.00     | Loose       | 52.30      | 0.71           |
| E2   | 80.60     | Consolidated | 53.05      | 0.70           |
| G1   | 328.50    | Loose       | 51.79      | 0.68           |
| G2   | 334.52    | Loose       | 51.99      | 0.76           |
| G3   | 346.90    | Loose       | 50.94      | 0.64           |

**DISCUSSION**

The formation of dolomite silts and sands is a diagenetic process recognized in Palaeozoic (Fu et al., 2004; Kahle, 2012; Machel et al., 2012; Poros et al., 2013), Mesozoic (Blank & Tynes, 1965; Rose, 1972; Chafetz & Butler, 1980; Ji et al., 2004; Richter et al., 2018) and Cenozoic (James et al., 1993; this study) carbonate deposits. In most cases this process has been documented in association with near-surface dissolution driven by meteoric waters (Blank & Tynes, 1965; Chafetz & Butler, 1980; James et al., 1993; Fu et al., 2004; Ji et al., 2004; Richter et al., 2018) perhaps entraining organic acids (Kahle, 2012). Similar karst-associated dolomite sediment has been observed in the Devonian Grosmont Formation of western Canada. These deposits have been described as ‘dolo fudge’ or ‘dolo gunk’ (Machel et al., 2012), because they host bitumen in intercrystalline pores, but the sediments were more generally described as ‘dolomite powder’ (Machel et al., 2012).
cause of the formation of such sediment is uncertain, but it has been speculated by to be associated with evaporite dissolution or even cryogenic mechanical weathering (Machel et al., 2012).

The diagenesis and burial history of the Grosmont Formation is reviewed by Machel et al. (2012). Significant sections of the Grosmont Formation are thought to have never been buried greater than ca 1000 m. Many karstification events have been interpreted to have affected the unit, but all post-date early dolomitization events, and occurred in either near-surface or shallow-burial settings. Although the timing of dolomite delithification is uncertain, ‘syn-depositional’ dolomite dissolution is not inconsistent with available evidence (Machel et al., 2012). Although the possibility of dolomite delithification in the Grosmont Formation by evaporite dissolution or cryogenic mechanisms cannot be discounted, the similarity in the resulting diagenetic product to Qatar’s karstic sediments (Table 1; Fig. 10), may argue for dissolution by meteoric waters, a process consistent with the structural and diagenetic history of the Grosmont.

The diffuse nature of the dissolution required for substantial formation of delithified dolomite deposits likely necessitates that they form prior to significant burial-related compaction and porosity-reduction, as is interpreted for Qatar Eocene deposits. The Cretaceous Edwards Formation (Blank & Tynes, 1965; Chafetz & Butler, 1980) was exposed soon after deposition, and has not been thought to have been deeply buried since (Barker et al., 1994). The Oligo-Miocene rocks of the Gambier ‘limestone’ (James et al., 1993) were thought to have been buried less than 300 m deep. In both cases, initial dolomitization has been interpreted to have occurred during early stages of diagenesis. Syn-sedimentary or very shallow-burial dolomites might be particularly susceptible to delithification in the meteoric realm due to both their near-surface formation (i.e. small sea-level falls can cause exposure), and perhaps, because of their initially low chemical stability relative to older dolomites (Graf & Goldsmith, 1956; Goldsmith & Graf, 1958; Lumsden & Chimahusky, 1980; Kupeč et al., 1993; Kaczmarek & Sibley, 2014).

Such diagenesis of platform dolomites might be more common along tectonically-active margins where post-depositional uplift is expected, such as occurred in Qatar during the Oligocene (Van Buchem et al., 2014).

As reviewed above, terms used to describe such dolomitic sediments are diverse, and include references to grain size (for example, ‘dolomite sands’; James et al., 1993), physical processes (for example, ‘crushed dolomite’; Zogović, 1966) and non-specific terms (for example, ‘dolomite powder’; Machel et al., 2012). The contention in this study is that the most appropriate term for dolomitic sediments interpreted to have formed through a near-surface diffuse dissolution processes is ‘dologrus’. ‘Grus’ is a term used when describing surface weathering, and is defined as: “an accumulation of angular, coarse-grained fragments (particles of sand and gravel) resulting from the granular disintegration by the processes of chemical and mechanical weathering of crystalline rocks (most notably granitoids) generally in an arid or semi-arid region” (Bates & Jackson, 1984). The term
‘dologrus’ is generally in keeping with the original definition of the geological term ‘grus’ as it applies to dolomitic rocks.

Dologrus has been interpreted to form in the vadose zone, associated with surficial weathering (Blank & Tynes, 1965; Rose, 1972; Chafet & Butler, 1980; Kahle, 2012). In Qatar, dologrus is not typically observed at the surface, and dolines are commonly filled with alluvium composed of fine siliciclastic sediment (Cavelier et al., 1970). However, most of Qatar is mantled by the Dammam Formation, which is in large part limestone. Dologrus from core E3 is interpreted to include soil pedds, implying that initial formation occurred in a near-surface setting prior to mobilization and transport-related sorting. The possibility that dologrus can also form in the shallow phreatic zone, however, cannot be discounted. In core E2 dologrus appears to have formed in situ, and its presence does not correlate with obvious exposure surfaces or significant stratigraphic horizons such as formation tops (Fig. 2). It is possible, if not likely, that congruent dissolution leading to dologrus formation can occur in the phreatic zone near the water table during aquifer recharge events. For instance, Whitaker et al. (2006) showed that undersaturated meteoric waters can directly flow through fractures to a water table greater than 60 m below ground surface. It is considered less likely that dologrus can form in the deeper phreatic zones, since, at least in Qatar, measurements show that the upper 50 m of the aquifer water column is supersaturated with respect to dolomite.

Kilometre-scale dolines are very common on the surface of Qatar (Eccleston et al., 1981).

Fig. 11. (A) and (B) Thin section images of dolomite sediment from Grosmont Formation showing dolomite crystal size variability. (C) Scanning electron microscope (SEM) image of Grosmont Formation dolomite showing rounded crystals. (D) SEM examples of hollow or pitted rhombs of dolomite from the Grosmont Formation. Thin section images are in plane polarized light.
(Fig. 1) and >15 m thick bodies of dologrus were encountered in both dolines penetrated for this study. If it is assumed that most Qatar dolines are underlain by similar dologrus deposits; hundreds of metres wide and tens of metres thick zones of delithified dolomite are likely very common in the Eocene strata of Qatar. The common occurrence of dologrus has been corroborated by local drilling engineers. Similarly altered deposits that have undergone significant burial might be difficult to recognize in the rock record, because compaction and recrystallization would likely yield rocks or perhaps ‘cave fills’ indistinguishable from other texturally oblitative dolomites. Magnetic susceptibility measurements on rocks suspected of having undergone delithification may distinguish such karst features, if the deposits entrain translocated soil sediments.

Intervals of dologrus in the near-surface (upper 20 m) may be identified using investigation methods such as Multiwave Analysis of Surface Waves (MASW) (Park et al., 1999), based on expected velocity differences between unconsolidated materials when compared with water-filled cavities or intact bedrock. For identification of deeper dologrus deposits, it is possible that a Reflection Microtremor (ReMi) (Louie, 2001) or similar analysis might delineate dologrus deposits at depths up to 100 m, although the scale of the dologrus body would need to be significant relative to the length of the geophone array and the distance between geophones (Louie, 2001). Borehole geophysical logging in cored or destructive boreholes including determination of P and S wave velocities is sometimes useful in calibrating such surfacic geophysical methods (Park et al., 1999). During drilling operations, zones of dologrus, although not typically a drilling hazard, could also likely be identified based on increased borehole penetration rate.

CONCLUSIONS

Dolomitic sediment, herein termed ‘dologrus’, is a common product of meteoric diagenesis affecting dolostones formed in shallow marine environments. Dologrus is interpreted to form as a result of diffuse dissolution in porous and permeable rocks prior to burial and compaction. This process is inferred to be driven by congruent dissolution of dolomite crystals at the crystal–pore-water boundary in the vadose or shallow phreatic zone as a result of diffusive water flow through rocks with high matrix permeabilities. Degradation of rock competency through this process can ultimately lead to subsurface collapse, upward stoping and the formation of related surface dolines.

ACKNOWLEDGEMENTS

The authors would like to thank Becky Rogala for her aid in the sampling of cores from the Grosmont Formation. We are indebted to Sabrina Skeat, Sallie Vest and Brooks Ryan for their help with figure creation and referencing. Noel James provided helpful advice as always, coining the term ‘dologrus’. We would also like to thank the Alberta Core Research Centre, operated by the Alberta Energy Regulator, for supplying samples from the Grosmont Formation. JMR is appreciative of PJ Moore for sharing his general insights into karst processes. Fiona Whitaker is appreciated for passing on her knowledge of the Qatar aquifer carbonate saturation states. We are indebted to Alexander Brassier and one anonymous reviewer for improving this manuscript with helpful comments. Finally, we are grateful to Charlie Kerrans for suggesting that the diagenesis of the Grosmont Formation might be an ancient analogue for the alteration observed in near-surface Qatar dolostones.

DATA AVAILABILITY STATEMENT

Research data are not shared.

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Manuscript received 22 July 2019; revision accepted 2 April 2020