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An overview of structurally-controlled dolostone-limestone transitions in the stratigraphic record

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ABSTRACT

In structurally-controlled dolomitization systems, there is a general consensus that the formation of dolostone-limestone transition, termed here as “dolomitization fronts”, is governed by either the presence of an ultra-low permeability zone (fluid barrier) or changes in dolomitization potential and kinetics. However, the actual processes controlling the abrupt termination of dolostone bodies and their corresponding morphology and dimension are still relatively poorly understood. To address these challenges, we aim to (i) review the different origin and styles of structurally-controlled dolomitization fronts in the stratigraphic record and (ii) provide a standardized framework and quantitative insight to describe and interpret dolomitization fronts.

To achieve this, field observations across geologic timescales and geodynamic settings are complimented with published data to document different styles of structurally-controlled dolomitization fronts. The results should that the following morphologies are associated with both tabular and columnar dolostone bodies: (i) lateral contact/bed-perpendicular fronts; (ii) vertical contact/bed-parallel fronts; and (iii) complex-shaped fronts at the distal part of dolostone bodies. This morphological information, when coupled with detailed petrography, mineralogical and geochemical data could help to accurately reveal the governing processes behind the termination of dolostone bodies and their corresponding reaction fronts geometries. Our review shows that the first front type is primarily controlled by the interplay between intrinsic properties of the host rocks, dolomitizing fluids, and self-organization process. In contrast, the second front type is governed by the presence of laterally continuous depositional, diagenetic, or structural fluid barriers, creating a significant permeability contrast across beds. The formation of complex-shaped fronts is interpreted to be controlled by a combination of original lithological composition and kinetics.

This overview provides the first multi-study categorisation of ancient dolomitization fronts and the controls on their formation at a range of scales. This improves our understanding of low temperature metasomatic processes, and their termination, in sedimentary systems. Furthermore, it highlights how accurate interpretation of the origin and styles of dolomitization fronts can improve our understanding of dolomitization processes, paleofluid flow, and distribution of economic resources in dolomitized carbonate platforms, which can be challenging to determine from the dolostone bodies themselves, where they have undergone multiple phases of recrystallization and diagenetic overprinting.

*Keywords: Dolostone; Geobodies; Fault/Fracture; High-temperature; Reaction front; Hydrothermal*
1. INTRODUCTION

Diagenetic reaction fronts are a common phenomenon within rocks that have undergone chemical alteration processes. This phenomenon occurs as a result of reaction and displacement of an original fluid with other fluids of a different temperature and composition (i.e. metasomatism) in chemically reactive and permeable rocks (Philips, 1991; Jupp and Woods, 2003). Depending on the composition, temperature and pressure of the incoming fluids, minerals in solution may become either undersaturated or oversaturated, leading to the formation of diagenetic reaction fronts to reinstate the system to equilibrium (Phillips, 1991; Woods and Fitzgerald, 1993; Jupp and Woods, 2003). To understand the formation of these reaction fronts, numerical models have evaluated the kinetics of the reaction and the preservation of mass (Hinch and Bhatt, 1990; Phillips, 1991). Furthermore, as many diagenetic reactions are volume preserving, synchronization between dissolution fronts and precipitation fronts has been invoked to retain the balance between dissolved components and precipitated mineral volumes (Putnis, 2009; Kondratiuk et al., 2015 and references therein).

The formation and occurrence of reaction fronts has long been discussed in a range of disciplines, including experimental physics (e.g. Jiang and Ebner, 1990; Phillips, 1991; De Wit, 2001; Jupp and Woods, 2003; Rongy et al., 2009) and chemistry (e.g. Mundschau et al., 1990; Sachs et al., 2002). In geological systems, chemical reaction fronts are commonly observed in both sedimentary and metamorphic rocks as a result of different metasomatic processes, including prograde metamorphism (Jamtveit et al., 1992; Nabelek and Labotka, 1993; Yardley and Lloyd, 1995; McCaig et al., 1995; Dong et al., 2017), cementation process in sandstone (Wei and Ortoleva, 1990), and calcite-to-clay replacement during the formation of terra rossa (Merino and Banerjee, 2008) as well as a few studies of dolomitization (Wilson et al., 1990; Nader et al., 2007; Budd and Mathis, 2015; Koeshidayatullah et al., 2020a; 2020b). In sedimentary systems, diagenetic reaction fronts can have far-reaching implications, such as controlling the spatial distribution of porosity (Broomhall and Allan, 1987; Wendte, 2006), accumulation of ore deposits (Harper and Borrok, 2007), fluid-rock interaction during CO$_2$ sequestration in subsurface reservoirs (Barlet-Gouedard et al., 2007; Ennis-King and Paterson, 2007; Nicot et al., 2011; Ulven et al., 2014) and unravelling dolomitization history (e.g. Wilson et al., 1990; Koeshidayatullah et al. 2020a; Stacey et al., 2020; Stacey et al., 2021).

Over the last several decades, structurally-controlled dolomitization has been extensively studied due to its economic and scientific importance (Davies and Smith, 2006; Sharp et al., 2010; Hollis et al., 2017). Structurally-controlled, hydrothermal dolomitization can occur in various geodynamic settings and involves fluids of varying temperatures and chemistry, such as in North America (Lavoie et al., 2005; Davies and Smith, 2006; Koeshidayatullah et al., 2020a; Stacey et al., 2020); Central Europe and
the UK (Ronchi et al., 2012; Lapponi et al., 2014; Hendry et al., 2015); China (Jiang et al., 2015; Jiang et al., 2016; Guo et al., 2016), and the Middle East (Sharp et al., 2011; Mansurbeg et al., 2016; Al-Ramadan et al., 2019). Overall, structurally-controlled dolomitization is usually associated with the presence of dolomite cement (e.g., saddle dolomite), hydro-brecciation, formation of dolomitization halos around faults, and discrete bodies that terminate in limestone (Martin-Martin et al., 2015; Rustichelli et al., 2017; Hollis et al., 2017; Koeshidayatullah et al., 2020a; Stacey et al., 2021). Therefore, our research is focused on structurally-controlled dolomitization because the occurrence of dolostone-limestone transition is more apparent in this system (e.g., generally a sharper boundary and distinct color difference between dolostone and limestone) when compared to other dolomitization processes, in particular reaction fronts that formed at lower temperatures (<50 °C).

Wilson et al. (1990) suggested a combination of mechanisms, including the magnesium source, hydrologic driving mechanisms, temperature and dolomitizing fluid circulation patterns control the formation of reaction fronts between dolostone and limestone during high temperature, structurally controlled dolomitization. Several studies have further captured systematic variations in Mg/Ca ratio, dolomite stoichiometry, trace element concentrations, and temperature across dolostone bodies (Nader et al., 2007; Koeshidayatullah et al., 2020b). In addition, numerical simulation suggests intrinsic host rock properties such as porosity, permeability, and reactive surface area (RSA) are critical to controlling the extent of structurally-controlled dolomitization by a range of fluid chemistry and temperatures (Yapparova et al., 2017; Benjakul et al., 2020). While these studies have laid important groundwork for understanding the formation of dolomitization fronts, the documentation of different styles of dolomitization fronts and controls on the termination of dolostone bodies in the geological record has yet to be presented. We therefore aim to provide the following:

- A systematic review on the current state of research regarding the origin and styles of dolomitization fronts by comparing different structurally-controlled dolostone bodies at various field locations (Fig. 1). Observations are compared with published studies in order to evaluate processes in different systems and better capture the variations in geometry and boundary conditions of dolomitization fronts.
- A standardized framework to describe and interpret dolomitization fronts in structurally-controlled dolomitization systems, and potentially dolomitization by different processes, by proposing a morphological classification of dolomitization fronts. Furthermore, we discuss statistical relationships between the dimension and geometry of dolostone bodies and the genesis of these different dolomitization fronts types.
- Discussion of the far-reaching implications of dolomitization fronts. Subsurface studies for energy production and energy storage typically rely heavily on statistical models of rock
property distribution. The contrast in rock physical properties between limestone and dolostone means that knowledge of geobody size and termination is critical to their accurate reproduction in geostatistical models. Furthermore, there is a growing need to integrate reactive transport models (RTM), and metasomatic studies within anthropogenic timescales to assess the impact of gas injection, particularly for carbon capture and storage. A consistent method of description and characterization of reaction fronts and geobody size is essential to inform and ground-truth the outputs of such models.

1.1. Terminology

This study focuses exclusively on structurally-controlled dolostone bodies, i.e. dolostone that unequivocally forms tabular and columnar bodies around and within faults and fault damage zones. Here, the geometry of the body is described either as (i) tabular, where a geobody is oriented parallel to bedding, and (ii) columnar, where the body is both perpendicular to the bedding and cross-cut different strata. In such structurally-controlled systems, the columnar bodies are often genetically related to the tabular bodies where the columnar bodies form adjacent to the fault, and the tabular bodies extend away laterally (Fig. 2). In some cases, dolostone bodies can also be formed within the fault or damage zones (can be either tabular or columnar depending on the geometry of the damage zones), for example during the hydrobrecciation processes (Fig. 2). However, the morphological association of columnar and tabular dolostone does not necessarily mean they formed at the same time or from the same fluids (Fig. 2; see discussion in Hollis et al., 2017).

In structurally-controlled systems, the geobodies often show a distinct colour contrast between dolostone and limestone, which makes identification of dolostone-limestone transition - often termed “dolomitization fronts” - in outcrop and drill core easier than in other systems. The term “dolomitization fronts” is typically used to describe the two-dimensional interface between dolostone and limestone across different scales and to represent the location where the dolomitization potential of the reactive fluids was progressively depleted (e.g. Wilson et al., 1990; Nader et al., 2007; Harper and Borrok 2007). Conversely, several field studies have documented the termination of dolostone bodies laterally and vertically into impermeable features such as filled fractures, stylolites or low permeability facies which need not have any direct relationship with the dolomitization potential of the fluids (e.g. Sharp et al., 2010; Martín-Martín et al., 2015; Hirani et al., 2018; Koeshidayatullah et al., 2020a). Consequently, there is a need to clearly define “dolomitization fronts” to avoid confusion. Here, we adopt the term “dolomitization fronts” to describe any location in space where a dolostone body displays either a vertical (i.e. at the base and top of the dolostone beds) or lateral (i.e. within
(beds) contact with the host rock, which is usually – but not exclusively - limestone (Fig. 2), in order to avoid any genetic connotation. The front might occur where there is either an apparent change in intrinsic depositional, structural or diagenetic property of the precursor rock, or where there is no apparent change in pre-dolomitization physical rock properties (i.e. it likely occurs as a result of a change in fluid chemistry, discontinuation of fluid supply or fluid driving mechanism) (Fig. 2). In outcrop, the contact between dolostone and limestone can be grouped into: (i) lateral or bed-perpendicular contacts which occur within beds (i.e. same lithofacies); and (ii) vertical or bed-parallel contacts which represent the transition across bedding or a low permeability horizon, such as a stylolite. The terminology used here also accounts for complex three-dimensional fluid flow that takes place during dolomitization. The formation of dolomitization fronts is often accompanied by the occurrence of diagenetic ‘halos’. In this paper, the term ‘halos’ is used to describe the partially dolomitized limestone located adjacent to the dolomitization fronts, essentially the transition zone from dolostone to limestone (Fig. 2). The width of a ‘halo’ is described as either thin (centimetre-scale) or thick (metre-scale).

1.2. Scale

In structurally-controlled dolomitization systems, dolostone bodies can occur discretely in multiple locations on carbonate platforms and can be up to several hundred metres in width (e.g. Davies and Smith, 2006; Martín-Martín et al. 2015; Hollis et al., 2017; Koeshidayatullah et al., 2020a; Breislin et al., 2020; Stacey et al, 2021). Typically, the occurrences of these discrete dolostone bodies are associated with the formation of both lateral and vertical dolomitization fronts within the host rocks. In detail, the transitions between dolomite (dolostone) and calcite (limestone), or between carbonate and non-carbonate minerals (e.g., quartz, barite, and other sulphide minerals) can occur at various scales from crystal (micro) to basin (mega) scale, independent of fluid source (Warren, 2000; Whitaker et al., 2004; Machel, 2004). At the mega (kilometre or basin) and macro (metre or outcrop) scales, both vertical and lateral dolostone-limestone transitions can appear simple, and apparently related to one or more depositional, diagenetic and structural barriers (Wilson et al., 1990; Nader et al., 2007; Sharp et al., 2010; Hirani et al., 2018) (Fig. 2). At the meso-scale (centimetre), dolostone-limestone transitions in core or hand-specimen may have either sharp or diffuse boundaries and often have an apparently simple geometry (Saller and Yaremko, 1994; Wendte, 2006; Davies and Smith, 2006). At the micro-scale (micrometre and smaller), petrographic analysis can show that the dolostone-limestone boundary is not always as sharp as observed at the meso- and macro-scale, and interlocking dolomite crystals are often found adjacent to calcite crystals or occur as discrete crystals within limestone (Hirani et al., 2018; Koeshidayatullah et al., 2020b). Furthermore, reaction fronts that form during the transformation from calcite to Mg-carbonates, including dolomite, in laboratory
experiments (e.g., Jonas et al., 2015; Jonas et al., 2017), and by numerical simulation (Beaudoin et al., 2014) are more complex. In particular, the boundary between calcite and dolomite crystals at the micro-scale is often more diffuse, and the geometry more complex, than at the meso- and macro-scale. Overall, although dolomitization fronts look simple in outcrop, their complexity is evident at the micro-scale.

2. CONTROLS ON THE FORMATION OF DOLOMITIZATION FRONTS

In general, dolomitization proceeds by a dissolution – re-precipitation reaction, and is often facilitated by elevated temperature, elevated fluid Mg/Ca ratio and reactive surface area whilst high pCO₂ and lower fluid pH will facilitate dissolution of the precursor limestone (Warren, 2000; Machel, 2004). In natural examples, the processes governing the transformation of calcite to dolomite (i.e. dolomitization process) have been studied in the laboratory; experiments have shown that such high-temperature transformations occur in multiple phases and are associated with the formation of diagenetic reaction fronts at each point in time (Kaczmarek and Sibley, 2014; Jonas et al., 2015; Müller and Küster 2017).

While the mechanisms governing structurally-controlled dolomitization are relatively well understood (Morrow, 1982; Warren, 2000; Machel, 2004; Davies and Smith, 2006; Hollis et al., 2017), processes governing the formation and styles of dolostone-limestone reaction fronts have not been widely discussed in the literature, likely due to the complex range of factors controlling the formation of dolomitization fronts at any given locality. Usually, the vertical contact (bed-parallel dolomitization fronts) is sharp and has a simple geometry whereas the lateral contact (bed-perpendicular dolomitization fronts) is often diffuse, and more complex in geometry (Amthor et al., 1993; Mountjoy and Amthor, 1994; Davies and Smith, 2006; Sharp et al., 2010; Rustichelli et al., 2017; Hirani et al., 2018; Koeshidayatullah, 2020b). In addition, complex-shaped dolomitization fronts may also occur where the rock physical properties are highly heterogeneous. Early work discussed the importance of advective processes on the migration of reaction fronts in both sedimentary and metamorphic rocks (e.g., dolostone-limestone), and constrained changes in temperature and fluid composition at reaction fronts (Wilson et al., 1990; Jamtveit et al., 1992). Furthermore, the styles and geometry of dolomitization fronts has been numerically modelled and suggested to be controlled by several factors, including Mg/Ca ratio, reactivity of bounding surfaces, and physiochemistry of dolomitizing fluids (Beaudoin et al., 2014; Yapparova et al., 2017). Here, we review the range of controlling factors that influence the geometry and styles of dolomitization fronts in the geological record, from the physical to the physiochemical factors:
**Permeability contrast** -- Many studies have highlighted the significance of laterally and vertically continuous permeability barriers in controlling the extent and termination of structurally-controlled dolostone bodies (e.g., Carmichael et al., 2008; Sharp et al., 2010; Beckert et al., 2015; Martín-Martín et al., 2018; Koeshidayatullah et al., 2020a). Dolomitization often terminates at these zones of permeability contrast, such as an interface between carbonate rocks and low-permeability mudrocks, at filled fractures, or beneath cemented horizons such as depositional omission surfaces, due to the low porosity and permeability of the feature. This permeability contrast prevents the advance of fluids and hence dolomitization. Similarly, bed-parallel fractures and stylolites may also inhibit fluid flow during diagenesis and dolomitization, leading to the formation of dolomitization fronts (Martín-Martín et al., 2018; Paganoni et al., 2018; Morad et al., 2018). For example, a low permeability depositional or structural barrier overlying a porous and permeable carbonate layer might drive the dolomitizing fluid laterally, rather than allowing it to continue to flow and react vertically, across beds. The presence of a laterally continuous, low permeability layer may govern the sharpness and geometry of the dolomitization fronts; for example, sharper fronts tend to develop where there is a greater contrast in permeability between beds as demonstrated from reactive transport modeling and field examples (Yapparova et al., 2017; Koeshidayatullah et al., 2020b). Overall, in structurally-controlled dolomitization systems, the presence of bed-parallel permeability contrast has a significant influence on the formation of bed-parallel dolomitization fronts and driving fluid migration preferentially in one direction (e.g. Sharp et al., 2010) whilst fractures can form bed-perpendicular fronts, particularly at the outcrop scale (e.g. Hirani et al., 2018).

**Intrinsic rock physical properties** -- Numerical simulation suggests that during dolomitization, intrinsic properties of the host rock, such as reactive surface area (RSA), original mineralogy (e.g. the presence of dolomite seeds or high-Mg calcite) and permeability heterogeneity have a significant control on the rate and extent of dolomitization (Yapparova et al., 2017; Benjakul et al., 2020). In ancient strata, the influence of the prior, physical properties of the host are often difficult to decipher and can only be inferred from the adjacent undolomitized or partially-dolomitized limestone. However, reactive transport models have shown that higher RSA (typical of mud-supported facies) can facilitate faster dolomitization rates than low RSA (grain-rich facies) in low-temperature systems (Al Helal et al., 2012; Gabellone and Whitaker, 2016; Yapparova et al., 2017). Since faster rates of dolomitization produce sharper and steeper fronts than slower rates of dolomitization, dolomitization fronts tend to be sharper and more vertical in muddier layers, compared to grainier beds, where fronts are often more diffuse and less steep (Yapparova et al., 2017).

**Kinetic and thermodynamic controls on dolomitization potential** -- Lateral termination (i.e. bed perpendicular dolomitization fronts) of structurally-controlled dolostone bodies are commonly
observed without the occurrence of distinct fluid barriers, such as fractures, or apparent changes in rock physical characteristics (Wilson et al., 1990; Yao and Demicco, 1997; Davies and Smith, 2006; Nader et al., 2007; Koeshidayatullah et al., 2020b). In these cases, the lateral transition between dolostone and limestone occurs as either tongue- or finger-shaped fronts, often with halos of partial dolomitization, which may have a higher porosity than the surrounding limestone or dolostone (Koeshidayatullah et al., 2020b). These fronts are interpreted to be controlled by changes in the kinetic or thermodynamic potential of the dolomitizing fluids (e.g., Wilson et al., 1990; Davies and Smith, 2006; Wendte, 2006; Merino and Canals, 2011; Koeshidayatullah et al., 2020b). The termination of structurally-controlled dolostone bodies and the resultant dolomitization front geometry has also been interpreted to be the product of changes in fluid temperature and pressure (Machel, 2004; Davies and Smith, 2006; Yapparova et al., 2017). This is in part because structurally-controlled dolomitization is often interpreted to occur from high temperature, pressurized fluids that were released from the deep subsurface via faults, leading to rapid depressurization and cooling (Davies and Smith, 2006; Corbella et al., 2014; Martin-Martin et al., 2015). Wilson et al. (1990) observed a cooling trend from the core to margin of a plume-shaped body (stable isotope temperature 175 to 120°C) in the Latemar Platform, Italy. This interpretation has been corroborated experimentally by precipitation of non-stoichiometric dolomite at lower temperatures (Kaczmarek and Thornton, 2017). Fluid temperature is also cited as having a significant control on the sharpness of dolomitization fronts, with high temperature fluids creating a sharper, more abrupt dolostone-limestone transition than lower temperature (<50 °C) fluids (Machel, 2004; Wendte, 2006; Yapparova et al., 2017).

Fluid pressure is widely invoked to be high during structurally-controlled dolomitization, and might govern the extent and geometry of dolostone bodies (e.g., Davies and Smith, 2006). Numerical modelling shows that a higher-pressure differential during dolomitization can create more laterally extensive dolostone bodies (Szymczak and Ladd, 2006, 2013). Aarnes et al. (2012) suggested the formation of diagenetic reaction fronts is associated with pressure build-up that can create fluid overpressure, which may either slow down the advancement of reaction fronts or terminate them, depending on the reaction temperature. However, such controls are difficult to interpret in natural settings, particularly since structurally-controlled dolomitization can occur from high pressure - high temperature fluids in a low-pressure, low-temperature setting (e.g., Stacey et al., 2021).

**Fluid properties** -- Typically, structurally-controlled dolomitization occurs from highly saline hydrothermal fluids (Machel and Lonnee, 2002; Machel, 2004; Davies and Smith, 2006). The salinity of a fluid might have a minor effect on the rate of dolomitization, by influencing fluid viscosity and density, and can form high angle bed-perpendicular dolomitization fronts through gravity segregation and stratification due to faster dolomitization in the upper, less dense, part of the fluid, (Yapparova et
Mapping the variation of fluid salinity across dolostone bodies through a detailed fluid inclusion study is theoretically possible. However, there is growing evidence that mixing processes between highly saline, deep crustal brines with seawater may be important to the formation of structurally controlled dolostone bodies (e.g. Koeshidayatullah et al., 2020; Stacey et al., 2021), and this might lead to wide spatial variations in fluid salinities that are difficult to disentangle from the replacement dolomitization process.

Reactive transport models of dolomitization have long emphasized the importance of a high fluid Mg/Ca ratio in facilitating dolomitization (e.g. Machel, 2004; Whitaker et al., 2004), implying that a decrease in Mg/Ca will likely terminate dolomitization. Numerical simulations suggest that Mg concentration is lower at the head of the dolomitizing fluid front, supporting the notion that the Mg/Ca ratio of the fluids is critical to the advance of the dolomitization front in 3D space (Yapparo et al., 2017; Benjakul et al., 2020). Koeshidayatullah et al. (2020b) demonstrated a systematic change from stoichiometric to non-stoichiometric dolomite inboard of a lateral dolomitization front, suggesting effective consumption of Mg during the precipitation of dolomite and a decrease in dolomitization potential by the advancing fluid. Dolomitization can only sustained if it is accompanied by the removal of Ca, and an increase in the Ca concentration of dolomite along some dolomitization fronts suggests that dolomitization might also terminate because of a failure to remove Ca as well as a decrease in the concentration of Mg (Morrow, 1982; Merino and Canals, 2011). The preservation of porosity in some halos (e.g. Koeshidayatullah et al., 2020b) suggests that Ca removal can be effective, however, with a net increase in porosity occurring where limestone has been dissolved and Ca is transported away from the dolomitization front.

**Self-organization or -acceleration process** -- The term geochemical self-organization was introduced by Ortoleva et al. (1987) who used it to explain the formation of chemical or textural patterns in minerals or rocks that cannot have been inherited. Self-organization has been invoked to explain the variation of geochemical and petrophysical properties within both low- and high- temperature dolostone bodies, based on a detailed analysis of variance in rock physical and geochemical properties (Budd et al., 2006; Budd and Mathias, 2015). Self-acceleration is a similar process, which describes an exponential increase in the concentration of Ca\(^{2+}\) that leads to precipitation of calcium-rich dolomite at the head of dolomitizing fluid, and a sudden depletion of magnesium concentration at the margin of dolostone bodies (Merino and Canals, 2011). Both self-organization and self-accelerating processes have been extensively invoked to explain the termination of dolostone bodies formed by a variety of processes (Wei and Ortoleva, 1990; Merino and Banerjee, 2008; Merino and Canal, 2011; Kondratiuk et al., 2015; Budd and Mathias, 2015; Yapparova et al., 2017). In particular, in high-temperature, structurally-controlled settings, self-accelerating processes can influence the geometry of bed-
perpendicular dolomitization fronts, leading to the formation of finger or tongue-like morphologies regardless of the presence or distribution of precursor anisotropies (Merino and Canal, 2011; Wei and Ortoleva, 2012; Szymczak and Ladd, 2012). Outcrop-based studies support this notion; Koeshidayatullah et al. (2020b) imparted dynamic self-accelerating and self-limiting dolomitization as a control on the evolution and style of bed-perpendicular dolomitization fronts. However, although self-organization may have an important role in both structurally-controlled dolomitization and the formation of dolomitization fronts, the actual process can be complex in natural settings, in particular for older rocks when they have undergone multiple phases of recrystallization and cementation (Budd and Mathias, 2015).

3. STUDY AREAS AND METHODS

We studied four natural examples of partially dolomitized carbonates across different geological timescales and geodynamic settings: (i) Middle Cambrian, Western Canada; (ii) Carboniferous, UK; (iii) Jurassic, Western Morocco; and (iv) Cretaceous, Spain (Fig. 3) to understand the factors governing the termination of structurally-controlled dolostone bodies. They share similar characteristics, typical of many structurally-controlled dolostone bodies (e.g. Davies and Smith, 2006; Sharp et al., 2010), such as discrete, columnar dolostone bodies, often with tabular components, and an apparent colour contrast with the host limestone. In addition, these locations each had an extensive outcrop, petrographic and geochemical database from prior studies providing information on the tectono-stratigraphic framework, depositional setting, origin of dolomitizing fluids and timing of dolomitization. All the field studies comprised dolomite bodies that formed in extensional basins which subsequently underwent thermal subsidence and orogenesis. Finally, the outcrops in these locations show exceptional occurrence of either abrupt or gradual transition between dolostone and limestone which encompass a range of different styles and dimension of dolomitization fronts.

3.1. Methods

In all study locations, dolostone bodies and their associated dolomitization fronts were mapped, and their distribution was measured in detail, including a description of the shape, size, and style of terminations. The width and thickness of both tabular and columnar dolostone bodies were measured by determining: (i) a reference point, such as fault, from which the width of dolostone bodies could be measured; (ii) the true bedding dip angle in order to have a reliable true vertical thickness of the bodies; and (iii) the width of halo zones (zone of partial replacement of limestone by dolostone) using outcrop measurements with a Jacobs staff and a TruPulse 2000 laser rangefinder for measurement of
inaccessible, steep cliff outcrops. In total, seventy-eight measurements (see Supplementary material) were made. Closely spaced (50 cm) samples were taken vertically and laterally across dolomitization fronts at twelve localities, and prepared as 40 µm thick polished sections for microscopic (transmitted light and cathodoluminescence) analysis.

A systematic dataset from published literature was compiled from studies of structurally controlled dolostone bodies formed throughout the Phanerozoic. From this dataset, dolostone bodies were quantitatively described across a range of time periods (Permian, Triassic, Jurassic, Cretaceous and Eocene) by using outcrop and satellite image photos within the paper (Table 1; see Supplementary material). A total of 34 measurements were added from this analysis including: (i) eight measurements (six tabular and two columnar) from dolostone bodies hosted in Permian carbonates, Oman (Beckert et al., 2015); (ii) seven measurements from four tabular and three columnar bodies from the Triassic, Latemar Platform, Italy (Wilson et al., 1990; Carmichael et al., 2008); (iii) nine measurements from tabular bodies hosted in the Upper Cretaceous carbonate, Spain (Dewit et al., 2012); and (iv) six tabular and three columnar bodies from Eocene-aged carbonates, Egypt (Hirani et al., 2018). Finally, one measurement was added for each of following: Cambrian dolostone, Western Canada (tabular bodies; Yao and Demicco, 1997) and Jurassic dolostone, Lebanon (Nader et al., 2007).

3.2. Study Area 1: Western Canada Sedimentary Basin (Cambrian)

The Western Canada Sedimentary Basin is situated within a region that has experienced a complex tectonic history from the Precambrian (Kubli and Simony, 1994; Lickorish and Simony, 1995) to the Cretaceous (Fig. 3A; Pana et al., 2019). The Western Canada Basin comprises thick sequences of dominantly carbonate rocks overlying regionally extensive basal sandstone aquifers for most of the Palaeozoic to Mesozoic, after which it evolved into a siliciclastic-rich system from the Cretaceous until the Recent (Creaney and Allan, 1990). This study focused on the Middle Cambrian carbonate-mudrock sequences (‘Grand Cycles’) of the Mount Whyte, Cathedral, Stephen and Eldon Formations situated within the Front Ranges of the Canadian Rocky Mountain and bounded by several major thrust faults (Fig. 3A). The Mount Whyte, Cathedral and Eldon Formations share similar lithofacies, being dominated by mudrocks, microbial mudstones and oncoidal grainstone. In addition, they all host large (100s of metre to km – scale) structurally-controlled dolostone bodies with a columnar core and tabular terminations. In the Cathedral and Eldon Formations, hydro-brecciation and zebra dolostone fabrics are more common than in the Mount Whyte Formation. Details of the sedimentological framework and dolomitization processes are provided by Yao and Demicco (1997), Collom et al. (2009), Koeshidayatullah et al. (2020a) and Stacey et al. (2021). Various processes have been invoked to explain dolomitization of the Middle Cambrian strata, including topographical-driven fluid flux (Yao
and Demicco, 1997), structural-controlled hydrothermal dolomitization (Jeary, 2002; Davies and Smith, 2006; Powell et al., 2006; Koeshidayatullah et al., 2020a), and release of overpressured crustal fluids during orogenesis (Vandeginste et al., 2005). Recent studies interpreted the timing of structurally-controlled hydrothermal dolomitization to be Cambrian with dolomitization initiated by seawater that was convected along normal faults during rifting and via an underlying sandstone aquifer, mixed with very hot and highly saline, Mg-rich fluids sourced from an underlying serpentinite by upward flow along faults (Koeshidayatullah et al., 2020a; Stacey et al., 2021).

3.3. Study area 2: Southern Pennine Basin, UK (Carboniferous)

The Pennine Basin was an intracontinental back-arc extensional basin that developed during the Devonian to Mississippian during subduction of the Rheic Ocean (Leeder, 1988); carbonate deposition took place on the footwalls of faults during the Mississippian (Fraser and Gawthorpe, 2003). In the Upper Carboniferous, the basin underwent thermal sag subsidence and then inversion along pre-existing NW-SE Caledonian normal fault systems. The first phase of dolomitization (phase D1) occurred on the margins of carbonate platforms, by the geothermal convection of seawater during the Mississippian – Serpukhovian (Frazer, 2014; Breislin et al., 2020). During basin inversion, fault reactivation led to structurally-controlled dolomitization (phases D2-D5) from hot, saline, basinal brines sourced from the adjacent hanging wall basins (Frazer et al., 2014; Breislin et al., 2020). This study focuses on phases D2 and D3, which occur along NW-SE and N-S trending faults, respectively (Fig. 3B).

3.4. Study area 3: Essaouira-Agadir Basin, Morocco (Jurassic)

The Essaouira-Agadir Basin is situated in the Western High Atlas, Morocco (Broughton and Trepanier, 1993) (Fig. 3C). The Meso- to Cenozoic succession in this basin was deposited on the passive margin formed after Atlantic rifting during the breakup of Pangea (Le Roy and Pique, 2001). Salt tectonics were active during this period (Hafid, 2000; Tari et al., 2013). This study focuses on the differentially dolomitized, open marine carbonate sediments that were deposited during the Lower (Upper Sinemurian – Lower Pleinsbachian) to Late (Oxfordian) Jurassic drift stage. The Lower Jurassic dolostone bodies are either tabular or columnar and petrographically comprise (i) fabric-preserving, porous euhedral dolostone and (ii) fabric-destructive subhedral to anhedral dolostone with an interlocking mosaic (Koeshidayatullah, 2019). Stable isotope, clumped isotope and trace element data indicates that the fabric-preserving dolostone formed from seawater at <50°C and was overprinted by fabric destructive dolomite from hotter, saline brines (~90°C) that had interacted with underlying Triassic evaporites and sandstones prior to dolomitization (Koeshidayatullah et al., 2019; Al Sinawi, 2021).
3.5. Study area 4: Maestrat Basin, Spain (Cretaceous)

The Maestrat Basin is an intraplate extensional basin located in the eastern part of the Iberian Chain (Salas et al. 2001) (Fig. 3D). The basin physiography and major structural elements follow the NW-trending Late Permian-Late Cretaceous Iberian rift basin with two basement fault systems, trending, NE-(Benicàssim) and NW-(Campello) (Fig. 3D). During the Upper Jurassic to Lower Cretaceous, several mini basins were formed, bounded by NW-trending normal faults (Salas et al., 2001). The Maestrat Basin is comprised of thick early Aptian to early Albian (4500 m) syn-rift sediments which are dominated by shallow marine carbonates and subordinate siliciclastic sediments at the very base and top of the sequence (Salas et al., 2001; Martín-Martín et al. 2013). During the Paleogene, the Maestrat Basin was inverted during the Alpine Orogeny, creating a fold-and-thrust belt in the easternmost part of the Iberian Peninsula. Bodies of structurally-controlled dolostone, up to 500 metres wide, are hosted in the Lower Cretaceous (Aptian), syn-rift shallow-marine carbonates of the Benassal Formation in the Benicàssim area (Fig. 3D). A study by Martín-Martín et al. (2015) shows that the dolostone bodies are mostly tabular, except in close proximity to crustal-scale faults where they form columnar bodies. Martín-Martín et al. (2015) interpreted dolomitization to have occurred under shallow burial conditions (500-750 m depth) during the post-rift stage from modified and heated Cretaceous seawater (80-150 °C).

4. RESULTS

4.1. Western Canada Sedimentary Basin (Series 2-Miaolingian, Cambrian)

4.1.1. Geometry and dimension of dolostone bodies

In the Western Canada Basin, the geometry and dimension of dolomite bodies within the Mount Whyte, Cathedral, and Eldon Formations were measured. A total of 36 tabular (n=26) and columnar (n=10) dolostone geobodies and their dolostone-limestone fronts were mapped on a regional scale by measuring body size in outcrop, and their textures examined in detail by logging and petrographical analysis. The detailed measurements of dolostone body and halo zone dimensions are summarized in Table 1. At the basin scale, individual dolostone bodies occur either parallel (tabular) or perpendicular (columnar) to the thrust sheets (Fig. 4A-D). In general, the columnar bodies are associated with normal faults that form perpendicular to the thrust sheet, whereas the tabular bodies occur as a lateral extension of the columnar bodies (Fig. 4A). The largest measured tabular dolostone body is ~6 km wide and ~72 m thick whereas the largest columnar dolostone body is ~82 m thick and ~8 m wide, both determined by laser rangefinder measurement (Table 1). In accessible exposures, the size of tabular dolostone bodies were measured to range from 0.08 to 27 m in thickness and 0.2 to 228 m in...
width (Table 1) whilst columnar bodies range from 1.3 to 22 m thick and 1.1 to 4.6 in width (Table 1). The thickness to width ratio of all the tabular bodies ranges from 0.01 to 0.5 (mean: 0.15). In contrast, the thickness to width ratio of all the columnar bodies shows much larger values, ranging from 0.4 to 11 (mean: 3.28).

4.1.2. Geometry and dimension of dolomitization fronts

Across the three formations, the tabular and columnar dolostone bodies commonly replace, and terminate within, bioturbated mudstone facies (Fig. 4C-D). In particular, the dolostone bodies are bounded by undolomitized, cemented oncoidal grainstone and mudrock beds at the top and base, respectively. From a distance, the transition between both tabular and columnar dolostone bodies into the limestone can be readily identified by the colour contrast between brown dolostone and grey limestone (Fig. 4A-B). At this scale, the dolomitization fronts are both lateral (within beds or bed-perpendicular) and vertical (bed-parallel) for both body types (Fig. 4C-D). Overall, the lateral transition between dolostone and limestone at this largest scale appears as a non-planar, tongue-shaped front for the tabular bodies (Fig. 4A-C). In contrast, the columnar bodies have sharp and planar lateral and vertical dolostone-limestone fronts. On closer observation, in outcrop, the lateral contacts between dolostone and limestone in both tabular and columnar bodies often cross bed-boundaries and occur either as tongue- or finger-shaped fronts with the tongue-shaped fronts usually occurring in a thicker-bedded facies (> 50 cm bed thickness). In contrast, finger-shaped fronts can be observed either in thinly bedded (10-15 cm thick bed) successions or at the edge of tongue-shaped fronts (Fig. 4C and 5A). On close examination, these reaction fronts are diffuse, with thick halo zones (up to 120 cm wide) (Table 1). For both columnar and tabular bodies, vertical contacts are typically non-planar and diffuse with thinner halo zones (up to 15 cm) when bounded by mudrock (Figs. 4D and 5B). In comparison, when bounded by stylolites, shales or pervasively cemented grainstone, morphologies are planar to non-planar with sharp terminations and very thin to no halos (Fig. 5C-D). The transition of dolostone to limestone in thin section (micro-scale) is much more diffuse than in the outcrop for all front types, with small, scattered isolated dolostone rhombs occurring in in the limestone, outboard of the front that was mapped in outcrop (Fig. 5E). This is not visible at hand sample and outcrop scale. Petrographical observation also shows that stylolites that occur at the limestone-dolostone boundary in outcrop formed after dolomitization (Fig. 5F).

4.2. Southern Pennine Basin, UK (Visean, Carboniferous)

4.2.1. Geometry and dimension of dolostone bodies

In this basin, three localities across the Derbyshire Platform were used to map the geometry and measure the dimension of both tabular (n=7) and columnar (n=3) dolostone bodies (Table 1). Five
paragenetic dolostone stages (D1-D5) follow the description of Breislin et al. (2020). Detailed measurements of various dolostone bodies in these localities are summarized in Table 1. At the basin scale, tabular D1 dolostone bodies occur on the southern margin of the carbonate platform, with a diffuse basal termination in Golconda Mine (latitude 53.089, longitude -1.6249) and no visible upper or lateral contacts (columnar and tabular bodies of D1 dolostone also form around E-W trending faults close to the Matlock Volcanic Complex; these were not included in this study as they formed at a low temperature (<50°C) from seawater (Breislin et al., 2020). Columnar dolostone bodies are typically observed along large, crustal-scale, NW-SE and NE-SW trending faults (D2 dolostone); in this study the largest such body was mapped along the Cinderhill Fault zone where it is greater than 8 km in length and 1-2 km in width, with the actual size obscured by Recent sediments (Fig. 3B). In this and other tabular bodies at this location, the thickness-to-width ratio of the dolostone body ranges from 0.01 to 0.38 (mean: 0.23). The smallest bodies were described at Brassington Quarry (locality 2; Fig. 3B) where several narrow, columnar bodies (D3 dolostone) formed along N-S trending faults. In outcrop, several individual tabular terminations to the columnar body that occurs along the Cinderhill Fault were observed at Parsley Hay (locality 1) with dimensions ranging from 5.5 m to 7.2 m wide and 1.2 to 2.3 m thick (Fig. 6A and Table 1). These dolostone bodies have a thickness-to-width ratio of 4.1 to 8.9 (mean: 6.2). Wider dolostone bodies occur in beds with low clay content, where clay-rich limestone is not replaced.

4.2.2. Geometry and dimension of dolomitization fronts

The dolomitization fronts in this study area exhibit a range of geometries. The nature of the outcrop means that dolostone bodies and dolomitization fronts cannot be observed from a distance. In outcrop, the lateral contacts occur as non-planar and diffuse finger-shaped fronts with thick halo zones (up to 52 cm). In contrast, the vertical contacts occur at bedding planes and stylolites and have very thin halo zones (up to 4 cm). At Hoe Grange (locality 3), a tabular termination occurs with some relict undolomitized limestone rafts (Fig. 6B); the exposure is small, but the minimum thickness of the body is estimated to be around 2.2 m and the width is more than 150 m. The vertical contact occurs at a karstified surface, delineated by a solution-pitted surface filled with soft clay (‘clay wayboard’ in local parlance) with no halo zone. Above this surface, the limestone is fine grained and chert rich (Fig. 6B). Here, the lateral contacts are usually non-planar and very sharp with thin halo zones (2.5 to 4.6 cm thick). At the micro-scale, dolostone-limestone fronts are more diffuse than in outcrop, with numerous, scattered dolomite rhombs in the adjacent clay-rich limestone (Fig. 6D-E).
4.3.1. Geometry and dimension of dolostone bodies

The distribution and geometry of various dolostone bodies was examined in two Jurassic carbonate successions in the Essaouira-Agadir Basin (EAB) (Table 1). A partially dolomitized Lower Jurassic (Upper Sinemurian to Lower Pliensbachian) succession was described from the Amsittene anticline, in the north of the EAB (Fig. 7A). Several well-defined tabular dolostone bodies (n=5) are present here, with an overall upward trend towards thicker and wider bodies from 5.2 to 7.1 m and 95 to 214 m, respectively (Fig. 7A). These tabular bodies show a very narrow range of body thickness-to-width ratio, from 0.03 to 0.06 (mean: 0.05). The lateral extent of the lowermost dolostone bodies cannot be clearly determined due to the absence of a distinct colour difference between dolostone and limestone. In these intervals, the halo zones are up to 1 m wide for the lateral contact and up to 50 cm for the vertical contact. In contrast, from the middle to uppermost part of the succession, the geometry and lateral extent of the dolostone bodies can easily be distinguished based on a colour contrast from dark grey to brown dolostone against light grey to white limestone. At two other localities, both tabular (n=6) and columnar (n=4) dolostone bodies were observed in the Upper Jurassic (Oxfordian) at the Tidili and Wintimdouane localities, in the southern part of the EAB (Fig. 7D). In both these locations, fabric-destructive dolomitization occurs along large (10s of kilometre scale) E-W trending strike-slip faults, forming tabular dolostone bodies up to 3 km wide and 120 m thick with tongue-shaped fronts. The geometry and dimension of these dolostone bodies are readily distinguishable from limestone by their colour contrast (brown dolostone and grey limestone). Within them, smaller (metre-scale) dolostone bodies form around normal faults that are several metres in length. The main features of these bodies are that they are highly fractured, have often undergone replacive calcitization and are commonly cross-cut by deep cutting solution pits filled with Oligo-Miocene siltstone and sandstone. Several of these individual tabular dolostone bodies were measured, with their width and thickness ranging from 8.2 to 162 m and 0.8 to 5.6 m, respectively.

4.3.2. Geometry and dimension of dolomitization fronts

In the Sinemurian succession of the Essaouira-Agadir Basin, lateral contacts are planar and very sharp following fracture corridors with no halo zones (Fig. 7B) whilst the vertical contacts are more diffuse and non-planar with halo zones up to 19 cm thick. While the lateral contacts in the middle to uppermost intervals appear very sharp and simple, petrographical analysis suggests that the contact between dolostone and limestone is more complex, diffuse, and non-planar as evident from the presence of scattered dolomite rhombs in the limestone beyond fracture corridors (Fig. 7C). In addition, there are several examples where the dolostone terminated into solution seams and low
permeability mudstone, which can only be observed in thin section (Fig. 7C). The dolostone-limestone transition cannot always be easily mapped in the outcrop due to pervasive fracturing and the presence of deep-cutting, metre-scale solution pits filled by a chaotic matrix-supported breccia with angular clasts along the fracture corridor (Fig. 7B). Where it is seen, the lateral contacts are often very diffuse and non-planar with halo zones up to 27.5 cm thick. In contrast, the vertical contacts are usually sharp and planar with thin halo zones (up to 4 cm), particularly where bounded by shale. The basal contact is usually more diffuse and non-planar with thicker halo zones (up to 12.5 cm) and typically follows a bed of platy corals. In the Oxfordian, the columnar bodies of non-fabric selective dolomite usually show sharp and planar lateral terminations with thin halo zones (up to 4.4 cm). There is no observed vertical contact for these columnar bodies. Finally, there are a few isolated and randomly distributed masses of dolostone (cm- to m-scale bodies) with diffuse, non-planar dolostone-limestone transitions surrounding them (Fig. 7E). At a micro-scale, a diffuse contact occurs when dolomite replaces boundstone and wackestone-packstone facies whilst sharp contacts are seen when dolomite replaces mudstone or where it is bounded by stylolites or fractures (Fig. 7F). Overall, the dolostone-limestone contact in thin section is more diffuse than at outcrop scale.

4.4. Maestrat Basin, Spain (Aptian-Albian, Cretaceous)

4.4.1. Geometry and dimension of dolostone bodies

In the Maestrat Basin, dolostone bodies are hosted in the Upper Cretaceous (Late Aptian-Early Albian) carbonates of the Benassal Formation replacing bioclastic packstone and peloidal grainstone facies (Sequence V; Martín-Martín et al., 2015). A total of 16 individual tabular (n=10) and columnar (n=6) dolostone bodies were measured (Table 1). These bodies commonly extend for up to 7 km away from the NW-SE trending Campello Fault and for up to 2 km from the NNE-SSW Benicàssim faults at Racó del Moro with an overall thickness of 150 m (Fig. 3D; Martín-Martín et al., 2015). At this scale, the columnar bodies are around 150 m thick and 14 m wide, typically occurring adjacent to the two major extensional faults (Fig. 3D). Overall, the dimension of these columnar bodies ranges from 30 to 150 m in width and 14 to 25 m in thickness. The average thickness to width ratio of these columnar bodies is 5.6 (1.7 to 10.7). Furthermore, km-wide tabular dolostone bodies are associated with these columnar bodies, extending away from the major faults, at the basin- and outcrop-scale (Fig. 8A-B). Several tabular dolostone bodies can be observed in outcrop at the Racó del Moro and Ferradura localities (Fig. 8C). In general, the tabular bodies are bounded by fine-grained micritic limestones and are pervasively cemented ooidal grainstone in the lower and upper part of the section, respectively. The body dimension ranges from 3.5 to 500 m wide to 0.5 to 25 m thick. The average thickness to width ratio of these tabular bodies is 0.09 (0.02 to 0.25).
4.4.2. Geometry and dimension of dolomitization fronts

In the Cretaceous strata of the Maestrat Basin, dolostone-limestone transitions in the tabular bodies form non-planar, tongue-shaped fronts, and either planar or non-planar fronts with a complex shape for the columnar bodies at both basin and outcrop scales. Non-planar lateral contacts are usually encountered in packstone-grainstone facies whilst mudstone facies exhibit planar contacts (Fig. 8B). These observations are revealed by the distinct colour contrast between brown dolostone bodies and grey limestone in the satellite images (i.e. at a basin scale) and outcrop (Fig. 8A-B). At Ferradura and Rocco del Moro, the vertical contact between tabular dolostone bodies and limestone is typically sharp and non-planar, occurring along bed-parallel stylolites (halos thickness up to 3.5 cm) although these stylolites formed both during and after dolomitization (Martín-Martín et al., 2018; Fig. 8D). In some instances, the vertical contact is less sharp and more planar, with halo zones of varying width, where it formed against low permeability limestone facies, such as mudstone or wackestone or pervasively cemented grainstone (up to 11 cm thick). In contrast, at the outcrop scale, lateral contacts often exhibit thick halo zones (up to 44.5 cm) with tongue-shaped fronts in thicker beds and finger-shaped reaction fronts with a diffuse boundary in thinly bedded succession. Overall, the dolostone bodies are generally thinner and narrower in the upper section compared to the lower sections. The reaction fronts of these bodies are typically non-planar with a complex geometry, and no observed halo zones.

4.5. Comparison across the stratigraphic record

The data described above was combined with the data extracted from the literature. Although the presence and thickness of halo zones associated with dolomitization in these published studies was not documented, we can still map the geometry and measure the dimension of dolostone bodies (Fig. 9A) while simultaneously describing the variation in dolomitization front styles. The compilation of data shows a strong positive (power-law) correlation between width and thickness of both tabular \( r^2=0.78 \) and columnar bodies \( r^2=0.77 \) (Fig. 9B). However, the overall relationship between width and thickness of these two types of dolostone bodies are different, following these equations (Fig. 9B):

\[ y = 11.4x^{1.034} \quad (1) \ \text{(Tabular Bodies)} \]
\[ y = 0.84x^{0.697} \quad (2) \ \text{(Columnar Bodies)} \]

where \( y \) is the width of dolostone bodies and \( x \) represents the thickness of dolostone bodies. The implication of this relationship is that in tabular bodies the width is always greater than the thickness (by factor of 10 or larger), whereas in the columnar bodies the width is always narrower than the
thickness (up to 12 times smaller). Furthermore, the thickness to width ratio of tabular dolostone bodies rarely exceeds 0.5 (0.01 to 0.62, mean: 0.14) while in the columnar bodies the ratio shows a wide range (0.15 to 27.4, mean: 5.3). Overall, the dimension and thickness-to-width ratio of tabular and columnar dolostone bodies are independent of both geological time period and geodynamic setting (Fig. 10A-B). In addition, the thickness to width ratio of columnar bodies is consistently larger than the tabular bodies (Fig. 10C).

From the outcrop data collected in this study, there are several clear relationships between the halo zone thickness and the style of dolomitization fronts, and between the thickness of halo zones and the width/thickness of the dolostone bodies (Figs. 11 A-D; see Supplementary material). In particular, the presence of tongue-shaped fronts is typically observed in wider and thicker dolostone bodies whereas in the thinner bodies, the finger-shaped fronts are more common (Fig. 11A-B; see Supplementary material). Furthermore, the thickness of halo zones at the vertical contact is strongly governed by the type of bounding lithofacies and planes (Fig. 11C-D; see Supplementary material).

Dolostone bodies bounded by low permeability carbonate facies tend to have more diffuse and thicker halo zones than those bounded by low permeability, non-carbonate facies. Furthermore, thicker, and wider, dolostone bodies are mostly bounded by low-permeability carbonate facies either in the upper or lower part, or both (Fig. 11C-D; see Supplementary material).

5. DISCUSSION

5.1. New Morphological Classification of Dolomitization Fronts

Dolomitization fronts associated with structurally-controlled dolostone bodies have been widely described across different scales and throughout the geological record (Wilson et al., 1990; Yao and Demicco, 1997; Davies and Smith, 2006; Nader et al., 2007; Sharp et al., 2010; Beckert et al., 2015; Martín-Martín et al., 2015; Rustichelli et al., 2017; Hirani et al., 2018; Koeshidayatullah et al., 2020b).

In this study, we have established that it is common to have several different types of dolomitization fronts in a single outcrop, field location or time period, although there are distinct patterns in the geometry and styles of dolomitization fronts across different scales. To date, no systematic classification has been proposed to describe the geometry and styles of dolomitization fronts. We therefore present a morphological classification system to unify the description of dolomitization fronts in structurally-controlled dolostone bodies and to facilitate systematic description and comparison between study areas. This will provide a framework in which to determine the controls on the termination of dolostone bodies and assess whether the geometry...
of dolostone bodies and dolomitization fronts can constrain the paragenesis of dolomitization processes.

Unifying the observations and measurements made in this study with data from other published studies, we propose that the style and geometry of dolomitization fronts can be classified into three major groups (Fig. 12 and Table 2): (i) vertical transitions from dolostone to limestone (broadly bed-parallel dolomitization fronts, recognizing that they can be bed-transgressive); (ii) lateral dolostone-limestone transitions (bed-perpendicular dolomitization fronts); and (iii) complex-shaped dolomitization fronts. In addition, there are, at least, three different contacts associated with the formation of dolomitization fronts and halo zones: (i) contact with no permeability barrier (e.g., homogenous carbonate or non-carbonate lithofacies); (ii) contact with reactive and non-permeable barrier (e.g., calcite or dolomite filling fractures); and (iii) contact with non-reactive and non-permeable barrier (e.g., mudrock, unfilled stylolite or fracture, or fracture-filled sulphide mineralization). Furthermore, a range of potential controls on the formation and geometry of dolostone bodies, and dolomitization fronts, are evaluated here.

5.1.1. Bed-parallel dolomitization fronts

Bed-parallel dolomitization fronts describe the vertical interface between dolostone bodies and either the upper or lower bounding beds, which can include both carbonate and non-carbonate rocks (Fig. 12). This type of reaction front is found at all scales and is typically concordant with stratigraphic architecture; dolomitization might be bed transgressive but dolomitization fronts are broadly parallel to bedding. Overall, this group can be subdivided into four sub-types of reaction front based on their geometry and contact characteristics (Fig. 12 and Table 2): (i) termination at facies with a presumed lower-permeability than the precursor limestone in the dolomitized layers (carbonate and non-carbonate lithofacies); (ii) discontinuity surfaces defined by low permeability clay-rich layers or low-permeability (cemented) layers such as omission surfaces; (iii) non-permeable (i.e. cemented) bed-parallel fractures; (iv) non-permeable bed-parallel pressure solution seams (i.e. stylolites).

i. Fronts formed at a contact with lower permeability bounding beds are observed in all field locations and reported in many studies (e.g., Wilson et al., 1990; Sharp et al., 2010; Beckert et al., 2015; Dong et al., 2017). The presence of such reaction fronts is often related to the occurrence of fine-grained lithofacies (lime mudstone), well-cemented carbonate facies (e.g. limestone that had undergone porosity occlusion by mineral precipitation prior to dolomitization), and ultra-low permeability non-carbonate facies (mudrock (shale), metamorphic, and igneous rocks) (Fig. 12). Two different styles are observed in this type, (a) sharp and planar bed-parallel fronts with thin halo zones when the dolostone bodies are
bounded by low permeability non-carbonate rocks (e.g., shale or metamorphic rocks; Fig. 5D-692
Cambrian example and Permian example in Beckert et al., 2015); and (b) sharp and non-planar
bed parallel fronts with thicker halo zones when the bounding beds are composed of low
permeability carbonate facies (e.g., lime mudstone or well-cemented grainstone facies).

ii. Low permeability layers associated with discontinuity surfaces were observed solely in the
Carboniferous, UK, where they were usually sharp and planar with no or very thin halo zones
(Fig. 6B). In this case, the presence of clay along the karst surface is likely to have prevented
the vertical migration of dolomitizing fluids by significantly reducing the permeability of the
karst surface (Fig. 12). Such contacts may be more widespread in the geological record
considering the close relationship between dolomitization and karstic surfaces (Rhodes et al.,
1984; Beckert et al., 2016) or sequence boundaries (Taghavi et al., 2006; Sharp et al., 2010).

iii. Fronts associated with bedding-parallel fracture planes can be observed in the Cambrian,
WCSB (Fig. 5C) and Cretaceous, Iran (Sharp et al. 2010) with a typically sharp and planar
dolomitization front and thin to absent halo zones (cm-scale; see Supplementary material),
depending on the types of filling material of these fractures. If the fractures are partially to
completely healed, they might have created anisotropy and behaved as a barrier, preventing
the flux of dolomitizing fluids across the adjacent beds, driving fluids laterally. Alternatively, if
they were dilatant, the fractures could have acted as a conduit for the lateral flow of
diagenetic fluids along the fracture planes, inhibiting the progression of the dolomitization
front vertically.

iv. Stylolite-bounded fronts have non-planar boundaries with variable thicknesses of halo zones.
Stylolite-bounded fronts occur when the formation of low-permeable stylolites predates
dolomitization. Such stylolites can be observed both in outcrop (macro-scale) and thin section
(micro-scale) at all study locations (e.g. Cambrian, WCSB, Fig. 5F; Cretaceous, Spain, Fig. 8D).
Where the stylolites are unfilled by cements, they are typically not associated with halo zones,
suggesting a sudden termination of dolomitization (e.g. Figs. 5B and F). However, thin halo
zones do occur when the stylolite is cemented by reactive minerals, such as dolomite and
calcite (Fig. 8D), implying that it became dilatant and a pathway for fluids.

The thickness of halo zones associated with bed parallel dolomitization fronts has no direct
relationship with the width and thickness of dolostone bodies, and can be up to 5 orders of magnitude
thinner than the dolostone bodies (Fig. 11C-D; see Supplementary material). Furthermore, the actual
style of dolomitization fronts (planar and non-planar) appears to depend on the geometry and
reactivity of the bounding surfaces (Figs. 5F, 7B, and 7F). Overall, the zones are thicker when the
contacts form against low permeability carbonate rocks and minerals than for contacts against non-
carbonate rocks and minerals (Fig. 11C-D; see Supplementary material). This suggests that the formation of a halo zone, indicative of a gradual termination of dolomitization, is strongly controlled by the reactivity of the barrier, with carbonate barriers allowing the residual dolomitizing fluid to react longer with the adjacent limestone than where the barrier is not formed of carbonate minerals. This observation is in a good agreement with a micro-scale numerical simulation on the development of dolomitization fronts based on the mineral reactivity in the barrier zones (Beaudoin et al., 2014).

While the thickness of the low permeability beds at dolostone-limestone contacts can vary, they are often considerably thinner than the dolostone bodies themselves (Figs. 6B and 8D; see Supplementary material), suggesting that bed-parallel fronts form as a result of permeability contrast than a change in actual rock permeability. This is consistent with simulation of fluid flow in sedimentary strata, which indicates permeability contrast and connectivity of permeable bodies is more important to effective permeability than actual permeability values (Jackson et al., 2005); in other words, dolomitizing fluids will be unable to move across a low permeability strata into the next bed and will therefore be preferentially channelled beneath it, even if it is very thin (<<1 meter). Such contacts typically have a sharp boundary in both outcrop and thin section with no to very thin halo zones. In combination, this suggests that dolomitization will stop rapidly where there is even a thin barrier or baffle to flow, and reactive fluids will be driven laterally beneath the barrier where they may continue to react.

5.1.2. Bed-perpendicular dolomitization fronts

Bed-perpendicular dolomitization fronts form perpendicular to bedding, within a single bed or crosscutting strata, and define the lateral termination of dolostone bodies. They are commonly, but not always, formed where there is no distinct lateral barrier to fluid flow (Fig. 12). This type of reaction front is the most commonly observed throughout the rock record, and was identified across the four study locations and in numerous examples in the literature. Bed-perpendicular fronts are scale-independent and have a range of geometries that can be categorized into (i) tongue-shaped, (ii) finger-shaped and (iii) fracture-bound (Fig. 12 and Table 2).

i. Tongue- and finger-shaped reaction fronts are often associated with tabular dolostone bodies and usually occur at a metre-scale (Table 1; see Supplementary material). They are present in all study areas and both display non-planar boundaries, typically with thick halo zones (up to 1 m wide) (Fig. 12) (e.g. Cambrian, West Canada, Fig. 5A; Carboniferous, UK, Fig. 6C; Jurassic, Morocco, Fig. 7E; Cretaceous, Spain, Fig. 8A; Triassic, Italy , Carmichael et al., 2008). In general, finger-shaped fronts are present where bedding planes and heterogeneous rock physical properties within beds are well pronounced, whereas tongue-shaped fronts occur when the bedding is thick or massive, in relatively homogenous strata. Although in some
instances these types can be readily distinguished, differentiation between the tongue- and finger-shaped fronts can be problematic because they can occur at the same place/position and overlap with each other. In particular, finger-shape fronts can occur at the margin or edge of tongue-shaped fronts when the host rocks are very heterogeneous (Fig. 5A). Such complexity has been numerically simulated to occur where there is a physical and chemical instability at the margin of reaction fronts, for example due to creation of porosity through dissolution (e.g., Wei and Ortoleva, 1990).

ii. Fracture-bound dolomitization fronts occur where the dolostone-limestone contact occurs against vertical or high-angle fractures or fracture corridors, which may be open or cemented (e.g. Figs. 7B and D). Typically, they show a sharp and planar boundary with a thin halo zone (up to 5 cm). This type of front may occur because (i) the fractures were not dilatant and so they inhibited lateral fluid flux; (ii) fractures were dilatant and so fluxed fluids vertically, instead of laterally; (iii) the fractures are deformation bands or healed by minerals that have a low permeability or (iv) there is a high shale-gouge ratio or clay smear that severely reduced the fracture permeability prior to dolomitization. The halo zones developed within fracture-bound fronts do not show any clear pattern with the dimension of dolostone bodies. In this type of front, it is important to determine the relative timing between dolomitization and formation of fractures in order to understand the controlling process behind the termination of dolostone bodies. For example, the Lower Jurassic dolostone bodies in the EAB basin, Morocco, appear to terminate laterally into fracture corridors based on field observations. However, petrographical analysis demonstrates that dolomitization took place before the formation of fracture corridors, evident from the presence of dolomite rhombs in the limestone outboard of the dolostone body and the fracture corridor. Here, it is evident that unravelling whether the faults/fractures were either a pathway or fluid barrier requires accurate interpretation of cross-cutting relationship between fractures and dolomitization processes from detailed petrographic examination and field observation.

Consequently, where dolostone-limestone fronts form at fractures, rapid termination of dolomitization is implied by the sharp, planar boundaries and thin or absent halo zones. In the same way as for bed-parallel fronts, dolomitizing fluids might have been redirected or vented. When there is no apparent rock physical anisotropy, or barriers to fluid migration, the formation of bed-perpendicular dolomitization fronts must be related to changes in the physio-chemical properties of the fluid and reaction kinetics. High-resolution mineralogical and geochemical analyses across dolostone bodies and dolomitization fronts in the Middle Cambrian, West Canada (Koeshidayatullah et al., 2020a) and Jurassic, Morocco (Koeshidayatullah, 2019) showed similar trends in magnesium
depletion and decrease in crystallization temperature at the dolostone-limestone transition. In particular, non-stoichiometric, calcium-rich (poorly ordered), dolomite formed at lower temperatures at the dolostone-limestone transition, and within halo zones, compared with stoichiometric (well-ordered), and hotter paleo-temperatures in dolomite in the core of the associated dolostone geobodies. Similar trends of decreasing dolomite stoichiometry and temperature were noted by Wilson et al. (1990) and Nader et al. (2007) whilst Hirani et al. (2018) showed that dolomite rhombs outboard of the dolostone-limestone contact in outcrop were zoned, planar, and consequently less mature, than within the core of the columnar dolostone body inboard of the reaction front.

Yapparova et al. (2017) proposed that bed-perpendicular dolomitization fronts are sharper when they are formed from higher temperature fluids. Field observations are largely consistent with this, since the bed-perpendicular dolomitization fronts in the Cambrian, Western Canada (100 to 230°C; Koeshidayatullah et al., 2020b) are typically sharper and more abrupt than observed in the Jurassic, Morocco (50 to 70°C; Koeshidayatullah, 2019) (Figs. 5E, 6D, 7C and 7E). However, the situation in natural outcrops is made complex by recrystallization of dolomite during subsequent fluid flux. For example, in the Cambrian of Western Canada, Koeshidayatullah et al., 2020b showed that the reaction front had back-stepped through time and that the dolostone-limestone contact observed in outcrop was a relic of the first phase of dolomitization. In addition, fluid temperatures are always >50°C, at which point the rate of dolomitization increases exponentially (e.g. Arvidson and MacKenzie, 1999), suggesting that cooling alone is insufficient to terminate dolomitization in structurally controlled dolostone bodies. Besides temperature, simulations also show how both fluid pressure and pressure gradient play a significant role in governing the dimension and morphology of fingered-reaction fronts, with the thickness, width, and morphology of dolostone bodies and their reaction fronts controlled by rapid pressure dissipation during the release of overpressurized hydrothermal fluids into a low-pressure environment (e.g., Szymczak and Ladd, 2012; Yapparova et al., 2017). Since overpressure is thought to have driven hydrobrecciation in the Cathedral Formation (Stacey et al., 2021) and also the formation of phases D2-D5 on the Derbyshire Platform (Frazer et al., 2014; Breislin et al., 2020), the importance of pressure release of front geometry should not be overlooked.

Detailed analysis of younger, low temperature dolomitization fronts (Budd et al., 2006; Budd and Mathias, 2015) and modelling (Merino and Canals, 2011) has invoked termination of dolomitization as an outcome of a self-organizational, and self-accelerating, processes. Such mechanisms explain why a dolostone-limestone front forms, for example as the result of a decrease in the Mg/Ca ratio of the dolomitizing fluid. This can lead to a decrease in dolomite stoichiometry and ordering at reaction fronts with no accompanying evidence for a sudden decrease in temperature or other fluid properties, such as salinity. Importantly, perhaps, thicker halo zones are often associated with tongue-shaped
fronts and tongue-shaped fronts are more common in thicker and wider dolostone bodies (Fig. 11A-B). Such phenomena are interpreted to be associated with the absence of distinct rock physical changes, and a more homogenous precursor texture, such that the termination of dolomitization was more gradual, creating tongue-shaped fronts with a gradual transition to limestone through the halo zone. Conversely, where there is greater anisotropy in the precursor limestone, for example, where beds are thinner, fronts are more fingered suggesting an irregular progression of the front along the higher permeability beds. In these cases, halo zones are thinner (Fig. 11A-B), suggesting a more rapid termination of dolomitization. In summary, the formation of fingered-reaction fronts and dolostone tongues at outcrop scale suggest a complex interplay between intrinsic host rock properties, temperature-pressure variation, and self-organization processes.

5.1.3. Complex-shaped dolomitization fronts

Complex-shaped dolomitization fronts describe a discontinuous, shapeless boundary between dolostone and limestone such that, for example, rafts of limestone are preserved within the dolostone (Fig. 12). Although this type of front is much less common than bed-parallel and -perpendicular fronts, it was observed in all study areas across different scales. In addition, complex fronts are more commonly associated with columnar dolostone bodies than tabular bodies (Figs. 5B, 6C, 7E and 8C). It is suggested that the formation of complex-shaped dolomitization fronts can be formed where either:

a) dolomitization is heterogeneous due to the presence of precursor template for preferential dolomitization, such as the presence of dolostone within burrows in mudstones (e.g. Cambrian, WCSB; Fig. 4D; Koeshidayatullah et al., 2020a). This can be important to the initiation of dolomitization by providing nucleation points (‘seeds’) by microbial mediation of dolomitization in burrows (Corlett and Jones, 2012; Gingras et al., 2012), from which anisotropic dolomitization progresses. Similarly, the presence of skeletal grains that were originally composed of high magnesium calcite or aragonite might create a complex template for dolomitization that could influence the geometry of reaction fronts. For example, complex reaction fronts were observed in Morocco where there are platy corals, originally composed of high Mg-calcite, and these grains as well as burrows were preferentially dolomitized (Fig. 7E).

b) Inhibition of dolomitization due to pre-existing anisotropy, for example where nodular, low permeability limestone remains un-dolomitized (e.g., Fig. 7E). Such limestone rafts might only be observed at the distal part of dolostone bodies, at the point where the dolomitizing potential of fluids was decreasing.
Finally, care should be taken to ensure that post-dolomitization events are considered. For example, in the Oxfordian strata of the EAB, complex-shaped fronts within the core of small fronts form as a result of partial dedolomitization, such that dolostone bodies appear to be isolated within limestone but in fact represent relics of the precursor dolostone (Fig. 6A).

From field observations, therefore, the formation of complex-shaped reaction fronts is related to facies heterogeneity. However, the extent to which intrinsic rock properties can control the morphology of dolomitization fronts can be difficult to unravel in natural settings, as it is not possible to directly observe the original properties of host rocks prior to dolomitization. Nevertheless, inferences can be made from the properties of the adjacent limestone at bed-perpendicular dolostone-limestone contacts. For example, in the Middle Cambrian, WCSB, dolostone bodies exhibit sharp dolomitization fronts where dolomitization occurred within a bioturbated mudstone, beneath an undolomitized, cemented oncoidal grainstone. Similarly, examples from the Jurassic, Morocco and Cretaceous, Spain, show a more diffuse and lower angle reaction front where the dolostone bodies replaced porous, ooidal grainstone (Figs. 7 and 8). The thickness of halo zones related to this front type are random and show no clear relationship with the dimension of the associated dolostone bodies. In all cases, detailed petrographical analysis is required to ensure that the relative timing of dolomitization, recrystallization and dedolomization is accounted for.

5.2. Implications

Dolomitization typically occurs in multiple phases and this multi-stage process is also responsible for the formation of dolomitization fronts. In particular, the spatio-temporal evolution of dolomitization processes, the source and direction of dolomitizing fluid flow at various scales, the fluid flow pathways and the paleotectonic history can be discerned from the geometry of dolostone bodies and their corresponding dolomitization fronts (Wilson et al., 1990; Nader et al., 2007; Hirani et al., 2018; Koeshidayatullah et al., 2020b). In the formation and evolution of dolomitization fronts, many studies assume that dolomitization fronts advance through time and terminate only once fluid supply is terminated or Mg/Ca ratio decreases beneath a critical value (e.g. Wilson et al., 1990; Wendte, 2006; Merino and Canals, 2011). This concept implies that dolomitization fronts would represent the youngest phase of dolomitization. This model, however, requires the dolostone to remain porous and permeable in the core of the body, which contradicts field observations that more porous dolostone is often observed at the reaction front (Wilson et al., 2007; Sharp et al., 2010; Koeshidayatullah et al., 2020). Koeshidayatullah et al. (2020b) suggested that this pattern of higher porosity and permeability at the reaction front provides evidence for retreat of the dolomitization fronts and implies that the observed dolomitization front is the oldest phase of dolomitization and therefore provides a window
into the formation of the fault-controlled dolostone body. Several studies have reported the presence of narrower paragenetically older bodies than younger bodies (Nader et al., 2007; Sharp et al., 2010; Hollis et al., 2017) and retreating reaction fronts are also observed in the crystal-scale experiment on solid-phase transformation from calcite to Mg-carbonate (et al., 2015; Müller and Krüse, 2017). This suggests that dolomitization fronts can, in some cases, provide a relic of the earliest stages of dolomitization, providing a window into the progression of dolomitization through time.

Our field observations show the importance of dolomitization front styles (bed-parallel and -perpendicular) on the distribution and variation of rock physical properties in differentially dolomitized carbonate platforms. In hydrocarbon reservoirs, reaction fronts are thought to have two opposite effects on petroleum migration pathways and reservoir quality. Dolomitization fronts can act as a diagenetic trap or seal if they are cemented, hence reducing porosity, or they might be porous, perhaps facilitating seal breach (e.g. Broomhall and Allan, 1987). Perhaps more importantly, dolomitization fronts can coincide with high permeability layers forming zones of preferential sweep and early water breakthrough during hydrocarbon production (e.g. Broomhall and Allan, 1987; Swart et al., 2005 Amel et al., 2015; Jafarian et al., 2017). Such an observation can be explained by the presence of a high porosity halo zone at the dolostone-limestone transition. Koeshidayatullah et al. (2020b) have shown that halo zones are one of the most porous intervals in structurally-controlled dolomitization dolostone bodies due to enhanced dissolution of calcite. This observation is further supported by three-dimensional numerical simulations where the dolostone “sweet spots” are situated proximal to the dolomitization fronts (Xiao and Jones, 2007).

Furthermore, the close relationship between dolomitization fronts and structural barriers (fractures or stylolites) suggest that the formation of dolomitization fronts may show differences in rock strength, and hence fracturing, across reaction fronts. For example, in the Cambrian of Western Canada (Koeshidayatullah et al., 2020a) and Upper Cretaceous of the Maestrat Basin (Figs. 5B, 5F and Fig. 8D), stylolites formed after dolomitization, perhaps because stress became concentrated at dolostone-limestone contacts. Similarly, dolomitization within Lower Jurassic limestone in the EAB appears to terminate at a fracture corridor, but petrographical observation shows that fracturing was focused at the dolostone-limestone boundary (Koeshidayatullah, 2019); i.e. fracturing post-dated dolomitization and was perhaps defined by the difference in rock strength between the two rock types. This is important in studies of partially dolomitized strata in the subsurface because zones of structural deformation at reaction fronts might facilitate fluid flow, and thereby create anisotropy that in hydrocarbon reservoirs that could lead to bypassing of matrix porosity and potential shortcutting of injected fluids during production.
The solid-phase transformation from calcite to dolomite is transport controlled, and dolomitization kinetics, reactive surface area, and porosity-permeability have thought to play an important role in controlling the geometry and propagation rates of dolomitization fronts in high temperature, structurally-controlled dolomitization system (Jonas et al., 2015; Yapparova et al., 2017; Koeshidayatullah et al., 2020b). Several studies have reported the close association between Mississippi Valley-type (MVT) mineralization (Pb-Zn-Ba) and dolomitization fronts (e.g. Harper and Borrok, 2007). In contrast, several examples from the Canadian Rockies (Kicking Horse Rim and Pine Point) show the mineralization is observed away from the reaction fronts and associated with latest phase of dolomitization (Powell et al., 2006). This phenomenon can be explained by the concept of retreating fronts introduced by Koeshidayatullah et al. (2020b) where the later phases of fluid flow would move closer to the fault or fluid source instead of extending away and becomes more saturated with secondary minerals. Wigley et al. (2012) indicate mobilization and preferential precipitation of trace metals, carbonates, and haematite at the reaction fronts through rock-fluid interactions during the charge of low pH, CO$_2$-bearing fluids into a formation. Such a process is interpreted to be induced by the presence of gradients in fluid chemistry, which significantly increases the saturation indices of certain secondary minerals at the reaction front (Merino and Canals, 2011; Wigley et al., 2012), but it has also been suggested that there is a preferential concentration of trace metals or ore minerals at reaction fronts, formed by the migration of dolomitization fronts through a self-cannibalization process (Merino and Canals, 2011). Regardless of the mechanisms, it is clear that marked changes in rock chemical properties occur at reaction fronts, including dolomitization fronts that can exert a strong control on mineral distribution.

Dolomitization fronts can also provide us with important information about how reactions proceed in carbonate strata. Numerical simulations have shown that rock-fluid interactions during sequestration of CO$_2$- can be transport-controlled (Kampman et al., 2014). During in-situ CO$_2$ sequestration into chemically reactive and permeable rocks, including carbonate and ultramafic rocks, one of the main concerns is how dissolution-precipitation in the host reservoir progresses and how reaction fronts develop (e.g., Wigley et al., 2012; Kampman et al., 2014; Ulven et al., 2014). In detail, the geometry of reaction fronts formed during CO$_2$ sequestration is thought to be controlled by kinetic rate constants and mineral reactive surface areas whilst their rate of propagation is governed by the rates of CO$_2$ dissolution, fluid flow, and the evolution of rock petrophysical properties (e.g., porosity and permeability) (Kampman et al., 2014). Reactions during CO$_2$ injection are associated with changes in the rock physical properties induced by the formation of chemical reaction fronts during precipitation-dissolution processes and numerical simulation has shown that the formation of fractures and types of fracture in CO$_2$ reservoirs is closely controlled by the magnitude of volume increase in rocks and
sharpness of reaction fronts (Ulven et al., 2014). Recent studies have shown that the fluids related to structurally-controlled dolomitization may be enriched in CO$_2$ (e.g., Robertson et al., 2019; Koeshidayatullah et al., 2020a), which means understanding the formation of dolomitization fronts could help to predict the physiochemical reactions that may take place in situ during sequestration of CO$_2$. However, there will be differences in reactivity; for example, reaction fronts formed by CO$_2$-injection can propagate into low permeable rocks (e.g., shale) because it has similar capillary properties and CO$_2$ can flow through diffusion, while dolomitization is typically associated with advection (Carey and Lichtner, 2011).

Overall, a systematic and detailed characterization of dolomitization fronts can help us to understand the physiochemical processes during fluid-rock interactions and to predict the distribution and variation of rock physical changes in a formation. In such cases, there are several key observations: (i) enhanced porosity-permeability, intense fracturing, and high concentration of ore minerals are often associated with dolomitization fronts, away from faults/fluid source and (ii) zones closer to the fluid source are typically characterized by significantly lower porosity and permeability due to multiphase recrystallization events that result in increased cementation and occlusion of pore space. Additionally, bed-perpendicular dolomitization fronts (e.g., tongue- and finger-shaped fronts) are characterized by thick halo zones with enhanced porosity and permeability when compared with other type fronts. Finally, the porosity enhancement and fracturing processes associated with structurally-controlled dolomitization process may have negative impact in hydrocarbon exploration or long-term gas storage, such as caprock or seal breach.

6. CONCLUSIONS

- Dolomitization fronts are commonly clearly visible in outcrops of structurally-controlled dolostone bodies and can occur at multiple scales and styles, independent from the geodynamic settings and timescales. Overall, dolomitization fronts often appear simplistic at the largest (basin) scale but can be complex at the centimetre to metre scale. Therefore, multiscale investigations, including petrographical analysis, is required to comprehensively describe the morphology of dolomitization fronts, and the relative timing of diagenetic events.

- Statistical comparison of structurally controlled dolostone bodies across stratigraphic records indicates that the relationships between the thickness and width of the tabular and columnar bodies are not random, but instead following strong, positive power-law correlations. Although both dolostone bodies have a similar positive thickness to width correlation, the
width of tabular bodies is always greater than their thickness (by factor of 10 or larger) while
the width of columnar bodies is always narrower than their thickness (up to 12 times smaller).

- Despite the complexities, the occurrence and style of dolomitization fronts in structurally
controlled dolostone bodies follows certain patterns and trends across geological timescales.
Therefore, a standardized framework to describe and interpret the origin and styles of
dolomitization fronts is proposed. This morphological classification defines: (i) bed-
perpendicular fronts which represent lateral contact between dolostone and limestone (ii)
bed-parallel fronts which represent vertical interfaces between dolostone and limestone; and
(iii) complex-shaped fronts at the distal part of dolostone bodies which are often shapeless.
For all front types, a halo zone, defined as a zone of partial dolomitization, may form on the
margins of the front and can be up to several metres wide/thick.

- Halo zones are thin or absent where bed parallel and bed perpendicular dolomitization fronts
coincide with a zone of permeability contrast, usually a low permeability baffle or barrier. This
suggests a rapid termination of dolomitization at these contacts, and perhaps re-routing of
the reactive fluid along, or parallel to, the discontinuity. Where halo zones are seen, they are
usually developed where the barrier is reactive – e.g. where carbonate minerals fill the
fracture or stylolite.

- Laterally continuous depositional, diagenetic, or structural fluid barriers, creating a significant
permeability contrast between or within beds play a significant role in the formation of bed-
parallel dolomitization fronts. In contrast, the bed-perpendicular fronts are often associated
with the absence of distinct fluid barriers and are primarily governed by the interplay between
intrinsic properties of the host rocks, potential of dolomitizing fluids, and self-organization
process. Combinations of original lithological composition and changes in fluid kinetics have
an important role during the genesis of complex-shaped fronts.

- The thickness of halo zones is widest in bed-perpendicular dolomitization fronts within tabular
dolostone bodies where dolomitization terminates within beds without evidence of
permeability contrast. In these beds, halo zone thickness shows a positive correlation with
the width and thickness of the tabular dolostone body. Where there is high vertical
heterogeneity, e.g. interbedded high and low permeability limestone, dolomitization fronts
tend to be fingered with thin halo zones. In contrast, thicker, more isotropic beds have wide
halo zones, suggesting that dolomitization terminated as a result of a decrease in the
dolomitization potential of the fluid.

- In structurally-controlled dolomitization systems, the presence of dolomitization fronts could
reveal important information that are otherwise difficult to unravel when the dolomitization
front is absent, such as recrystallization history, evolution of the fluid composition during
dolomitization and subsurface fluid flow pathways. Furthermore, understanding the origin
and styles of dolomitization fronts could improve our characterization of physiochemical
processes in hydrocarbon reservoirs and carbon capture sequestration.

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Figure 1. Map showing the distribution of the four study areas (World map is obtained from NASA/Goddard Space Flight Centre Scientific Visualization Studio). Additional information such as the study focus, geodynamic setting and evolution, and overall dolomitization processes are also highlighted here.
Figure 2. A schematic diagram showing various termination styles of structurally-controlled dolostone bodies laterally and vertically. It is important to note that the term dolomitization front has always been used ambiguously in previous work.
Figure 3. Geological map of different study areas. Western Canada Sedimentary Basin, the map shows the different outcrop locations (yellow arrow: 1: Whirlpool Point, 2: Saskatchewan river crossing, 3: Icefield parkway, 4: Bow lake). (B) Derbyshire Platform, Southern Pennine Basin, UK, studied outcrops are marked by yellow stars (1: Parsley Hay, 2: Brassington Quarry, 3: Hoe Grange). (C) Essaouira-Agadir Basin, Western High Atlas, Morocco. Here, three outcrop locations were investigated, one in Liassic (red star) and two for Oxfordian (yellow stars). (D) Maestrat Basin, Spain, two main localities were utilized (yellow arrows).
Figure 4. Different scales of dolostone bodies and dolomitization fronts observed in the Middle Cambrian successions, Canada. (A-B) Basin-scale tabular and columnar dolostone bodies with tongue-shaped fronts. (C) Outcrop-scale tongue-shaped fronts showing non-planar, diffuse lateral fronts at the margin of tabular bodies. (D). Diffuse and non-planar vertical transition between tabular dolostone bodies and mudstone in the Whirlpool point locality (locality 1).
Figure 5. Different scales of dolomitization fronts observed in the Middle Cambrian, Canada. (A) Finger-shaped fronts (lateral contact) in the margin of tabular bodies. (B) Non-planar, undulated vertical transition between dolostone bodies and mudstone. (C-D) A combined, outcrop-scale finger-shaped fronts and stylolite-bounded fronts as lateral and vertical transitions, respectively. The main difference is (D) bounded by shale. (E-F) Micro-scale dolomitization fronts where sharp transitions between dolomite crystal and limestone is observed with the presence of no bounding surface (E) and stylolite (F), respectively.
**Figure 6.** Different scales of dolomitization fronts observed in the Carboniferous, Derbyshire Platform, UK. (A) Massive D2 dolostone body (sensu Breislin et al., 2020) with its associated tongue-shaped and complex-shaped fronts (lateral termination) and non-planar vertical contact observed in the Parsley Hay location. (B) Example of tabular dolostone bodies bounded in the upper part by clay-coated karstic surface within the uppermost contact of the D2 body. (C) D3 dolostone forming haloes around N-S trending faults in the Carboniferous, UK. Lateral terminations of these bodies are appeared sharp in the field. (D) Note the presence of scattered dolomite rhomb in the limestone (yellow arrows). (E) Fabric-destructive dolomite with planar-s crystal replaced the limestone.
Figure 7. Different scales of dolomitization fronts observed in the Jurassic, Morocco. (A) Basin-scale dolostone bodies in the Lias succession, EAB with colour distinction between dolostone and limestone. (B) A distinctive separation between dolostone and limestone by fracture corridors observed in the Liassic succession, Morocco. (C) In contrast with the outcrop observation, diffuse boundary between dolostone and limestone is observed in the micro-scale. This is indicated by the presence of floating dolomite rhomb in the adjacent limestone (yellow arrows). (D) Basin-scale tabular dolostone bodies in the Oxfordian succession, EAB. (E) An example of complex-shaped fronts which follow the presence of porous, platy corals within the sediment. (F) Diffuse boundary between dolostone and limestone recognized under thin section. Note the presence of scattered dolostone rhombs.
Figure 8. Different scales of dolomitization fronts observed in the Cretaceous, Maestrat Basin, Spain. (A) Basin-scale tabular dolostone bodies with tongue-shaped fronts (lateral contact) and sharp vertical contact. (B) Outcrop-scale vertical contact of the large tabular bodies (A) which show a planar, sharp transition between dolostone and cemented packstone-grainstone facies. (C) Lateral and vertical terminations of structurally-controlled bodies in the Maestrat Basin, the lateral termination displays gradual, tongue-shaped fronts while the vertical termination is bounded by bed-parallel stylolite. (D) Stylolite-bounded fronts (vertical contact) with thin halos zone observed in this study area.
Figure 9. (A) A cross plot between the thickness and width of dolostone bodies across various geological timescales as observed in this study and published literatures. (B) A cross plot between the width and thickness of both tabular and columnar bodies. Although both bodies show strong positive power-law relationships, the relationships between the thickness and width are different as evident from the power-law equations.
Figure 10. Temporal distribution of tabular and columnar dolostone bodies across geologic periods. (A) Distribution and variation of the width of dolostone bodies. (B) Distribution and variation of the thickness of dolostone bodies. (C) Distribution and variation of the thickness-to-width ratio of dolostone bodies.
Figure 11. (A-B) Cross plots between halos thickness (lateral transition) and width/thickness of dolostone bodies. For the lateral transition, the tongue-shaped front is the most commonly observed type in geologic records. Furthermore, the tongue-shaped fronts are typically thicker than other types. (C-D) Cross plots between halos thickness (vertical transition) and width/thickness of dolostone bodies. Among different types of vertical transition, thick halos zone is often associated with the low-permeability carbonate facies.
**Figure 12.** A genetic classification scheme of dolomitization fronts. Left panel shows the bed-parallel termination while the right panel displays both bed-perpendicular and complex-shaped fronts.
### Table 1. Measurements of different dolostone bodies from the four study locations.

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<th>Location</th>
<th>Thickness (m)</th>
<th>Width (m)</th>
<th>Thickness/Width Ratio</th>
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<th>Halos Thickness Vertical Transition (cm)</th>
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<td>1.2</td>
<td>1.8</td>
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<td>Max</td>
<td>Mean</td>
<td>SD</td>
<td>Max</td>
<td>Mean</td>
</tr>
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<td>2.2</td>
<td>4.5</td>
<td>2.8</td>
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</table>

Maestrat/Cretaceous (Tabular) (N=10)

| Min  | 0.5  | 3.5  | 0.02 | 8.5  | 0.5  |
| Max  | 150  | 7000 | 0.25 | 44.5 | 12   |
| Mean | 38.1 | 1025 | 0.09 | 26.6 | 6.0  |
| SD   | 53.8 | 1974.2 | 0.06 | 12.7 | 4.3  |

Maestrat/Cretaceous (Columnar/Massive) (N=6)

| Min  | 30   | 14   | 1.7  |
| Max  | 150  | 25   | 10.7 |
| Mean | 96.7 | 19.3 | 5.6  |
| SD   | 40.1 | 4.2  | 3.4  |

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Table 2. A genetic classification of structurally-controlled high temperature dolomitization fronts.

<table>
<thead>
<tr>
<th>Dolomitization Fronts Group</th>
<th>Type</th>
<th>System</th>
<th>Host Rock Heterogeneity</th>
<th>Fluid Barrier</th>
<th>Shape</th>
<th>Contact</th>
<th>Halos</th>
<th>Controls</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No to Thin</td>
<td>Presence of depositional aquitard (through cementation or original low permeability facies)</td>
</tr>
<tr>
<td></td>
<td>Depositional Facies</td>
<td>Facies or Diagenesis-related</td>
<td>High Heterogeneity</td>
<td>Reactive to Non-Reactive</td>
<td>Planar to Non-Planar</td>
<td>Sharp when associated with non-reactive facies Diffuse when related to reactive facies</td>
<td>No to Thin (&lt; 5 cm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>Very Thin</td>
<td>Presence of clay coating that reduced the permeability</td>
</tr>
<tr>
<td>Bed-parallel termination</td>
<td>Karst-Bound</td>
<td>Structural and Diagenesis-related</td>
<td>High Heterogeneity</td>
<td>Non-Reactive</td>
<td>Planar to Non-Planar</td>
<td>Sharp</td>
<td>No to Thin</td>
<td>Presence of discontinuity plane</td>
</tr>
<tr>
<td>(Between beds)</td>
<td>Fracture-Bound</td>
<td>Structural and Diagenesis-related</td>
<td>Not affected</td>
<td>Reactive to Non-Reactive</td>
<td>Planar</td>
<td>Sharp if not filled by carbonate mineral Diffuse if filled Sharp to Diffuse</td>
<td>No to Thin</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Very Thin</td>
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<tr>
<td></td>
<td>Stylolite-Bound</td>
<td>Facies-Related Diagenesis-Related</td>
<td>Low Heterogeneity</td>
<td>Reactive to Non-Reactive</td>
<td>Non-planar</td>
<td>No to Thin</td>
<td>Thin to Thick (&gt; 5 cm)</td>
<td>Changes in physiochemical properties of dolomitizing fluid</td>
</tr>
<tr>
<td>Bed-perpendicular termination (Within beds)</td>
<td>Scalloped/Tongue</td>
<td>Intrinsic host rock and Fluid chemistry-related</td>
<td>Low Heterogeneity</td>
<td>No Barrier</td>
<td>Non-planar</td>
<td>Diffuse</td>
<td></td>
<td>Changes in physiochemical properties of dolomitizing fluid and rock properties of limestone</td>
</tr>
<tr>
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<td>Finger</td>
<td>Intrinsic host rock and Fluid</td>
<td>High Heterogeneity</td>
<td>No Barrier</td>
<td>Non-planar</td>
<td>Diffuse</td>
<td>Thin to Thick</td>
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<tr>
<td>Fracture-bound</td>
<td>Chemistry-Related</td>
<td>Not affected</td>
<td>Reactive to Non-Reactive</td>
<td>Planar</td>
<td>Sharp</td>
<td>No to Very Thin</td>
<td>Presence of discontinuity plane</td>
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<td>Structural-Related</td>
<td>Facies or Diagenesis related</td>
<td>High Heterogeneity</td>
<td>Reactive to Non-Reactive</td>
<td>Non-planar</td>
<td>Diffuse</td>
<td>Thin</td>
<td>Presence of porous and reactive grain components (e.g. HMC mineralogy)</td>
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</table>