Whitaker, F., & Frazer, M. A. (2018). Process-based Modelling of Syn-depositional Diagenesis. In Y. Xiao, F. Whitaker, & T. Xu (Eds.), *Reactive Transport Modelling: Application to subsurface energy and environmental problems* (1st ed., pp. 107-156). Wiley.
<https://doi.org/10.1002/9781119060031.ch3>

Peer reviewed version

Link to published version (if available):
[10.1002/9781119060031.ch3](https://doi.org/10.1002/9781119060031.ch3)

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Process-based modelling of syn-depositional diagenesis

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3.1 Introduction

Carbonate rocks are of global importance both as economically significant reservoirs for oil and gas and as aquifers for water supply. On deposition, most carbonate sediments transmit fluids through matrix porosity, and thus they act as single-permeability systems. However, the reactivity of their constituent minerals makes them especially prone to chemical diagenesis – the alteration of minerals and of pore volume and geometry that occurs largely as a result of water:rock interaction. This can involve precipitation of pore-occluding cements or generation of secondary mouldic, linked-vug and channel porosity, and even cave formation (Moore, 1989). Diagenesis can strongly impact the performance of these rocks as reservoirs and aquifers by modifying the spatial distribution of primary (depositional) porosity and permeability that together determine key properties of storage and flow (Skalinski et al., 2013). Even minor diagenetic changes in porosity can result in major shifts in permeability at core scale, and significantly enhance both the heterogeneity and scale dependence of permeability (Whitaker & Smart, 2000). In addition, diagenesis can affect rock strength and ductability, wettability and absorption characteristics, and control their response to acidization and measurement of porosity via wireline logs (Roehl & Choquette, 2012). Developing a predictive understanding of carbonate diagenesis is thus of critical economic importance.

Reservoir geologists are often called upon to predict diagenetic modification of rock quality across a carbonate platform based on core samples and downhole data for a limited number of sites, and seismic data that is rarely of sufficient resolution to image most diagenetic features. This relies on a workflow which involves inferring diagenetic process from product, and predicting distributions based on an understanding of controls on process (e.g. Dickson & Kenter, 2014). For example, petrographic and geochemical evidence may suggest a given phase of cement was precipitated close to the water table, and thus, by reference to models of the spatial configuration of modern water tables in carbonate environments we may predict a near-horizontal zone of cementation controlled by the paleo-position of sea-level. This approach has enabled geologists to effectively highlight potential mechanisms and conditions for carbonate diagenesis within the context of a geological history (e.g. Hollis, 1998; Hollis & Walkden 1996). However, it is only relatively recently that the application of process-based models has allowed us to quantitatively assess the relative merits and shortcomings of mechanisms hypothesized by these more inferential methods (e.g. Frazer et al., 2014).

This contribution provides a review of the status of process-based forward modelling of syn-depositional diagenesis. The unstable mineralogy and high matrix porosity and permeability means that carbonate sediments are at their most vulnerable to diagenesis soon after deposition. We review the processes of syn-depositional diagenesis and the application of reactive transport models

(RTMs) to understand controls on the rates, distribution and nature of alteration. The limitations of simulating reactions within a static sedimentological framework are then explored, and an alternative approach presented that involves explicit coupling of stratigraphic and diagenetic forward models. Applications of this approach to understanding fundamental controls on early meteoric diagenesis within a sequences stratigraphic framework are explored using examples of simulations of modern, Cenozoic, Mesozoic and Paleozoic platform carbonates. Learnings for outcrop studies are compared to those for reservoirs where constraints on system behavior are less well known, but where forward stratigraphic–diagenetic modelling offers potential to generate fully 3D models to help reduce uncertainty in prediction of reservoir properties key to efficient extraction of hydrocarbons.

3.2 Fundamentals of syn-depositional carbonate diagenesis

Syn depositional (also termed “eogenetic”) diagenesis involves alteration within the context of carbonate deposition and platform growth, close to the surface, involving oceanic or meteorically-derived waters. The reactivity of carbonate minerals makes them prone to rapid alteration whenever they encounter fluid chemistries with which they are not at equilibrium. This can lead to a complex diagenetic record of changing environmental conditions. This is particularly the case where primary minerals are dominated by metastable minerals such as high-Mg calcite and aragonite. Most carbonate sediments are precipitated from seawater, either directly or by biotic-mediation. The mineralogy of biogenic sediments is determined primarily by the type of calcifying organism, but that of primary precipitates reflects the Mg/Ca of the fluid from which they precipitated. As such aragonite is the dominant primary marine precipitate at present, and during periods in the past when sea water had a similarly high Mg/Ca ratio (“aragonite seas” Sandberg 1983), whilst low Mg/Ca ratios in seawater (“calcitic seas”) promote the precipitation of calcite. This initial mineralogy can have profound implications for the diagenetic potential and thus the evolution of porosity and permeability within the sediment. High-Mg calcite is most reactive and is more prone to neomorphic replacement by low-Mg calcite, accompanied by minimal pore-structure rearrangement. Aragonite tends to stabilize to low-Mg calcite via dissolution-precipitation. Typically, this leads to extensive porosity rearrangement as aragonitic grains are dissolved and pore-filling calcite cements are precipitated either locally or down the flow path. Alteration of low-Mg calcite to form dolomite can further modify the porosity and permeability, and increase mechanical strength, and is discussed by Xiao et al (this volume).

Active circulation of seawater through the accumulating sediments can lead to precipitation of marine cements (James & Jones 2015). Platform margins may cement rapidly where permeability and hydrodynamic energy are high, whilst in quiescent environments a slow sedimentation rate can permit marine hardground formation (Tucker 1993). Excessive marine cementation can totally occlude porosity, but moderate cementation at grain-grain contacts can help preserve porosity to depth by strengthening the rock against compaction (Choquette & James 1987). However, within cm of the sediment surface organically-matter oxidation can significantly modify the carbonate chemistry of the porewaters, leading to dissolution or precipitation depending on the reactivity of the organics and availability of sulfate and iron (Mackenzie, 2005). Marine hardgrounds have been widely recognized as an important control on later fluid flow (Read & Horbury, 1993; Christ et al., 2012; Shekdar et al., 2014), but the impact of early marine dissolution or stabilization of aragonite has received less attention in the geological literature (Christ et al., 2015).

In areas of restricted seawater circulation, evaporation can increase fluid density and generate the potential for downward “reflux” under the influence of gravity through the underlying sediments. If temperature and fluid chemistry are favorable, this can lead to the replacement of limestone by dolomite and the precipitation of diagenetic gypsum (Machel 2004; Machel & Mountjoy 1986). RTM of this variant of syn-depositional diagenesis is discussed in detail by Xiao et al in Chapter 4 of this volume.

Carbonate units predominantly build during the transgressive stages of a sea-level cycle, with the rate of accommodation generation being closely linked with the rate of relative sea-level rise (eustatic sea-level rise plus subsidence). Because carbonate platform sediments tend to accumulate to sea-level when the platform is flooded, even a relatively minor fall in relative sea-level will expose sediments deposited in a shallow marine environment to meteoric fluids. Exposure-driven diagenesis plays an integral role in the sequence stratigraphic development of a carbonate platform, and importantly, has the potential to modify sediments across sequence boundaries (Matthews & Frohlich 1987; Tucker 1993). In fact, while many sequence stratigraphic studies focus on understanding the depositional phases of a platform, the resulting sediment packages are separated by unconformities that represent extended periods of subaerial exposure. These periods of exposure, and the meteoric diagenesis that occurs during these periods, represent the default state of many carbonate platforms, with phases of deposition occurring only briefly throughout their history. This was especially true during ice-house periods, when high amplitude variations in sea level meant those platforms that were not drowned by the rapid sea-level rise were left high and dry for much of their early history, interrupted by only relatively short episodes of marine flooding and sediment deposition (Paterson et al., 2006; 2008).

Carbonate sediments formed in marine waters are at a state of disequilibrium when exposed to meteorically-derived waters. As such, it is not unusual for these periods of exposure to play a primary role in establishing the porosity and permeability architecture within a platform early in its diagenetic history. Meteoric diagenesis is characterized by a complex series of dissolution-precipitation reactions which are distributed within a spatial framework defined by hydrological zones (Figure 3.1). Sediments above the water table reside in the vadose or unsaturated zone where pores are filled by a mixture of water and air. The water table forms the upper boundary of a lenticular shaped body of freshwater – the freshwater lens - that floats upon the underlying denser saline water. This saline zone is separated from the freshwater lens by a zone of intermediate salinity water termed the mixing zone which provides a route for discharge of meteoric waters. It is widely accepted that each of these hydrological zones plays host to a distinct combination of diagenetic processes.

Figure 3.1: Schematic cross-section through a young carbonate island illustrating the distribution of hydrological zones established in response to meteoric recharge within which develop distinct diagenetic products ("hydro-zones").

Fluid chemistries and fluxes within each of these hydrological zones provide a framework for understanding and predicting the distribution of diagenetic processes and products during periods of meteoric exposure (e.g. Whitaker et al. 1997). Because they are defined by hydrological processes, the extent and position of these zones are highly dynamic, with the potential to respond quickly to changes in boundary conditions (Whitaker & Smart 2007a,b). The elevation of water table is tied to sea-level and the thickness of the lens is controlled by the effective recharge, the size and geometry of the exposed area and the permeability of the rock hosting the lens. Discharge of meteoric water occurs via the mixing zones, increasing in magnitude towards the coast, and leading to compensatory inflow of seawater beneath the mixing zone.

This brief introduction illustrates how diagenetic systems are the product of a complex interplay between solute transport and reaction processes that occurs over a wide range of temporal and spatial scales. Reactive transport modeling (RTM) represents a powerful tool to understand the structural complexity of these systems, the coupling between hydrological and geochemical mechanisms, and the time scales and spatial distribution of diagenesis. Syn-depositional diagenesis presents a particular challenge, as a result of the interactions between episodes of sediment deposition and overprinting by repeated episodes of meteoric diagenesis. While our understanding of carbonate sedimentary processes and the distribution of their products has advanced significantly in recent years, aided through the use of forward sediment models, our capacity for quantitative prediction of diagenetic alteration has failed to advance at a similar rate. This is especially true for systems where the impact of chemical alteration is not clearly confined by depositional boundaries. However, even in systems where diagenesis has followed the original depositional framework, we often fail to accurately predict which facies will be most affected. The remaining parts of this chapter explore two approaches to address this problem, their contributions to understanding syn-sedimentary diagenesis, potential and their current limitations.

3.3 Understanding syn-depositional diagenesis through RTM

3.3.1 Marine Diagenesis

Whether carbonate sediments are formed in the marine or lacustrine environments, diagenesis commences immediately upon deposition. At this earliest stage, cementation and micritization are generally recognised as the dominant rock-altering processes in effect. The recent review of marine cementation by Christ et al. (2015) highlights a broad relationship between water depth and rates of marine cementation based upon several coincident factors. Specifically, near-surface waters with their higher energy and warmer waters are likely to be more favourable to marine cementation. Thus in areas of shoaling, in particular at platform margins and on windward coasts, wave set-up and tidal action can pump warm (high CaCO_3 supersaturation) seawater through the young sediments (Longuet-Higgins 1983; Przyborska 2014). Such higher-energy environments are often characterised by well-sorted and grainy sediments and/or reefs, and the high permeability enhances the flux of cementing fluid, promoting cementation throughout a thicker package of sediments (James et al., 1976; Marshall 1985). Marine cements are currently dominated by aragonite and high-Mg calcite, and regional differences in seawater chemistry may account for the more rapid cementation rate reported from reefs in the Red Sea (Friedman et al. 1974) compared with the eastern Pacific (Cortes 1997).

In contrast, in environments dominated by mud deposition low sediment permeability reduces circulation and thus localise cementation to form thin hardgrounds (Shin 1969). In environments where little to no sediment deposition occurs over long timescales, hardground formation is the primary process underway. Rates of marine cementation within near-surface sediments are often

reported as a time to achieve lithification due to cement precipitation and range from a year, to many thousands of years (Christ et al., 2015). These time scale estimates, along with the dependence of marine cementation upon water temperature and hydrodynamic energy suggests that this process is sensitive to fluctuations in climatic and oceanographic boundary conditions on an annual to millennial time scale.

RTMs have become an established tool for the simulation of the role of degradation of organic matter, directly or indirectly, in driving submarine diagenesis. This work focuses largely on the deep ocean, where solute transport is dominantly diffusive, and models incorporate a range of enzymatic reactions, organisms and oxidants (see review by Arndt et al., 2013). Studies are largely motivated by the importance of these reactions for global cycling of elements in the marine system, and carbonate dissolution and precipitation are often viewed simply as factors which need to be corrected for (Thullner et al., 2009). However, recent work has suggested that syn-depositional precipitation of marine carbonates may be a major player in the carbon cycle (Schrag et al., 2013), and these authigenic carbonates can provide important new insights into paleo-environmental conditions (e.g. Arndt et al., 2009).

RTMs have been applied to quantify diagenetic dynamics in marine sediments (Thullner et al., 2005, Jourabchi et al., 2005). The dominant diagenetic processes within the submarine environment reflect the redox environment, but are also affected by the sedimentary iron cycle (Stoessel, 1992; Soetaert et al., 2007). The sequential utilization of terminal electron acceptors (O_2 , NO_3 , $Mn(VI)$, $Fe(III)$, SO_4^{2-} and CH_4) results in a characteristic redox zonation, and associated shifts in carbonate saturation state, favouring either carbonate dissolution or precipitation. The former dominates in the oxic and nitrogeous zones, where degradation of organic matter and associated secondary redox reactions generally acidify porewaters (Pfeifer et al., 2002). Below the nitrogenous zone, the picture becomes more complex. A number of anaerobic biogeochemical reactions have been invoked as triggers of authigenic carbonate precipitation, (Woods et al., 1999; Greene et al., 2012; Bergmann et al., 2013). Some anaerobic processes (e.g. Fe and Mn reduction) unambiguously increase porewater pH (Soetaert et al., 2007), promoting supersaturation. Other processes, like sulphate reduction, affect both pH and DIC and have complex effects on carbonate saturation state dependent on both initial conditions and reaction rate (Meister, 2013; Soetaert et al., 2007). Crucially, none of these metabolic pathways function in isolated geochemical environments, and so RTMs are critical to tease apart the evolution of carbonate saturations state in both the space and time domains.

Sea floor depth is major factor affecting the processes controlling organic carbon oxidation and thus porewater chemistry (Thullner et al., 2009). Most RTM studies in the marine environment are focused on the deeper benthic environment (>200m water depth). This is characterized by low rates of sediment and organic matter supply, relative homogeneity in types of organic matter, low rates of bioirrigation and microbial diversity, and transport is dominantly by diffusion. RTM simulations in shallow marine environments need to incorporate the effects of temporal variations from semi-diurnal and diurnal to seasonal time scales, as well as more complex sediment deposition/erosion dynamics, and advective exchange of fluids driven by tides and currents. In addition, organic matter loads tend to be much more heterogeneous, deriving from a range of different sources and including pre-processed terrestrial or fossil organic matter that may be more refractory (Arndt et al., 2013). Finally, in shallow systems active bioirrigation promotes loss of reducing species to water column and thus promotes reoxidation within the sediment (Thullner et al., 2009).

Simulations of redox-driven carbonate diagenesis are generally limited to a few 10s of centimeters below the sea floor driven by rapid decay of labile organic compounds, and fail to consider the effect of degradation of the most refractory compounds over much longer distances on geological timescales (Middelburg, 1989). In contrast, diagenesis driven by reflux of dense brines generated by evaporation of sea water in restricted settings has been simulated in over distances of 10s of

kilometers and timescales up to millions of years (Xiao and Jones, this volume and references therein). However, there is clear scope for RTM simulations of reflux systems to consider organic-mediation of reactions, given their potential impact on syn-sedimentary dolomitization.

3.3.2 Vadose zone diagenesis

When a fall in relative sea-level exposes the young carbonates to meteoric water, there is a radical shift in diagenetic environment. Vadose zone diagenesis occurs in a hydrologically and geochemically complex environment in which flow of diagenetic fluids occurs in pores where gas is often present, and relative permeability evolution can potentially play an important role in controlling diagenetic processes (Brooks & Whitaker, 1997). While net porosity generation is positively correlated with recharge (Whitaker and Smart., 2007b) the dynamics of CO₂ dissolution and degassing from recharge waters are responsible for modulating the spatial distribution of cementation and dissolution within the vadose zone and the top of the water table. Specifically, CO₂ dissolution within descending recharge waters increases their potential for CaCO₃ dissolution through the production of carbonic acid. Degassing of CO₂ from these waters can drive cementation through a reverse of this reaction.

In addition to CO₂ in rainfall sourced from the atmosphere, CO₂ is primarily generated in soil by microbial and root respiration processes. As a consequence, recharge waters that infiltrate through soil often have an inherently higher potential for diagenetic alteration than waters that flow over bare rock surfaces. Thick, low permeability and laterally continuous soils also act to limit upwards loss of CO₂ to the atmosphere, effectively increasing the net dissolution potential of recharge waters. However, where effective pathways for CO₂ degassing exist, recharge waters may re-equilibrate with atmospheric PCO₂ and precipitation may result. In this case, net dissolution may be minor but local transport of CaCO₃ from regions of high to low PCO₂ conditions may occur. As such, the distribution and extent of soil development on a carbonate island can play a significant role in determining the rates and patterns of diagenesis within the vadose zone.

The nature of fluid flow within the vadose zone also plays an important role in determining the character of diagenesis. In a vadose zone where fluids simply percolate downwards to the water table through matrix porosity, dissolution is concentrated within the upper vadose zone, where waters are at greatest disequilibrium. Solutes are then transported to the water table and freshwater lens. Through time, positive feedbacks between flow rate and dissolution in the vadose zone lead to the development of connected vug, channel and fracture porosity. This enables a fraction of the recharge to bypass the vadose zone, thereby reducing rates of vadose zone diagenesis (Whitaker et al. 2006; Whitaker & Smart 2007b, Smart et al. 2011). In thin vadose zone systems, where capillary rise above the water table extends to the surface, evaporation can drive upward transport of water and solutes into the bedrock or soil. Evaporation will drive precipitation of low-Mg calcite cements beneath and within the soil, forming a range of pedogenic calcretes and reducing porosity in the part of the upper vadose zone (Whitaker & Smart, 2007b).

Little attention has been paid to modelling carbonate diagenesis within the vadose zone above the water table, at least in part because of the additional complexities a multi-phase system with temporal variations in fluid saturation. Xiao and Jones (2006) simulate exposure of aragonitic sediments under humid conditions and suggest vadose dissolution may extend some 10 m below the exposure surface, whilst minimal alteration is reported under semi-arid conditions. Whitaker et al. (2011) present a higher resolution study which also incorporates the effects of biotic CO₂ generation and transpiration, and incorporates temporal variation in rainfall at a range of timescales. These simulations suggested that rainfall has limited dissolutional potential, and in a semi-arid climate such as characterises the northern Bahamas can generate c.0.5% porosity over 10 ky. Dissolution is focused in the upper 10-20 cm and declines rapidly with depth. However, shallow vadose dissolution is enhanced by CO₂ generated by soil microbial activity and root respiration at depths >20 cm. Deep

rooting vegetation, which characteristically develops in arid to semi-arid settings, can significantly increase the PCO_2 of vadose air (Figure 3.2). However, total dissolution is primarily a function of total rainfall, due to both higher fluid flux and reduced CO_2 degassing with increasing pore water content.

Figure 3.2. RTM simulations of vadose zone diagenesis showing production and concentration of CO_2 resulting from bacterial and root respiration for three contrasting vegetation systems (a and b). Root water uptake and resulting calcite precipitation rates for differing rates of transpiration (c and d). After Whitaker et al. (2011).

Whitaker et al. (2011) also examine drives for precipitation of calcite in the vadose zone, in the absence of aragonite. A combination of CO_2 degassing and evaporation drives near-surface precipitation of calcite, resulting in cementation focused in the upper 10 cm of the vadose zone. A second drive for precipitation is solute exclusion during root water uptake, which can result in localised precipitation to depths >1 m below the exposure surface and may account for formation of rhizocretions. The vadose zone is highly dynamic, and responds to individual storm events, sequences of storms and seasonal climatic variations. The resultant net changes in porosity mask the effect of repeated cycles of dissolution and precipitation, which could significantly reorganize pore structure within the vadose zone.

The overall control of vadose zone thickness was studied by Xiao and Jones (2006), where a 50 m and 100 m vadose zone was simulated to represent exposure during ice-house lowstands, under a humid climate (represented by a 0.5 m/yr recharge flux on the top boundary of the domain). These simulations show that the dissolution potential of the waters recharging the vadose zone is largely depleted within the shallowest part of the vadose zone. As a result there is no drive for diagenesis within the deeper vadose zone or at the water table, and reactions within the underlying hydrozones remain largely unaffected.

Figure 3.3. Porosity evolution of a carbonate platform at 50 and 100 ky under a humid climate for two sea level lowstand scenarios (original fractional porosity specified as 0.35). Red horizontal line is the water table. Blue area represents enhanced calcite dissolution and porosity increase below the exposure surface and also within the mixing zone near the coast due to focused fluid flow, which is more obvious with a thinner vadose zone (Xiao & Jones, 2006a).

3.3.3 Freshwater lens diagenesis

Most recharge to the water table occurs following high intensity storm events. High permeability conduits permit rapid transmission of calcite-undersaturated recharge waters to the water table, even with a thick vadose zone (Jocson et al., 2002; Whitaker et al., 2006). This effect is not shown in the simulations of Xiao and Jones (Figure 3.3) which assume flow through an equivalent porous media. Bypass flow also supplies terrestrial organic matter from the surface and soil to support CO₂ generation within the freshwater lens (Whitaker and Smart, 2007a). Rapid bypass flow can drive dissolution at considerable depth (>100 m) beneath the exposure surface (Whitaker et al. 2006). Studies of freshwater lens geochemistry in modern eogenetic carbonates universally suggest that aragonite stabilisation and subsequent dissolution of CaCO₃ is widespread, and occur at higher rates in more humid climates (Budd 1988; Whitaker & Smart 2007b). Mixing between recharge waters and those at the top of the freshwater lens has been invoked to account for observations of dissolution at the water table (Mylroie & Carew, 1990). However, simulations based on a range of waters from the modern Bahamas suggest that this process has limited potential, and may even drive minor cementation depending on composition of end-members (Whitaker and Smart, 2007b).

Notwithstanding the net increase in dissolved calcium in meteoric groundwaters in carbonate island aquifers, there are zones where cements are precipitated, at least during some time periods. At the water table, cementation can be driven by degassing of CO₂ generated within the freshwater lens, with precipitation forming a water-table calcrete (e.g. Perry et al., 1989). As discussed above for marine porewaters, high rates of organic matter oxidation by sulfate reduction can cause calcite supersaturation, generating cements that might be distinguished by a dull cathodoluminescence indicative of reducing conditions. Finally, in mixed-mineralogy settings incongruent dissolution should be considered. Thus, for example, dolomites and evaporite minerals are more soluble than calcite in meteoric waters, and their dissolution will result in calcite precipitation (Wigley, 1973).

The recharge of calcite undersaturated meteoric water to the water table provides the basis for simulations of calcite dissolution in the freshwater lens, which show dissolution focused at shallow depth below the water table. Sainz-Garcia et al. (2011) simulated rates of porosity generation of 2% in 10 ky at the water table, with dissolutional potential consumed within 6 m. Higher vertical resolution simulations by Cooper and Whitaker (2011) suggest greater focus at the water table, with very rapid porosity generation (up to 17%/ky), declining rapidly with depth below water table (See Figure 3.4b below). Cooper (2015) confirmed the importance of grid resolution, but also examined sensitivity to recharge rate and chemistry of recharge waters sampled in the Bahamas. This additional generation of dissolutional potential leads to dissolution rates that are three times greater than that generated by rainwater percolation alone.

The importance of constraining the geochemistry of waters delivered to the freshwater lens is highlighted by contrasting the results shown in Figure 3.3. with the work of Xiao and Jones (2006). The equilibration of recharge waters within the vadose zone results in little or no change in porosity within the lower vadose zone and freshwater lens. However, incorporating bypass-flow, though specifying discrete fractures through a 50 m thick vadose zone, allows for focused dissolution and aragonite stabilisation (Figure 3.4). Under a humid climate this system generates porosity within fractures that reach the water table at a rate of some 0.5% in 10 ky, whilst in the adjacent matrix flow parts of the aquifer stabilization of aragonite to calcite reduces porosity by 0.4% in 10 ky. Simulations of a calcitic aquifer (Cooper and Whitaker, 2011; Sainz-Garcia et al. 2011) confirm that, in the absence of aragonite, the bulk of the freshwater lens is diagenetically inactive. However, this work does not consider the effect of degradation of organic matter, generated at or just below the land surface, which has the potential to generate additional acidity, at depth with the freshwater lens (Whitaker and Smart, 2007a).

Figure 3.4: RTM results illustrating the distribution of porosity (by fraction) in a carbonate platform in which by-pass flow occurs due to the presence of conductive fractures. The platform was specified with a starting porosity of 0.3 (30%) and an initial mineralogy of 100% aragonite. By pass flow leads to porosity enhancement in the fractures and cementation around the locations where fractures meet the water table and thus deliver CaCO_3 saturated waters to the freshwater lens (from Xiao and Jones, 2006).

3.3.4 Mixing Zone Diagenesis

Dissolution and precipitation can occur as a result of mixing between waters of different chemical composition due to the non-linear dependence of CaCO_3 saturation on factors that include ionic strength and pH (Runnels, 1969). Mixing between meteoric water equilibrated with the limestone aquifer and seawater results in mixtures which are calcite undersaturated, providing the seawater fraction in the mixture is $<10\%$ (Plummer 1975). This is expressed in modern mixing zones as pervasive dissolution of allochems and matrix, formation of a macroscopic “swiss cheese” texture and the development of laterally extensive cave networks (Back et al. 1979; Smart et al. 1988; Smart et al. 2006). Studies of modern mixing zones indicates that dissolution is enhanced both because meteoric waters mix with groundwater of seawater salinity which is close to calcite equilibrium (rather than supersaturated seawater), and because of the oxidation of organic matter suspended in the density gradients of the mixing zone (Smart et al. 1988; Whitaker & Smart 1997a). Oxidation of organic carbon exhausts dissolved oxygen, but continued oxidation is possible by reduction of sulfate derived from mixing with underlying saline groundwater. Re-oxidation of sulfide in the overlying oxygenated waters will also drive dissolution by formation of sulfuric acid. Alternately, if the fraction of seawater in the mix is high, other dissolved ions are present and critically if the PCO_2 is close to atmospheric, mixing with fresh groundwaters can cause precipitation of carbonate cements (Frank and Lohmann, 1995; Csoma et al., 2006). Laboratory experiments to determine controls of calcite dissolution and precipitation in fresh-salt water mixing zones by Singurindy et al (2004) confirm these controls and generate a simple scale-independent transport theory that agrees well with observations from field studies at a number of sites.

RTM simulations of the fresh-salt water mixing zone indicate that dissolution increases with the PCO_2 of the lens waters, and the fluid flux, which is controlled by the island width and recharge rate and increases significantly close to the coast (Sanford and Konikow, 1989; Cooper and Whitaker 2011; Figure 3.5). Dissolution rates are greatest the upper (fresher) part of the mixing zone where transport enhances mixing. However, simulations by Rezaei et al. (2005) suggest that close to the coast, maximum dissolution shifts to in the lower (more saline) part of the mixing zone because of a very active convection cell that develops there, rather than where undersaturation is greatest. These results are largely confirmed by the work of Xiao and Jones (2006) but they are also extended by the observation of increased cementation near the platform margin on the order of 5% porosity loss over 100 kyr, due to the increased circulation of seawater beneath the mixing zone. This underlines

the important role of RTM simulations of systems where the interplay between transport and reaction is non-trivial. Saturation index calculations are useful but fail to show how much calcite is dissolved, as this is strongly influenced by mixing rate. No RTM simulations have attempted to incorporate the effect of organically-mediated processes within the mixing zone, but a higher PCO_2 saline end-member both increases dissolution rate and shifts the locus of maximum dissolution to the lower part of the mixing zone (Rezaei et al., 2005).

Figure 3.5. RTM simulations showing strong climatic control on meteoric dissolution for a half of a small (1 km wide) strip island comprising calcite with 30% porosity and horizontal and vertical permeability of 10^{-10} and 10^{-11} m^2 . Recharge chemistry is that of modern low lying carbonate islands in the Northern Bahamas, with a PCO_2 of 1 % at 25°C (Whitaker and Smart, 2007b), mixing at the lens base with modern local seawater. a) 2D simulations show increase in the lens thickness in direct proportion to recharge. Porosity generation is focused at the water table and in the mixing zone adjacent to the coast, but in the interior the mixing zone is diagenetically-inert. Dashed white line is the 50% isochlor which marks the midpoint of the mixing zone. b) Very high spatial resolution 1D simulations of the zone immediately beneath the water table that show exponential decay in rate of porosity generation with depth below the water table, with >99% of dissolution focused in the upper 10 cm of the freshwater lens but an increase in dissolution in direct proportion to recharge rate. c) Variation in mixing zone dissolution rate with depth (note change in vertical scale) at increasing distance from the coast. After Cooper & Whitaker (2011) and Cooper (2015).

The fresh-salt water mixing zone has previously been invoked as a potential environment in which dolomite could form, as waters undersaturated with respect to calcite may remain dolomite supersaturated, due to the high dolomite supersaturation of seawater. Badiazamani (1973) suggested that “Dorag” dolomite could form from mixed waters (5-50% seawater) undersaturated with calcite yet supersaturated with dolomite. This model was subsequently invoked by Land (1973) and numerous subsequent workers to account for dolomites not associated with evidence of brine salinity reflux. However, Hardie (1987) demonstrated that the range of salinities over which dolomite formation may be thermodynamically favourable to formation of non-stoichiometric dolomite is negligibly small. Kinetic considerations also cast doubt on mixing zone dolomites, based on significant difference between the rate of dolomite precipitation relative to that of calcite dissolution in the mixing zone (Plummer, 1975). Furthermore, modern mixing zones are characterized by either the absence of dolomite, or only very small amounts of dolomite (e.g. Plummer et al., 1976, Smart et al., 1988; Csoma et al., 2004). Not surprisingly therefore RTM simulations fail to show any dolomite forming within the mixing zone. Any minor amount of dolomite which may form within specific (generally higher salinity) zones within the mixing zone (e.g. Ward & Halley, 1985) may be related to organically-mediated processes and occur in spite, rather than because of, the process of groundwater mixing. Mixing zones may be related to dolomitization simply by providing the pump

for circulation of salt water in the near coastal zone (Whitaker & Smart, 1993), as illustrated by RTM simulations of Xiao et al., 2013 (see also Xiao & Jones, Chapter 4 of this volume).

3.4 Challenges in reactive transport modelling of syn-depositional diagenesis

Within the past 15 years, the application of RTM technology has provided quantitative constraints on the distribution and rate of syn-depositional diagenetic processes in carbonate systems, and potential responses to external drivers. Results of simulations have also been used to constrain sets of rules to represent the effects of diagenesis within forward sediment models of early diagenesis (see section 3.4 below). However, the number of workers applying these techniques remains small, and emphasis has been heavily on understanding dolomitisation, particularly by brine reflux (see Chapter 4 of this volume). RTM studies of meteoric systems are starting to provide quantitative insights into the role of climate and soil development in carbonate diagenesis, but this work is in its infancy. The important role of biological processes has been demonstrated by RTM simulations of the vadose zone, and is known from biogeochemical studies of modern systems to also extend below the water table. Simulations of marine porewater chemistry simulate a range of metabolic pathways that may be important for carbonate diagenesis, but the effects of these on the sediments remain to be fully explored. Significant scope exists for development of models of meteoric systems that evaluate these effects, incorporating the complexities of advective solute transport which are assumed to be minor in marine systems. As our capacity to model individual hydrological zones develops, there is an opportunity for a more integrated approach, coupling processes at the bedrock surface and within the soil, with those in the vadose zone and in the underlying phreatic zone.

In addition to considering only a subset of reactions known to be influential, models developed to date tend to ignore the complexity of the pore structure and thus of solute transport in natural systems. Typically, only a single rock type is considered, or any spatial trends in initial physical properties are extremely simplistic. As a result, the simulated distributions of diagenetic products only resemble field observations in the most general terms, and fail to replicate features such as the heterogeneity in diagenetic alteration and sharp diagenetic fronts often seen in the field. This not only hinders application of simulation results to further understanding the operation of diagenesis in more complex geological examples, but also undermines confidence of non-modelers in the utility of the modelling process.

Recent simulations of dolomitisation have demonstrated the impact of incorporating greater geological realism in initial rock properties at a range of spatial and temporal scales in generating more complex and geologically realistic output (Gabbellone et al. 2016). Where there are positive feedbacks between diagenesis, permeability and fluid flow, models with simple initial distribution of porosity and permeability may be poorly suited for direct application to most simple natural systems. In addition, while many geologists may consider (at least qualitatively) the role of depositional facies in controlling heterogeneities in porosity and permeability, it is much rarer to consider the effects of the distribution of geochemical properties such as reactive surface area and mineralogy. It is still unclear to what degree inherited rock property distributions play a role in determining the locations of preferential flow paths and/or regions of enhanced diagenetic alteration. Simulations suggest that the initial rock parameters (reactivity or permeability) that are most predictive of final diagenetic rock properties likely reflect the Damkohler number (the ratio of reaction rate to the rate of solute advection; Phillips 1991; Whitaker et al., 2012).

In general, RTM simulations model the change in porosity due to mineral transformations, dissolution and precipitation, but permeability is inferred, most commonly using the Carmen-Kozeny relationship. Simulations of dolomitisation by Budd and Park (2017), have shown the effect of the

positive feedbacks resulting from diagenetic porosity enhancement on replacement of calcite with dolomite. Heterogeneity in initial porosity and permeability fields, and consequent focusing of reactive fluids, results in the development of pronounced perturbations in the geometry of the dolomite front. In contrast, stabilization of aragonite to less dense low-Mg calcite might be expected to become self-limiting, at least where precipitation occurs local to dissolution. However, such simplistic conclusions, based solely on the volume of the solids, ignore the effect of the change in pore geometry for example by dissolution of aragonitic grains and precipitation of pore-filling secondary calcite.

Arguably the most critical simplification of most RTM simulations of early carbonate diagenesis is that they fail to account for the influence of changing paleo-environmental conditions – perhaps the definitive aspect of syn-depositional diagenesis. The timescales involved in most diagenetic processes (thousands of years to hundreds of thousands of years) are extended relative to the changes in boundary conditions known to play a role in controlling diagenesis. For example, shallow meteoric diagenesis is responsive to individual storms, wet seasons and secular changes in climate from decadal timescales to those linked with changes in glacio-eustatic sea-level. We currently have little understanding whether the effects of boundary condition variations on shorter timescales can be accurately represented over longer time periods using simple time-averaged boundary values.

Changing sea-level will have a dramatic effect on elevation of the water table, and thus the thickness of the vadose zone, as well as on the position and dimensions all diagenetic hydro-zones which develop below the water table. The dynamic and transient nature of these hydrological zones means that a sedimentary package may experience diagenesis within multiple zones over time, and may even be subject to repeated sequences of diagenetic alteration as these zones migrate in response to cyclic changes in relative sea-level (Figure 3.6). The response of the hydro-zones to changing sea-level also depends upon the platform geometry. Thus, for a steep-sided platform, the margin defines the coastline largely independent of the magnitude of sea-level fall. In platforms with a gently inclined surface, even a small magnitude drop in relative sea-level can result in a significant lateral shift in the position of the coastline and associated geometry and flux within the freshwater lens and particularly the mixing zone (Read & Horbury, 1993).

Critical boundary conditions include, not only the elevation of sea level relative to the platform surface, but also the rate of meteoric recharge and the degree of soil development and vegetative cover which determine the potential for meteoric dissolution (Whitaker & Smart, 1997). The meteoric hydrological system will also differ between a platform isolated from terrigenous input and a land-attached platform, where significant recharge may be sourced from the continental hinterland. The latter may include non-carbonate lithologies, which would influence both flow and fluid chemistry. As such, carbonate diagenetic products represent a record of fluid-rock equilibration that may be interpreted petrographically to constrain a sequence of fluid rock encounters (Figure 3.6). However, the resulting complexity presents a significant challenge to the understanding of syn-depositional diagenesis.

Figure 3.6: a) A conceptual sequence stratigraphic scenario integrating syn-depositional diagenesis. **t1**: Cycle A is deposited as relative sea level rises (transgressive sequence) and is then subjected to alteration by a meteoric diagenetic system as relative sea level falls to **t2**. Cycle B is deposited during second transgressive phase (ending at **t3**) but during the subsequent exposure event (**t4**) meteoric diagenesis cross-cuts the A/B cycle boundary. Cycle C is deposited during a significant rise in relative sea level (**t5**), but the subsequent low stand (**t6**) is insufficient to expose the entire carbonate platform. Instead, meteoric alteration is restricted to two smaller hydrological systems beneath platform margin islands. These islands also restrict flow of ocean water to the platform interior, allowing evaporative concentration and dolomitization of platform interior sediments by brine reflux. These processes do not penetrate deep enough within the succession to overprint previous diagenetic phases. These processes cease upon the re-flooding of the platform and deposition of Cycle D (**t7**), which occurs before the final meteoric alteration phase in **t8** during which the meteoric system overprints the diagenetic phases that record the **t6** diagenetic system. These periods of deposition and exposure lead to the production of two internally complex, but spatially related diagenetic geobodies. The internal architecture of these geobodies formed because of the events detailed in **a)**, can be seen in **b)**. The diagenetic events that produced Geobody 1 leads to seven possible paragenetic sequences being recorded within 11 different regions within the geobody. The spatial complexities of diagenesis at **t6** (**a**) lead to a more

complex internal architecture within Geobody 2, which contains 12 paragenetic sequences arranged within 27 paragenetic regions. Such a conceptual exercise helps us understand the complexities that could arise from even a relatively simplistic scenario. In reality, the 3D nature of these diagenetic process, as well as their temporally and spatially transitory nature will lead to greater levels of complexity.

A limited number of RTM simulations have recently explicitly considered carbonate diagenesis within an evolving sedimentary framework, focusing on dolomitisation by seawater (Garcia-Fresca et al., 2012; Palmer et al., 2014; Frazer et al., 2015; Gabellone et al., 2016). However, whilst the availability of the requisite computational power to undertake such simulations is becoming less of a limitation, the ability to efficiently implement such developments currently provides a baffle to development. An alternative approach is to approximate the effect of diagenesis within the framework of forward stratigraphic models, and this is the focus on the remaining part of this review.

3.5 Coupled forward stratigraphic-diagenetic models

3.5.1 Stratigraphic forward models (SFM)

Stratigraphic forward models (SFMs) simulate the spatial distribution of sediment accumulation as a function of sediment production, erosion, transport and deposition processes, and the evolution of accumulation over time to build sedimentary sequences. SFMs of carbonate systems vary in complexity both in terms of the granularity with they consider different sediment factories, and the range and complexity of controls on sediment accumulation that are included. All recognize the primary importance of interactions between eustacy and subsidence that together determine accommodation, with the depth (light) dependence of production rate, and some also include the effects of wind and wave energy and/or climate on physical and biological systems. SFMs have been used by the sedimentological community to test conceptual sequence stratigraphic models by simulating the development of stratal relationships in response to the (often non-linear) interactions between this complex set of controls from first principles. These have generated insights ranging in scale from controls on development of high-frequency meter-scale depositional cycles to predictions of seismic-scale sequence stratigraphic architecture. SFMs have also been used to replicate and understand the geological complexity of well-constrained outcrop examples, as well as to simulate subsurface datasets and generate inputs for reservoir models and flow simulations.

3.5.2 Carbonate diagenesis and sequence stratigraphy

The conceptual framework for interpreting carbonate depositional systems using a sequence stratigraphic approach was developed from observations of the geometries and attributes of siliciclastic systems (Sarg 1988; Crevello et al., 1989). The changes in relative sea-level that control deposition also exert a fundamental control on early diagenetic processes (Goldhammer et al., 1990; Tucker, 1993; Read & Horbury, 1993 and references therein) via their effect on fluid composition and flux, as well as duration of subaerial exposure. These workers postulated that, for example in a transgressive sequence tract (TST - sediments accumulated during periods of rising relative sea-level) marine calcite cements, increasing in abundance towards to maximum flooding surface, may be an important diagenetic feature. Sequences deposited during periods of high relative sea level (HSST) were thought to be characterized by formation of cements, vuggy and mouldic porosity and possibly dolomitisation occurring during higher-frequency sea-level falls. Sequences deposited during falling and low stands (LST) should show a greater effect of diagenesis associated with subaerial exposure, with vadose dissolution and karstification overprinting meteoric cements, vuggy and mouldic porosity. Tucker (1993) stressed that within these simple temporal contrasts lateral variation might be anticipated, with proximal areas showing more meteoric diagenesis than distal parts. Meteoric

processes were thought to be more important under more humid conditions, with the indicative diagenetic feature of more arid conditions being dolomitisation by brines. However, because of diagenetic overprinting, consideration of stacking patterns was also seen as important, with the suggestion that progradational, aggradational and retrogradational sequences are each characterized by distinct patterns of syn-sedimentary carbonate diagenesis on the larger-scale.

The integration of a conceptual model for diagenesis within a sequence stratigraphic context provides a spatial and temporal framework and can significantly improve the interpretation of key geological observations. Such an approach has been applied to end member humid and arid meteoric diagenetic systems by both Read & Horbury (1993) and Tucker (1993). Universally applying the learnings from these simple end-member studies however, is often not possible, as diagenetic processes do not act consistently through time. Temporal changes in the dominance of sediment producing organisms, along with secular seawater chemistry variations, together determine sediment aragonite content, and thus the degree of potential syn-depositional diagenetic alteration. Changes in the magnitude and frequency of relative sea level change can also dramatically change patterns of meteoric overprinting. As such, greater temporal resolution in geological characterization is required if conceptual models are to contribute to meaningful predictions of diagenesis.

Csoma and Goldstein (2004, 2006) achieved this through the identification of “diagenetic salinity cycles” within the paragenetic sequences preserved beneath unconformities formed during subaerial exposure. The diagenetic products record a progression from marine conditions, through the mixing zone to the meteoric environment and back through the mixing zone to marine conditions, suggesting a relative sea level fall and rise. This provides a valuable framework for description and prediction of diagenetic responses to sea-level changes at the depositional cycle scale within the sequence stratigraphy. However, individual cycles may be more difficult to interpret where diagenetic overprinting occurs during repeated exposure cycles, characteristic of periods of higher amplitude eustasy. In addition, the nature of such cycles might be expected to vary with depth below the water table, and systematically from proximal to distal locations, for example in response to variations in the diagenetic activity of the mixing zone (as shown in Figure 3.5). Thus, whilst such simple models are conceptually attractive, there is considerable complexity that may be critical to reservoir quality prediction but is difficult, perhaps impossible, to address without redress to quantitative modelling.

3.5.3 Integrating diagenesis into SFMs – 1D and 2D modelling

Although conceptual models provide a clear indication of the potential of incorporating diagenetic processes within SFMs, development of such models has not been widely attempted. Matthews and Froelich (1987) simulated deposition of a 1D column of aragonitic sediment that filled accommodation generated during periods of rising relative sea level. When sea-level fell, these sediments were subject to meteoric diagenesis within hydrological zones of fixed thickness that migrated vertically through the sediment column in response to changes in relative sea level. The user specified the nature and rate of diagenesis, which was uniform within each hydro-zone. This model showed that the relationship between diagenetic alteration and the subaerial exposure surface forming the top of the sediment column at the time of diagenesis was obscured by the complexity of the glacio-eustatic sea-level history. It would be impossible to unravel the diagenetic history of the simple stratigraphic sequence by traditional stratigraphic and sedimentological methods, and the authors concluded that forward modelling is the preferred approach to analysis of syn-depositional sequences.

Using a 1D model it is impossible to evaluate the impact of lateral variations in the thickness of the hydro-zones, which would for example enhance mixing zone diagenesis close to the coast, whilst in the platform interior diagenesis in the freshwater lens should be greater. This limitation was overcome by development of a 2D model (CARB2D⁺), based on the SFM of Bosence and Waltham (1990), which allowed simulation of syn-depositional diagenesis within a time-varying framework of hydrologically-defined diagenetic zones (Whitaker et al. 1997, 1999). CARB2D⁺ includes both spatially varying sediment texture and spatial variations in the distribution and size of meteoric hydro-zones controlling syn-sedimentary diagenesis. The water table varies with sea-level, whilst the geometry of the lens and mixing zone depend on the island size and geometry, meteoric recharge, and upscaled permeability. Whitaker et al. (1997) present simulations of the diagenetic evolution of an aggrading 6 km diameter carbonate platform subject to the same types and rates of diagenetic processes as modelled in 1D by Matthews and Froelich (1987). This includes mixing zone dolomitisation, though given our understanding of the importance of carbonate dissolution in the mixing zone, this is perhaps more usefully viewed as mixing zone porosity.

Results are summarized in Figure 3.7. The glacio-eustatic sea-level curve from the past 500 ky, combined with a simple linear rate of subsidence, resulted in short periods of subtidal sediment accumulation (total duration 65 ky) interspersed with extended periods of exposure (total duration 435 ky). Most of the depositional sequences that formed are separated by unconformities representing >60 ky exposure, during which meteoric diagenesis affected the accumulating platform sediments. Simulations show a clear stacked sequence of diagenetic zones, which were readily recognizable because of their lateral continuity and distinct trends in diagenetic evolution from platform interior to margin, which could not be represented in a 1D model. Apparent spatial

Figure 3.7 a) Relative sea-level curve showing periods of exposure of the top of the aggrading platform (green), with depositional units and subaerial unconformities numbered by oxygen isotope stages. b) Residence time in diagenetic hydro-zones and c) at the water table, during periods of platform top exposure. Grey shading differentiates water table residence time during individual sea-level low stands. d) Simulated distribution of calcite and e) dolomite. Diagenetic geobodies are numbered for the depositional sequences defined by the overlying unconformity and to which they might be supposed to relate genetically, although as shown in c) this association is coincidental and geobodies result from overprinting during several separate low stands. After Whitaker et al. (1997).

associations between unconformity surfaces and underlying diagenetic zones suggest causality, but these are misleading and each diagenetic geobody is instead a product of overprinting during a number of separate low stands. For a given sea-level curve, differences in subsidence rate (controlling accommodation) simply condense platform-top stratal sequences, but they exert a major control on their diagenetic evolution by increasing the extent of diagenetic overprinting. In this example, steep margins prevented significant progradation of the platform. This maintained a constant spatial distribution of hydro-zone thickness over time relative to sea-level, and meant that diagenetic patterns resulted solely from vertical migration of hydro-zones. This work does not aim to simulate specific platform, but it is noted that stacked sequences of mixing zone caves are described in the margin of the eastern Yucatan by Smart et al. (2006), though given the more extensive platform and lower subsidence, the periods of time involved here are likely to be substantially higher.

Jones et al. (2004) assessed the utility of CARB2D+ to predict early diagenesis in a Pennsylvanian reservoir example, the Northwest Extension of the Salt Creek Field in the Midland Basin of West Texas. The reservoir interval consists of cyclically stacked wackestones, packstones and oolitic-skeletal grainstones. Early diagenesis has significantly modified reservoir quality by pore filling meteoric cements and fabric-selective dissolution to generate abundant mouldic porosity. To investigate model application in a data-poor environment, a representative 2D section was defined using an initial surface, the external platform (decompacted) geometry, a regional scale burial history and literature constraints on Pennsylvanian sea level and climate.

Most simulations using different sea-level amplitude and frequency cycles resulted in very different platform geometries from that observed. For the simulation that best fitted the seismic architecture (eustasy dominated by 400 ky cycles), cumulative residence time of sediments in different hydrozones was tracked for a semi-arid climate (Figure 3.7). Simulated freshwater lens and mixing zone residence times show distinct lateral trends, as expected from the thickness of these hydrozones with distance from the coast, and distinct vertical trends in response to lower order sea-level cycles. At the time of platform demise, the simulated post-early diagenesis porosity distribution is highly heterogeneous. The largest simulated increase in porosity (up to 30 %) was associated with dissolution in the freshwater lens. Porosity occlusion (up to 35 %) is dominated by cementation in the vadose zone and the freshwater lens, primarily due to the reprecipitation of calcite derived from surface dissolution, but also from the stabilization of aragonite to calcite. Early porosity distribution was generated using diagenetic rate data from RTMs and hydrozone residence times from CARB2D+, and compacted (based on sediment texture) to reservoir depth. Comparison of predicted reservoir porosity to data from ooid grainstone intervals in seven cored wells shows a relatively good match, though with overestimation of both the lowest (<10 %) and highest (30-40 %) porosity classes. Using the proportion of different pore types and predicted reservoir porosity generated a good match to observed reservoir permeability distribution.

Figure 3.8. Architecture of NW Extension of Salt Creek defined from 3D seismic data shown for a) Synthetic sea-level curve used in CARB2D+ to model b) residence time in meteoric diagenetic hydrozones shown here for windward platforms margin. c) Predicted and observed porosity and permeability for ooid grainstones in 7 cored interior and marginal wells. After Jones et al. 2004.

3.5.4 3D forward stratigraphic-diagenetic models (FSDM)

CARB3D+ was developed to enable simulation of more complex platform geometries, sedimentary architectures and diagenetic patterns in 3D (Figure 3.8). It differs from the earlier model in employing an explicit simulation of the evolving hydrodynamic environment resulting from interaction of waves and currents with the bathymetry, and resulting sediment transport. The new model also introduced an alternative mode of parameterization of diagenetic rates. Within each hydro-zone, the rates of diagenesis are spatially variable and determined by the climate *via* its effects on the flux of reactive fluids and geochemically determined diagenetic potential. This potential is controlled by the degree of soil development and associated biological activity. Grain-size dependent reaction rates and feedbacks between the evolving porosity-permeability characteristics and distribution of the hydro-zones are also included. The rules governing diagenesis are derived both from RTM studies (described in section 3 of this paper), and from hydrochemical studies of modern carbonate islands (e.g. Whitaker and Smart, 2007a & b).

CARB3D⁺ can also model the effect of early meteoric dissolution and precipitation of cements on porosity and permeability. The model tracks progressive changes in the volumes of cement and fabric-selective (matrix) and non-fabric selective (secondary karstic) porosity. Primary permeability is determined directly from porosity and is dependent on grain size, following the approach of Lucia (2007). Dissolutional porosity is portioned between fabric selective and non-fabric selective porosity, but cementation preferentially reduces fabric selective porosity. Non-fabric selective porosity is modelled as the progressive enlargement of capillary tubes (analogous to touching-vug porosity) with an assumed spacing, allowing the simple prediction of secondary permeability using the Kozeny-Carman model. Total porosity and permeability are the sum of both fabric selective and non-fabric selective components.

Figure 3.9. Outline structure of CARB3D⁺ including extrinsic controls (blue), model components (green) and primary outputs.

3.5.5 Application of CARB3D+ to understanding carbonate sedimentation and syn-sedimentary diagenesis

Over the last ten years CARB3D+ has been used in industry and academia for training, to investigate controls on platform development, and to understand specific reservoirs and outcrop analogues. Some applications have developed a single large complex model of a specific reservoirs, whilst others have involved rapid modelling of multiple facies realizations. The resulting high vertical-resolution geological models that can be up-scaled and input to standard reservoir simulators. More fundamentally, CARB3D+ modelling has underlined the critical need to integrate studies of syn-depositional diagenesis with the stratigraphic evolution of carbonate build-ups and identified gaps in our understanding of governing processes. Here we summarize a range of applications of the code by our group, and collaborators in industry and academia, which are in the public realm (Table 3.1). These range from the Recent and the Cenozoic, for which we have more confidence that modern sedimentological and diagenetic processes can be reasonably applied, to the deeper past, where biota, soils, atmospheric and seawater composition have at times been quite different. Because of the important control on sediment texture of both flux of diagenetic fluids and sediment reactivity, we include both studies of the distribution of sediment texture and exposure surfaces from FSM as well as specific simulation of syn-sedimentary diagenesis.

Case Study	Age	Focus	Data	Period	Platform Dimensions	Ref and Figure
Cocos Keeling	Modern	Control of hydrodynamics on facies distribution	Hydrodynamic data, sediment samples and satellite interpretation	1 ky	13 x 18 km, <10 m thick	Our Fig 10a-f Paterson et al. (unpublished data)
Caicos	Modern	Control of hydrodynamics on facies distribution	Satellite interpretation and sediment samples	1 ky	100 x 70 km, <10 m thick	Our Fig 10g-i Paterson et al. (unpublished data)
Generic simulations compared with North Andros core	Pleistocene	Control of facies and sea-level on cementation below exposure surfaces	Porosity from Pleistocene core, modern hydrochemistry and RTM	0.5 My	3.5 km diameter, 40 m thick	Our Fig 14 Smart & Whitaker (unpublished data)
La Molata, Cabo de Gata, South East Spain	Late Miocene	Heterozoan to photozoan sedimentation; effects of eustasy on complex volcanic basement	Outcrop mapping, petrography geochemistry	3.4 My	>4 km diameter, 150m thick	Our Fig 12 Kaczmarek et al. 2009
Natuna, Sarawak Basin, Indonesia	Mio-Pliocene	Control of eustasy and subsidence on sedimentation and hydrozone residence time	Seismic, core and well-logs from reservoir	4 My	4 x 8 km, 105 m thick	Our Fig 13 Paterson et al., 2006 and 2008
North Madura, East Java Basin, Indonesia	Early Miocene	Controls on mound coalescence and platform demise	3D seismic from potential reservoirs	4 My	1 – 7 km diameter, 360 m thick	Our Fig 11 Hughes et al., 2008
Lombardy, Italy	Triassic	Controls on platform progradation and marine cementation, development of rigorous workflow.	Outcrop mapping, petrography geochemistry		8 x 10 km diameter, 500 m thick	Berra et al., 2010
Latemar, Italy	Triassic	¹ Cyclicality in stacking patterns ² Climatically controlled diagenesis & tracer experiments to evaluate pore connectivity	Outcrop mapping, petrography geochemistry	1 My	2.5 km diameter, 170 m thick	¹ Forkner et al., 2010; Our Fig 15 ² Whitaker et al., 2014
Salt Creek, West Texas	Carboniferous	Porosity and permeability from meteoric diagenesis	Logs, 3D seismic and core	1 My	3.4 x 5 km 160 m thick	Our Fig 8 Jones et al., 2006
Tengiz, Caspian Sea	Carboniferous	Diagenetic response to switch from aggradation to progradation and implications for reservoir quality	Seismic, well log, core, petrography geochemistry, isotopes		17 x 20 km, 500m thick	Our Fig 16 Frazer et al., 2010

Table 3.1 Applications of CARB3D+

3.5.5.1 Prediction of sediment distribution and platform architecture using CARB3D+

Syn depositional diagenesis is controlled both by extrinsic parameters (fluid flux and geochemistry) and intrinsic parameters, primarily the permeability and reactivity of the substrate. The latter are strongly facies controlled, with fine grained materials having lower permeability, but also higher effective reactive surface area. The capacity of the model to generate geologically reasonable facies

distributions was evaluated by Paterson et al. (unpublished data) by comparison of maps of the distribution of current speed and sediment texture generated by CARB3D+ and observational data. Wind and open ocean current speed and direction, and initial surface geometries based on modern bathymetry were specified for two platforms of contrasting size; south Cocos (Keeling) platform in the Indian Ocean and the rather larger Caicos platform in the Caribbean. Figure 3.10 shows good agreement between synthetic facies maps and those based on sediment sampling and analysis of Landsat imagery by Kaczmarek et al. (2010) which postdates the modelling work. Current speeds on the simulated south Cocos platform also show a good match with those measured for passages between the barrier islands and across the platform. However, to replicate the distribution of reefs requires simulation more than one principal wind direction to reflect the monsoonal climate (not possible at the time of the original study).

Over time, the vertical stacking of these spatial patterns of sediment distribution gives rise to a complex 3D geometry of permeability and reactivity. The evolution of platforms during “ice-house” periods of high frequency and high amplitude glacio-eustatic sea-level fluctuations is complex and gives rise to rhythmic patterns of carbonate sedimentation (Burchette & Wright 1992, Read, 1995). These patterns are often used for lateral correlation between wells or outcrop sections, as well as to infer timescales for sediment accumulation. Paterson et al. (2006) used CARB3D+ to systematically investigate the effects of key controls on accumulation and sedimentary architecture of isolated ice-house platforms. Longer period (4th order) sea-level cycles were shown to dominate over high frequency (5th order) cycles. Subsidence rate exerts a fundamental control on stacking patterns and the number of “missed beats” – when the platform top remains emergent at sea-level maxima – which create non-Milankovitch sequence boundary frequencies.

In greenhouse periods, the relatively low amplitude of sea-level fluctuations results in a quite different pattern of sediment accumulation for isolated carbonate platforms. Forkner et al. (2010) compared synthetic stacking patterns driven by eustatic oscillations that result from Milankovitch astronomical forcing, generated using CARB3D+, with a well-studied measured stratigraphy. Three sets of cyclic parameters were compared using Fischer plots created from 1D columns extracted from a 3D model of the well-studied Mid Triassic Latemar Platform of Northern Italy. They demonstrated how the use of Milankovitch insolation as a proxy for high frequency eustasy can generate a succession with vertical stacking trends highly comparable to those observed in outcrop and importantly provides a process-based approach for constraining this key input to SFMs. Although the suggestion that stacking patterns can be interpreted in terms of Milankovitch-driven (“allogenic”) cyclicity in sea level often underpins conceptual models of sequence stratigraphy, some have suggested that such patterns are illusory or related to auto-cyclic processes (“allogenic” cyclicity, Burgess, 2008). Cooper and Smart (2010) generated CARB3D+ synthetic stratigraphies for isolated carbonate platforms using both stationary Milankovitch cyclic and random sea level drivers to evaluate statistical approaches for distinguishing allogenic and autogenic cyclicity. This suggested

Figure 3.10. Evaluation of CARB3D+ sediment modelling by comparison to modern Cocos-Keeling platform (a-f) and Caicos platform (g-i). Synthetic facies (f and i) are compared with direct observation of facies distribution based on sample characterization (a, after map of Smithers, 1994) and that inferred by an analysis of Landsat imagery (by Kaczmarek et al. (2010) (c and h). For Coco-Keeling we also show predicted current velocity (d), and resulting redistribution of coarse and fine sediments (e). Paterson et al., unpublished data.

that the exponential distribution test for Poisson related distributions used by Burgess (2008) is not capable of reliably identifying stationary cyclic behaviour, whilst the layer thickness inventories test devised by Bailey and Smith (2005) generally detected cyclicity in the Milankovitch cyclic successions and, given a timescale calibration, the frequency of the main drivers.

Gulden and Simo (2012) used CARB3D+ to test field-observation-derived hypotheses that describe functional relationships between carbonate system characteristics and platform geometry as defined by the progradation-aggradation ratio (P/A). The novel aspect of this study was the “ensemble” approach employed, where by the numerical engine of the code was decoupled from the graphical user interface to enable many model realizations. This approach was directed at understanding systems for which ‘best’ parameter values are unknown and verification data are limited. The P/A, which describes the temporal translation of the break in depositional profile that defines the platform margin, can be calculated from outcrop data or seismic profiles, and can be related to accommodation history and sediment supply. The characteristics of the ensemble of simulations show that aggrading and prograding platforms are the most common geometries, with a trade-off between a system’s tendency to prograde and to aggrade. The initial bathymetry is more important than system characteristics in controlling P/A; deep, steeply sloping basins favor aggradation and shallow, gently sloping basins favor progradation. Backstepping is less common, but most likely in deep, steeply sloped basins with weak, shallow reef production and in systems with increasing accommodation and many high-amplitude, high-frequency sea-level oscillations. Downstepping is rare, especially in deep basins with steep platform slopes. Strongly negative relative sea-level change is near-necessary for downstepping, together with small-amplitude, high-frequency sea-level oscillations and healthy margins. FSM using CARB3D+ provides a link between seismically resolvable features (such as P/A) which characterize the platform architecture and facies proportions and sediment characteristics on the platform that are key to reducing the uncertainty in reservoir quality prediction. However, because of their commercial potential, the nature of these relationships remains confidential.

A combination of seismic data and 3D FSM was also used by Hughes et al. (2008) to explore how interactions between tectonism, eustasy, carbonate accumulation rate, and environmental stresses impact the nucleation, growth, and demise of Early Miocene carbonate platforms from the East Java Basin (Figure 3.11). Combining seismic visualization with FSM sensitivity analysis enabled quantification of the controls on the platform evolution, and suggested the growth and demise of the platforms was controlled more by carbonate productivity rates than tectonic subsidence. The carbonate platforms in this area appear to have initiated with seven mounds which, with high productivity and low accommodation, amalgamated to form a single large platform. Lower productivity causes isolated platforms or partially amalgamated platforms. After amalgamation, the platform appears to have drowned, and the FSM simulations suggest that this could have been driven by low productivity (less than 1m/kyr), even at low subsidence rates (0.04m/kyr). This indicates the key role of stressing the system, perhaps by additional nutrients causing a reduction in light levels and favoring a change in biota from coral-dominated to red-algal dominated. Such a change has been reported from the Modern (Hallock et al., 1993) and associated with platform drowning of Tertiary buildups in Turkey and Spain (Bassant et al., 2004).

The inverse of this scenario, a transition from heterotrophic to phototrophic conditions, was simulated by Kaczmarek et al. (2009) for the Upper Miocene at La Molata, Cabo de Gata region of south-eastern Spain, constrained by detailed outcrop work high-resolution constraints on stratal geometry, lithological heterogeneity and relative sea-level history (Franseen et al., 1993). Whilst CARB3D+ lacks the functionality to incorporate input of volcanoclastics or megabreccia formation, the synthetic stratigraphy does honor most of the important aspects observed in outcrop, within the unconformity-bound depositional sequences (Figure 3.12). Geometries reflect the interactions between high-magnitude, high-frequency fluctuations in relative sea-level, and the substantial (~200m) and complex paleotopography of the Neogene volcanic substrate, as well as changes in the character of the carbonate factory over time. Heterozoan-dominated sequences are most accurately modeled using lower maximum carbonate production rates over a broad range of water depths, and photozoan-dominated units are best modeled with production-depth curves that have higher

maximum values but lower depositional depth ranges. Sequence stratigraphy, pinning-point relative sea-level curves and magnetostratigraphy provide tight constraints on third- and fourth-order fluctuations which control sequence development. In addition, higher frequency fifth-order cyclicity is suggested by meter-scale cycles in both the lower heterozoan units, and the uppermost photozoan sequence.

Figure 3.11. a) PGS Seismic data showing amalgamated platform in North Madura with b) growth pattern interpreted from time slices. In c) four selected slices illustrate stages in platform growth, with nucleation and amalgamation of separate mounds, then drowning caused by reduction in production rate, d) as simulated using CARB3D+ and displayed as 2D section marked in red in c). After Hughes et al. (2008).

Figure 3.12. Outcrop photograph, static geological model built from outcrop data (Franseen et al., 1993) and forward sediment model for the La Molata Outcrop. After Kaczmarek et al. (2010).

3.5.5.2 FSDM – simulation of diagenetic hydrozones

The importance of understanding the facies proportional and texture of accumulating sediments is clear when simulations of coupling sedimentology and early diagenesis are examined. Paterson et al (2008) simulate the repetitive and cumulative overprint of meteoric diagenesis in icehouse platforms. Although the residence time within all meteoric hydrozones is characterized by a high degree of lateral continuity, there is more limited vertical continuity, with significant variations on a fourth order sequence scale across the platform (Figure 3.13). The frequency and magnitude of sea-level variation, subsidence rate and climate are shown to be fundamental controls on residence time in diagenetic hydrozones, as well as on the distribution of sediment texture and platform architecture (Paterson et al., 2006). In addition to the sedimentological response to rate of dissolutional lowering of the land surface, climate also controls the freshwater-lens thickness and the depth and width of the mixing zone for a given distance from the coast.

There is a hierarchy of eustatically driven overprint cycles that accords with the principles of sequence stratigraphy, with higher-frequency cyclicity modifying the primary signal generated by lower-frequency cycles. Third-order cycles are identified as a critical control on the overall extent of meteoric diagenetic modification of the platform, whilst 4th order cycles control the vertical distribution of diagenesis within the platform. Meteoric alteration is minimal for 3rd and 4th order Transgressive System Tracts (TST) and greatest for 3rd and 4th order Highstand System Track (HST). Fifth order cycles are often missed beats, generating prolonged exposure and long vadose zone residence times, but have only a minor impact on freshwater lens and mixing zone residence times. Diagenetic overprinting is greater at lower subsidence rates; in high-subsidence regimes sediment packages move below the zone of meteoric-water influence rapidly. Higher effective recharge can increase the thickness of freshwater lens and mixing zones which increases residence times significantly. Residence times in the vadose zone can be directly linked to a sequence stratigraphic framework. However, for the freshwater lens and the mixing zone, this is only possible with good constraints of the elevation of sea-level minima.

3.5.5.3 FSDM – simulation of diagenetic processes

Although there is broad agreement on the nature of the products of diagenesis within different hydrozones (James and Choquette 1990; Moore 1989 and references therein), uncertainties remain about the distribution and the rate of diagenesis (e.g. compare Melim 1996 and Whitaker et al., 2006). Paterson et al. (2008) thus focused on using CARB3D+ cumulative residence times as a surrogate for the extent of meteoric diagenesis for an isolated platform. This version of the model required the user to specify processes and rates of syn-depositional diagenesis within each hydrozone, to explicitly simulate the evolve of early meteoric diagenesis through time. Thus, one possible distribution of calcite cementation, porosity and permeability is shown in Figure 3.13 g-i. This shows well-developed lateral continuity, with differences from margin to interior and between windward (boundstone-dominated) and leeward margins, and significant vertical contrasts on a fourth order sequence scale.

Subsequent model development included internal parameterization of diagenetic rates based on climate and soil type (see section 5.3.2), parameters that can be inferred from sources such as global climate models and reconstructions of paleogeography, as well as characterization of paleo-exposure surfaces at outcrop or from core/downhole geophysics. The chemical potential and recharge rate at the surface provides the drive for diagenesis and the distribution of sediment texture and mineralogy in the underlying sediment column determines the vertical distribution of dissolution and precipitation. The power of this approach is shown in Figure 3.14, which compares the change in non-fabric selective porosity due to increasing cement abundance simulated by CARB3D+ and core data from the northern Bahamas (Smart & Whitaker unpublished data compared with data from Beach, 1995). Pleistocene and Holocene carbonates show peaks in cementation below individual paleo-exposure surfaces (Figure 3.14a), superimposed on a general increase in cementation with depth (Figure 3.14b). Field observations in modern systems (Whitaker & Smart 2007a, b; Cooper et al., 2016) and RTM simulations (Whitaker et al., 2011; Cooper, 2015) suggest near-surface dissolution during recharge events/seasons driven by organic acids and high CO₂ production, combined with low CO₂ degassing. During subsequent dry periods evapotranspiration and CO₂ degassing then drive calcite precipitation at and below the surface. These processes lead to preferential cementation of finer-grained sediments due to the combined effect of greater effective reactive surface area, higher retention of water against gravity drainage, and capillary rise from the top of the freshwater lens.

Figure 3.13. CARB3D⁺ simulations for an isolated platform based on Miocene Natuna, Sarawak Basin, Indonesia. 2D sections through a 3D model show distribution show facies (a), residence time in vadose zone (b), freshwater lens (c) and mixing zone, (d) given the sea-level curve (e, with eustatic (black curve), subsidence (red line) and “relative” sea-level variations (red curve). Cross sections parallel (x-x') to principal wind direction (red/blue line) shown in map g. Based on Paterson et al., 2008. In addition, we show one set of potential distributions of calcite cement (h), porosity (i) and matrix permeability (j).

The model generates an exponential reduction in porosity occlusion by shallow vadose dissolution-cementation below the exposure surface. Furthermore, porosity loss in the muddy platform interior occurs at almost twice the rate simulated for the boundstone-dominated margins. Synthetic 5th order sediment cycles are rather thicker (average 4.6 m) than those observed in core, due to the higher subsidence rate specified (4-10 times that on North Andros, McNeil 2005). The synthetic sequences will be less altered than those observed in the cores, both because higher subsidence rates modelled will decrease the degree of overprinting, and because the 41 ky (obliquity-driven) cyclicity modelled is higher frequency than the 100 ky (eccentricity-driven) cycles that dominated over the last 0.9 My (Zachos et al. 2001). The net effect is laterally continuous zones of alteration

associated with individual cycle tops, superimposed on an increase in vadose zone diagenesis with depth (age) due to diagenetic overprinting.

Figure 3.14. Comparison of a) porosity data and core photo from a single depositional package, and b) a stack of depositional packages separated by unconformities, from Pleistocene 5e deposits on North Andros Island, Bahamas (adapted from Beach, 1995) with c) synthetic non-fabric selective porosity data from a CARB3D+ simulation, with unconformities shown as dashed lines (Smart & Whitaker, unpublished data).

Using CARB3D+ Paterson et al. (2008) confirmed that high amplitude eustatic sea-level fluctuations characteristically result in a high degree of overprinting which can obscure diagenetic signatures in ice-house platforms. Whitaker et al. (2014) evaluate conceptual models that suggest greenhouse platforms are likely to show significantly less diagenetic overprinting because of the shorter duration of exposure to meteoric waters (Read, 1998). Simulations based on the Latemar platform, with progressive reduction of accommodation over time, demonstrate that overprinting may also occur in greenhouse carbonates at times of low accommodation generation (Figure 3.15). In the Cyclic unit, a combination of short duration of exposure and rapid subsidence below the influence of meteoric processes do limit the impact of meteoric diagenesis. Reducing accommodation in the Transition and Condensed units, means low amplitude eustatic oscillations will produce multi-cycle superimposed diagenetic events overprinting the same volume of sediments, generating an apparently simple distribution of diagenesis which might readily be interpreted as resulting from a single exposure event.

These simulations also provide a comparison of the diagenesis that might be expected in a small isolated platform under contrasting climatic end-member diagenetic scenarios (Whitaker et al. 2014). Aridity effects include not only low recharge rate, but also a thin /discontinuous soil cover,. In contrast, the humid climate simulation had a twenty times higher recharge and a thick laterally continuous soil cover, which resulted in more rapid surface lowering and subsurface dissolution. Results show how the higher rate of dissolutional surface lowering during subaerial exposure under a more humid climate, controls the graininess of the platform *via* its effect on energy levels across the platform top during the subsequent transgression. CaCO_3 dissolved at the surface is re-

precipitated in the semi-arid simulation as vadose cements, whilst in the humid simulation cementation is more extensive and occurs also within the freshwater lens, reflecting more rapid percolation to the water table. However, associated subsurface meteoric dissolution generates significant secondary porosity under a more humid climate. This reflects both the additional drive for dissolution in the lens provided by subsurface oxidation of surface-derived organics in the lens, and enhanced mixing zone dissolution because of higher soil CO₂ and increased specific discharge. The impact of these effects is most marked during periods when slower subsidence causes diagenetic overprinting from repeated exposure events. Thus, whilst in our arid climate simulations meteoric diagenesis is only a second order modifier of depositional porosity and permeability, humid diagenesis can completely dominate over control of reservoir quality by depositional facies.

The study of Whitaker et al. (2014) illustrates a further strength of FSM; the rapid generation of high vertical resolution fully-3D representations of rock properties that are directly amenable to quantitative analysis. After accounting for the effect of compaction (to 2 km burial depth), synthetic stratigraphies from CARB3D⁺ were used as a basis for streamline flow simulations to better understand the impact of depositional and diagenetic heterogeneity on flow behavior. Simple tracer experiments were undertaken, using numerically-efficient streamline simulations to track particles. This allowed quantitative comparison of sweep pattern, sweep efficiency and recovery factor to understand which elements of the permeability structure are important in channeling and baffling flow in complex reservoirs, and how this is impacted by differences in subsidence and climate for a greenhouse platform. Two sets of features appear to control post-burial fluid flow through the synthetic platforms; low permeability laterally continuous horizons (such as separates the Transition zone from the overlying Condensed zone) and the development of karstic permeability. Simulations suggest that karstification under humid conditions could give rise to permeability several orders of magnitude higher than observed in core, where they would likely be recorded as zones of low or no recovery. Such extreme permeability features are well known at shallow depth (Whitaker and Smart 2000; Smart et al., 2006), and their persistence at depth has been observed from bit drops and loss of circulation (e.g. Wallis 1993). They can also be inferred from flow behavior during production of reservoirs (e.g. Putney et al. 2008; Ronchi et al. 2009) the effect of karstification may be difficult to distinguish from that of fracturing, which can also be focused on platform margins.

The effects of dissolution and karstification during syn-depositional diagenesis, are offset by the reduction of matrix porosity by compaction and precipitation of cement, both in meteoric hydro-zones but also in the marine environment. Early marine cements are a particular feature of platform carbonates accumulating in seas with a high carbonate saturation, as proposed for Triassic seawaters in equatorial latitudes (e.g. Riding and Liang, 2005). Berra et al. (2016) use CARB3D⁺ to simulate the development of a spectacularly well-exposed high-relief Triassic carbonate platform in the Central Southern Alps, Italy, where early fibrous radiaxial isopachous marine cements occludes fabric-controlled porosity in the mud-free slope facies and margin belt. Simulations confirm that meteoric diagenesis is negligible due to the arid climate and lack of soil, and the diagenetic history is dominated by the progressive reduction of the original porosity by marine cement precipitation and sediment compaction, in agreement with field observations. In the model the cementation rate is constant and is a function solely of duration of exposure to seawater. Efficiency of cementation is strictly related to the sediment type: cementation is uniform and extensive in the slope facies; it is less homogeneous in the platform interior, where porosity is lower due to the abundance of more compressible fine-grained sediments.

Figure 3.15. a) 2D section oriented along principle wind direction through 3D simulation of the Latemar platform showing platform architecture and facies distribution, arbitrary divisions into cyclic, transitional and condensed units (each 300 ky) reflecting overall reduction in accommodation shown in b) sea-level curve. c) 3D distribution in half the platform (cut along line of 2D section) showing connate water saturation for arid and humid simulations at three time intervals during single-phase tracer experiment. Blue and red vertical lines mark position of injector (I) and producer (P) wells. After Whitaker et al. (2014).

CARB3D+ has also been used to generate interpretative frameworks for understanding the potential impact of syndimentary diagenesis within active carbonate oil fields. The Tengiz field in Kazakhstan is an isolated carbonate platform of Devonian and Carboniferous age with a stratigraphic thickness of over 2km (Weber et al., 2003; Collins et al., 2006). Its internal reservoir property distributions were thought to be strongly influenced by diagenetic processes (Kenter et al., 2010) and the extensive influence of syn-sedimentary meteoric diagenesis was not identified until recently (Dickson & Kenter, 2014). The application of CARB3D+ to this platform has helped provide a broad prediction of the stratigraphic architecture, facies distribution and meteoric influence on this system

Figure 3.16. Stratigraphy of Unit 1 in Tengiz after Collins (2006) compared to synthetic stratigraphy generated using CARB3D+. After Frazer et al. (2014).

within a spatial framework (Figure 3.16; Frazer et al. 2014). Specifically, CARB3D⁺ simulations, conditioned against well and log data, identified four spatial zones within which eustasy, platform subsidence and deposition/erosion combine to develop distinct internal patterns of meteoric alteration. The platform accumulated over an extended period recording the transition from greenhouse to icehouse conditions. The associated patterns of meteoric alteration ranged from minor, para-sequence bound alteration, where all meteoric alteration within a sediment package could be directly tied to the exposure surface at its top, to boundary-transcendent, extensive meteoric alteration where repeated exposure to meteoric fluids associated with many overlying exposure surfaces lead to complete recrystallisation and extensive cementation. The simulations also suggest a contrast in the degree of diagenetic overprinting between areas of greater or lesser progradation in the Serpukhovian.

The range of examples presented above emphasize the strong control on deposition and diagenesis of platform carbonates exerted by the interplay of biological, climatic and environmental factors, as well as antecedent topography, tectonics and eustacy. Because of the considerable spatial and temporal variations in these controlling factors and the complex interactions between them, a wide

range of depositional architectures is observed in the geological record, with an array of associated diagenetic overprints. Berra et al. (2016) systematically describe an iterative workflow that can be used to derive the parameters needed to produce a numerical model mirroring the development of a real platform, and illustrate this workflow by simulating development of the Triassic Esino Limestone succession of the Central Southern Alps, Italy using CARB3D⁺. This study combined knowledge of the architectural, sedimentological and diagenetic features of the outcrop with data from modern and ancient analogues, using sensitivity analysis to tune parameter values within ranges defined from field, laboratory and uniformitarian constraints. In this, and other examples described here, the development of the numerical model allowed an understanding of the effects of the interaction between productivity, environmental energy and creation of accommodation space on the architecture of the carbonate system and the depositional and diagenetic facies, which can be challenging to interpret from observation of the geological products alone. Equally important, they also provide a fully-3D digital numerical model that can be used for the parameterization of the petrophysical properties of selected complex geological bodies at outcrop or in the subsurface, with potential application to reducing uncertainty in exploitation of carbonate reservoirs. However, it is important to remember that models always retain properties which may limit their ability to mimic real systems, their results may be affected by the processes included, computational algorithms used, temporal and spatial scale of discretization and uncertainties in parameterization and other input data.

3.6 Discussion and Conclusion

While diagenesis has long been a challenge of reservoir management in carbonate lithologies, many decades of characterisation-focussed studies have failed to provide a clear path to generating spatial predictions for the distributions of diagenetically-controlled reservoir properties. This does not undermine the value of characterisation studies as primary sources of data, but does clearly demonstrate the need for an integrated framework within which these complex and often confusing observational datasets may be interpreted and extrapolated for reservoir prediction. Understanding the link between diagenetic products and their formative processes, along with the external influences on their operation, provides a methodology that intrinsically incorporates geological observations and concepts within a spatial framework defined by fundamental laws of chemistry and physics.

Young carbonate sediments are highly reactive and prone to syn-sedimentary diagenesis, which often has a significant impact on pore types and connectivity, and can also play a crucial role in establishing a template for later diagenetic fluid flow. Changes in relative sea level, along with prevailing climatic conditions (arid vs humid) are the primary controls on the duration, severity and spatial distribution of syn-sedimentary diagenesis at the platform scale. These overarching external conditions determine the size and position of the four primary hydrological zones; the vadose zone, the freshwater lens, the mixing zone, and the marine zone. Each presents different conditions for diagenetic alteration of the carbonate sediments. If relative sea level fluctuates over a large vertical range at high frequency, rapid migration of these zones can lead to extensive "overprinting" of meteoric diagenetic products across sequence boundaries, making the final products difficult (and often impossible) to separate into a clear parasequence. Factors such as dominant depositional facies, soil development, and spatial and temporal variability in recharge play important secondary roles in local conditions for diagenesis.

Moving from conceptual to numerical models of syn-sedimentary diagenesis requires careful geological characterisation of diagenetic products as well as quantitative formalisation of existing knowledge in areas of hydrology and chemistry. This formalisation process has revealed that our understanding of some key diagenetic processes still incomplete. For example, there are knowledge

gaps relating to the impact of biogeochemical processes on diagenesis. Furthermore, formalisation frequently requires data on observable temporal and spatial timescales to be scaled appropriately to provide effective values suitable for the formulations inherent within numerical simulations. Some of these questions may be answered by direct observation of diagenesis under controlled laboratory conditions, whilst others require field characterisation in modern carbonate systems to identify key aspects of, and interactions between, the hydrological, geochemical and biological systems driving diagenesis.

The quantitative rigor offered by computational reactive transport modelling allows us to critically evaluate conceptual models for diagenesis and generate new predictive concepts. The ability to generate multiple chemically and physically constrained realisations of our diagenetic concepts allows us to explore underlying controls and determine the impact of our geological uncertainty on the results. However, much of this potential remains largely unrealised, partly because of the small community of specialist users with the expertise to apply the available technologies. Simple models can reveal new insights, but can be misleading if they fail to consider all key processes, or to simulate behaviour at appropriate spatial and temporal scales (which might require much finer resolution than previously anticipated). There is also a critical need to incorporate feedbacks between diagenetic changes in mineralogy and porosity, and the resulting evolution of the pore geometry and hence both permeability and reactivity.

One of the key benefits offered by RTM simulations is the ability to predict diagenesis at time scales beyond those that can be examined in the laboratory. They allow us to explore the operation of processes in environments not represented in the modern or under conditions that are challenging or impossible to observe directly. Once sufficient data is gathered on the operation of diagenetic processes through field and lab experiments, the physical and chemical rules that underpin RTM allow us to extrapolate (within uncertainty bounds) to their operation within these more exotic conditions, and at geologically relevant timescales. This allows us access to an entire field of numerical experimentation driven by geological concepts. RTMs offer an improved capability to predict carbonate diagenesis by i) helping to develop better conceptual models based on chemically and physically realistic scenarios; ii) providing quantitative estimates of rates and distribution of diagenesis, and iii) describing diagenetic trends and geobodies which can be used to populate reservoir models.

However, we are only recently starting to realise the potential of this approach. While RTM has provided some key insights into the operation of diagenetic processes, the sophistication in representing geochemical and hydrological processes has often been offset by a reduction in geological realism, undermining their applicability. The most critical aspect of this lack of realism is the lack of stratigraphic development during diagenesis and thus, strictly speaking, no RTM of truly syn-depositional diagenesis has been developed to date. Sequence stratigraphy provides the simplest means of generating a spatial and temporal framework within which to understand the evolution of diagenesis in response to changes in relative sea-level and climate. However useful such conceptual models are, they remain fundamentally unsuitable for reservoir modeling due to their limited ability to generate specific predictions of the spatial distribution and extent of diagenetic and depositional processes.

The incorporation of algorithms that represent the syn-depositional diagenetic changes, resulting from hydrological and geochemical processes, within stratigraphic forward models offers a novel route to predict syn-sedimentary alteration of primary porosity and mineralogy. A major advantage over RTMs is that it allows explicit consideration of the controls on, and feedbacks between, sedimentological and diagenetic processes. Outcome is a prediction of the development of paragenetic sequences (as envisaged by Csoma and Goldstein's (2004) diagenetic salinity cycles) at

locations distributed across the platform in full 4D (at multiple locations through time). We have described development of this approach, culminating in the model CARB3D⁺, and application to a range of platform types, sea-level histories and climatic settings from Modern to Paleozoic.

CARB3D⁺ offers a means of distributing petrophysical data in the inter-well environment and generating valuable 3D datasets with 100% data coverage which enable us to extract dimensions, temporal and geometric relationships. The model enables assessment of sensitivity of diagenesis to controlling parameters and uncertainty, such as response to sea level and initial surface topography. CARB3D⁺ also provides geologists and engineers with a shared mental picture of the subsurface geology and a common understanding of important concepts. Finally, by preserving insights from our understanding of process, CARB3D⁺ can be used for building reservoir models which may better honour actual 3D distributions than do those which rely primarily on geostatistics.

There are inherent limitations to both RTM and FSDM, but also clear synergisms between the two approaches to modelling syn-sedimentary diagenesis. The explicit process-based simulations of diagenesis generated using RTMs have been used as one important source of data from which to develop rules sets that govern diagenesis within the meteoric hydrozones within CARB3D⁺. In the other direction, it is possible to use complex geometries and distribution of rock properties from CARB3D⁺ as input to more geologically realistic RTMs. Each approach represents a different solution to the compromise between the ability on the one hand to explicit simulation of process (a strength of RTM), and on the other to consider the effect of sedimentation and boundary conditions that vary in time and space (via coupled FSDM). The ultimate target must be to explicitly simulate diagenesis by RTM within the context of a forward stratigraphic model. Irrespective of the potential of such a tool, prediction of syn-sedimentary diagenesis for periods in the geological past (rather than in modern systems) will continue to be plagued by considerable uncertainty. This arises not least because the data to constrain model inputs remains highly uncertain, particular for reservoirs during the exploration phase. Irrespective of such limitations, process-based models remain the only real route through which “soft” geological concepts can have a direct impact on the spatial distributions of properties that are deployed to reservoir applications.

Acknowledgements

We thank Yitian Xiao for editorial support, and for the long-standing collaboration in application of RTM to understanding carbonate diagenesis. We are grateful for the contribution of colleagues, including Peter Smart, Gareth Jones, Steve Kaczmarek, Fabrizio Berra and John Reijmar, and many more who are not named but also played a role in developing our ideas. The misconceptions and simplifications remain entirely of our own making. Development of CARB3D⁺ was carried out in collaboration with Peter Smart at the University of Bristol and David Waltham and colleagues at RHUL, and funded via the Bristol Carbonates Consortium by Chevron, Conoco-Phillips, Eni, ExxonMobil, Petrobras and Shell. We acknowledge the fruitful discussions and the integrity, persistence and good humor of colleagues who have worked with us in developing model applications to outcrop and reservoir examples. Miles Frazer thanks Chevron Energy Technology for their support and review of this work

References

- Arndt, S., Jorgensen, B.B., LaRowe, D.E., Middelburg, J.J., Pancost, R.D., Regnier, P. 2013. Quantifying the degradation of organic matter in marine sediments: A review and synthesis. *Earth Sci. Rev.* 123, 53-86.
- Back, W., Hanshaw, B.B., Pyle, T.E., Plummer, L.N., Weidie, A.E., 1979. Geochemical significance of groundwater discharge and carbonate solution to the formation of Caleta Xel Ha, Quintana Roo, Mexico. *Water Resour. Res.* 15, 1521–1535.

- Badiozamani, K., 1973. The dorag dolomitization model, application to the middle Ordovician of Wisconsin. *J. Sediment. Petrol.* 43, 965–984.
- Bailey, R.J., Smith, D.G., 2005. Quantitative evidence for the fractal nature of the stratigraphic record: results and implications. *Proc. Geol. Assoc.* 116, 129–138.
- Bassant, P., Van Buchem, F., Strasser, A., Lomando, A., 2004. A comparison of two Early Miocene carbonate margins: The Zhujiang Carbonate Platform (Subsurface, South China Sea) and the Pirin Platform (Outcrop, Southern Turkey). *Amer. Assoc. Petrol. Geol. Mem.* 80, 153–170.
- Beach, D.K., 1995. Controls and effects of subaerial exposure on cementation and development of secondary porosity in the subsurface of Great Bahama Bank. *Amer. Assoc. Petrol. Geol. Mem.* 63, 1–33.
- Bergman, K.D., Grotzinger, J.P., Fischer, W.W., 2013. Biological influences on seafloor carbonate precipitation. *Palaos* 28, 99–115.
- Berra, F., Lanfranchi, A., Smart, P.L., Whitaker, F.F., Ronchi, P., 2016. Forward modelling of carbonate platforms: Sedimentological and diagenetic constraints from an application to a flat-topped greenhouse platform (Triassic, Southern Alps, Italy). *Mar. Pet. Geol.* 78, 636–655.
- Bosence, D.W.J., Waltham, D.A., 1990. Computer modeling the internal architecture of carbonate platforms. *Geology* 18, 26–30.
- Brooks, S.M., Whitaker, F.F., 1997. Co-evolution of early diagenesis and vadose zone hydrology of Holocene carbonate sands. *Earth Surf. Proc. & Land.* 22, 45–58.
- Budd, D.A., 1988. Aragonite-to-calcite transformations during fresh-water diagenesis of carbonates: insights from pore-water chemistry. *Geol. Soc. Amer. Bull.* 100, 1260–1270.
- Budd, D.A., Vacher, H.L., 1991. Predicting the thickness of fresh-water lenses in carbonate paleo-islands. *J. Sediment. Res.* 61, 43–53.
- Budd, D.A., Park, A.J., 2017. Formation of bed-scale spatial patterns in dolomite abundance during early replacive dolomitization: I. Mechanisms and feedbacks revealed by reaction-transport modeling. *Sedimentology*. (in revision).
- Burchette, T.P., Wright, V.P., 1992. Carbonate ramp depositional systems. *Sediment. Geol.* 79, 3–57.
- Burgess, P.M., 2008. The nature of shallow-water carbonate lithofacies thickness distributions. *Geology* 36, 235–238.
- Choquette, P.W., James, N.P., 1984. Diagenesis 12. Diagenesis in limestones - 3. The deep burial environment. *Geosci. Canada*. 3–35.
- Christ, N., Immenhauser, A., Amour, F., Mutti, M., Preston, R., Whitaker, F.F., Peterhänsel, A., Egenhoff, S.O., Dunn, P.A., Agar, S.M., 2012. Triassic Latemar cycle tops—Subaerial exposure of platform carbonates under tropical arid climate. *Sediment. Geol.* 265, 1–29.
- Christ, N., Immenhauser, A., Wood, R.A., Darwich, K., Niedermayr, A., 2015. Petrography and environmental controls on the formation of Phanerozoic marine carbonate hardgrounds. *Earth Science Rev.* 151, 176–226.
- Collins, J.F., Kenter, J.A.M., Harris, P.M., Kuanysheva, G., Steffen, D.J.F.K.L., 2006. Facies and reservoir-quality variations in the late Visean to Bashkirian outer platform, rim, and flank of the Tengiz buildup, Precaspian Basin, Kazakhstan. *Am. Assoc. Petrol. Geol., Mem.* 88, 55–95.
- Cooper, K.C., 2015. Biogeochemistry of an eogenetic karst island: implications for diagenesis. Unpublished PhD Thesis, University of Bristol, 246 pp.
- Cooper, K., Smart, P., 2010. Is Milankovitch cyclicity recognisable in carbonate sequences? Numerical experiments using the forward model CARB3D+, in: *Amer. Assoc. Petrol. Geol. Internat. Conf.* (Abstract).
- Cooper, K.C., Whitaker, F.F., 2011. Diagenetic patterns in a small carbonate island setting: a reactive transport study. *Karst Waters Instit. Spec. Publ.* 16, 17–19.
- Cooper, K.C., Whitaker, F.F., Anesio, A., Naish, M., Reynolds, D., Evans, E., 2016. Dissolved organics carbonate transformations and microbial community response to variations in recharge waters in a shallow carbonate aquifer. *Biogeochem.* 128, 215–234.
- Cortés, J., 1997. Biology and geology of eastern Pacific coral reefs, *Coral Reefs*, 16 (suppl.), S39–S46.
- Crevello, P., Sarg, J.F., Read, J.F., Wilson, J.L., (eds.), 1989. Controls on carbonate platform to basin development. *Soc. Econ. Paleontol. Mineral. Spec. Publ.* 44, 405 pp.

- Csoma, A.E., Goldstein, R.H., Pomar, L., 2006. Pleistocene speleothems of Mallorca: implications for palaeoclimate and carbonate diagenesis in mixing zones. *Sedimentology* 53, 213–236.
- Csoma, A.E., Goldstein, R.H., Mindszenty, A., Simone, L., 2004. Diagenetic salinity cycles and sea-level along a major unconformity. Monte Composauro, Italy. *J. Sediment. Resear.* 74, 889-903.
- Dickson, J.A.D., Kenter, J.A.M., 2014. Diagenetic evolution of selected parasequences across a carbonate platform: Late Paleozoic, Tengiz Reservoir, Kazakhstan. *J. Sediment. Res.* 84, 664–693.
- Forkner, R.M., Hinnov, L.A., Smart, P., 2010. Use of insolation as a proxy for high-frequency eustasy in forward modeling of platform carbonate cyclostratigraphy - A promising approach. *Sediment. Geol.* 231, 1–13.
- Frank, T.D., Lohmann, K.C., 1995. Early cementation during marine-meteoric fluid mixing: Mississippian Lake Valley Formation, New Mexico. *J. Sediment. Res.* 65.
- Franseen, E.K., Goldstein, R.H., Whitesell, T.E., 1993. Sequence stratigraphy of Miocene carbonate complexes, Las Negras area, southeastern Spain: Implications for quantification of changes in relative sea level. *Amer. Assoc. Petrol. Geol. Mem.* 57, 409-434.
- Frazer, M., Whitaker, F., Hollis, C., 2014. Fluid expulsion from overpressured basins: Implications for Pb-Zn mineralisation and dolomitisation of the East Midlands platform, northern England. *Mar. Pet. Geol.* 55, 68–86.
- Frazer, M., Whitaker, F., Hollis, C., 2015. Understanding the Development of Dolomite Geobodies using Reactive Transport Modelling: The Importance of Platform Growth. *Proc. 15th Bathurst Conf. (Abstract)*, Edinburgh, UK.
- Friedman, G.M., Amiel, A.J., Schneidermann, N., 1974. Submarine cementation in reefs: example from the Red Sea. *J. Sediment. Petrol.* 44, 816-825.
- Gabellone, T., Whitaker, F., Katz, D., Griffiths, G., Katz, D., Sonnenfeld, M., 2016. Controls on reflux dolomitisation of epicritic-scale ramps: insights from reactive transport simulations of the Mississippian Madison Formation (Montana and Wyoming). *Sediment. Geol.* 345, 85-102.
- Goldhammer, R.K., Dunn, P.A., Hardie, L.A., 1990. Depositional cycles, composite sea level changes, cycle stacking patterns, and the hierarchy of stratigraphic forcing - examples from platform carbonates of the Alpine Triassic. *Geol. Soc. Amer. Bull.* 102, 535-562.
- Green, S.E., Bottjer, D.J., Corsetti, F.A., Berelson, W.M., Zonneveld, J.P., 2012. A subseafloor carbonate factory across the Triassic-Jurassic transition. *Geology* 40, 1043-1046.
- Gulden, L., Simo, A., 2012. Understanding Progradation-Aggradation Ratios of Isolated Carbonate Platforms: A Forward Sediment Model Approach. *Amer. Assoc. Petrol. Geol. Article #90142*, Ann. Conv. April 22-25, Long Beach, California.
- Hallock, P., Mullerkarger, F.E., Halas, J.C., 1993. Coral-reef decline. *Res. Explor.* 9, 358–378.
- Hardie, L.A., 1987. Dolomitization: a critical view of some current views. *J. Sediment. Petrol.* 57, 166–183.
- Hollis, C., 1998. Reconstructing fluid history: an integrated approach to timing fluid expulsion and migration on the Carboniferous Derbyshire Platform, England. *Geol. Soc. London, Spec. Publ.* 144, 153–159.
- Hollis, C., Walkden, G., 1996. The use of burial diagenetic calcite cements to determine the controls upon hydrocarbon emplacement and mineralization on a carbonate platform, Derbyshire, England. *Geol. Soc. London, Spec. Publ.* 107, 35–49.
- Hughes, T.M., Simo, J.A.T., Ruf, A.S., Whitaker, F., 2008. Forward sediment modeling of carbonate platform growth and demise, East Java Basin: Example North Madura. *Proc. Indonesian Petrol. Assoc. 32nd Annual Convection*, IPA08-G-117, 10pp.
- James, N.P., Choquette, P.W., 1988. Diagenesis 9-. Limestones - The Meteoric Diagenetic Environment. *Diagenesis* 11, 161–194.
- James, N.P., Jones, B., 2015. *Origin of Carbonate Rocks*. John Wiley & Sons.
- James, N.P., Ginsburg R.M., Marszalek, D.S., Choquette P.W., 1976. Facies and fabric specificity of early subsea cements in shallow Belize (British Honduras) reefs, *J. Sediment. Petrol.* 46, 523-544.
- Jocson, J.M.U., Jenson, J.W., Contractor, D.N., 2002. Recharge and aquifer response: Northern Guam Lens Aquifer, Guam, Mariana Islands. *J. Hydrol.* 250, 231–254.
- Jones, G.D., Whitaker, F.F., Barnaby, R., Thomas, M., Tseng, H-Y, Xiao, Y., 2004. Predictive Modeling of Sedimentology and Early Diagenesis in an Icehouse Isolated Carbonate Platform: Salt Creek Field,

- West Texas. Amer. Assoc. Petrol. Geol. Hedberg Meeting on Structural Diagenesis, Austin, Texas, Feb. 2004.
- Jourabchi, P., Van Cappellen, P., Regnier, P., 2005. Quantitative interpretation of pH distributions in aquatic sediments: a reaction–transport modeling approach. *Am. J. Sci.* 305, 919–956.
- Kaczmarek, S.E., Bova, J., Whitaker, F.F., Leadbeater, T., Franseen, E., Smart, P.L., Goldstein, R., 2009. From conceptual models to outcrop-based forward models using CARB3D+: Preliminary findings from La Molata, Cabo de Gata, S.E. Spain. *Amer. Assoc. Petrol. Geol. Ann. Conv.* June, 2009; Denver Colorado.
- Kaczmarek, S.E., Hicks, M.K., Fullmer, S.M., Steffen, K.L., Bachtel, S.L., 2010. Mapping facies distributions on modern carbonate platforms through integration of multispectral Landsat data, statistics-based unsupervised classifications, and surface sediment data. *Am. Assoc. Pet. Geol. Bull.* 94, 1581–1606.
- Kench, P.S., 1998. Contemporary sedimentation in the Cocos (Keeling) Islands, Indian Ocean: interpretation using settling velocity analysis. *Oceanogr. Lit. Rev.* 4, 645.
- Kench, P.S., 1997. Contemporary sedimentation in the Cocos (Keeling) Islands, Indian Ocean: interpretation using settling velocity analysis. *Sediment. Geol.* 114, 109–130.
- Kenter, J.A.M., Tankersley, T., Skalinski, M., Harris, P., Levy, M., Dickson, T., Jacob, G., 2010. Tengiz field (Republic of Kazakhstan) unit 1 platform static model: Using a hybrid depositional - Diagenetic approach. *SPE Casp. Carbonates Technol. Conf.* 2010 1, 128–136.
- Land, L.S., 1973. Contemporaneous dolomitization of middle Pleistocene reefs meteoric water, North Jamaica. *Bull. Mar. Sci.* 23, 64–92.
- Loyd, S.J., Berelson, W.M., Lyons, T.W., Hammond, D.E., Corsetti, F.A., 2012. Constraining pathways of microbial mediation for carbonate concretions of the Miocene Monterey Formation using carbonate-associated sulfate. *Geochim. Cosmochim. Acta* 78, 77–98.
- Lucia, F.J., 2007. Carbonate reservoir characterization. New York, Springer-Verlag, 336 pp.
- Machel, H.G., 2004. Concepts and models of dolomitization: a critical reappraisal. *Geol. Soc.* 235, 7–63.
- Machel, H.G., Mountjoy, E.W., 1986. Chemistry and environments of dolomitization - A reappraisal. *Earth Sci. Rev.* 23, 175–222.
- Mackenzie, F.T., 2005. Sediments, Diagenesis, and Sedimentary Rocks: Treatise on Geochemistry, Second Edition, Volume 7. Elsevier, 446 pp.
- Marshall, J.F., 1985. Cross-shelf and facies related variations in submarine cementation in the Central Great Barrier Reef, *Proc. 5th Coral Reef Sym.*, 3, 509–512.
- Matthews, R.K., Frohlich, C., 1987. Forward modeling of bank-margin carbonate diagenesis. *Geology* 15, 673–676.
- McNeill, D.F., 2005. Accumulation rates from well-dated late Neogene carbonate platforms and margins: *Sediment. Geol.* 75, 73–87.
- Meister, P., 2013. Two opposing effects of sulfate reduction on calcite and dolomite precipitation in marine, hypersaline and alkaline environments. *Geology*. 41, 499–502.
- Melim, L.A., 1996. Limitations on lowstand meteoric diagenesis in the Pliocene-Pleistocene of Florida and the Great Bahama Bank: Implications for eustatic sea-level models. *Geology* 24, 893–896.
- Middelburg, J.J., 1989. A simple rate model for organic matter decomposition in marine sediments. *Geochim. Cosmochim. Acta* 53, 1577–1581.
- Moore, C.H., 1989. Carbonate diagenesis and porosity. Elsevier.
- Mylroie, J.E., Carew, J.L., 1990. The flank margin model for dissolutional cave development in carbonate platforms. *Earth Surf. Proc. Land.* 15, 413–424.
- Palmer, T., Whitaker, F., Gabellone, T., Frazer, M., Garcia-Fresca, B., 2014. Evaluating Links Between Sequence Stratigraphy and Reflux Dolomitisation of the Permian San Andres Formation. AAPG Annual Convention and Exhibition, Houston, Texas, USA April 6–9, 2014 Article #90189.
- Paterson, R.J., Whitaker, F.F., Jones, G.D., Smart, P.L., Waltham, D., Felce, G., 2006. Accommodation and Sedimentary Architecture of Isolated Icehouse Carbonate Platforms: Insights from Forward Modeling with CARB3D+. *J. Sediment. Res.* 76, 1162–1182.
- Paterson, R.J., Whitaker, F.F., Smart, P.L., Jones, G.D., Oldham, D., 2008. Controls on Early Diagenetic Overprinting in Icehouse Carbonates: Insights from Modeling Hydrological Zone Residence Times Using CARB3D+. *J. Sediment. Res.* 78, 258–281.
- Perry, E.C., Swift, J., Gamboa, J., Reeve, A., Sanborn, R., Marín, L.E., Villasuso M., 1989. Geologic and environmental aspects of surface cementation, north coast, Yucatan, Mexico. *Geol.* 17, 818–821.

- Pfeifer, K., Hensen, C., Adler, M., Wenzhofer, F., Weber, B., Schulz, H.D., 2002. Modeling of subsurface calcite dissolution, including the respiration and reoxidation progresses of marine sediment in the region of equatorial upwelling off Gabon. *Geochim. Cosmochim. Acta* 66, 4247-4259.
- Phillips, O.M., 1991. *Flow and Reactions in permeable Rocks*. Cambridge University Press.
- Plummer, L.N., 1975. Mixing of sea water with calcium carbonate groundwater, *in* Whitten, E.H.T., ed., *Quantitative models in the earth sciences: Geological Society of America Memoir* 142, 219–236.
- Plummer, L.N., Vacher, H.L., Mackenzie, T., Bricker O., Land, L.S., 1976. Hydrochemistry of Bermuda: A case history of ground-water diagenesis of biocalcarenes. *Geol. Soc. Amer. Bull.* 87, 1301-1316.
- Putney, K.L., Collins, J.F., Harris, P.M., Zhumagulova, A., Fischer, D., 2008. Reservoir characterisation of the Korolev Field, North Caspian Basin, Kazakhstan. *Am. Assoc. Petrol. Geol. Search & Discovery Article* 20055.
- Read, J.F., 1985. Carbonate facies models. *Amer. Assoc. Petrol. Geol. Bull.* 69, 1-21.
- Read, J.F., 1998. Phanerozoic carbonate ramps from greenhouse, transitional and ice-house worlds: clues from field and modelling studies. *Geol. Soc., Lond., Spec. Publ.* 149, 107-135.
- Read, J.F., Horbury, A.D., 1993. Eustatic and tectonic controls on porosity evolution beneath sequence-bounding unconformities and parasequence disconformities on carbonate platforms. *In* Horbury, A.D. and Robinson, A.G. (Ed.), *Diagenesis and Basin Development. Amer. Assoc. Petrol. Geol. Studies in Geology* 36, 155-197.
- Rezaei, M., Sanz, E., Raeisi, E., Ayora, C., Vázquez-Suñé, E., Carrera, J., 2005. Reactive transport modeling of calcite dissolution in the fresh-salt water mixing zone. *J. Hydrol.* 311, 282–298.
- Riding, R., Liang, L., 2005. Seawater chemistry control of marine limestone accumulation over the past 550 million years. *Rev. Española Micropaleontol.* 37, 1–11.
- Roehl, P.O., Choquette, P.W., 2012. *Carbonate petroleum reservoirs*. Springer Science & Business Media.
- Ronchi, P., Ortenzi, A., Borromeo, O., Claps, M., Zempolich, W.G., 2009. Diagenetic processes and their impact on the petrophysical properties in Kashagan carbonate platform reservoir (Carboniferous Kazakhstan). *Am. Assoc. Petrol. Geol. Ann. Conf.*, Denver, June 2009.
- Runnels, D.D., 1969. Diagenesis, chemical sediments, and the mixing of natural waters. *J. Sedim. Petrol.* 39, 1188–1201.
- Sainz-Garcia, A.M., Molinero-Huguet, J.J., Saaltink, W.M.W., 2011. Numerical modelling of coastal aquifer karst processes by means of coupled simulations of density-driven flow and reactive solute transport phenomena. *Car. Evap.* 26, 19-27.
- Sandberg, P.A., 1983. An oscillating trend in Phanerozoic nonskeletal carbonate mineralogy. *Nature* 305, 19–22.
- Sanford, W.E., Konikow, L.F., 1989. Simulation of calcite dissolution and porosity changes in saltwater mixing zones in coastal aquifers. *Water Resour. Res.* 25, 655–667.
- Sarg, J.F., 1988. Carbonate sequence stratigraphy. *Soc. Econ. Palaeontol. Mineral. Spec. Publ.* 42, 155-181.
- Schrag, D.P., Higgins, J.A., Macdonald, F.A., Johnston, D.T., 2013. Authigenic carbonate and the history of the global carbon cycle. *Science* (80-.) 339, 540–543.
- Shekhar, R., Sahni, I., Benson, G.S., Agar, S.M., Amour, F., Tomás, S., Christ, N., Always, R., Mutti, M., Immenhauser, A., Kabiri, L., 2014. Modelling and simulation of a Jurassic carbonate ramp outcrop, Amellago, High Atlas Mountains, Morocco. *Pet. Geosci.* 20, 109–123.
- Shinn, E.A., 1969. Submarine lithification of Holocene carbonate sediments in the Persian Gulf. *Sedimentol.* 12, 109-144.
- Singurindy, O., Berkowitz, B., Lowell, R.P., 2004. Carbonate dissolution and precipitation in coastal environments: laboratory analysis and theoretical consideration. *Water Resour. Res.* 40., W4401.
- Skalinski, M., Kenter, J.A., Jenkins, S., Tankersley, T., 2013. Updated Rock Type Definition and Pore Type Classification of a Carbonate Buildup, Tengiz Field, Republic of Kazakhstan (Russian). *SPE Caspian Carbonates Technol. Conf.* 1–16.
- Smart, P.L., Dawans, J.M., Whitaker, F.F., 1988. Carbonate dissolution in a modern mixing zone, South Andros Island, Bahamas. *Nature* 335, 811-813.
- Smart, P.L., Beddows, P.A., Coke, J., Doerr, S., Smith, S., Whitaker, F.F., 2006. Cave development on the Caribbean coast of the Yucatan Peninsula, Quintana Roo, Mexico. *Geol. Soc. Am. Spec. Pap.* 404, 105–128.

- Smart, P.L., Richards, D.A., Beck, W., Whitaker, F.F., 2011. Hydrochemistry of drip waters in an intergranular flow carbonate aquifer: Turks and Caicos Islands. *Carbonate Geochemistry, Carbonate Geochemistry: Reactions and Processes in Aquifers and Reservoirs*, Madison, Wyoming, Karst Waters Institute Special Publication 16, 65-68.
- Smithers, S.G., 1994. Sediment facies of the Cocos (Keeling) Islands. *Atoll Resear. Bull.* 407, 1-34.
- Soetaert, K., Herman, P.M.J., Middelburg, J.J., 1996. A model for early diagenetic processes from the shelf to abyssal depths. *Geochim. et Cosmochim. Acta* 60, 1019–1040.
- Stoessell, R.K., 1992. Effects of sulphate reduction on CaCO_3 dissolution and precipitation in mixing zone fluids. *J. Sediment. Petrol.* 62, 873-880.
- Thullner, M., Van Cappellen, P., Regnier, P., 2005. Modeling the impact of microbial activity on redox dynamics in porous media. *Geochim. Cosmochim. Acta* 69, 5005–5019.
- Thullner, M., Dale, A.W., Regnier, P., 2009. Global-scale quantification of mineralization pathways in marine sediments: a reaction–transport modeling approach. *Geochem., Geophys., Geosyst.* 10, Q10012.
- Tucker, M.E., 1993. Carbonate diagenesis and sequence stratigraphy, in: *Sediment. Rev.* pp. 51–72.
- Vest Jr, E.L., 1970. Oil fields of Pennsylvanian-Permian horseshoe atoll, west Texas. *Am. Assoc. Petrol. Geol. Memoir* 14, 185-203.
- Walles, F. E. 1993. Tectonic and diagenetically-induced seal failure within the south-western Great Bahamas Bank. *Marine Petroleum Geology*, 10, 14-28.
- Ward, W.C., Halley, R.B., 1985. Dolomitization in a mixing zone of near-seawater composition, late Pleistocene Northeastern Yucatan Peninsula. *J. Sediment. Petrol.* 55, 407-420.
- Weber, L.J., Francis, B.P., Harris, P.M.M., Clark, M., 2003. Stratigraphy, lithofacies, and reservoir distribution, Tengiz Field, Kazakhstan. *Amer. Assoc. Petrol. Geol. Mem.* 83, 351-394.
- Whitaker F.F., Smart, P.L., 1997. Climatic control of hydraulic conductivity of Bahamian limestones. *Groundwater* 35, 859-868.
- Whitaker, F.F., Smart, P.L., 2000. Characterising scale-dependence of hydraulic conductivity in carbonates: evidence from the Bahamas. *J. Geochem. Explor.* 69, 133-137.
- Whitaker, F.F., Smart, P.L., 2007a. Geochemistry of meteoric diagenesis in carbonate islands of the northern Bahamas: 1. Evidence from field studies. *Hydrol. Process.* 21, 949–966.
- Whitaker, F.F., Smart, P.L., 2007b. Geochemistry of meteoric diagenesis in carbonate islands of the northern Bahamas: 2. Geochemical modelling and budgeting of diagenesis. *Hydrol. Process.* 21, 967–982.
- Whitaker, F.F., Xiao, Y., 2010. Reactive transport modeling of early burial dolomitization of carbonate platforms by geothermal convection. *Am. Assoc. Pet. Geol. Bull.* 94, 889–917.
- Whitaker, F.F., Smart, P.L., 1993. Saline groundwater circulation in carbonate build-ups: an overview and case study from the Bahamas. In Horbury, A.D. and Robinson, A.G. (Ed.), *Diagenesis and Basin Development*. *Amer. Assoc. Petrol. Geol. Studies in Geology* 36, 113-132
- Whitaker, F.F., Paterson R.J., Johnston, V., 2006. Meteoric diagenesis during sea-level lowstands: evidence from modern hydrochemical studies on northern Guam. *J. Geochem. Explor.* 89, 420-423.
- Whitaker, F., Smart, P., Hague, Y., Waltham, D., Bosence, D., 1997. Coupled two-dimensional diagenetic and sedimentological modeling of carbonate platform evolution. *Geology* 25, 175–178.
- Whitaker, F., Smart, P., Hague, Y., Waltham, D., Bosence, D., 1999. Structure and function of a coupled two-dimensional diagenetic and sedimentological model of carbonate platform evolution. *Soc. Econ. Palaeontol. Mineral. Spec. Publ.* 62, 339-356.
- Whitaker, F.F., Al-Helal, A.B., Gabellone, T., Griffiths, G., 2012. Integrated reactive transport modelling: challenges and opportunities for improved prediction of diagenetic impact on reservoir quality. *Proceedings of the TOUGH Symposium 2012*, LBNL, Berkeley, California, 6pp
- Whitaker, F., Cooper, K., Smart, P., Al-Helal, A.B., Xiao, Y., 2011. Predicting carbonate diagenesis: emerging insights from reactive transport modelling. *Proceedings of the 14th Bathurst Conference (Abstract)*, Bristol, UK.
- Whitaker, F.F., Felce, G.P., Benson, G.S., Amour, F., Mutti, M., Smart, P.L., 2014. Simulating flow through forward sediment model stratigraphies: insights into climatic control of reservoir quality in isolated carbonate platforms. *Pet. Geosci.* 20, 27–40.
- Wigley, T.M.L., 1973. The incongruent solution of dolomite. *Geochim. Cosmochim. Acta* 37, 1397-1402.

- Woods, A.D., Bottjer, D.J., Mutti, M., Morrison, J., 1999. Lower Triassic large sea-floor carbonate cements: Their origin and a mechanism for the prolonged biotic recovery from the end-Permian mass extinction. *Geol.* 27, 645–648.
- Xiao, Y., Jones, G.D., 2006. Reactive transport modeling of carbonate and siliciclastic diagenesis and reservoir quality prediction. Abu Dhabi International Petroleum Exhibition and Conference held in Abu Dhabi, U.A.E., SPE Paper 101669.
- Xiao, Y., Whitaker, F.F., Al-Helal, A.B., Stafford, S., Gomez-Rivas, E., Guidry, S., 2013. Fundamental approaches to dolomitization and carbonate diagenesis in different hydrogeological systems and the impact on reservoir quality distribution. *Internat. Petrol. Technol. Conf.* 2013, IPTC paper 16579, 16pp.
- Zachos, J.C., Pagani, M., Sloan, L., Thomas, E., Billups, K., 2001. Trends, rhythms and aberrations in global climate 65 Ma to present. *Science* 292, 686-693.