1 Introduction

1.1 Motivations and objectives

Carbonate rocks are important hydrocarbon reservoir rocks and have attracted great attention of petroleum geologists since the rise of petroleum industry. It is estimated that around 50–60% of the world's conventional oil and gas resources are reservoired in carbonate rocks (Burchette, 2012). In comparison with clastic rocks, carbonate rocks are more sensitive to diagenesis because the formation and preservation of most secondary pores in carbonate rocks are directed controlled by diagenetic fluid-rock interactions. In the past few decades, the study of diagenesis has been an important basic work for carbonate reservoir characterization and exploration, with the fundamental goal of precisely predicting the influence of diagenesis on reservoir quality and heterogeneity at multiple spatial-temporal scales. With the development of oil and gas exploration, the accuracy of reservoir heterogeneity characterization is increasingly required, and the classical description and conceptual diagenetic models based on observational results can no longer meet the requirements of precise prediction of high-quality reservoirs. As such, quantifying diagenesis with relevant fluid-rock interaction processes has become a rising field of research and is attracting an increasing attention.

The study of diagenesis has a long history with various methods. The current approaches for carbonate diagenesis study (e.g., petrographic observation, mineralogical and geochemical analyses of drilling core samples) are mostly diagenetic products-based. Although these methods help to trace the origins and chemical properties of diagenetic fluids and reveal the diagenetic environment through qualitative description and elemental-isotopic signals of rock samples, they cannot provide quantitative constraints of the diagenesis-mineral-porosity co-evolution. Meanwhile, these methods are more or less limited in terms of spatial-temporal resolution (Xiao et al., 2018), which introduces great uncertainties to reservoir quality prediction, especially in areas that are poorly explored or away from well control. Besides, there remains some controversies regarding carbonate diagenesis that cannot be well explained by the current classical research approaches.

Numerical simulation (represented by reactive transport modeling; RTM) of diagenetic fluids-rock interactions is an emerging method for diagenesis study. Preliminary studies in the past two decades have shown that this approach is effective to quantitatively/semi-quantitatively evaluate the diagenetic processes and their impacts on reservoir properties, and hosts broad development and application prospects because of its economic efficiency and flexible spatial-temporal resolution (Xu et al., 2004; Xiao et al., 2018). At present, the RTM approach has been applied in both natural diagenesis (including carbonate and clastic rocks) at geological scale and artificial diagenesis at production scale (e.g., Whitaker and Xiao, 2010; Gabellone et al., 2016; Zhang et al., 2019; Hamon et al., 2021). Nevertheless, these findings will never be the final conclusions for RTM study of diagenesis, as there is always a contradiction between the complexity of real geological diagenetic events and the simplification of setting models. Thus, ever since the RTM method was applied in diagenesis study, a constant objective has been setting up geological and numerical models and parameters more closely to the diverse real geological environments.

To enrich the fluid-rock interactions theory associated with carbonate diagenesis and to reduce uncertainty of reservoir quality prediction, this thesis provides forward modeling of the two important diagenetic processes (i.e., dolomitization and karstification) using RTM approach, focusing on the spatial-temporal evolution of minerals and porosity, diagenetic trend and their potential controlling factors. The results are used and try to explain some of the controversies in current diagenesis study. RTM simulation of diagenesis has also been employed in a case study (the Ordovician Majiagou Formation, Ordos Basin, China), which helps to reconstruct the diagenesis-porosity evolution of carbonate rocks in a more accurate way than previous studies, and also provides new clues for further prediction of high-quality reservoirs.

1.2 State of the art and scientific challenges

1.2.1 Overview of carbonate diagenesis

(1) Definition and classification

The formation of sedimentary rocks goes through two main stages. The first stage includes

weathering, transport, deposition, and other geological processes that predate burial of sediments, which is broadly defined as sedimentation and involves a variety of physical, chemical, and biological processes. The second stage involves various post-sedimentation (i.e., during burial) geological processes, known as diagenesis and metamorphism. Therefore, the carbonate diagenesis refers to any physical, chemical and biological process that alters carbonate rocks after sedimentation (until metamorphic conditions are reached) (Nader, 2017). In terms of the duration and process, the sedimentation stage is characterized by short time and rapid progress, while the diagenesis experienced prolonged time and slow progress. No matter what the sedimentary rocks look like today, they are the result of a long period of diagenetic alteration. In general, the study of diagenesis of sedimentary rocks includes the multiple diagenetic process and their controlling factors, involving various issues such as lithification of initial loose sediments, element redistribution and mineralization, and rock porosity evolution. Particularly, for carbonate rocks, when the ambient conditions of the rocks and intrinsic fluids change, or upon migration of extrinsic fluids into a rock-mass, processes such as dissolution, precipitation, and mineralogical and porosity-permeability changes may occur. These issues are directly related to the spatial-temporal distribution and evolution of mineral and hydrocarbon resources in sedimentary rocks, and the basic theory of the formation process of sedimentary rocks. Therefore, investigation of carbonate diagenesis has become a fundamental task for the exploration and development of hydrocarbon carbonate reservoirs.

The classification of diagenesis of sedimentary rocks can be varied. According to the type of driving force, diagenesis can be divided into physical-dominant processes (e.g., compaction), chemical-dominant processes (e.g., mineral precipitation, dissolution and replacement) and biological-dominant processes (e.g., bacterial sulfate reduction and biomineralization) (Huang, 2010). In terms of the influence on hydrocarbon reservoirs, diagenesis can be constructive (reservoir spaces increase), destructive (reservoir spaces decrease) or retentive (reservoir spaces adjustment and preserve) (Zhang et al., 2014). According to the different lithofacies of sedimentary rocks, diagenesis can also be divided into carbonate diagenesis, sandstone diagenesis, mudstone (shale) diagenesis, etc. (Bjørlykke and Jahren, 2012). In addition to the above classification schemes, considering the sensitivity of carbonate to the variations in

ambient environmental conditions and pore fluid properties, the most common classifications of carbonate diagenesis are based on diagenetic environment (realm) and diagenetic stage (relative time).

(2) Diagenetic environments (realms)

The concept of "diagenetic environment" is used to characterize the environmental conditions and pore fluid properties under which the diagenesis occurs, which is also frequently named "diagenetic realms" (Fig. 1.1). Due to the coverage of new sediments, diagenetic environment is distinct from the sedimentary environment, including physical properties (e.g., temperature, pressure and flow pattern of pore water), chemical properties (e.g., water composition, pH and Eh values) and biochemical properties. The diagenetic environment changes continuously as the sediments are buried or briefly exposed and then burial, or tectonically uplifted to the surface after burial. As such, the physicochemical conditions controlling the diagenetic process are also changing, and the most important controlling factor is the properties of pore water.
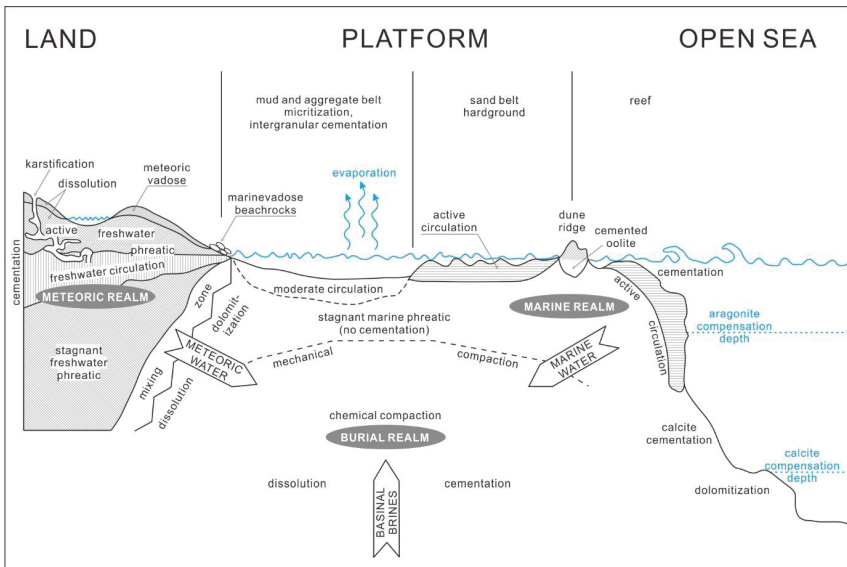

Figure 1.1 Schematic representation of the major carbonate diagenetic realms and related processes in a carbonate platform (modified after Moore, 2001; Nader, 2017).

Carbonate sediments can be involved in several types of pore fluid condition including marine seawater, meteoric freshwater and burial fluid. Each pore fluid type could result in specific fluid-rock interactions that can be identified by unique mineral assemblages, rock fabrics and geochemical indicators. Meanwhile, each digenetic realm, which is inherently associated with the prevailing type of fluid, constitutes a unique diagenetic environment. According to the properties (origins) of the pore fluid and whether it fills with the pore spaces, five types of diagenetic environment of carbonate rocks can be classified: seawater environment, meteoric water environment, seawater-meteoric water (mixing water) environment, burial environment and telogenetic environment (Fig. 1.1).

Seawater diagenetic environment is also called submarine diagenetic environment. Generally, the supratidal zone is in the sub-environment of vadose seawater and the intertidal-subtidal zone is in the sub-environment of phreatic seawater. Seawater diagenesis occurs in an early syngenetic stage just after the sediments deposition, and is characterized by pervasive cementation (e.g., isopachous fibrous aragonite/calcite cementation), mineral replacement (e.g., evaporative pumping- and shallow seepage reflux-related dolomitization) and biological effects (e.g., bioturbation and microbial-related micrite envelope).

Meteoric diagenetic environment is associated with the intermittent short-term exposure (generally less than 1 Ma) of carbonate sediments during the periods of relative sea level fall. Bounded by water-table (phreatic surface), the meteoric diagenetic environment consists of a vadose zone in the upper part and a phreatic zone in the lower part. According to the saturation state of $CaCO_3$ in the pore water, the vadose sub-environment can be further divided into a dissolution zone that is featured by fabric-selective dissolution and karstification caused by undersaturated meteoric water, and a precipitation zone that is featured by minor meniscus, pendent and spelean cementation. The phreatic sub-environment comprises three distinct zones: an upper dissolution zone where the (high pCO_2-containing) pore water is still unsaturated with regard to carbonate and moldic and vuggy porosities are well developed; a mid-precipitation zone where the pores are filled with $CaCO_3$-saturated water and active water circulation promotes rapid cementation (e.g., equant calcite cement) and porosity destruction; a lower

stagnant zone where the equilibrium between pore water and $CaCO_3$ has been established and cementation is weakly developed due to the absence of water circulation and replenishment.

Mixing water diagenetic environment is the mixing zone between the seawater phreatic sub-environment and the meteoric phreatic sub-environment. In humid climate, the carbonate shelf and carbonate platform could have a wide mixing zone. The best known diagenesis in mixing water environment is mixed-water dolomitization. However, in the past two decades, the mixed-water dolomitization model has been intensively questioned in terms of thermodynamics, and researchers have gradually realized that the mixed-water model cannot explain the genesis of thick-bedded and massive dolostone in geological formations. It should be also noted that the seawater, meteoric water and mixing water environments are all at surface/near-surface settings, within which the diagenesis occurs without coverage of now sediments and has a relatively small influencing depth. As such, these three diagenetic environments are collectively called the near-surface diagenetic environment.

Following the accretion of overlying sediments, the initial carbonate sediments are subjected to burial diagenetic environment when they are at depths beyond the reach of near-surface diagenetic processes. Generally, burial diagenetic environment can be further divided into shallow-medium-deep burial sub-environments. Burial diagenesis is typically represented by the pervasive compaction and pressure solution. In addition, in some areas with special basin thermal evolution history and tectonic events, diverse diagenetic processes, such as mineral dissolution (e.g., organic acids-related burial dissolution), cementation (e.g., fractures/fault controlled calcite, dolomite and gypsum/anhydrite precipitation) and replacement (e.g., basinal brines- and hydrothermal-driven dolomitization) might also occur. These burial diagenesis can be distinguished from near-surface diagenesis by particular petrological features and geochemical indicators.

Finally, telogenetic environment refers to the re-exposure of carbonate rocks to near-surface diagenetic environment (mostly meteoric water environment) due to regional tectonic uplift after medium-deep burial and mineral stabilization. Under the action of CO_2-containing surface water or groundwater, carbonate rocks are easily subjected to weathering, dissociation,

transport and redeposition, forming various karst landforms, cave systems and porous rocks.

(3) Diagenetic stages

Diagenetic stage is generally used to describe the evolution of different diagenetic processes (diagenetic sequences) and the temporal characteristics of diagenetic alteration. Since the temporal factor in the geological history is a relative one, there are many schemes for the division of diagenetic stages proposed by different researchers, with different terms and emphasis, and the classification standards have not been unified yet.

Typically, the diagenetic stages of carbonate rocks can be simply classified into eogenesis, mesogenesis and telogenesis, which imply information of both the temporal characteristics and environmental conditions of the diagenetic processes. To be specific, eogenesis refers to the diagenetic processes that occur just after sediments deposition and before burial, involving marine, meteoric water and mixing water diagenetic environments. Alternatively, eogenesis is frequently described as early diagenesis. Mesogenesis is commonly used to describe the various diagenetic processes that occur under long-term burial conditions. Finally, telogenesis refers to the diagenetic processes that occur under surface/near-surface conditions when the carbonate rocks are tectonically uplifted after burial and (once again) subject to meteoric diagenetic environment.

1.2.2 Classical diagenesis characterization approaches

The purpose of classical diagenesis characterization for carbonate reservoirs is to describe and explain specific diagenetic processes in a relative time frame by integrating a variety of analytical techniques. In general, the following results should be obtained by diagenesis characterization: 1) identifying and defining the various diagenetic facies (processes) based on the features and distributions of diagenetic products; 2) organizing the various diagenetic processes in chronological order and trying to reconstruct a complete diagenetic sequence; 3) inferring about the origins and chemical properties of multi-types of fluid that are responsible for the diagenetic processes; 4) clarifying the physico-chemical conditions and their evolution at different diagenetic stages. Ultimately, based on the above results, a conceptual geological model can be established to explain the environmental conditions of various fluid-rock

interactions and the co-evolution of diagenesis and reservoir properties. Several classical approaches are commonly used for carbonate diagenesis characterization, and are briefly presented below.

(1) Petrography and mineralogy

Petrographic observation is a basic work for diagenesis study and can be carried out at different scales such as outcrops, drilled cores and microscopic thin sections. Descriptions based on petrographic observation are mostly qualitative and are made on rock textures, features and distribution of the various diagenetic products (e.g., dissociated carbonate fragments, cements and replacive minerals), and the types and amount of pores and fractures (often combined with porosity-permeability measurement). Particularly, the different diagenetic facies (processes) should be placed in chronological order based on cross-cutting relationship of the diagenetic products. As such, a preliminary diagenetic sequence is established, waiting to be further verified by mineralogical and geochemical analyses. For microscopic petrology, in addition to the common light microscope, several strengthening methods, such as scanning electron microscope (SEM), cathode-luminescence and fluorescence microscopes, are also occasionally used, which help to obtain a higher magnification (10–100,000 times) and to better identify the diagenetic sequence (i.e., multi-stage cementation) and the hydrocarbon-bearing character of reservoir rocks, respectively.

Mineralogical analysis is usually done by means of X-ray diffraction and electron probe microanalysis (EPMA) techniques. In general, mineralogical analysis in diagenesis study aims to: 1) identify some unknown and clay minerals that are difficulty to recognize from thin section observations; 2) determine the absolute content (or mineral-distribution map) of diagenetic minerals (e.g., replacement dolomite, calcite and gypsum/anhydrite cements); 3) assess dolomite stoichiometry and crystal ordering that are potentially related to the degree of dolomitization. Compared with petrographic observation, mineralogical analysis provides more lithology- and diagenesis-dependent quantitative data to assess the relative strength of diagenetic alteration and the distribution of diagenetic products at micro-scales (core samples and thin section).

(2) Geochemistry and fluid inclusions

Diagenetic products-based geochemical and fluid inclusions analyses are effective and have been widely applied to determine the diagenetic environments, trace the origins and chemical properties of diagenetic fluids, and date the diagenetic processes. The methods for geochemical analysis of carbonate samples (powdered bulk samples or in-suit microsamples) are various, mainly including carbon and oxygen stable isotopes, strontium isotope, major and trace elements (including rare earth elements; REE), U-Pb isotopic dating and clumped isotopes.

Isotopic analyses of powdered carbonate samples are usually carried out on a specialized isotope ratio mass spectrometer (e.g., Thermo Scientific 253 Plus MS and Finnigan Triton Plus thermal ionization MS). To be specific, carbon and oxygen isotopes are often used to determine the origin of diagenetic fluids (e.g., normal or modified seawater) and mineral precipitation temperature because they are sensitive to fluid properties and temperature. Other factors involved in diagenetic processes, such as the influence of organic carbon and meteoric water, can also be assessed by comparing isotopic values of different samples (Yang et al., 2001; Xiong et al., 2019). Strontium isotope is often used to roughly estimate the age of some specific diagenetic facies (e.g., replacement dolomite), by comparing the measured isotopic values with the evolution curve of marine Sr isotopic values (Nader, 2017). Diagenetic fluids with different sources also show different isotopic features. For instance, crust-sourced (affected by meteoric water or radiogenic silicate minerals) fluids have relatively higher Sr isotopic values, while the mantle-sourced fluids yield relatively lower Sr isotopic values (Huang, 2010).

Major and trace (including REE) elements analyses are carried out using an Inductively Coupled Plasma Mass Spectrometery (ICP-MS; for whole-rock bulk samples) which can be also coupled to a Laser Ablation device (LA-ICP-MS; for in-situ analysis). In the last decade, major and trace elements, especially the rare earth elements, have been widely applied to trace geochemical properties of fluids (such as seawater and pore water) preserved during carbonate deposition and diagenesis (Tostevin et al., 2016; Li et al., 2019). In addition, other diagenetic processes such as meteoric water leaching, terrigenous (detrital) contamination and deep-sourced hydrothermal alteration can be also identified based on special REE distribution

patterns (Hood et al., 2018; Gong et al., 2021). This is mainly due to that the rare earth elements have similar electron configurations and geochemical properties, and are likely subjected to distinct REE fractionation under different diagenetic environments. Thus, rare earth elements of diagenetic mineral could delicately record the variation of ambient environmental conditions during diagenesis, by forming specific REE distribution patterns.

U-Pb isotopic dating is a mature and commonly used technique in geochronology research. It has been widely used in minerals with high U content, such as zircon, monazite, apatite and garnet. In contrast, the development and application of U-Pb isotope dating technique in diagenetic carbonate minerals lag behind relatively and are limited because of the extremely low U content in carbonate rocks. Nevertheless, Shen et al. (2019) developed a laser ablation in situ U-Pb dating method that is suitable for ancient marine carbonate rocks and effectively applied it in the study of diagenetic sequence and pore evolution. This method holds a great potential for determining the accurate formation time (absolute age) of multi-stage carbonate cements, which helps us better understand the diagenetic sequence and reconstruct porosity evolution history, especially in deep-burial carbonate reservoirs that have experienced complex diagenetic alteration by multiple fluids in multi-cycle superimposed basins.

Clumped oxygen isotopic analysis is an emerging method developed in recent years for carbonate diagenesis research and is regard as a new paleo-thermometer. As mentioned above, although oxygen stable isotopic signal could reflect fluid properties and temperature, the results are hindered by two variables (i.e., original/diagenetic fluids chemistry and precipitation temperature) and thus are highly uncertain (Nader, 2017). In contrast, clumped oxygen isotopic analysis is based on the principle of temperature-dependent formation of an isotoplogue of CO_2 with a mass of 47 within the carbonate minerals ($^{13}C^{18}O^{16}O_2^{2-}$ ionic groups). Thus, the clumped oxygen isotope value ($\Delta 47$) is independent of the fluid $\delta^{18}O$ composition and only reflects temperature (Ghosh et al., 2007). Recently, the clumped isotope paleo-thermometry has been applied to constrain precipitation temperature and to calibrate fluid models with related to dolomite formation (Murray and Swart, 2017; Li et al., 2020).

Analysis of fluid inclusions trapped in diagenetic minerals (e.g., cements) is one of the few