
Process based modeling of the karstification processes in the region of Tulum, Mexico.

thesis presented at the
FACULTY OF SCIENCES
CENTER FOR HYDROGEOLOGY AND GEOTHERMICS
(CHYN)
UNIVERSITY OF NEUCHÂTEL, SWITZERLAND

for the degree of
DOCTOR OF SCIENCES

presented by
AXAYACATL MAQUEDA

accepted on the recommendation of

Prof. Philippe RENARD
Prof. Stephen A. MILLER
Prof. Franci GABROVŠEK
Prof. Rachid ABABOU
Dr. Fabien CORNATON

DEFENDED ON SEPTEMBER 30th, 2017

IMPRIMATUR POUR THESE DE DOCTORAT

La Faculté des sciences de l'Université de Neuchâtel
autorise l'impression de la présente thèse soutenue par

Monsieur Axayacatl MAQUEDA

Titre:

**“Process based modeling of the
karstification processes in the region
of Tulum”**

sur le rapport des membres du jury composé comme suit:

- Prof. ass. Philippe Renard, directeur de thèse, Université de Neuchâtel, Suisse
- Prof. Stephen A. Miller, Université de Neuchâtel, Suisse
- Prof. ass. Franci Gabrovsek, Karst Research Institute, Postojna, Slovénie
- Prof. Rachid Ababou, Institut de Mécanique des Fluides, Toulouse, France
- Dr Fabien Cornaton, DHI-WASY, Berlin, Allemagne

Neuchâtel, le 22 septembre 2017

Le Doyen, Prof. R. Bshary



Abstract

Caves are important since they are preferential paths for groundwater flow. Knowledge of caves or karst is essential for proper management of water resources, but the exploration of caves is a major challenge. An alternative to study caves and their structure is to simulate the processes related to cave growth. The motivation of this thesis is to study large karst networks in the region of Tulum, Mexico. The objective of the study is to understand how and why the cave systems formed in this region.

The first step was to do a review of the information available on the study area. During field work in the study area we observed the propagation of the sea tidal wave into the karst network. This observation lead to question what would be the effect of tidal induced water exchange between caves and surrounding limestone. A conceptual model and a numerical model were developed to quantify dissolution in these conditions. Results show that water exchange can lead to significant mineral dissolution, or cave growth. This dissolution process is additional to dissolution occurring at cave wall surface, therefore the superposition of both dissolution process may explain the fast paced cave growth rate needed to explain the large karst networks in the area.

Additionally, a numerical model framework was developed to simulate the development of fractures into conduit networks. The simulation of development of synthetic networks can provide insight on the development of real caves.

Keywords: speleogenesis, karst, calcite dissolution, coastal aquifers, mixing-zone, tides

Résumé

Les grottes sont importantes car elles constituent des voies préférentielles pour l'écoulement des eaux souterraines. La connaissance des grottes ou du karst est essentielle pour une bonne gestion des ressources en eau, mais l'exploration des grottes est un défi majeur. Une alternative pour étudier les grottes et leur structure est de simuler les processus liés à la croissance des grottes. La motivation de cette thèse est d'étudier de grands réseaux karstiques dans la région de Tulum, au Mexique. L'objectif de l'étude est de comprendre comment et pourquoi les systèmes de grotte ont été formés dans cette région.

La première étape consistait à examiner les informations disponibles sur la zone d'étude. Pendant le travail sur le terrain d'étude, nous avons observé la propagation de la marée dans le réseau karst. Cette observation conduit à se demander quel serait l'effet de l'échange d'eau induite par les marées entre les grottes et le calcaire environnant. Un modèle conceptuel et un modèle numérique ont été développés pour quantifier la dissolution dans ces conditions. Les résultats montrent que l'échange d'eau peut conduire à une dissolution minérale importante, ou à la croissance des grottes. Ce processus de dissolution s'ajoute à la dissolution qui se produit à la surface de la paroi de la grotte, donc la superposition du processus de dissolution peut expliquer le taux de croissance rapide des grottes nécessaire pour expliquer les grands réseaux karstiques dans la région.

En plus, un cadre de modèle numérique a été développé pour simuler le développement de fractures dans des réseaux de conduites. La simulation du développement de réseaux synthétiques peut donner une idée du développement de grottes réelles.

Mots-clefs: speleogenesis, karst , dissolution de la calcite, aquifères côtiers, zone de mélange, marées

Acknowledgements

This research work was funded by the Swiss National Science Foundation grant 20001L-1411298 (Project Xibalba).

I would like to thank Philippe Renard, my thesis director, for all the support along the thesis. Thanks for all the freedom to find my research path and the encouragement to follow it.

I want to thank Martin Hendrick for all the great discussions during the PhD. The final chapter of this thesis is inspired in your work on karst networks. Thanks for your friendship outside working hours and teaching me French along a few beers. It would have not been the same living in Neuchâtel without you.

I would like to thank Fabien Cornaton for motivating me to change from surface to groundwater. Thanks for encouraging my curiosity. I would have never made a PhD if our paths have not crossed.

Thanks to Amigos de Sian Ka'an for bringing attention to study the site. Thanks to the cave divers that bravely explore the cave network and helped us: Bil Phillips, Simon Richards, Leo, Xibalba Dive Center, Quintana Roo Speleological Survey. Thanks to the Geological Survey of Austria team working in Tulum. Special thanks to Arnulf Schiller, your calmness during fieldwork was truly inspiring.

I would like thank the students that worked along us in Tulum: Cécile Vuilleumier, Gregory Kaeser, Thomas Hossler. Also, thanks to Prof. Pierre Perrochet for your helpful discussions on the work.

Thank you Christopher, Jonas, Dan, Amandine, Daniel. I'll miss the apéros among Biology and Hydrogeology, students from different groups can get along really well.

Thanks to my family for supporting me in spite of distance. Claudia, thanks for believing in your husband working on a PhD. Thanks for your support and patience. The years spent working on this project are full of good memories thanks to you.

Contents

1	Introduction	1
2	Speleogenesis review	3
2.1	Introduction	3
2.2	Minerals in karst landscapes	5
2.3	Calcite equilibrium chemistry	5
2.3.1	Solutes molar concentrations and Ion Activity	9
2.3.2	Saturation Index	14
2.3.3	Hydrothermal karst and mixing corrosion	14
2.3.4	Calcite equilibrium discussion and summary	17
2.4	Calcite dissolution kinetics	18
2.4.1	Dissolution rate in porous media	21
2.4.2	Dissolution in fractures	24
2.5	Physical changes after mineral dissolution	26
2.5.1	Physical changes due to dissolution in porous media	27
2.5.2	Physical changes due to dissolution in fractures	38
2.6	Telogenetic and eogenetic karst	41
2.7	Vuggy porous media and macropores	43
2.8	Review discussion	44
3	Study area	47
3.1	Introduction	47
3.2	Geographical setting and bathymetry	48
3.3	Geological setting	49

3.3.1	Cretaceous to Upper Miocene geological history	49
3.3.2	Pleistocene to Holocene geological history	52
3.4	The Ox Bel Ha Karst system	62
3.4.1	Position in the sedimentary sequence	62
3.4.2	When did speleogenesis occur?	67
3.4.3	Ox Bel Ha system during sea level changes	68
3.5	Available data about geochemistry and groundwater flow	70
3.5.1	Mineral composition	70
3.5.2	Groundwater chemistry	71
3.5.3	Groundwater flow velocity	74
3.5.4	Aquifer Recharge	74
3.5.5	Preferential dissolution	77
3.6	Data acquired from CHYN team field work	77
3.6.1	Tides	78
3.6.2	Geochemistry	80
3.6.3	Drillings, tracer tests, flux imager	83
3.6.4	Limestone physical properties	89
3.7	Conclusion	90
4	Speleogenesis models	91
4.1	Introduction	91
4.2	Evolution of porous media hydraulic properties after mineral dissolution . . .	92
4.2.1	Governing equations	93
4.2.2	Numerical implementation	95
4.2.3	Analytical solution and model validation	97
4.3	Dissolution in fractures	98
4.3.1	Governing equations	99
4.3.2	Numerical implementation	101
4.3.3	Model validation	106
4.4	Conclusion	109

5	Dissolution front development around karst features due to tidal pumping in eastern Yucatan Peninsula coast	111
5.1	Introduction	111
5.2	Study area	114
5.2.1	Geological setting	114
5.2.2	Aquifer characteristics	115
5.3	Methods	116
5.3.1	Tide measurement	116
5.3.2	Reactivity sources for mineral dissolution	116
5.3.3	Conceptual model of porosity development	117
5.3.4	Governing equations	119
5.3.5	Simulation of dissolution and porosity evolution	121
5.3.6	Parameters for porosity evolution simulations	126
5.4	Results	127
5.4.1	Validation of numerical solution results	127
5.4.2	Porosity evolution simulations	128
5.5	Discussion	131
5.5.1	Mass transport and inflow water type effect on dissolution front development	132
5.5.2	Estimations of wall-retreat rate	133
5.6	Conclusions	134
6	Evolution of fracture networks	137
6.1	Introduction	137
6.2	Examples of cave geometry	138
6.3	Fracture network evolution simulations	139
6.4	Discussion and conclusion	148
7	Conclusions	151
7.1	Main results	151
7.2	Future developments	153
7.2.1	For conceptual development	153

7.2.2 For the study area	154
Appendix	155
A Code developed for the thesis	155
References	157

Chapter 1

Introduction

A significant fraction of the global population depends on groundwater as a water source. Groundwater supply is compromised either by over-extraction or pollution. Caves are an important element of groundwater systems since they are preferential paths for groundwater and pollutants. Challenges posed by water resource management require a proper knowledge of caves geometry and topology. However, caves are difficult to survey considering the physical challenges of human exploration, or even impossible considering survey efforts are constrained by economics.

One alternative to overcome the gap in information about caves is to simulate their development. The specific term given to process related to cave growth is speleogenesis. In this thesis, speleogenesis is explored through the simulation of physical processes such as groundwater flow, mass transport, mineral dissolution (reaction) and changes in petrophysical properties following dissolution.

The motivation of this thesis are large underwater karst systems located in the eastern coast of Yucatan Peninsula in Mexico in the region of the city of Tulum. The largest one is Sistema Ox Bel Ha with 270 km of connected underwater karst conduits. The total length of explored underwater conduits in the region is 1388 km. Additionally, there are 277 km of explored dry caves.

The purpose of this thesis is to apply speleogenesis knowledge to answer the following questions: Why such large karst systems formed at the eastern coast of the Yucatan Peninsula? What can we learn from these cave systems that helps us to understand other caves? These broad questions need to be subdivided into several specific questions to obtain

satisfactory answers.

The first specific question is: what are the available tools to study speleogenesis? Research on the processes that drive cave development have interested researchers for a long time. The knowledge on caves has been enriched from other fields of science: aqueous geochemistry, fluid physics, and mathematical and numerical developments to solve physics problems. The current state of research is the acknowledgement that karst networks are the result of groundwater flow and mineral dissolution acting over soluble rocks. Conceptual models to explore speleogenesis, the physics and chemistry behind them, and their implementations are described in detail in Chapter 2 of this thesis.

The second specific question is: what do we know about the study area? Karst networks in the study area have been studied by explorers and scientists in the last 50 years. Chapter 3 of this thesis reviews the information available: karst conduit maps, groundwater chemistry, groundwater recharge and flow conditions, aquifer mineralogy, topography and geological data. Chapter 3 also describes the data collected during this thesis work. This information is the base to generate hypothesis on karst development for the study area.

Chapter 4 describes the simulation tools developed by adapting previous research on speleogenesis to study speleogenesis under the specific conditions of the study area.

While carrying field work in the study area, some particular characteristics the site caught our attention: limestone is very porous, ocean tides propagate into the aquifer far away inland, conduit walls are not impermeable to flow. These observations lead to question if available conceptual models of karst development could explain the particularities of the study area. The answer was no and a new conceptual model of karst development impulsed by tides was developed. This model, its validation and application to study speleogenesis are presented in Chapter 5.

The last question is: can the simulation of speleogenesis produce structures that resemble networks similar to the study area or others? Chapter 6 approaches to this question by conducting continues simulations of fracture enlargement by flow and mineral dissolution. Results are compared to real networks and a discussion is provided.

Finally, a summary presentation of our results is presented in Chapter 7 followed by recommendations for future development.

Chapter 2

Speleogenesis review

2.1 Introduction

Speleogenesis is the name given to the natural processes contributing to the development of caves (Klimchouk et al., 2000). Caves were a subject worth of human curiosity for the mere fact of their existence.

The first hypothesis of cave formation were based on field observations that were collected at the same time chemistry was advancing as a science in the 18th century. It was recognized that groundwater was directly linked to cave formation but hypothesis differed on where the rock dissolution was happening: either in the vadose or phreatic zone. From the chemistry point of view there were two main advances. The finding that water with less suspended solids was more capable to dissolve limestone and hypothesis on the contribution of carbon dioxide on limestone dissolution. Every hypothesis was heavily influenced by the place where the observation was made. If thermal waters were present the cave formation was attributed to them. If a volcano was close, cave formation was attributed to volcanic gases. If a surface stream sunk into the ground, cave formation was linked to mechanical erosion by flow sediments (Shaw et al., 2000). Due to these punctual observations, by the end of 19th century, there were three main theories on cave formation:

1. by mechanical erosion caused by sediment grains in subsurface water flow;
2. by mineral dissolution caused by groundwater flow in the vadose zone;
3. by mineral dissolution caused by groundwater flow in the phreatic zone.

Every theory was regarded as the unique explanation for speleogenesis in all known caves. Later, it was acknowledged that these processes and others, may occur in the same cave contributing to speleogenesis according to the characteristics of the local environment. A more complete historical perspective of early theories about cave formation is provided by Shaw et al. (2000). Conceptual development in early theories established the relationship between caves and carbonate aquifers which resulted in the concept of *karst*.

Karst is a term with multiple meanings. It can be used to describe a landscape that contains caves, and having an extensive underground drainage system which develops in soluble rocks such as limestone and gypsum (Ford and Williams, 2007). Karst is also used to describe landforms, such as caves or sinkholes, which originate due to the dissolution of carbonate rocks.

If we focus on the groundwater aspects, the present conceptual model of flow in karst is divided in three main components: recharge, flow and discharge (White, 2002). Recharge is either concentrated in sinkholes or distributed in all the aquifer when rainfall percolates the soil. Flow occurs either through matrix, fracture or conduit permeability and then water exits the aquifer through springs. The most visible and specific feature in karst aquifers are the conduits that form networks. The conceptual models of karst development then logically focus on the enlargement of fractures to become conduits. However, flow and dissolution occurs also in the matrix and smaller fractures.

The following review reassesses the physical and chemical processes relevant to the formation of karst landforms. Caves develop in rock composed of different minerals, this review is focused on the dissolution of calcite. The first section of the review focuses on the minerals. The second section focuses on the dissolution reaction, describing reactive transport in porous media, fractures and conduits. The third section treats the physical changes such as porosity increase in porous media or aperture enlargement in fractures. The split between reactions and physical changes is just conceptual because both processes occur at the same time. The only major difference is time scale: chemical reactions occur over hours to days while observable physical changes such as conduit enlargement occur over years.

2.2 Minerals in karst landscapes

The majority of sedimentary carbonate minerals is biogenic in origin, meaning these minerals are composed by skeletal hard parts of organisms. A smaller fraction of carbonate sediments is formed abiogenically, meaning heterogeneous mineral precipitation in water or diagenesis in already deposited sediments (Morse et al., 2007). Biogenic skeletal carbonates are different to abiogenic ones in terms of porosity, permeability, reaction surface area or mineral composition. Reaction surface area is an important variable because it controls the interactions between the mineral and water. Carbonate rocks are mainly a mixture of aragonite (CaCO_3), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and magnesite (MgCO_3). This review focuses on calcite.

There are two approaches to study calcite dissolution: equilibrium and kinetics chemistry. They are complementary to study speleogenesis. Equilibrium chemistry is used to assess the reactivity of water to minerals, it allows knowing if speleogenesis occurs or not. Kinetics chemistry allows estimating the rate of alteration of minerals by dissolution.

2.3 Calcite equilibrium chemistry

The purpose of this section is to provide a background on solubility of minerals theory, the special characteristics of carbonate equilibria compared to other minerals, the measurements in water samples required to estimate carbonate equilibria, and the practical way do these calculations. The section finishes with a discussion of the presented topics.

Carbonate rock dissolution reactions can occur both forward and in reverse. Equilibrium means dynamic equilibrium where the forward and backward reaction rates are equal, thus the total amount of reactants and products remain constant. The calcite dissolution reaction in pure water is shown in equation (2.1). The

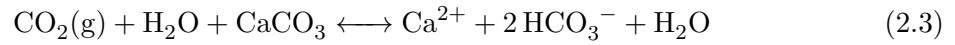


The amount of dissolved calcium Ca^{2+} is equivalent to the amount of dissolved carbonate CO_3^{2-} . Assuming the calcite solubility product is equal to $K_{\text{calcite}} = 10^{-8.48}$ (Appelo and Postma, 2010, p. 176) and assuming Ca^{2+} ion activities are equal to molar concentrations (mol per liter of water) the mass action equation (2.2).

$$\begin{aligned}
K_{calcite} &= [Ca^{2+}][CO_3^{2-}] = [Ca^{2+}]^2 = 10^{-8.48} \\
[Ca^{2+}] &= 10^{-4.24} = 5.75 \times 10^{-5} \text{ mol/L} \approx 0.06 \text{ mmol/L}
\end{aligned}
\tag{2.2}$$

0.06 mmol per liter is equivalent to 2.4 mg L⁻¹ of Ca²⁺ in solution. However, one can observe that average groundwater has a Ca²⁺ mass concentration in solution an order of magnitude higher than the expected amount estimated for pure water. Groundwater in nature is not pure, and contains many solutes that can increase the solubility of carbonate minerals. The most significant solute in groundwater in terms of increased calcite solubility is carbon dioxide (Appelo and Postma, 2010, p. 178).

The full reaction between carbon dioxide CO₂ and CaCO₃ is shown in equation (2.3).



The reaction between calcite and carbon dioxide is significant because CO₂ is relatively abundant in soils and groundwater. However, the reaction is complex and needs to be decomposed in the intermediate reactions in order to understand the effect of pH on carbonates species. When CO₂ dissolves in water, gas phase CO_{2(g)} becomes CO_{2(aq)} and a fraction of the carbon dioxide in the aqueous phase associates with water to form carbonic acid (H₂CO₃) as shown in equation (2.4).



CO_{2(aq)} occurs at the same time as carbonic acid H₂CO₃ and is more abundant. In order to simplify a convention is adopted and both species CO_{2(aq)} and H₂CO₃ are summed (Appelo and Postma, 2010, pag. 179) resulting in equation (2.5) where H₂CO₃^{*}=CO_{2(aq)} + H₂CO₃.



Subsequently H₂CO₃ dissociates in water and releases two protons H⁺ which associate with the CO₃²⁻ from calcite to form bicarbonate HCO₃⁻. Since the concentration of CO₃²⁻ is reduced by the presence of free protons, the concentration of dissolved carbonates species

H_2CO_3^* , HCO_3^- , CO_3^{2-} depends on the pH of the solution. The reactions and mass actions constants needed to calculate the species concentration in solution are as follows (2.6,2.7,2.8) (Appelo and Postma, 2010, pag. 180).

CO₂ dissolution in water (hydration): $\text{CO}_{2(\text{g})} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CO}_3^*$

$$K_H = [\text{H}_2\text{CO}_3^*]/[\text{P}_{\text{CO}_2}] = 10^{-1.5} \quad (2.6)$$

Carbonic acid dissociation: $\text{H}_2\text{CO}_3^* \longleftrightarrow \text{H}^+ + \text{HCO}_3^-$

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3^*] = 10^{-6.3} \quad (2.7)$$

Carbonate and bicarbonate depending on pH: $\text{HCO}_3^- \longleftrightarrow \text{H}^+ + \text{CO}_3^{2-}$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 10^{-10.3} \quad (2.8)$$

The dominant species in a carbonates solution with a pH below 6.3 is H_2CO_3^* (non-dissociated carbonic acid and $\text{CO}_{2(\text{aq})}$). In a solution with a pH between 6.3 and 10.3 the predominant carbonate species is bicarbonate HCO_3^- . Figure 2.1 shows the distribution of carbonate species as a function of pH .

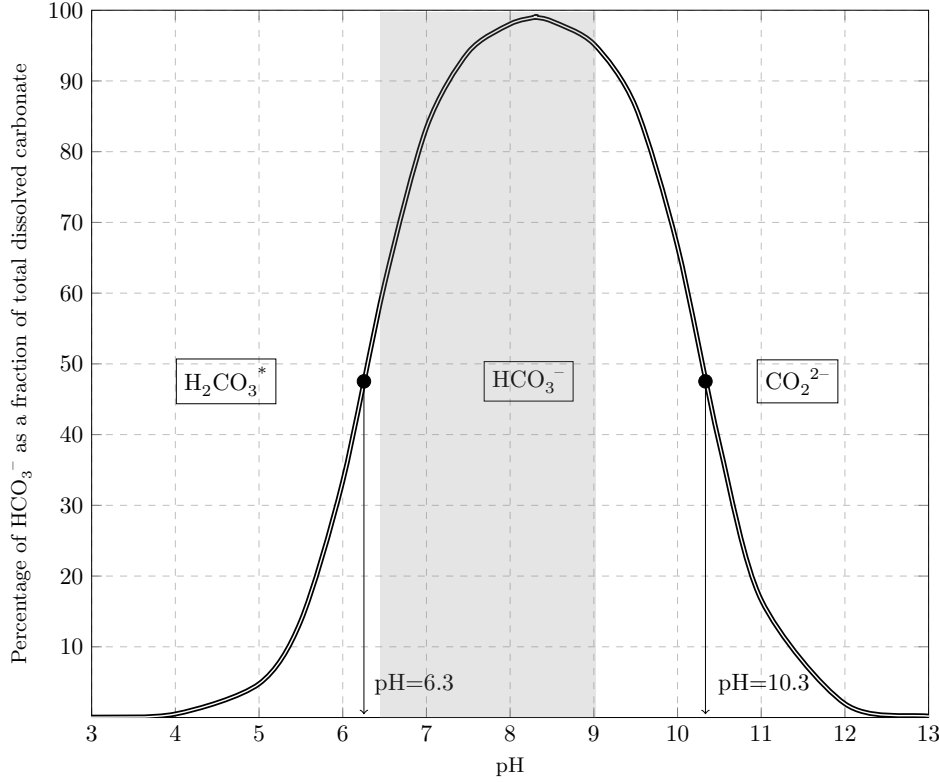


Figure 2.1: H_2CO_3^* , HCO_3^- , CO_3^{2-} percentages of total dissolved carbonate as function of pH, adapted from (Appelo and Postma, 2010, pag. 180). Shaded area in gray shows the pH range for common karst groundwaters. In this interval HCO_3^- as a fraction of total of dissolved carbonate ranges from 60 to 100%.

The sum of dissolved carbonate species is given by the following mass balance equation; where the total inorganic carbonate species (TIC) is the sum of the concentrations of carbonic acid, bicarbonate and carbonate (Appelo and Postma, 2010, p. 181)

$$\Sigma\text{CO}_2 = \text{TIC} = m_{\text{H}_2\text{CO}_3^*} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} \quad (2.9)$$

Thus, the carbonate system speciation is defined by equations (2.6), (2.7), (2.8) and (2.9). There are four equations but 6 unknowns: H_2CO_3^* , P_{CO_2} , H^+ or pH, HCO_3^- , CO_3^{2-} , $\Sigma\text{CO}_2 = \text{TIC}$. Thus, to solve this equation system it is necessary to measure in water sample at least two variables to define the remaining four (Appelo and Postma, 2010, p. 183). The variables that can be measured in water samples in order of complexity of the test are:

- pH and alkalinity (acid neutralizing capacity = $m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}}$)

- total inorganic carbon (TIC)
- carbon dioxide partial pressure (P_{CO_2})

The reaction between $\text{CO}_2(\text{g})$ and calcite is shown in equation (2.3). The mass action equation is the following and the solubility product K is obtained by combining the calcite dissociation reaction (2.1) with the reactions of the carbonate system (2.6), (2.7) and (2.8) (Appelo and Postma, 2010, p. 191):

$$\frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[P_{\text{CO}_2}]} = 10^{-6.0} = K \quad (2.10)$$

Assuming water is at equilibrium with $\text{CO}_2(\text{g})$ from the atmosphere, $P_{\text{CO}_2} = 10^{-3.5}$, water will contain 0.44 mmol L^{-1} of Ca^{2+} . Comparing this result with equation (2.2) shows that the amount of carbon dioxide found in the atmosphere increases calcite solubility by a factor of approximately 7. However, groundwater can have P_{CO_2} values 100 times higher than the atmosphere due to bacterial activity in soils (Appelo and Postma, 2010, p. 186). Then, the expected Ca^{2+} concentration in groundwater is approximately 2 mmol L^{-1} or 33 times the solubility of calcite in pure water.

2.3.1 Solutes molar concentrations and Ion Activity

The assumption that molar concentrations of ions are equivalent to the activity of those ions in solution was made to simplify the explanation of the carbonate species system. However, mass action equations (e.g. 2.2 and 2.10) are valid only for the activity of ions. The activity of an ion is the measured concentration corrected by accounting for electrostatic shielding and the formation of aqueous complexes (Appelo and Postma, 2010).

Electrostatic shielding/Ionic strength effect

Solutions are assumed as electrically neutral, meaning there is the same number of anions and cations in solution, or electroneutrality. The electroneutrality assumption is valid only at the macroscopic level. At the ion size level, electroneutrality does not apply because ions are charged particles with a region of influence around them. For example, a cation will

have in its vicinity a positive electrical potential, thus different than the average potential of the solution that is 0. Thermal motion of ions in a solution (Brownian motion) makes other cations and anions enter and exit the vicinity of the cation. Due to the electrical potential of the cation, anions will then stay longer on average in the vicinity of the cation. The time-averaged effect of the continuous movement and electrical potential is that anions will have an affinity to stay around cations and viceversa. Due to the structure of the water molecule and the oxygen atom having a higher electronegativity compared to hydrogen atoms, the molecule is not neutral (Murray, 2004). The hydrogen atoms are weakly positive and the oxygen atom is weakly negative, see figure 2.2.

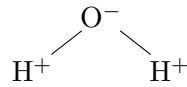


Figure 2.2: Water molecule

In solutions with an extremely low solute content, the solute ions most probably will have water molecules in their vicinity. For example, calcite will dissolve into calcium and carbonate ions that will be surrounded by water molecules (Murray, 2004), see figure 2.3.

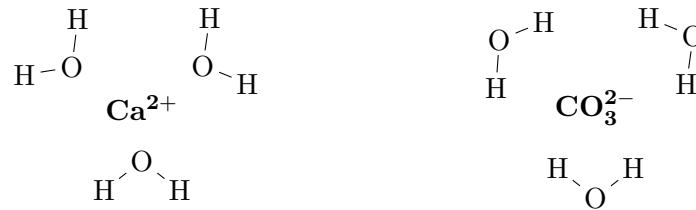


Figure 2.3: Carbonate and calcium ions in a very low solute content solution. The shielding by water molecules will reduce the probability of Ca^{2+} and CO_3^{2-} to encounter themselves in the solution, react and precipitate as solids.

Water molecules will shield Ca^{2+} and CO_3^{2-} ions from interacting with each other. The solute ions will behave as if they were present in a smaller concentration than they really are, this is the origin of the concept of activity coefficient. The activity coefficient γ accounts for the relationship between the ion chemical activity and the real concentration in solution. See equation (2.11) (Appelo and Postma, 2010) where activity A and concentration C are expressed in mol units:

$$A = \gamma C \tag{2.11}$$

The strength of the interaction between solute ions and water molecules depends on electrical charges described by Coulomb's Law. The force between two charged particles depends on the particle charge magnitude and the distance between the particles. Applying this concept to aqueous solutions, the charge magnitude depends on the ion charge. Monovalent ions, like Na^+ and Cl^- , product of NaCl solution, will attract less strongly molecules compared to divalent ions like Ca^{2+} and CO_3^{2-} . However, since the water molecule electrical potential is small, the effect on the activity is almost negligible. Thus, the activity coefficient is almost 1 and the ion concentration in mol units in solution is almost equal to ion activity, see A region in figure 2.5.

In solutions with moderate solute content, the probability of a solute ion Ca^{2+} of encountering another solute ion of opposite charge, CO_3^{2-} , is greater. Thus, they should meet, react and precipitate. However, it is extremely uncommon to find pure calcite solutions in nature. For example, if NaCl is added to a pure calcite solution, negative charge Cl^- ions will surround Ca^{2+} ions even if a bond is not formed. The same situation happens for negatively charged CO_3^{2-} ion that get surrounded by positive Na^+ and water molecules, see figure 2.4. Since the electrical potentials of Na^+ and Cl^- are higher than water molecules the electrostatic shielding is stronger than the one produced only by water molecules, the reduction in ion activity is greater (Murray, 2004). See B region in figure 2.5.

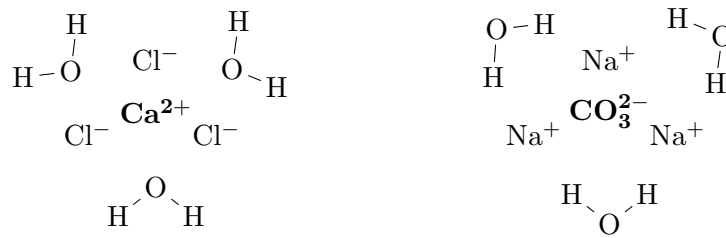


Figure 2.4: Carbonate and calcium ions in a moderate solute content solution. Na^+ and Cl^- ions surround the ions produced by calcite dissolution even if they don't bond. The electrostatic shielding prevents Ca^{2+} and CO_3^{2-} from coming together and precipitate.

The total amount of ions (electrical charges) in solution is measured by ionic strength. Ionic strength is estimated with the charge of an ion (z_i) and the molality (z_i) of such ion as shown in equation (2.12):

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (2.12)$$

The greater the ionic strength of the solution, the lower the activity coefficient for each ion in solution as explained by electrostatic shielding. Several theories use ionic strength and the ion size parameter to model the ion activity coefficient, the simplest one is the Debye-Hückel model (Appelo and Postma, 2010).

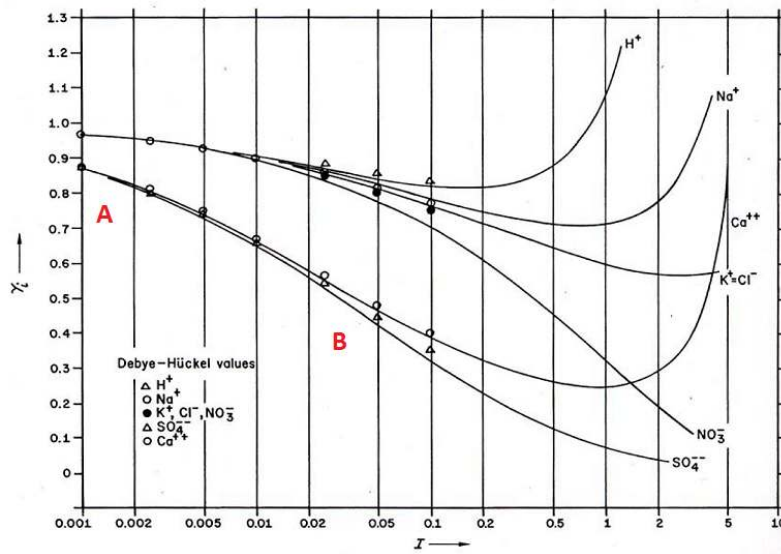


Figure 2.5: Activity coefficients for some ions as a function of Ionic Strength. Solutions with extremely low solute content are in zone A and solutions with moderate solute content in zone B. Modified from Garrels and Christ (1965).

Aqueous complexes

Free ions in an aqueous solution may come close enough, become attached and considered new species. These new species are called ion pairs or aqueous complexes. Ion pairs are separated by water molecules but share their first hydration shell (H_2O molecules around ion). Aqueous complexes occur when ions are in contact and share electrons (Murray, 2004). Ion pairs and complexes are described in figure 2.4. Examples are major cation complexes such as CaSO_4^0 , CaF^+ or CaOH^+ . For example, the total calcium concentration in a solution is distributed among Ca^{2+} , CaHCO_3^+ , CaSO_4^0 , CaCO_3 , CaOH^+ and CaHSO_4^+ . Therefore the mass balance of calcium is expressed in equation (2.13):

$$\Sigma\text{Ca} = m_{\text{Ca}^{2+}} + m_{\text{CaHCO}_3^+} + m_{\text{CaSO}_4^0} + m_{\text{CaOH}^+} + \dots \quad (2.13)$$

The formation of complexes can be described by equilibrium equations known as ion-association reactions and the corresponding mass action constant is named stability constant. These equations are very similar to mineral dissolution ones (Appelo and Postma, 2010).

Electrostatic shielding and aqueous complexes are part of the same process. However, for a better understanding and modeling of the process it was divided in two parts. The activity coefficients and ion activities are estimated to initiate an ion-pairing calculation. These variables are used to calculate the activities of the complexes. Then, molal activities of complexes are estimated that allow the calculus of improved mass balances and a better estimate of ionic strength. This iterative process ends when no significant improvement of the estimate of ionic strength is found. The ion pairing iterative process is solved numerically by PHREEQC software (Parkhurst and Appelo, 2013), see figure (2.6).

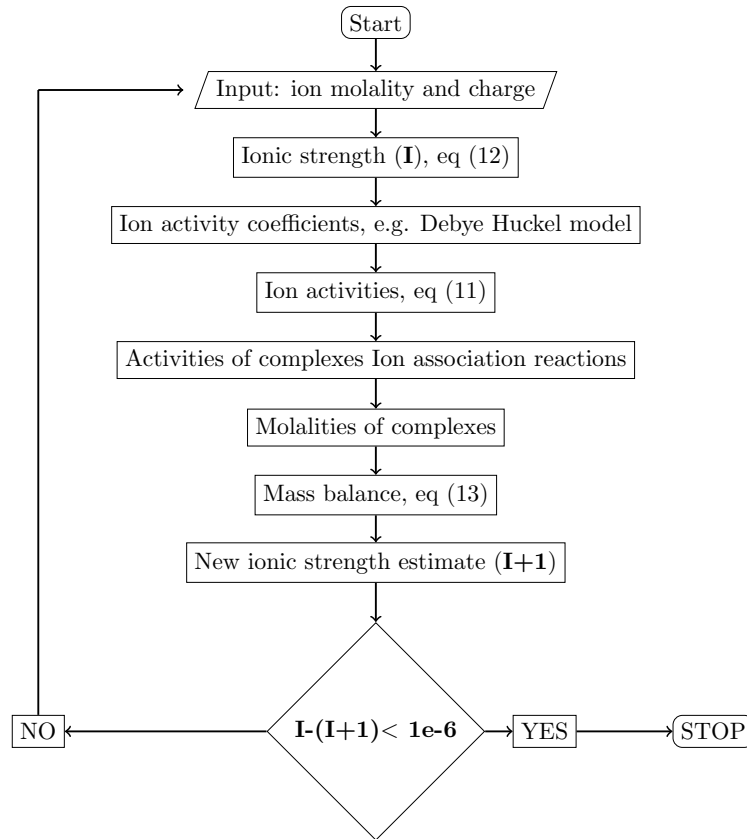


Figure 2.6: Iterative process of speciation of ions accounting for electrostatic shielding and the formation of complexes

Ion activity effect on mineral dissolution

The observable effect of a reduction in the activity coefficient of an ion is an increase in the solubility of minerals (Appelo and Postma, 2010). The formation of ion pairs and complexes tends to further increase carbonate solubilities in waters where I (ionic strength) exceeds 0.01. Thus, in seawater with $I \approx 0.7$ and zero dissolved CO_2 , calcite is 480 times more soluble than pure water. Electrostatic shielding accounts for 2-fold increase in solubility and ion pairs or complexes account for a 240-fold increase in calcite solubility from pure water to seawater (Langmuir, 1984).

2.3.2 Saturation Index

The Mineral Saturation Index (SI) used today was first proposed by Langmuir (1971) based on mineral stability research (equilibrium constants) made by Garrels and Christ (1965). Based on data like temperature, and concentrations of Ca^{2+} , HCO_3^- , field measured pH and the concentration of other ions that influence ion-pairing. Whether water is undersaturated, saturated or supersaturated can be determined by comparing the equilibrium constant K_c , see equation (2.1) the ion activity product IAP of calcite in water. For calcite, saturation index is calculated with equation (2.14). A negative SI indicates undersaturation (dissolution potential). $SI = 0$ indicates saturation and a positive value of SI indicates supersaturation (precipitation potential). Equilibrium constant K is obtained from experiments on dissolution based on thermodynamic theory. Thus *equilibrium constants* vary with water temperature. More information can be found in Appelo and Postma (2010, p. 132-133).

$$SI = \log \left(\frac{IAP}{K} \right) \quad (2.14)$$

2.3.3 Hydrothermal karst and mixing corrosion

Besides groundwater with high dissolved CO_2 concentration there are other sources of reactivity related to speleogenesis, among them hydrothermal karst and mixing corrosion.

Hydrothermal karst is caused by the rise of geothermal waters rising from depth. Those waters may be saturated with carbon dioxide which may originate from the metamorphism

of carbonate rocks or from volcanic activity (Dublinsky, 2000). Volcanic activity is also related to hydrogen sulfide gas $\text{H}_2\text{S}_{(\text{g})}$ that produces sulfuric acid when dissolved in water.

(Bögli, 1964) proposed that the enlargement of capillary joints and narrow fractures into karst conduits can not be explained only by the relationship between water, calcite and carbon dioxide. Reactive surface water can infiltrate and become groundwater but it would eventually saturate and lose its capacity to dissolve minerals. Thus, the enlargement of conduits in large conduit networks must be driven by other process. Bögli analyzed the mixing of waters with different CO_2 concentrations using the solubility curve of calcite in water as a function of CO_2 . This relationship between CO_2 in equilibrium with CaCO_3 was first developed by Tillmans (Greenfield and Baker, 1920) and later improved by Zehender et al. (1956).

Figure 2.7 shows the divide between the zone of precipitation of calcite (above the thick black line) from the water that dissolves calcite (aggressive). A straight line formed by two points over the solubility curve is always in the aggressive water zone. This straight line represents the sum of all possible mixes between two water samples: W_1 and W_2 . Every time waters with a different CaCO_3 content mix, the result is an increase in calcite solubility provided there is no exchange of carbon dioxide with the surrounding environment (closed CO_2 system). This additional solubility was named mixing corrosion by Bögli.

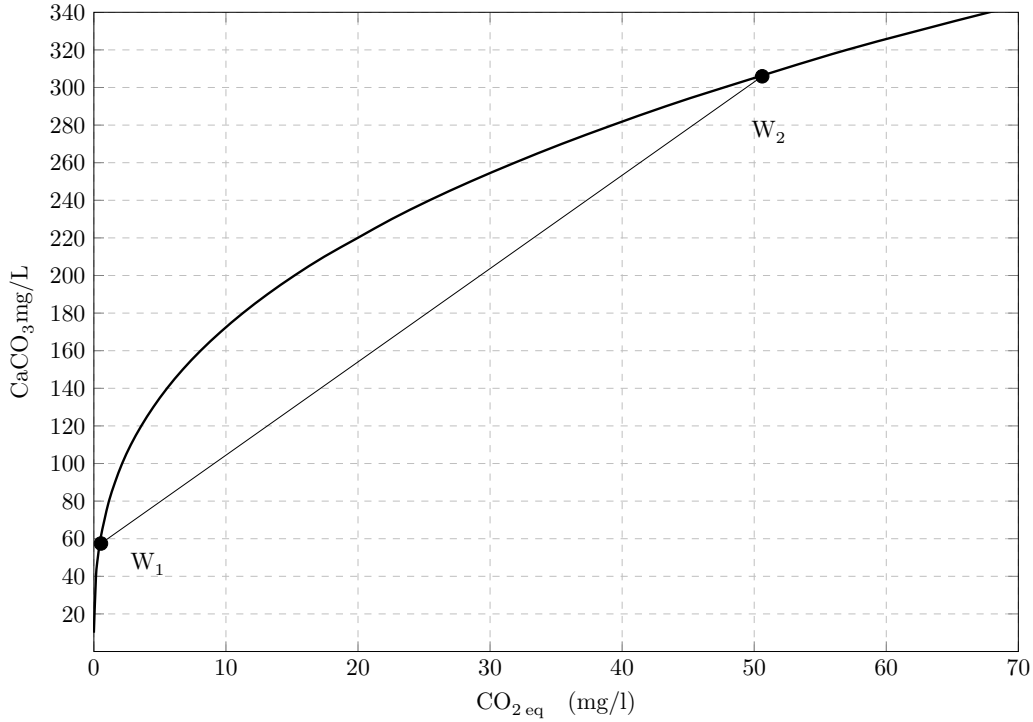


Figure 2.7: Solubility curve for calcite in water depending on carbon dioxide concentration, (thick black line). Mixing corrosion (thin line), adapted from (Bögli, 1964).

The calcite solubility model on which Bögli based his mixing-corrosion hypothesis relied on equation (2.15) where C is the CO_2 concentration in equilibrium with calcite, K is a constant that accounts for temperature influence Table 1a in Zehender et al. (1956), f is a constant that accounts for effects caused by non carbonate ions in solution Table 1b in (Zehender et al., 1956), CaH is Calcium Hardness of water in French Degrees and KH is the ratio Carbonate Hardness versus Alkalinity of water in French Degrees. Constant f , that accounted for ion effects, was estimated based on Total Hardness and Carbonate Hardness of water. Bögli, based also on Zehender's carbonate equilibria model, proposed that water temperature had an influence in calcite dissolution. Waters of different temperatures mixing would have an additional effect beyond the CO_2 difference between them.

$$C = \frac{K}{f}(CaH)(KH)^2 \quad (2.15)$$

Bögli presented his work one year before the publication of the modern carbonate system model developed by Garrels and Christ (1965). Alan Howard (1966) verified analytically one

year later Bögli's hypothesis using Garrel's carbonate system model and obtained smaller but similar increases in calcite solubility after mixing, thus proving the existence of mixing-corrosion.

Wigley and Plummer (1976) further assessed the mixing-corrosion effect, they found mixing waters could cause:

1. calcite supersaturation when Ca^{2+} or CO_3^{2-} have different activities but the same dissolved CO_2 concentration in end-member solutions.
2. undersaturation when calcite saturated waters with different dissolved CO_2 concentration are mixed.
3. undersaturation when saturated solutions with different ionic strength are mixed, i.e. fresh and sea water.
4. undersaturation when saturated solutions at different temperatures mix.

2.3.4 Calcite equilibrium discussion and summary

As reviewed in the previous sections, the main theoretical concepts behind calcite dissolution are the following:

1. Mass action (equilibrium) constants
2. The effect of CO_2 on calcite solubility
3. Carbonate species concentrations depending on pH
4. Measurements of dissolved Ca^{2+} in water samples
5. The difference between ion activity and molar concentration driven by aqueous complexes and electrostatic shielding.
6. The concept of Saturation Index SI
7. Mixing corrosion

All those concepts are included in the dissolved ion speciation software PHREEQC (Parkhurst and Appelo, 2013). Calculations done in PHREEQC account for the effects of

solution temperature and ion activity. Thus, the most simple approach to make calcite *SI* calculations is to measure temperature, pH, alkalinity and cation/anion, and then process the data in PHREEQC.

The Saturation Index is a useful tool but it is not the final answer to explain mineral dissolution or precipitation. The most common example of supersaturation with mineral precipitation is seawater. The thermodynamical concepts behind Saturation Index do not account for metastable mineral phases (more than 1 equilibrium state) and do not consider that reaction rates are controlled by mineral surface geometry or impurities causing kinetic inhibition (Morse et al., 2007). Calcite equilibrium chemistry allows estimating the potential of mineral dissolution or precipitation. However, potential does not ensure a reaction will occur, or it may occur at a rate so slowly that it is practically inhibited. Thus, to overcome these limitations calcite dissolution kinetics approaches are reviewed in the following section. In consequence PHREEQC is used only to estimate dissolution potential but not applied directly to calculate dissolution kinetics.

2.4 Calcite dissolution kinetics

Equilibrium chemistry relies on basic laws such as thermodynamics to explain mineral solubility. In contrast, kinetics chemistry relies only on dissolution experiments and dissolution conceptual models that are rough approximations to the dissolution process or even ignore processes. Conceptual models rely on what can be observed and measured in dissolution experiments. Dissolution can be observed in two ways, either indirectly by observing changes in the solution chemistry or directly by measuring changes in the mineral surface geometry (the solid-liquid interface) (Morse et al., 2007). The first method has been the most commonly used since the early developments in solution chemistry dating from the 1930s with important breakthroughs in the 1960s. The second method relies on more recent developments in microscopic imaging allowing to observe directly the reaction surface, measure it and track geometry and volume changes.

Present dissolution kinetics conceptual models rely on solution chemistry concepts because it was the only alternative to observe dissolution. Dissolution reactions are relatively slow, but increasing the ratio of mineral crystal surface area by crushing the minerals or using strong acids makes even very slow rates measurable. In the solution chemistry approach,

the surface area in contact with the solution needs to be quantified. Quantifying the mineral surface area is a problem still unsolved (Morse et al., 2007), thus dissolution kinetics based on the solution chemistry approach need a relatively arbitrary assumption on surface area. So far, microscopic imaging has only been applied to quantify the reaction surface area and observe crystal formation, but a new conceptual model has not yet been formulated.

After the development and validation of the mineral Saturation Index developed by Langmuir (Langmuir, 1971), researchers identified several cases of water from carbonate aquifers that were undersaturated with calcite. The undersaturation of groundwater suggested that kinetics of calcite in natural environments may be relatively slow. Thus, the importance of studying calcite dissolution kinetics.

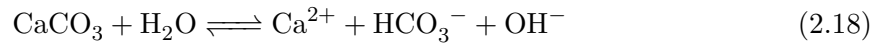
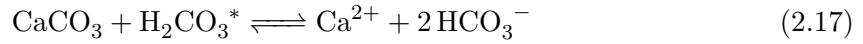
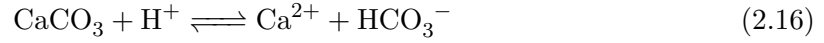
Based on previous research showing the importance of mass transport processes in calcite dissolution rate, Plummer and Wigley (1976) hypothesized that the rate of dissolution of any mineral is dependent on:

1. Rate of transport of reactants and products between mineral surface and the bulk solution.
2. Rate of heterogeneous reaction at the mineral surface. Heterogeneous means a reaction occurring in two phases. In this case it is the dissolution reaction at the liquid-solid interface.
3. Rates of homogeneous reactions within the solvent. Homogeneous means reaction in one single phase. In this case it is applied to describe reactions in the liquid phase.

What researchers observe in a dissolution experiment is a superposition of these three limiting processes. Plummer and Wigley (1976) set up an experiment with powdered calcite and assumed that by stirring the solution, the limiting effect of mass transport rate between mineral surface and bulk solution is minimized. Also, they assumed homogeneous reactions are very fast, thus not limiting the rate. Under these assumptions the measured calcite dissolution rate is probably determined only by the kinetics of heterogeneous surface reactions. In this experiment the reaction surface area was estimated from the mineral weight and assuming every mineral grain was a rhombohedron.

Plummer et al. (1978) formulated a conceptual model based on the results of dissolution experiments. Dissolution is explained by 3 reversible reactions shown in equations (2.16),

(2.17) and (2.18).



These reactions are integrated in the net rate of dissolution that covers both dissolution and precipitation in equation (2.20) where r is the specific dissolution rate in $\text{mmol cm}^{-2} \text{s}^{-1}$ units.

$$r = \frac{\partial[\text{Ca}^{2+}]}{\partial t} \quad (2.19)$$

$$r = k_1[\text{H}^+] + k_2[\text{H}_2\text{CO}_3] + k_3[\text{H}_2\text{O}] - k_4[\text{Ca}^{2+}][\text{HCO}_3^-] \quad (2.20)$$

Equation (2.20) is known as the PWP equation. It is remarkable theoretical development but its applicability in karst development models is limited by three factors: flow conditions found in karst and the reaction surface area quantification problem.

The origin of the PWP equation is a dissolution experiment where the solvent solution is stirred to minimize the limiting effects of mass transport between the bulk solution and mineral surface. Groundwater laminar flow probably occurs in fractures that develop into karst conduits. Under laminar flow conditions, the transport of mass between mineral surface and bulk solution is molecular diffusion. Thus, dissolution kinetics applied to karst must account for mass transport between the mineral surface and the bulk solution.

If the PWP equation is applied to study dissolution in porous media, an assumption of the reaction surface area to volume ratio A/V , in L^2/L^3 units, needs to be made. As explained before, measuring reaction surface area is a challenging problem, while possible heterogeneities in reaction surface area are found in carbonate rock. As explained in section 2.2, the biogenic origin of calcite implies differences in reaction surface area depending on which organisms deposited calcite in first place.

Despite these issues, the PWP equation is the base for dissolution kinetics conceptual models applied to karst that will be reviewed in the following sections, both for groundwater flow in fractures and porous media. The implicit assumption in these models is that the most important processes of karstification take place in the phreatic zone under closed-system conditions (Buhmann and Dreybrodt, 1985). This assumption implies groundwater got CO_2 either by being in equilibrium with the atmosphere before infiltration or by getting saturated by soil CO_2 . Once surface water becomes groundwater, the amount of dissolved carbon dioxide is assumed as constant.

2.4.1 Dissolution rate in porous media

A conceptual pore scale model of calcite dissolution kinetics in a porous medium was developed by (Buhmann and Dreybrodt, 1985). The model is derived from describing flow in between two parallel planes and then adapting it to a porous medium. The geometrical model is shown in figure 2.8. A water film of thickness 2δ is wrapped by two parallel planes of calcite. The flux of ions F is given by PWP equation (rate r in 2.20) and the transport rate from the mineral surface to bulk solution is calculated assuming molecular diffusion as mass transport mechanism. Flux F can be interpreted as an effective dissolution rate that takes into account the mass transport limit that occurs on the flow conditions of karst environments.

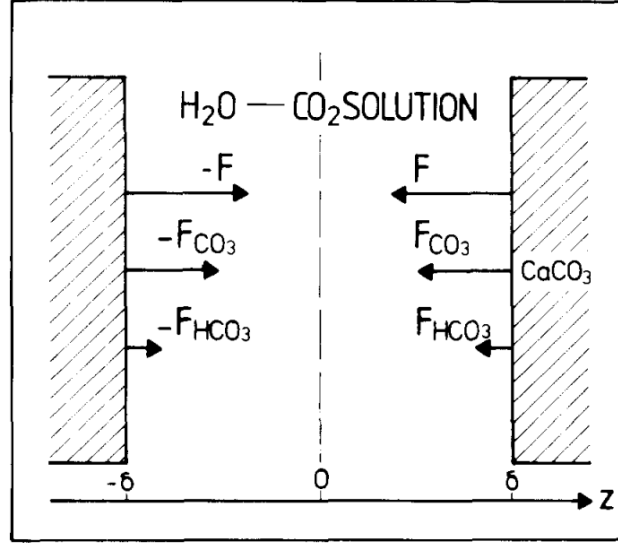


Figure 2.8: Geometrical model of calcite dissolution in a system closed to the atmosphere (Buhmann and Dreybrodt, 1985)

Besides theoretical development, Buhmann and Dreybrodt (1985) conducted dissolution experiments and their results could be explained by equation (2.21). α is an experimental constant in cm s^{-1} , $[\text{Ca}^{2+}]_{\text{eq}}$ is the calcium equilibrium concentration as a function of distance δ , dissolved carbon dioxide concentration P_{CO_2} , and temperature $[\text{Ca}^{2+}]_{\text{av}}$ is the experimentally measured value of Ca^{2+} concentration.

$$F = \alpha \{ [\text{Ca}^{2+}]_{\text{eq}} - [\text{Ca}^{2+}]_{\text{av}} \} \quad (2.21)$$

The distance δ is a very important variable in this conceptual model. Figure 2.9 shows the calculated values of the constant α for experiments at different temperatures, CO_2 partial pressures and separation of parallel plates δ . For lower values ($\delta < 0.005\text{cm}$) the calculated constant α is almost the same for turbulent and laminar flow. Buhmann and Dreybrodt (1985) concluded that for thinner water films mass transport between mineral surface and bulk solution does not limit the dissolution reaction and the effect of mass transport in dissolution reaction rate can be ignored up a distance $\delta = 0.01\text{cm}$.

δ (cm)	$P_{\text{CO}_2} = 1 \cdot 10^{-2}$ atm.			$P_{\text{CO}_2} = 3 \cdot 10^{-2}$ atm.			$P_{\text{CO}_2} = 5 \cdot 10^{-2}$ atm.			$P_{\text{CO}_2} = 1 \cdot 10^{-1}$ atm.		
	5°C	10°C	20°C	5°C	10°C	20°C	5°C	10°C	20°C	5°C	10°C	20°C
(a) Laminar flow:												
0.001	0.714	1.6	7.14	0.606	1.1	3.33	0.666	1.19	3.33	0.833	1.39	3.23
0.002	1.3	2.8	13.3	1.18	2.1	6.25	1.25	2.25	5.26	1.05	1.73	3.33
0.005	3.13	6.4	21.7	2.13	3.5	8.93	1.49	2.5	5.0	1.06	1.73	3.33
0.01	5.26	9.6	21.7	2.04	3.5	8.7	1.49	2.47	4.76	1.06	1.73	3.23
0.02	5.13	9.5	18.2	2.0	3.46	6.9	1.46	2.44	4.76	1.05	1.70	3.17
0.05	4.76	8.4	16.1	2.0	3.3	6.5	1.43	2.43	4.67	1.04	1.68	3.07
0.1	4.08	7.7	12.7	1.89	3.25	5.9	1.4	2.29	4.46	1.01	1.61	2.95
(b) Turbulent flow:												
0.001	1.08	3.3	9.75	0.63	1.08	4.1	0.655	1.17	3.37	0.82	1.37	3.5
0.003	2.9	7.3	22.0	1.8	3.3	9.5	1.97	3.32	8.14	2.28	3.5	6.0
0.005	5.08	10.2	27.5	2.9	5.1	13.0	3.13	5.09	10.4	3.3	4.7	7.8
0.01	8.6	15.1	34.0	5.4	8.75	17.0	5.2	7.3	13.0	4.54	6.05	9.0
0.02	13.2	20.5	45.0	8.2	11.3	19.0	6.9	8.9	13.9	5.5	7.0	10.2
(c) Ca^{2+} concentrations at saturation:												
$[\text{Ca}^{2+}]_{\text{eq}}$	6.4	5.5	4.1	16.6	14.4	11.0	24.3	21.4	16.9	38.8	35.1	28.0

Figure 2.9: Calculated value of α in 10^{-5}cm s^{-1} for various pressures of CO_2 , temperatures and film thicknesses δ for (a) laminar flow, (b) turbulent flow. Part (c) gives the calculated Ca^{2+} concentrations in $10^{-4} \text{mmol cm}^{-3}$ (Buhmann and Dreybrodt, 1985)

To describe dissolution in porous media, the distance δ is substituted by the pore size (Baumann et al., 1985). Then, from the flux equation (2.21) they derived the calcite dissolution rate

$$r = \frac{S}{V_p} \alpha (C_{eq} - C) = k (C_{eq} - C) \quad (2.22)$$

where S is the effective surface area of porous media volume, α the experimental constant from equation (2.21), C_{eq} is the Ca^{2+} equilibrium concentration and C the solution Ca^{2+} concentration. Constants S , V_p and α are integrated into constant k

Equation (2.22) provides a reasonable approximation of dissolution occurring in porous media for pore sizes up to $0.005 - 0.01 \text{cm}$. Equation (2.22) is the result of calcite dissolution experiments. In spite of its simplicity it accounts for mass transport between mineral surface and bulk solution in pore space. It is simpler to implement in a simulation compared to the PWP model (equation 2.20) because it is a linear model and there is only 1 solute species to take into account in a reactive transport simulation. Equation (2.22) will be used in this thesis as the dissolution kinetics model for porous media.

2.4.2 Dissolution in fractures

Dissolution in fractures is also limited by the mineral reaction surface rate and the mass transport rate between the mineral surface and the bulk flow solution. The mineral dissolution reaction rate different to the one applied to porous media. The PWP equation was developed using pure calcite. Dissolution experiments in natural limestone show a different behavior, when the solution approaches equilibrium the calcite dissolution rate diminishes. Thus, it is not linear. Eisenlohr et al. (1999) explain the rate decrease by impurities being released from the calcite rock during dissolution and adsorbing into the reaction surface where they act as inhibitors. The observable effect is that dissolution experiment's results need to be explained by using higher order kinetics. Dreybrodt et al. (2005b) propose an empirical model for natural limestones where the dissolution rate depends on how far the solution is from equilibrium concentration c_{eq} . Dissolution far from equilibrium can be explained by equation (2.23) that is linear, $n = 1$. At a certain Ca^{2+} content, the dissolution rate slows down and is estimated using equation (2.24). The point at which dissolution kinetics change is named switch concentration c_s and (Dreybrodt et al., 2005b) assumed it to occur at $c_s \approx 0.8 c_{eq}$.

$$r = k_1 (1 - c/c_{eq})^n \quad \text{for } c < c_s \quad (2.23)$$

$$r = k_n (1 - c/c_{eq})^n \quad \text{for } c \geq c_s \quad (2.24)$$

Flow in a fracture can be laminar or turbulent. It depends on fracture geometry and hydraulic boundary conditions. In laminar flow, the transport of ions from mineral surface to bulk solution is driven only by molecular diffusion. For laminar flow, equation (2.25) shows the dissolution rate for solutions far from equilibrium $c < c_s$ where $k_1 = 4 \times 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$ is the kinetic constant, D the molecular diffusion coefficient, a the fracture aperture, c calcite concentration and c_{eq} calcite equilibrium concentration. Equation (2.26) applies to solutions close to equilibrium $c \geq c_s$ in laminar flow where kinetic constant is equal to $k_n = 4 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ and reaction order $n = 4$.

$$r = \frac{k_1}{1 + (k_1 a)/(3D c_{eq})} \left(1 - \frac{c}{c_{eq}}\right) \quad \text{for } c < c_s \quad (2.25)$$

$$r = k_n \left(1 - \frac{c}{c_{eq}}\right)^n \quad \text{for } c \geq c_s \quad (2.26)$$

For turbulent flow, Dreybrodt et al. (2005b) hypothesized the existence of a zone where mass transport between the mineral surface and the bulk solution is driven only by molecular diffusion. They named this zone diffusion boundary layer *BDL*, see figure (2.10). The higher the turbulence in flow (Reynolds number) the thinner is *BDL*. Thus, at a certain flow speed, *BDL* is minimized by turbulence and the dissolution reaction is only controlled by the surface rate. Thus, in turbulent conditions it is necessary to calculate the mass transport limited rate and the surface reaction rate and use the one that gives the slower rate.

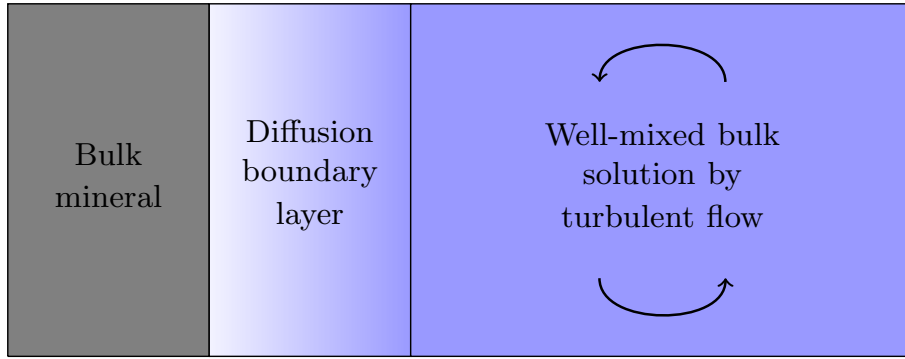


Figure 2.10: Diffusion boundary layer

The thickness ϵ of *BDL* depends on the fracture aperture a and the Sherwood number Sh defined by Dreybrodt et al. (2005b) shown in equation (2.27). For water at temperatures found in karst, the calculation of the Sherwood number is done with equation (2.28) where f is the fracture friction factor, and Re the Reynolds number.

$$\epsilon = a/Sh \quad (2.27)$$

$$Sh = \frac{(125f)(Re - 1000)}{1 + 1257.3 \sqrt{f/8}} \quad (2.28)$$

Once BDL thickness is known, equation (2.29) is the dissolution rate F limited by diffusive mass transport in turbulent flow.

$$F = D(c_{eq} - c)/\epsilon \quad (2.29)$$

Equations (2.30) and (2.31) give the dissolution rate limited by reaction surface rate in turbulent flow for $c < c_s$ and $c \geq c_s$ with $n = 4$.

$$F = k_1 \left(1 - \frac{c}{c_{eq}}\right) \quad (2.30)$$

$$F = k_n \left(1 - \frac{c}{c_{eq}}\right)^n \quad (2.31)$$

The conceptual model of (Dreybrodt et al., 2005b) provides a useful tool to simulate karst development in natural limestones. The effect of the switch from linear reaction to 4th order reaction rate can explain the development of long phreatic karst networks. Once the reaction rate slows near equilibrium water can travel thousands of meters without reaching equilibrium. Thus, a fracture far away from the inlet can grow, albeit slowly. Equations (2.25), (2.26), (2.30) and (2.31) will be used in this thesis to estimate the dissolution reaction rate in fractures.

2.5 Physical changes after mineral dissolution

The basis to describe speleogenesis is the principle of mass conservation. The mass of mineral dissolved can be converted into wall retreat for fractures or porosity increase in porous media. In this section the effects of mineral dissolution on the physical properties of porous media and fractures are reviewed.

2.5.1 Physical changes due to dissolution in porous media

Porosity

Porosity increase due to mineral dissolution is estimated according to equation (2.32) (Rezaei et al., 2005) where ε_0 is the initial porosity, R is a dissolution rate from equation (2.22), V_m is calcite molar volume, $\varepsilon(t)$ is the porosity after dissolution time t .

$$\varepsilon(t) = \varepsilon_0 (1 + R V_m t) \quad (2.32)$$

Permeability

The relationship between porosity and permeability is complex. Research on the porosity-permeability relationship has usually not been conducted with the specific perspective of karst development. Available knowledge comes mainly from applied rock physics in the field of oil industry and the emerging questions of carbon dioxide sequestration. It is important to recognize the source of knowledge because there are implicit assumptions from other fields of research that may or may not be valid in karst development. The general and conceptual relationship between porosity and permeability is shown in figure (2.11) adapted from Hiatt and Kyser (2000). The most common way to plot the relationship is a log-linear graph where the log scale is used for permeability and linear scale for porosity.

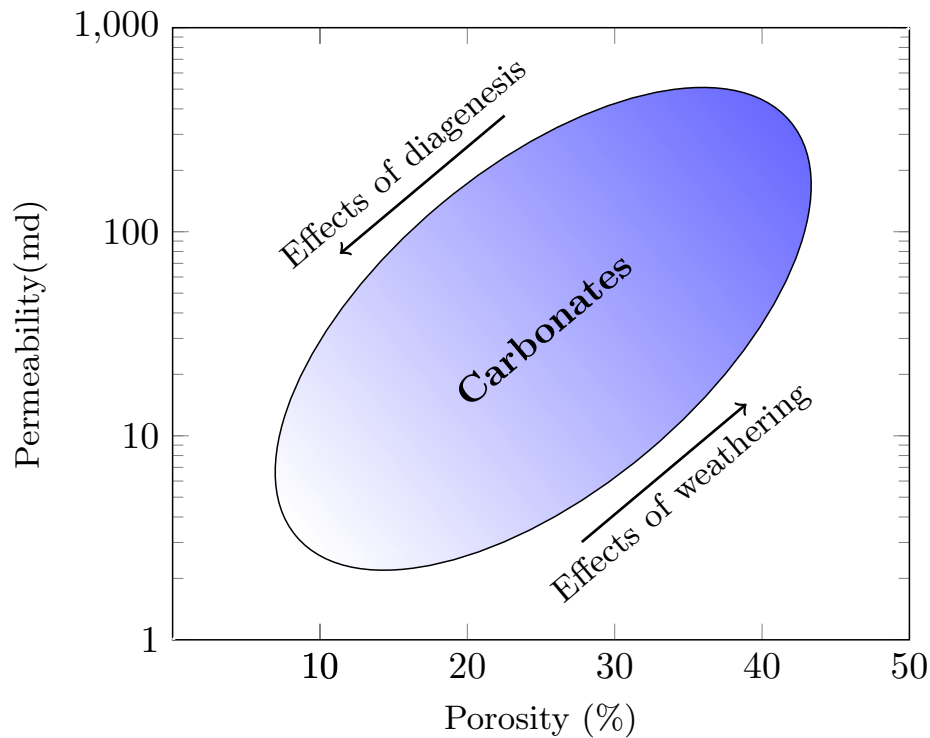


Figure 2.11: General relationship between porosity and permeability carbonate rocks, effects of weathering and diagenesis. Adapted from Hiatt and Kyser (2000)

Diagenesis is the name given to the processes that transform sediments into sedimentary rocks. In general, diagenesis involves a loss of porosity and permeability driven by the compaction caused by sediment burial and mineral precipitation in the pore space. Weathering is the breakdown and chemical alteration of rocks when they're exposed to Earth's atmosphere. Mineral dissolution related to groundwater flow can be described as chemical weathering and generally it causes an increase in porosity and permeability. Trends in porosity-permeability were described as general, diagenesis may not always lead to porosity loss. For example, recrystallization of aragonite into calcite leads to porosity aggregation which may not change overall porosity but greatly increases permeability (Hanshaw and Back, 1979). In spite of exceptions, the general trends are valid to describe the evolution of carbonates.

Data coming from the oil industry is mainly sourced from rocks samples that have undergone diagenesis. Rock samples come either from drilling cores at several km depth or carbonates buried at depth brought to surface by plate tectonics. Thus, these samples are representative of the process of porosity and permeability loss and every sample represents only a stage of diagenesis. Since porosity does not changes during measurements, these

measurements are known as static.

Figure 2.12 shows a compilation of published data sets of porosity and permeability. The relationship is influenced by the size of grains composing the rock, see figure 2.12-2. Figures 2.12-3 and 2.12-4 shows that reef limestone (biogenic) has a greater permeability for relatively low porosity values compared to abiogenic carbonates. Figure 2.12 shows the effect of mineral composition on the relationship. Dolostone (dolomite) has a higher permeability for a certain porosity when compared to limestone (calcite).

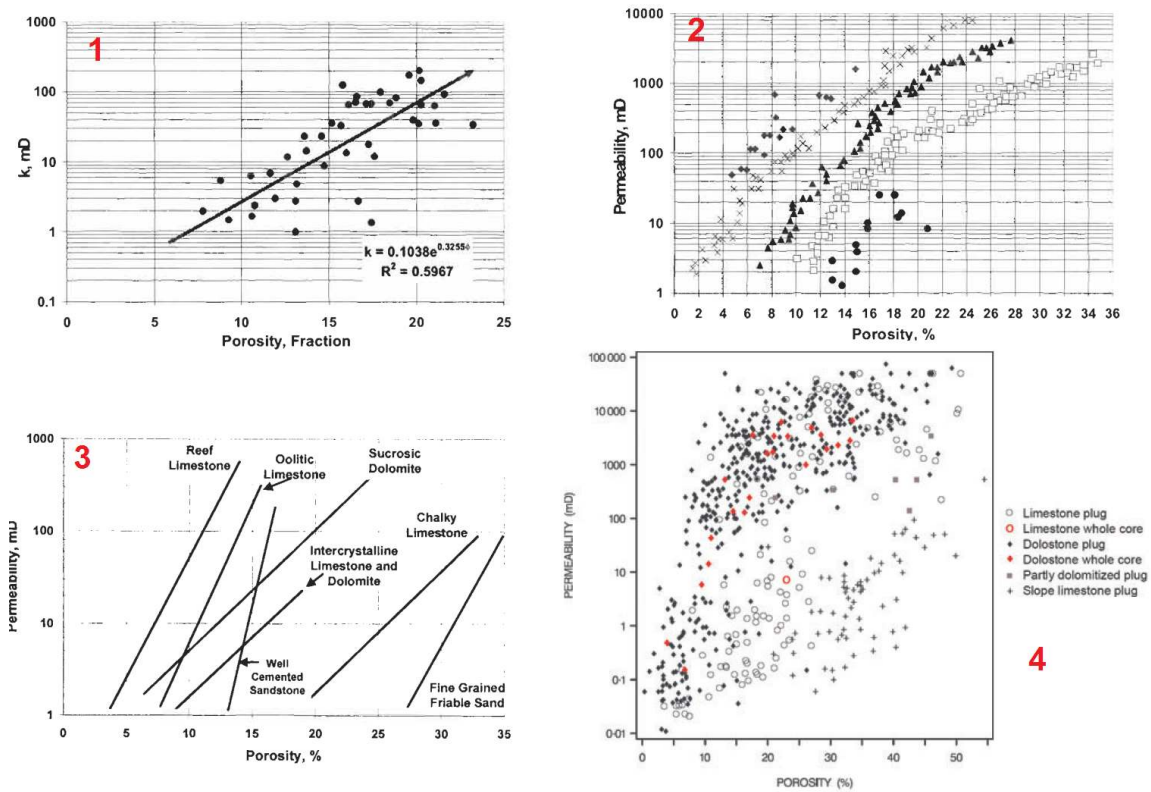


Figure 2.12: 1) Porosity and permeability in sandstone oil reservoir. Rock properties depend on: 2) grain size, from left (coarse grains) to right (clayey sandstone), 3) rock grain origin, 4) mineral composition. 1,2 and 3 (Tiab and Donaldson, 2004), 4 (Ehrenberg et al., 2006)

Based on theoretical considerations and measurements, some models have been proposed for the porosity-permeability relationship. The most common is the Kozeny-Carman model shown in equation (2.33) where k is the permeability in milliDarcy, Φ the porosity fraction and s_{Vgr} is the specific surface area of a porous material. Since s_{Vgr} is difficult to measure in rock samples, a fitting constant a is used to fit experimental data with the Carman-Kozeny equation (Tiab and Donaldson, 2004).

$$k = \left(\frac{1}{2s_{Vgr}^2} \right) \frac{\Phi^3}{(1 - \Phi)^2} = a \frac{\Phi^3}{(1 - \Phi)^2} \quad (2.33)$$

Porosity and permeability have also been fitted to a power law model, see equation (2.34) (Tiab and Donaldson, 2004). A higher exponent b yields a greater increase in permeability for a unit change in porosity.

$$k = a \Phi^b \quad (2.34)$$

Bernabé et al. (2003) made a review of processes altering the porosity-permeability relationship, among them: compaction, elastic deformation, thermal cracking, mineral dissolution and deposition. Equation (2.35) shows the model they proposed where k_0 and Φ_0 are the initial permeability and porosity and exponent α fits the model to experimental data. The value of exponent α depends on the process altering the rock, for either increasing or decreasing porosity.

$$k = k_0 \left(\frac{\Phi}{\Phi_0} \right)^\alpha \quad (2.35)$$

Another way to measure the porosity-permeability relationship is through dissolution experiments. The basis of the experiments is to make water with high carbon dioxide concentration in solution flow through rock samples to cause mineral dissolution and making continuous measurements of head loss and flow rate to calculate permeability. Porosity changes are measured directly using X-ray tomography and indirectly by tracking the solution chemistry. Since the rock is altered during measurements, permeability measurements are known as dynamic. Bernabé et al. (2003) found that dissolution experiments with high CO_2 in solution produce results that fit to exponents higher than 3 in equation (2.35).

Results from Gouze and Luquot (2011) show that the porosity-permeability relationship depends on the acidity (dissolved CO_2 concentration) of water used in the dissolution experiment. The rock used in the experiment is oolitic limestone from Middle Jurassic

Mondeville formation in the Paris Basin which mineral composition is 99% calcite. Increases in permeability were explained by pore effective hydraulic radius and tortuosity. Dissolution increases pore radius and reduces tortuosity. Model results shown in figure 2.13 shows that under equivalent flow conditions waters of different acidity produces different increases in porosity and permeability. The water with lower $pH = 3.21$ is not the one that produces a higher overall permeability. Under the experiment conditions, water with intermediate $pH = 3.51$ produces the highest increase in permeability because reactive water reaches deeper (compared to $pH = 3.21$) increasing permeability over the limestone sample scale.

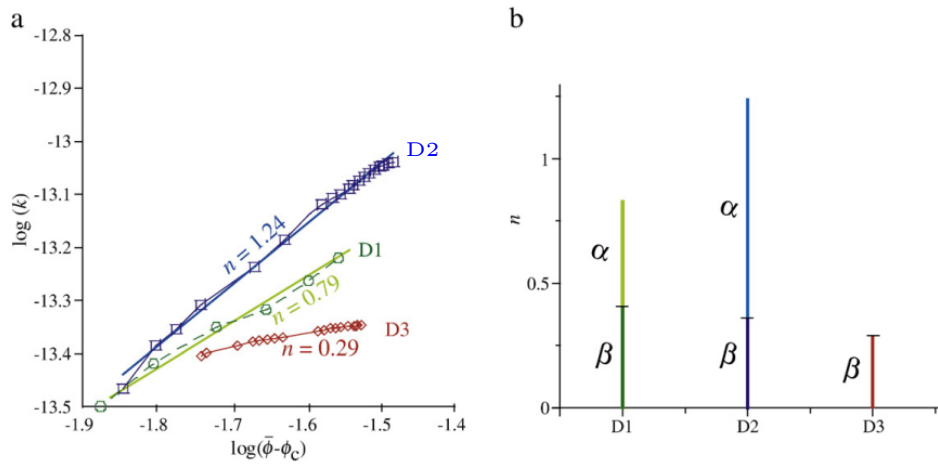


Figure 2.13: 3 dissolution experiments with different pH in water: D1 - 3.21, D2 - 3.51, D3 - 4.02. Plot *a* shows the porosity-permeability relationship during the experiment. n is the exponent in Bernabé model (equation 2.35). Plot *b* shows the relative contribution of pore size increase α and tortuosity decrease β to the overall permeability increase (Gouze and Luquot, 2011)

Another recent dissolution experiment conducted by Menke et al. (2015) where CO_2 saturated brine at $pH = 3.1$ an 10 MPa was injected through a rock sample of 99.1% calcite limestone oolite from the Upper Lincolnshire formation (England) from the Middle Jurassic period. The experiment was run from porosity fraction 0.15 to 0.25 and permeabilities between 7,000 mD to 500,000 mD. A power law, $k = 1.4 \times 10^{-7} \Phi^{5.16}$, was found to fit well the data. A power law was also used to describe the data on figure 2.12. The use of power laws to describe the porosity-permeability relationship is limited to the interval of porosity of experiments. As porosity approaches to 1, permeability should approach infinity for practical purposes. However, this trend is not reflected in power laws.

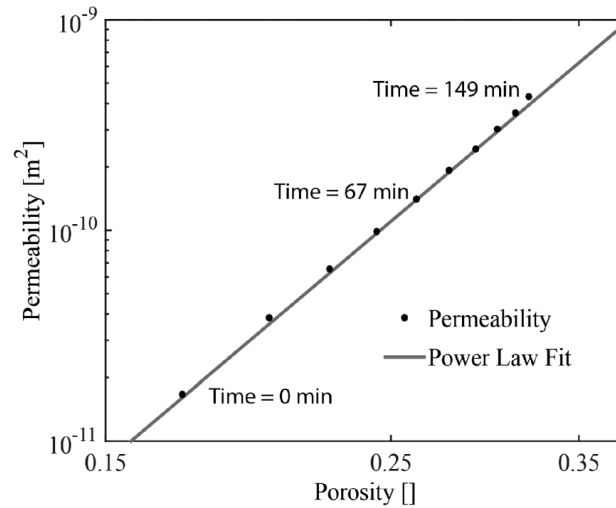


Figure 2.14: Porosity and permeability evolution in dissolution experiment (Menke et al., 2015)

Figure 2.15 shows a plot of the published porosity and permeability measurements of Noiriél et al. (2009), Gouze and Luquot (2011) and Menke et al. (2015). The dissolution experiments only cover a limited span of porosity increase as opposed to static measurements of porosity and permeability, see figure 2.12. Also, water in these experiments is quite acidic ($pH = 3 - 4$) compared to groundwater in karst where pH is usually between 5 and 8. It is expected that karst water would produce a different porosity-permeability relationship. However, it is still unknown since no experiment has been done using the reactivity found in karst waters.

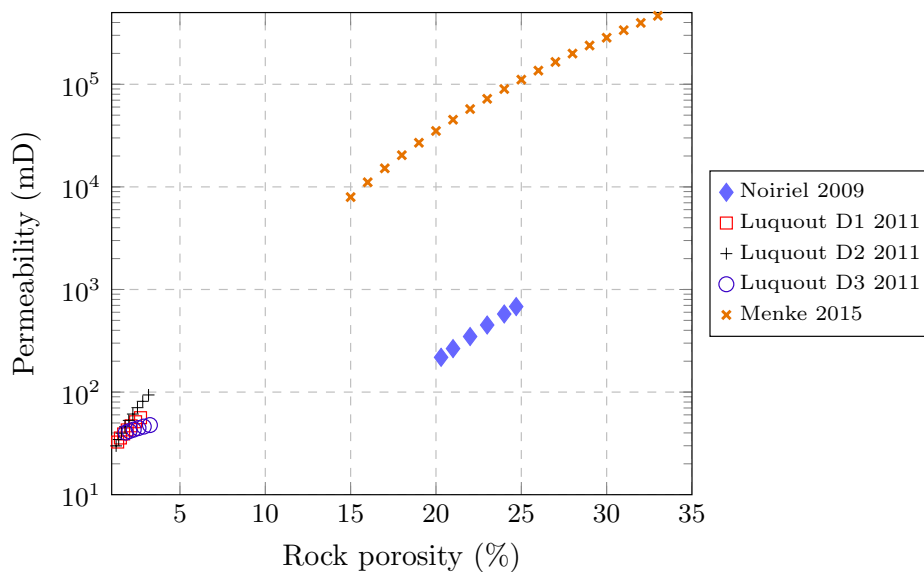


Figure 2.15: Porosity and permeability evolution in dissolution experiments

Another way to assess the porosity-permeability relationship is by using numerical models at pore scale to simulate the evolution of porosity and permeability along mineral dissolution. Simulations have the advantage of enabling analysis of porosity and permeability evolution at the pore scale. The following numerical simulation of the evolution of permeability was done by Nogues et al. (2013). The core of the simulation is a reactive transport model that simulates the reaction between carbonates and water with high $p\text{CO}_2$ pressure. The pore network geometry is based on a synthetic oolitic dolostone and the model size is $1.87 \times 1.87 \times 1.87$ millimeters. Water in the domain is in equilibrium with minerals and is displaced by water with pH of 3, 4.3, 5.1 and 6 depending on the simulation. Figure 2.16 shows a plot of porosity versus the exponent α needed to represent the porosity-permeability relationship according to the model of Bernab  shown in equation 2.35. The most interesting result is that exponent needed to explain the porosity-permeability relationship depends on the stage of porosity evolution. There is a region between porosity values of 0.15 and 0.25 where the exponent $\alpha = 3$ can explain the relationship. This region matches the range of reported porosities from laboratory dissolution experiments. However, when dissolution continues above porosities of 0.25 the increase in permeability needs a higher order relationship. No dissolution experiment has been conducted for porosity over 0.30 – 0.35 to validate the numerical simulation results.

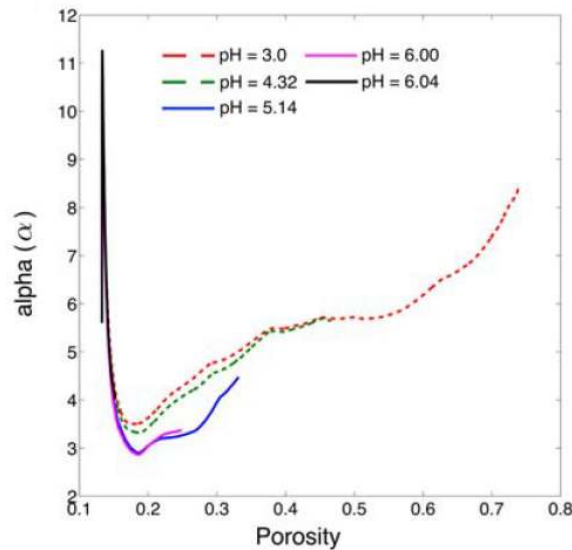


Figure 2.16: The order of the porosity-permeability relationship may depend on the porosity stage of evolution (Nogues et al., 2013)

This review shows that the porosity-permeability relationship in carbonate rocks is quite

complex. It depends on petrophysical properties such as mineral composition and grain size, rock origin (biogenic) and diagenesis. However, it also depends on the water acidity driving dissolution process. Finally, it was shown that the relationship can be modeled by a power law (equation 2.35) but the order of this law depends on the stage of porosity evolution.

It is possible to include all this complexity in a karst development model but all the variables have been studied at a scale of centimeters or even smaller. It is known that petrophysical properties have an effect on porosity-permeability relationship but no publications related to the spatial distribution of petrophysical properties at a scale relevant to karst development were found.

In this thesis, the Bernabé model (equation 2.35) is used to describe the porosity permeability relationship. It captures the general trend, but it is necessary to be aware that some characteristics of permeability evolution may not be captured by this simplified model.

Storage

The relationship between porosity and specific storage S_s is given by equation (2.36) (De Marsily, 1986) where ε is porosity, C_B and C_F are bulk porous medium and fluid compressibility, ρ is the fluid density and g the gravitational constant. The porosity increase is followed by an increase in storage capacity and hydraulic conductivity of the porous medium.

$$S_s = \rho g [(1 - \varepsilon) C_B + \varepsilon C_F] \quad (2.36)$$

Reaction surface area

Gouze and Luquot (2011) demonstrated experimentally that the reaction surface area of porous pure calcite rock samples decreases after mineral dissolution. This kind of research shows there is a trend in the evolution of reaction surface area. However research on this topic is still in the early stages and general conclusions can not yet be made from a limited number of experiments. In this work, it was assumed that the reaction surface area remains constant after porosity increases.

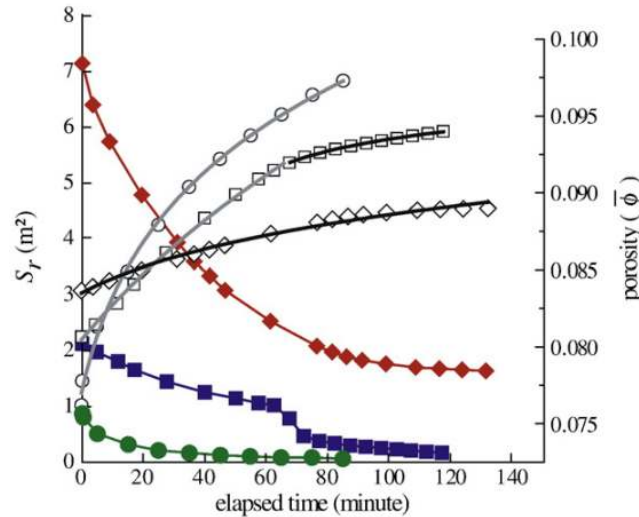


Figure 2.17: Decrease of reaction surface area after porosity increase caused by mineral dissolution (Gouze and Luquot, 2011)

Rock compressive strength

Limestone is a composite material composed of carbonate grains and cement keeping grains together. Figure 2.18A shows an abiogenic grainstone. It is assumed that ooids (grains) have an abiogenic origin. The white material keeping them together is calcite cement probably precipitated in the vadose zone. Figure 2.18 is an example of biogenic grainstone. Organism skeletons are still visible and some of them are partially dissolved. All grains are kept together by calcite cement (in white color) probably precipitated in the phreatic zone.

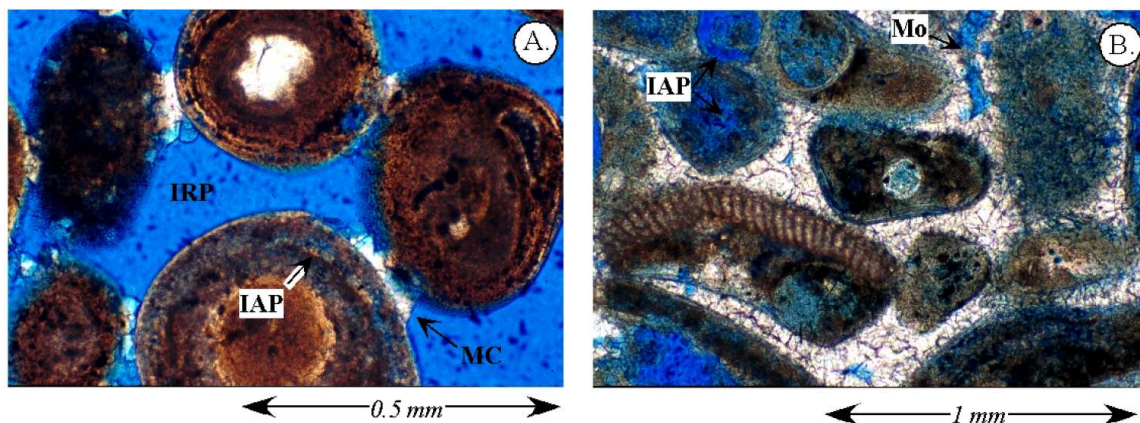


Figure 2.18: A) Abiogenic ooid limestone from Exhuma Islands, Bahamas. These ooids have been partially dissolved yielding intraparticle porosity (IAP). Some calcite has precipitated as meniscus cement (MC) commonly precipitated in the vadose zone. B) Biogenic Pleistocene skeletal grainstone from Bermuda. Some grains are partially dissolved creating intraparticle and moldic (Mo) porosity. The white color is calcite cement typically precipitated in the phreatic zone. Both thin sections taken from (Hiatt and Kyser, 2000)

Both carbonate rock thin sections have the same general structure: grains and cement. The only difference between them is the origin of the carbonate grains and how the calcite cement precipitated. A hypothesis can be made: if reactive water flows through the pores, rock dissolution occurs, and at certain stage of porosity increase the composite material becomes unstable either by losing mechanical resistance or because the calcite cement keeping grains together dissolved. The macroscopic effect will be the disintegration of the rock, becoming grains, before the material is completely dissolved.

The mechanism described in the previous section is a reasonable hypothesis but no dissolution experiment has been conducted focusing on the evolution of the mechanical properties of carbonate rocks. What has been observed is the relationship between rock porosity and uniaxial compression strength. This research was driven by the need to assess the stability of underground mines. Denis et al. (1987) tested samples from Lutetian (Eocene) limestone from an underground quarry. The limestone is biogenic with grain diameter between 0.1–0.5 mm. Figure 2.19 shows the results of uniaxial compression tests on limestone samples with different measured porosity. The relationship is clear: higher porosity is related to lesser mechanical strength. For the lower porosities the strength is 14 MPa, for porosity of 0.42 the strength has reduced to 3 MPa. Rock samples with porosity above 0.42 were not analyzed in this experiment, however it can be hypothesized that is the relationship stays linear for higher porosity values, compression strength is equal to zero for porosity equal to 0.46. Figure 2.20A shows the results of the Brazilian test. Usually, rocks have a tensile strength 10 times less than compressive strength. Unsaturated rock has a higher tensile strength when compared to saturated rock. Figure 2.20B shows the relationship between compressive strength and degree of saturation for two samples with porosity $n = 0.37$ and $n = 0.416$. Full saturation reduces compressive strength by 50%. These trends may not be applicable to all limestone. These rock samples are 90% calcite and the rest is quartz and clay. The authors explain the relationship between saturation and strength by the presence of clay impurities in the limestone. Clay expands when it saturates and it may create internal stresses on the rock that reduce the overall strength. Anyway, the relationship between porosity and strength is clear.

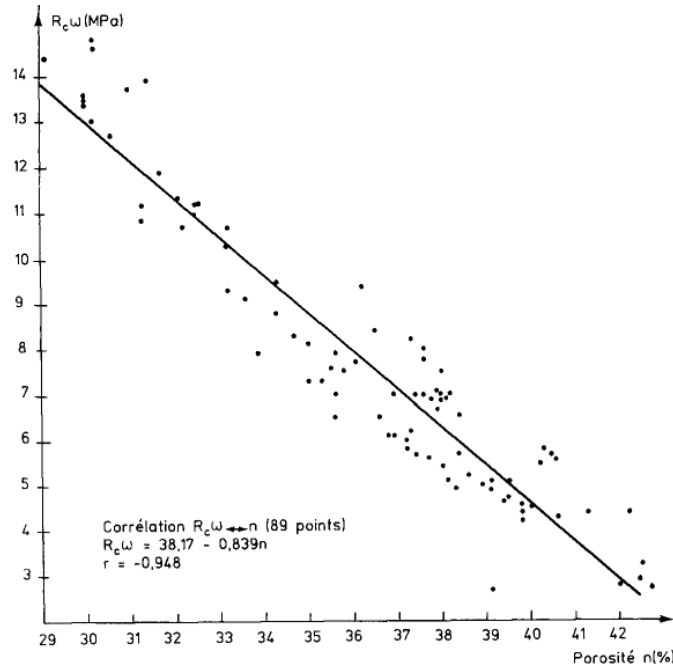


Figure 2.19: Correlation between porosity and uniaxial compression strength for water saturated calcite, from Denis et al. (1987).

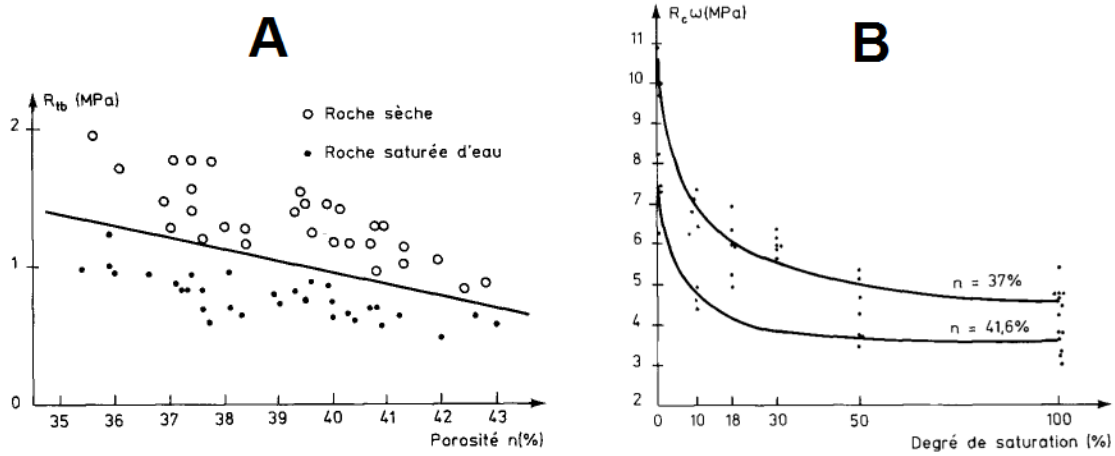


Figure 2.20: A) Correlation between porosity and indirect tensile strength (Brazilian test) unsaturated and saturated calcite, B) Relationship between saturation degree and uniaxial compression strength for two sample with porosity $n = 0.37$ and $n = 0.416$ from Denis et al. (1987).

Hatzor et al. (2010) assessed the mechanical stability of a karstic cavern in Israel through numerical simulations of cavities. The mineral composition of limestone is unknown but they conducted compression tests for samples with different porosities. Figure 2.21 shows the relationship between uniaxial compressive strength and bulk porosity. The trend in porosity reduction suggests that the limestone sample loses all mechanical resistance before

grains composing the rock are fully dissolved.

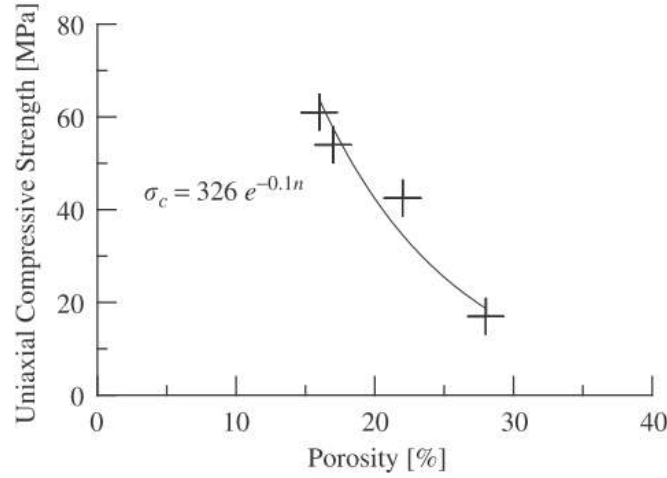


Figure 2.21: Relationship between uniaxial compressive strength $R(MPa)$ and bulk porosity in Bina limestone, Israel. Figure from Hatzor et al. (2010).

The relationship between porosity and mechanical strength has been only of limited interest for researchers. There are few publications, but the published results are sufficient to consider which effect may have the loss of mechanical resistance in speleogenesis. However, heterogeneities in limestone mineral composition are unsuitable for generalizing these results for all limestones. For this thesis, it is assumed that mineral dissolution needs to increase rock porosity until 0.95 for full dissolution of porous medium.

2.5.2 Physical changes due to dissolution in fractures

Fracture aperture

The dissolution kinetics model for fractures of (Dreybrodt et al., 2005b) yields a result in $\text{mol cm}^{-2} \text{s}^{-1}$ units. The implicit assumption in this model is that mineral reaction occurs only in the mineral surface. Thus, mineral dissolution causes wall retreat. Assuming a fracture is represented by two parallel planes, wall retreat Δa can be estimated by multiplying the dissolution rate (see section 2.4.2) by a time period Δt where dissolution is active and calcite molar volume V_m , as shown in equation 2.37.

$$\Delta a = 2 F \Delta t V_m \quad (2.37)$$

Mechanical stability of underground cavities

Small fractures can grow into conduits of several meters in diameter as results of mineral dissolution. After a certain size, the stresses in rocks forming the conduit wall may be sufficient to cause a partial collapse. Partial collapse refers to the breakdown of cavity sections where mechanical stresses are concentrated due to cavity geometry, fractures or rock heterogeneities. It's partial because the cavity remains open and collapse breccia accumulates on the floor. Partial collapse modifies the geometry and the size of the conduit. If the cavity is still in the phreatic zone, the conduit geometry may no longer be related to the water flow and chemistry. If the conduit is in the vadose zone and inactive from the conceptual model of reactive flow driven speleogenesis, the conduit may grow just because of mechanical instability. If the conduit is close to the terrain surface, collapse can create a sinkhole at the surface.

Researchers have tried to find the size and geometry of cavities that collapse based on rock mechanical properties and fractures. An empirical relationship has been found between cavity span s (horizontal distance from cavity wall to wall) and the thickness of the roof L (distance from cave ceiling to terrain surface). For smaller s/L ratios, meaning thinner roofs and wider cavities, the cavity requires higher rock strength to be stable (Parise and Lollino, 2011).

A more detailed study was conducted by Hatzor et al. (2010) where numerical simulations of cave stability were performed based on the conceptual model shown in figure 2.22. The main cavity geometry properties are horizontal span B and roof thickness h . In addition to cavity dimensions (span, height and roof thickness), variables such as intensity of joint/fractures, orientation of joints, shear stress of joints and strength of rock were considered. Simulation results, also in figure 2.22, show the boundary (thick black line) between stable(safe), marginally stable and unstable (unsafe) cavities depending on the span B and roof thickness h . Cavities with roof thickness less than 6 meters are unstable regardless the horizontal span B . Deeper cavities are more stable. However, it is very probable that cavities in the range of 20 – 30 m are intersected by a fracture or a joint causing instability. Thus, the stability of cavities beyond a horizontal span of 30 m is compromised. The shaded area that indicates marginal stability represents cavities where stresses cause partial collapse of the cavity.

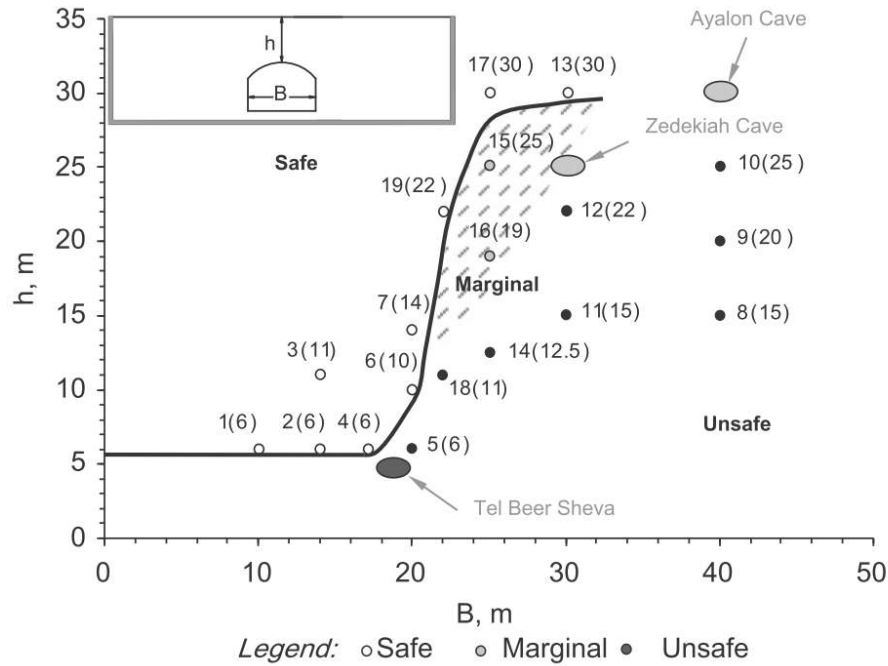


Figure 2.22: Results of cavity stability numerical simulations. Based on the rock and fracture properties of the studied limestone block, the stability is assessed for cavities with different spans B and roof thickness h , from (Hatzor et al., 2010)

These results can not be extrapolated into general rules about speleogenesis. Results depend on limestone mechanical properties, and the spatial distribution and orientation of fractures and joints in the limestone block. However, two concepts can be integrated into speleogenesis. The first one is that after a dissolution conduit reaches a certain size partial collapse may occur. From that point in the conduit evolution, it's geometry is no longer dependent solely on groundwater flow conditions. Thus, the conceptual model of conduit enlargement caused by reactive water flow can be applied to conduits up to 15 – 30 m depending on the limestone properties, fractures, bed joints and roof thickness. The second important concept for speleogenesis is that conduit growth may be driven by a superposition of dissolution and partial collapse if the conduit is in the phreatic zone. If the conduit is in the vadose zone, growth may only be driven by partial collapse.

This research is based on the conceptual model of conduit enlargement driven by the flow of water reactive to limestone. A further development would be to couple a model of mineral dissolution and rock mechanics to study speleogenesis.

2.6 Telogenetic and eogenetic karst

The past sections briefly reviewed the concepts developed to explain the growth of caves. In this section, the applicability of these concepts to study speleogenesis is assessed. It is clear that karst occurs on carbonate rocks, but carbonate rocks have different origins and diagenesis evolution as explained in section 2.5.1.

To make a distinction between speleogenesis occurring in very different settings, Mylroie and Mylroie (2007) proposed the concept of eogenetic and telogenetic karst. Telogenetic is the name given to karst that develops in carbonate rocks that have been buried and underwent diagenesis at depth in Earth's crust, and porosity and permeability were reduced by mechanical compaction, mineral substitution, recrystallization or other processes. Eogenetic is the name given to karst that develops on younger carbonate rocks that underwent meteoric diagenesis close the Earth's surface where the initial porosity and permeability of sediments has not been altered by compaction.

Figure 2.23 shows the differences between eogenetic and telogenetic karst. Speleogenesis starts in eogenetic karst right after the deposition of sediments. In telogenetic karst, development starts until tectonics bring carbonate rocks closer to the surface where they get in contact with meteoric waters (groundwater).

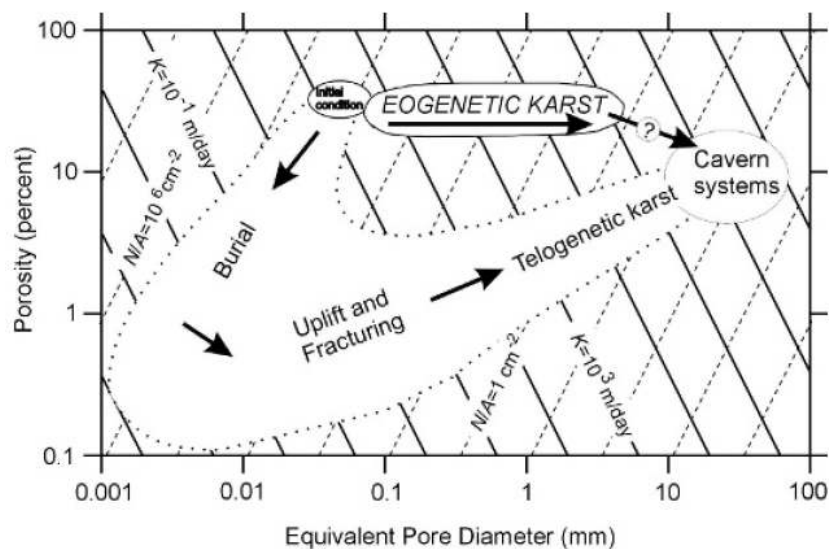


Figure 2.23: Differences between eogenetic and telogenetic karst, from (Mylroie and Mylroie, 2007)

Since telogenetic karst is related to tectonics, it is usually found in terrains such as

mountain ranges. Due to the high relief, water flow is driven by steep gradients. In contrast, eogenetic karst is found on carbonate islands, or emerged continental carbonate platforms. Hydraulic gradients in these regions are less steep and flow near to the ocean is influenced by sea tides.

As described in the previous sections, the conceptual model of mineral dissolution for porous media can be coupled to Darcy's law to simulate reactive transport and thus speleogenesis. The model of dissolution for fractures can be coupled to Darcy-Weisbach equation or Manning-Strickler flow equations to simulate fracture enlargement. Depending on the type of karst, eogenetic or telogenetic, and hydraulic conditions, any of the models can be used to simulate speleogenesis.

The fracture model is ideal to simulate telogenetic karst because it assumes mineral dissolution reaction occurs only at the fracture wall. This assumption is adequate because carbonate rocks in telogenetic karst have very low porosity and permeability. Thus most of the groundwater flow occurs in the fracture network or along bedding planes inside a limestone block.

In eogenetic karst, the fracture or conduit walls can not be assumed as impermeable because carbonate rock has significant porosity and permeability. Water exchange between a karst conduit and the surrounding carbonate matrix has been observed in the Santa Fe river in Florida (Moore et al., 2010). This is a surface river that flows into a sinkhole and then flows through a conduit network. During baseline flow conditions, distributed aquifer recharge makes calcite saturated matrix water flow into the conduit. When storms increase river flow, the hydraulic gradient reverses and unsaturated river water flows into the matrix. Only during storm flow conditions unsaturated water comes in contact with conduit wall and speleogenesis can occur.

A similar situation has been observed in eogenetic karst San Salvador Island in Bahamas where the phenomena driving the water exchange between sinkholes and matrix is sea tides (Martin et al., 2012). During low tides, calcite saturated water flows from the matrix into a sinkhole and during high tide unsaturated water flows from the sinkhole into the matrix surrounding it. Thus, mineral dissolution probably occurs only during high tide. The water exchanges between a cavity, conduit or sinkhole, can be better described by flow and dissolution reaction in porous media.

2.7 Vuggy porous media and macropores

The reviewed conceptual models of flow and reaction may not be sufficient to describe speleogenesis. Between fracture and porous media flow are intermediate limestone conditions, such as limestones with centimeter scale vuggy macroporosity with biogenic origin. Figure 2.24 shows limestones samples collected from the karstic Biscayne aquifer in southeastern Florida with porosity up to 81% (Sukop et al., 2013). The origin of vugs is related to molds of burrows, solution enlarged burrows 2.24B, interburrow vugs 2.24A, moldic fossils or root molds 2.24C.

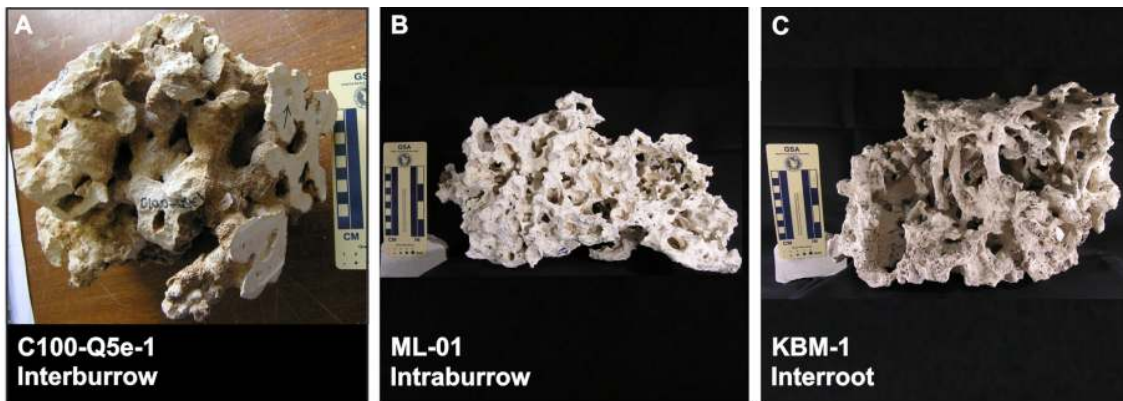


Figure 2.24: Limestone samples with macropores, from (Sukop et al., 2013).

The presence of vuggy macroporosity in a karst aquifer implies the need to have a triple porosity model that includes matrix, connected vugs, and conduit permeability. However, flow at the vug scale in connected vug structures needs a different representation apart from Darcy's law or conduit flow. Sukop et al. (2013) applied Lattice Boltzmann flow computations to pore geometry models obtained by X-ray tomography. Figure 2.25A shows results of the flow simulations, the apparent hydraulic conductivity depends on hydraulic gradient or flow velocity. Slower flow encounters a higher conductivity when compared to faster flow. Figure 2.25B shows the porosity-permeability relationship for vuggy limestones and the Kozeny-Carman model fit.

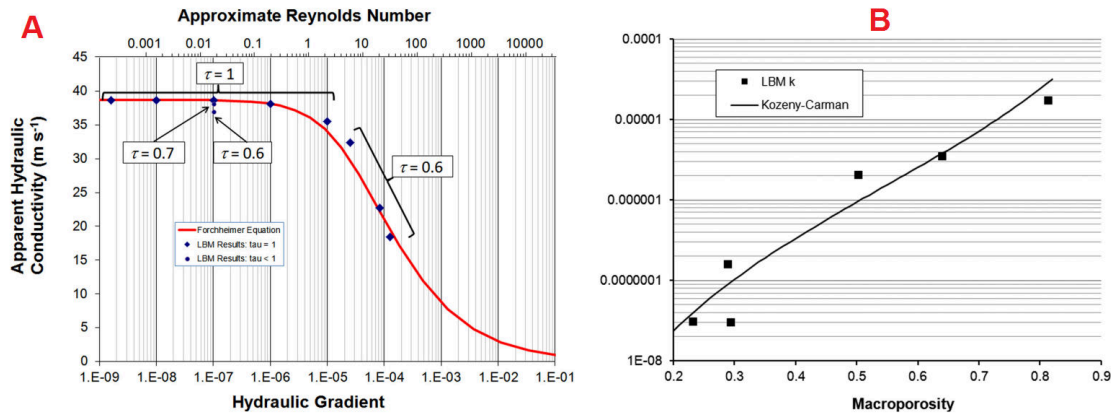


Figure 2.25: A) Apparent hydraulic conductivity is a variable depending on flow velocity, B) Porosity-permeability relationship for vuggy porosity limestone, from (Sukop et al., 2013).

Layers of limestone with connected vuggy pores have been identified as preferential groundwater flow paths in the karst Biscayne aquifer in Florida (Cunningham et al., 2006). Since the description of the importance of connected vugs for groundwater flow is relatively recent, the only conceptual development on how to describe flow in this limestone is the publication from (Sukop et al., 2013). No dissolution experiment has been conducted on vuggy limestones, and no conceptual model has been developed to describe mineral dissolution.

2.8 Review discussion

This review covers the most important natural processes related to speleogenesis. It incorporates solution chemistry, mineral dissolution kinetics, and the physical changes in limestone after dissolution occurs. Finally, an assessment on the utility of these concepts to describe real karst is proposed.

If karst can be conceptualized as a double porosity system composed by matrix and conduit permeability, the conceptual models presented here are ideal to simulate the speleogenesis processes. If karst is a triple porosity system composed by matrix, connected vugs, and conduit permeability, undergoing speleogenesis occurring in the connected vugs can not be simulated with the present extent of research. Thus speleogenesis simulations in this work consider only the enlargement of fractures into conduits and porosity and permeability increase in porous limestone.

Another topic related to speleogenesis that appears to be requiring further research is the

effect of rock porosity increase (weathering) on the mechanical strength of the porous matrix and conduits. The main conclusion that can be made so far is that flow and chemistry can explain conduit geometry until it reaches a size where mechanical stresses complement or drive entirely the evolution of the conduit geometry.

Chapter 3

Study area

3.1 Introduction

The study area is located around the city of Tulum on the eastern coastal plain of the Yucatan Peninsula in Mexico. This area was selected because more than 1000 km of underwater caves have been mapped by explorers in the region. The world's longest underwater cave systems are found here. South of the city of Tulum, the Ox Bel Ha karst network covers 242 km of connected conduits. In addition, the conduits are rather large and shallow which makes them accessible for speleological survey and mapping. The geology is rather simple because most of the formations are young and have not been deformed by later tectonic events. A large amount of observations and data on the karst systems of the region has already been collected and published. All these characteristics make the area particularly interesting to study speleogenesis and to attempt to model those processes.

This chapter describes the study area from two perspectives. On the one hand, we use published data and review them. This part is focused on the main topics relevant for speleogenesis. This includes an overview of the regional and local geologic setting, the limestone mineralogy, the groundwater geochemistry, and the hydrogeological boundary conditions. On the other hand, we conducted three main field campaigns in the area during this project. The field campaigns were made in collaboration with the Austrian Geological Survey and the Amigos de Sian Ka'an NGO in Mexico. The data acquired during these campaigns are also summarized in this chapter and discussed in the framework of speleogenesis. They provide additional information related to sea tide propagation into the aquifer, groundwater geo-

chemistry and limestone physical properties such as porosity, permeability and mechanical resistance.

3.2 Geographical setting and bathymetry

The Yucatan Peninsula is a partially emerged carbonate platform. Figure 3.1 shows the position of the study area and the bathymetry of the Yucatan carbonate platform. The source of underwater elevations is the Earth's Relief from ETOPO1 Model (Amante and Eakins, 2009). The cell size of the source raster is 1 arc-minute or approximately 2 km. The platform edge is assumed to be where depth increases from 100 to 3000 m in a short horizontal distance. The West and North platform edges are between 150 and 250 km from the present shoreline.

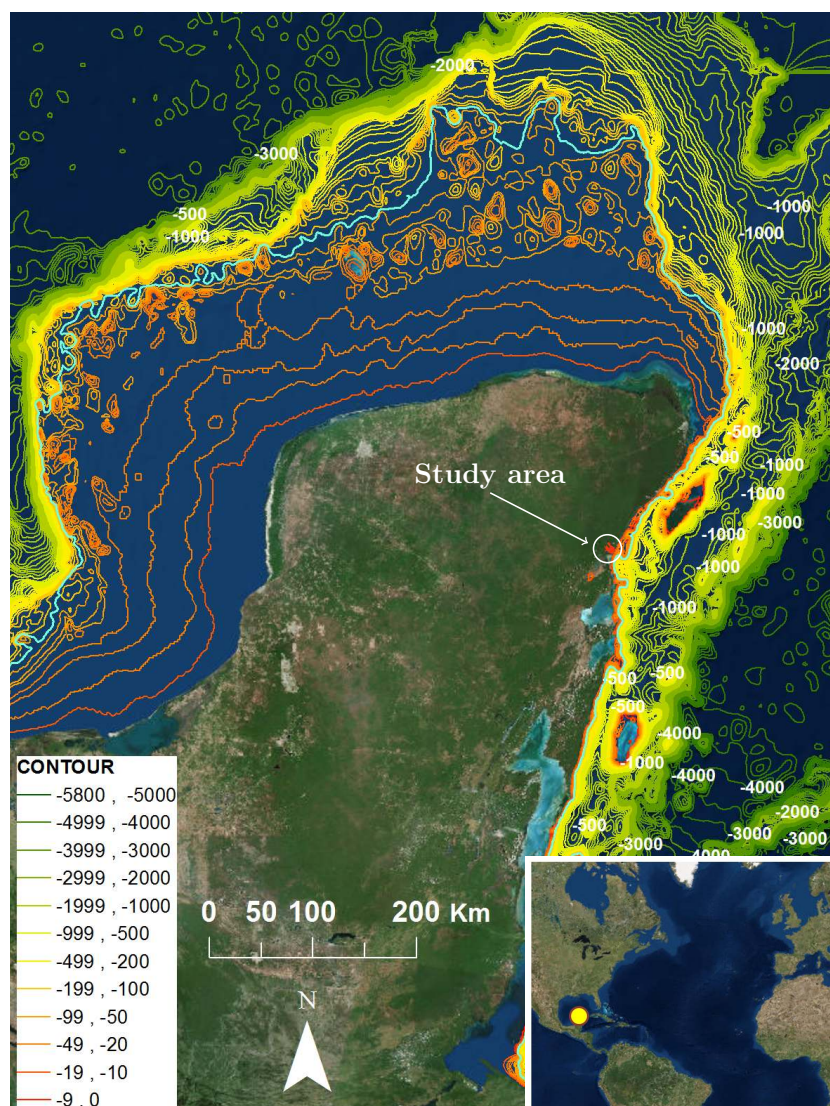


Figure 3.1: Extension of Yucatan Carbonate platform. The light blue line indicates the platform edge at depth of 100 m is indicated with light blue. Depth contour map elaborated with data from Amante and Eakins (2009)

Figure 3.2 shows that the continental shelf has a minimal extension in the study area. The present shoreline is precisely at the drop from 0 to 1000 m depth. Sea level oscillations of 100 m in the study area only produce sea regressions between 1 and 10 km.

3.3 Geological setting

3.3.1 Cretaceous to Upper Miocene geological history

During the Cretaceous, 145 to 66 Million years before Present (<http://www.stratigraphy.org>), the Yucatan Peninsula was covered by the sea and stayed submerged until the Pleistocene.

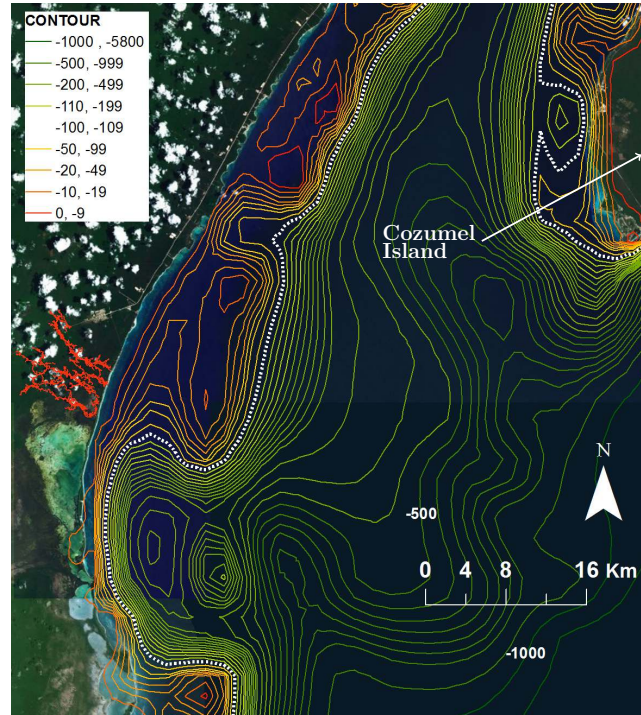


Figure 3.2: Ox Bel Ha system is shown in red color in center left, plotted with data from (QRSS, 2013). Depth of 100 m is indicated with a white dashed line. Depth contour map elaborated with data from Amante and Eakins (2009)

On average there is approximately more than 1300 m of Cretaceous sediments on top of a metamorphic basement. During Paleogene and Neogene, 66 to 2.6 Million years BP, approximately another 1000 m of sediments accumulated on shallow-sea conditions (Lopez Ramos, 1973). Tectonic uplift in the Yucatan limestone shelf started in the Oligocene, 33.9 to 23 Million years BP, continued into the Pleistocene and stopped around the Middle Pleistocene 800,000 years BP (Szabo et al., 1978).

In the study area, no deep drillings have been done to determine the stratigraphic sequence. However, in the early 1970s, seismic profiles were made in the coast of Quintana Roo as shown in figure 3.3 (Del Castillo and Vivas, 1973). Seismic profile number 11 is approximately 20 kilometers north of Ox Bel Ha karst system. Profile 11 is shown in figure 3.4. From left to right, the profile starts approximately 8 km from the coast and there is light slope until the depth of 900 m is reached at point A at 25 km from the coast. The slope of sea bottom in this region is approximately 3.5%. At 15 km from the coast two inverted faults were inferred marked with symbol 3. The approximate depth of the basement is indicated with symbol 1. The basement is at approximately 2000 meters below sea level at 25 km from the coast and sedimentary rocks are approximately 1500 m thick. Unconsolidated

sedimentary strata is indicated by number 2. Sediments with symbol *P* were identified as Pelagic (open sea) origin and sediments with symbol *T* as a sequence of turbidity current layers. The peak at point B was identified at the boundary between the Yucatan continental shelf and Yucatan Basin at approximately 80 km from the shore. The basement at this point is 3000 m below sea level and sedimentary rock is 2000 m thick. The interpretation of this profile 11 suggests the presence of a highly irregular basement covered by horizontally stratified sediments.

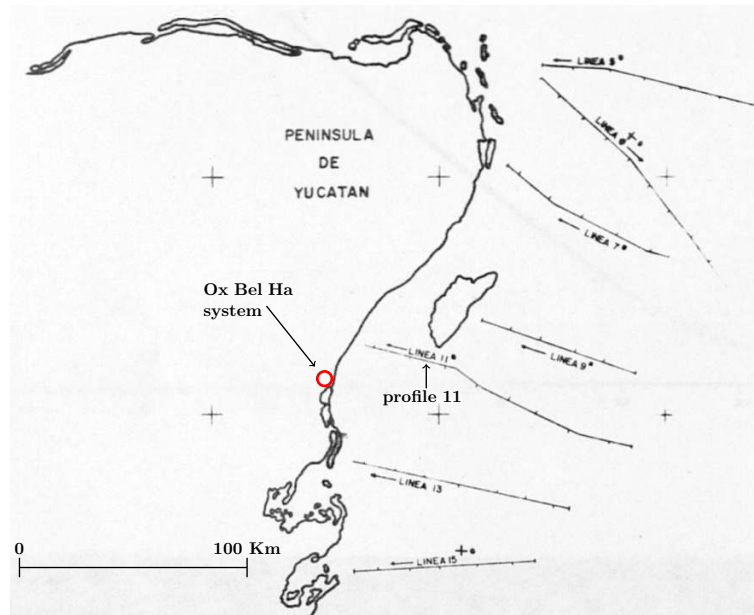


Figure 3.3: Seismic profiles made in Quintana Roo coast and the position of Ox Bel Has system

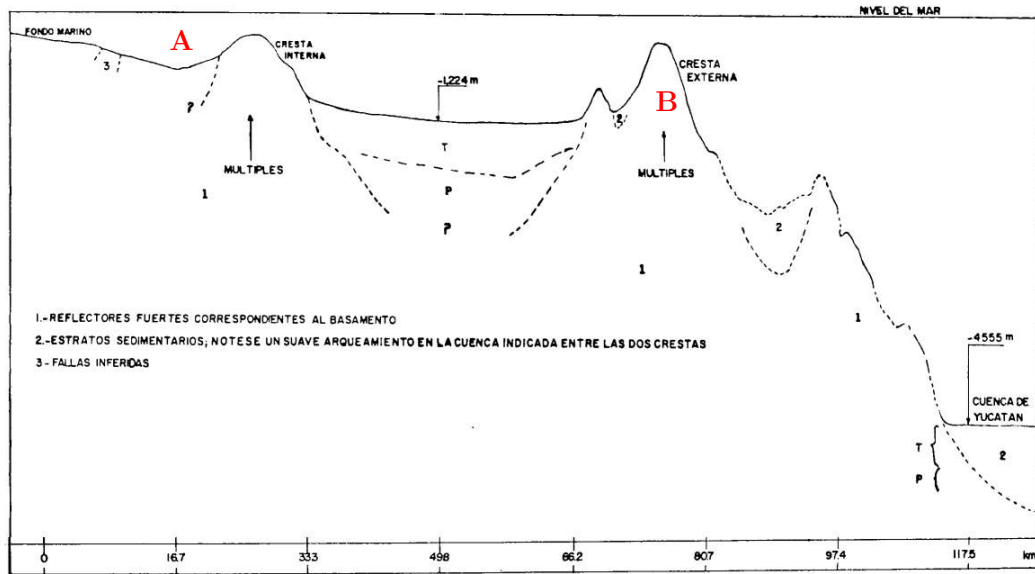


Figure 3.4: Profile 11 interpretation from Del Castillo and Vivas (1973)

Magnetic measurements suggest the existence of a magnetic basement at 2000 m below sea level near Cozumel island (Angeles, 2006) located 45 km Northeast of the study area. This basement depth estimation is consistent with seismic data. Thus, it is assumed that in the study area the thickness of carbonate layers is at least of 1500 m. Since sediments have not been deformed by tectonic forces, it can be assumed that most of the stratigraphic sequence between the basement and the Upper Pliocene is composed by horizontal beds of fine grain carbonate sediments.

At the end of the Cretaceous a large asteroid impacted in the northwest region of the Peninsula. A 200 km crater was formed named Chicxulub Bauer-Gottwein et al. (2011) Since the area was still under sea level, the crater became a sedimentary basin. The impact crater border is at approximately 150 km from the study area. The impact breccia of the crater is highly reactive to water and has been related to high permeability in the Yucatan Peninsula. However, the impact breccia has not been observed in the study area.

3.3.2 Pleistocene to Holocene geological history

The Yucatan Peninsula was submerged until Quaternary glaciations made it emerge from the sea during the last 800,000 years. The origin of glaciations is still under debate, but research show glaciations started 3 million years ago and became progressively more intense. Between 3 and 0.8 million years ago, glaciations had a 40,000 year cycle. 800,000 years ago

glaciations changed to a 100,000 years cycle that lead to enough accumulation of ice yielding significant changes in sea level. The amplitudes of sea level change in early glaciations are unknown because several coastal areas underwent subsequent tectonic uplift, but precise measurement was done for more recent sea level changes. Interglacial periods were detected at 630, 330, and 200 thousand years ago (Lambeck et al., 2002).

Figure 3.5 shows past sea level estimations up to 450,000 years before present. Estimations are based on coral fossils from many sites around the world including Caribbean Sea islands (Fleming et al., 1998) and sediments from the Red Sea (Rohling et al., 1998). During glaciations 1,2,3,4,5 the sea level was lower than present level. In contrast, sea level was higher only for two interglacial periods.

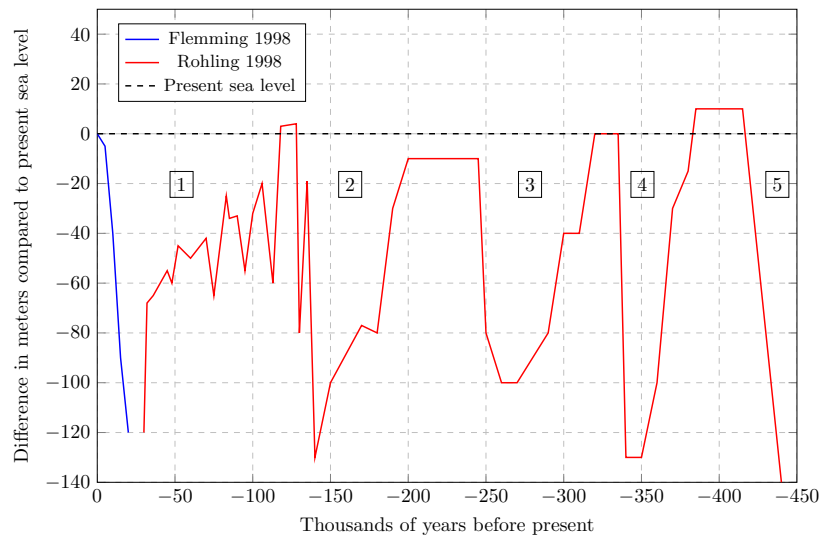


Figure 3.5: Sea level in the past 450,000 years, data from Fleming et al. (1998) and Rohling et al. (1998).

The emergence of Yucatan Peninsula created new depositional environments such as a reef-rimmed carbonate platform. The Eastern boundary of the Yucatan carbonate platform is rimmed by the Mesoamerican Barrier Reef System. The barrier spans from the northeastern tip of the Yucatan Peninsula, down to Belize, Guatemala and the Bay Islands in Honduras. Figure 3.6 shows the location of the reef barrier in the study area. The crest of the reef barrier is between 400 and 1000 m away from the present shoreline.

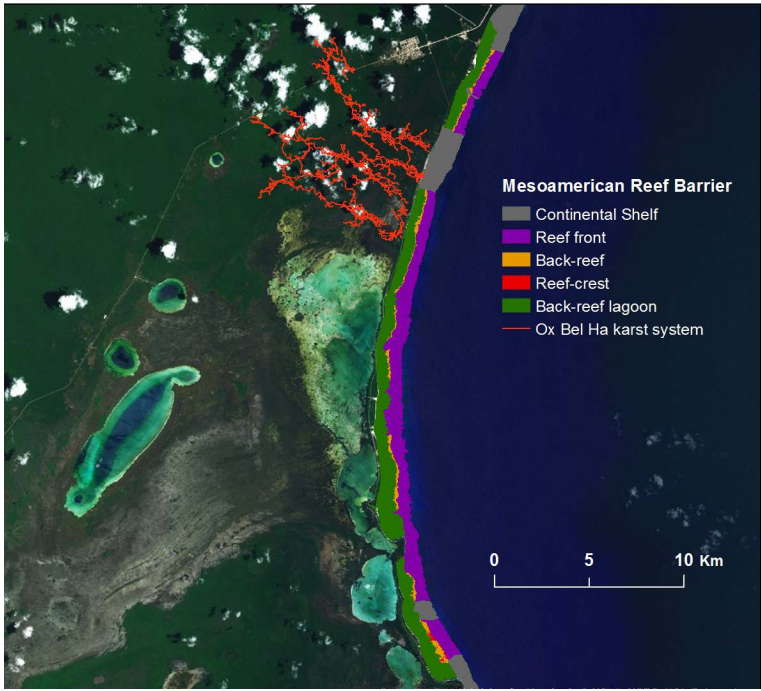


Figure 3.6: The crest of the barrier reef is between 400 and 1000 m from the present shoreline in the study area. Reef data from CONABIO (2016).

The structure of sediments related to the reef barrier sedimentation environment is unknown in the study area. No drilling campaign has been conducted to produce a stratigraphic sequence model of Miocene and Pleistocene limestones. Thus, it is necessary to compare the study area with an analogue site to infer what may be the structure of sediments. Pomar and Ward (1995) proposed the deposition model for reef-rimmed carbonate platforms shown in figure 3.7 based on observations of an Upper Miocene coral reef platform in the island of Mallorca in Spain.

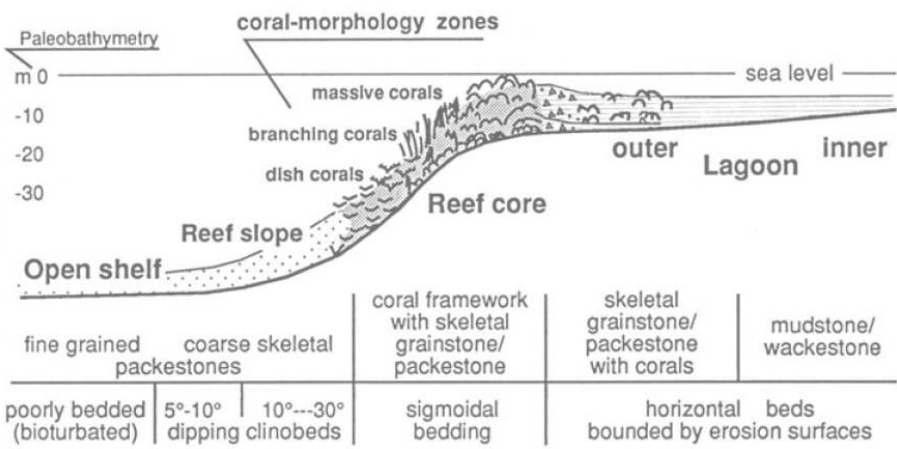


Figure 3.7: Facies model for the reef-rimmed Lluçmajor carbonate platform, from Pomar and Ward (1995)

The main feature in the model is the coral reef barrier that responds to sea level changes. Four main lithofacies are accounted in this model:

1. The *back-reef lagoon* is characterized by horizontal sediment bedding composed mainly by skeletal remains of corals and eroded fragments of older limestones.
2. The *reef-core* is characterized by having sigmoidal bedding and it is composed by lithified coral skeletons. The S shaped curve of bedding orientation is caused by corals growing on top of older corals during a sea level rise cycle.
3. The *reef-slope* is composed by coralline algae and coral debris and it dips seaward gently, i.e. less than 10° .
4. The *open-shelf* facies is composed by bioturbated (poorly bedded) fine grain limestones.

It is possible to identify with ease the reef-crest and the back-reef lagoon depositional environments on present conditions shown in figure 3.6. However, as shown in figure 3.5, the sea level has oscillated several times during Pleistocene and Holocene. Thus, the coral reef has advanced landward and seaward depending on sea level and the shoreline could have prograded according to the model proposed by Pomar and Ward (1995) shown in figure 3.8.

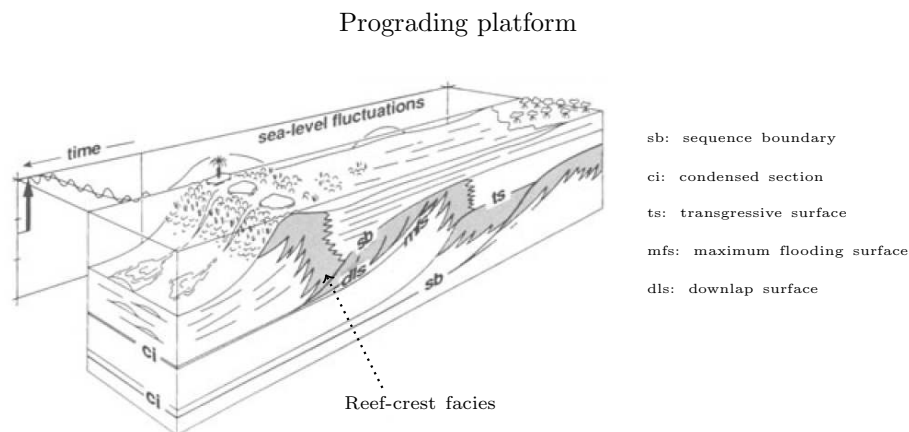


Figure 3.8: High-frequency reefal platform depositional sequence in a prograding platform, from Pomar and Ward (1995). The prograding platform is composed of stacking aggrading sediments deposited during sea level rises.

The depositional model of Pomar for the study area is just a hypothesis. However, researchers have identified some of the facies of this depositional model for Pleistocene and Holocene in the study area. Ward and Brady (1979) found that during high stands of sea

level, such as the Upper Pleistocene, sedimentation on the *back-reef lagoon* produced progradation of the shoreline of the study area. Ward and Halley (1985) suggested Pleistocene sediments in the eastern coast of Yucatan Peninsula form a wedge over older Miocene and Pliocene limestone. Figure 3.9A shows the location of the boreholes, the distance from the northernmost to the southernmost one is approximately 100 km, and the study area is just on the southern tip of the borehole covered area. An important feature is the caliche layer (subaerial calcareous crust) that develops during sea level regressions at the terrain surface when soil water evaporates and leaves dissolved minerals behind. The presence of this layer allowed to infer that sediments corresponding to at least 3 sea level fluctuations are found on the coastal plain of Eastern Yucatan Peninsula. The objective of Ward and Brady (1979) was to characterize the strandplain sediments on top of the stratigraphic column. The analysis of the beach-ridge plain suggested the deposition environment was a prograding shoreline with waves and longshore currents. The source of sediments was identified as eroded fragments of older limestones (sand) and back-reef lagoon sediment. This carbonate body dimensions were estimated between 3 and 10 meters thick and between 500 m to 4 km wide, see figure 3.9B. It is very porous and permeable grainstone dated to the last Pleistocene interglacial highstand of sea level which occurred approximately between 120,000 and 130,000 years ago. On topographic highs of the older limestone below this body there are clusters of corals with even higher porosity and permeability.

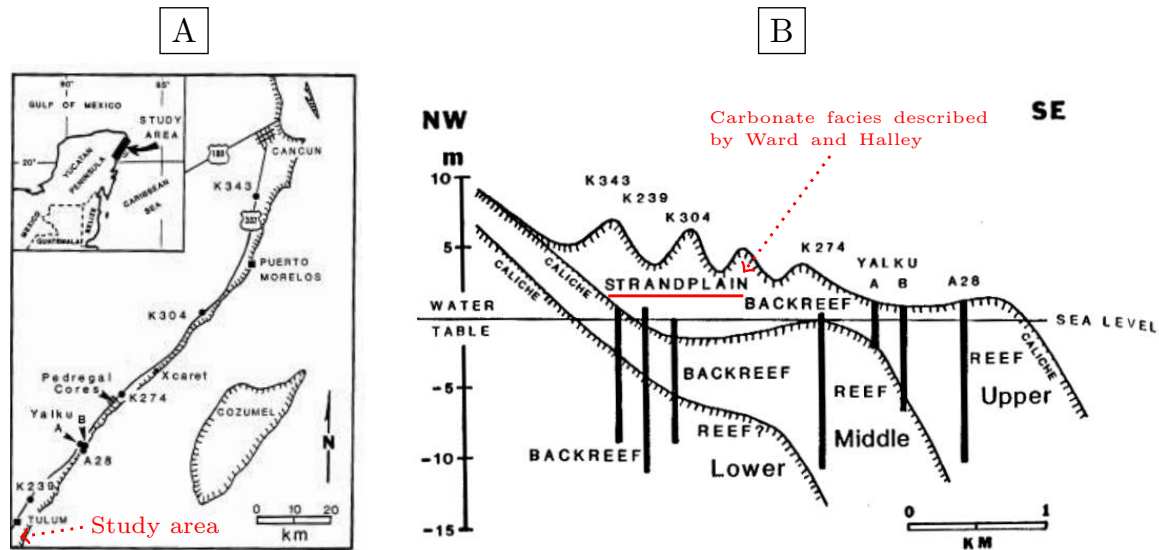


Figure 3.9: A) Location of boreholes for stratigraphic research relative to the study area, and B) Hypothetical cross section showing 3 sequences of reef formation corresponding to different sea level oscillations, taken from Ward and Halley (1985). Note the similarity to the deposition model shown in figure 3.8.

The general stratigraphic sequence between two caliche crusts is shown in figure 3.10. The top of the sequence is caliche crust. The sequence of strata corresponds to the sediment grain size distribution in a shoreline which is correlated with energy in the deposition environment. In the foreshore where waves breaks and upper shoreface (0 to 3 m depth) sediment is coarse sand while in deeper environments such the lower shoreface (5 to 10 m depth) sediment is finer sand and silt (Bjørlykke, 2010).

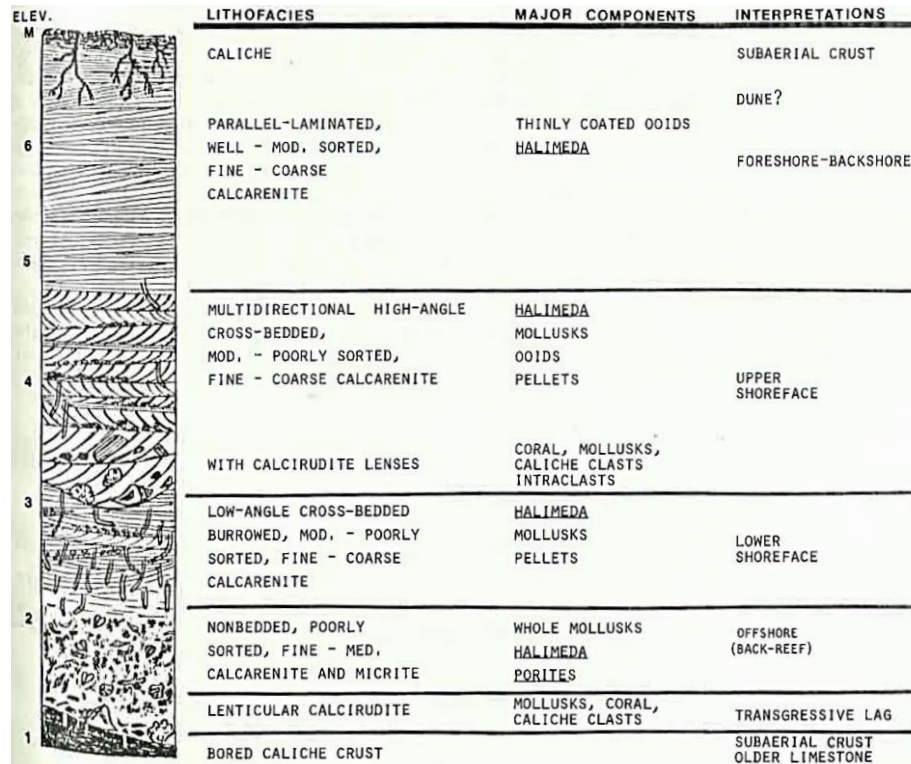


Figure 3.10: General stratigraphic sequence of Pleistocene limestone in the study area, from Ward and Brady (1979)

In the context of a carbonate platform with a reef barrier, the carbonate body described by Ward and Brady (1979) is the back-reef lagoon environment. This carbonate body represents only one cycle of shoreline transgression. Its thickness gives an order of magnitude of deposition rates in every sea level fluctuation and by consequence the thickness of Pleistocene sediment layers.

Another important component in the sedimentation model is the coral reefs. Fossil coral reefs on the eastern coast of Yucatan Peninsula have been described by Blanchon (2010) in a site 50 km North of the study area. The research was focused on the impact of 6 m elevation of sea level during the last interglacial high-stand. The carbonate facies were identified along several transects approximately 250 m long. One transect is shown on figure 3.11A. The strata in yellow represents beach and lagoonal sediments deposited during sea level regression. The corals are Ac (*Acrophora cerviconis*), Ap (*Acrophora palmata*), Ap mix, Ma (*Montastrea annularis*), Maf (*Montastrea faveolata*), Map (*Monstastrea "organ pipe"*) and Pp/Pf (*Porites porites* and *Porites furcata*) species. bCa and cCa represent branching and crustose Coralline Algae respectively. The reef crest is dominated by *Acrophora Palmata*

coral. The back of the crest is dominated by *Montastrea* and *Porites* corals. The sediments at the front and back of the reef crest are coral gravel. Below the reef crest there is a mixture of all coral species. The seaward extent of this transect shows another lower reef crest. The stratigraphic sequence genesis is shown in figure 3.11B. It explained how the Ap coral could grow during the last sea level high stand while the lower reef could not grow due to sediment flux or erosion of open marine conditions.

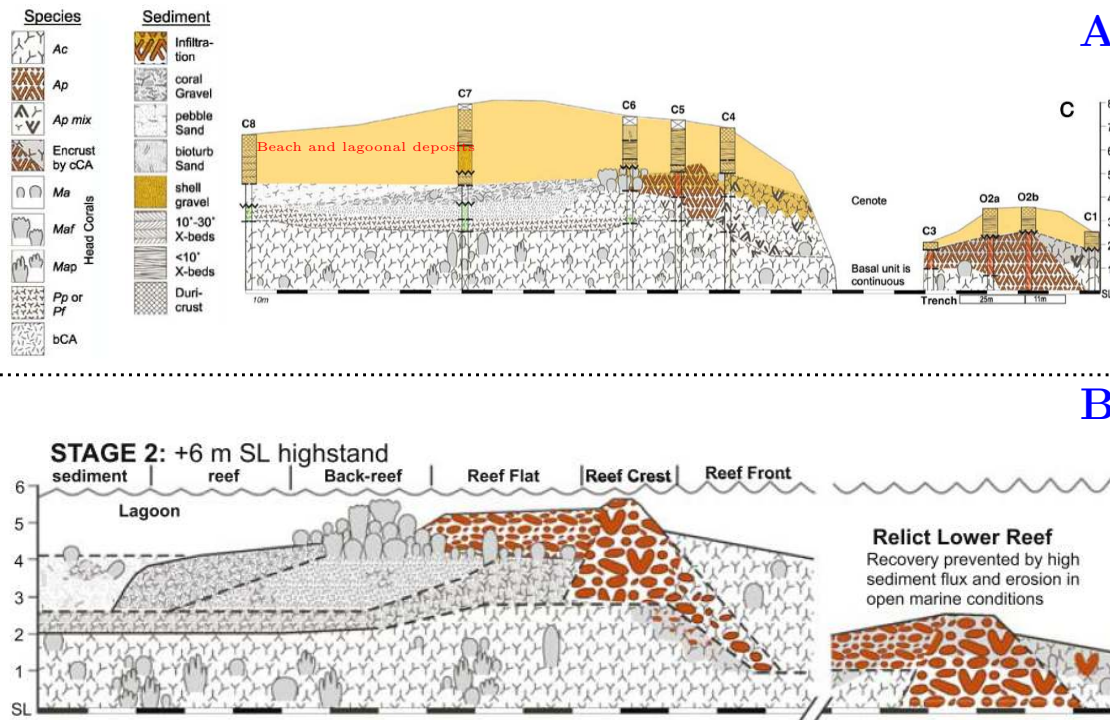


Figure 3.11: A) Reef development during the last sea level highstand, B) Cross section of a relict reef on Xcaret, both figures from Blanchon (2010). Vertical units are meters above present sea level. The horizontal scale is 10 meters per tick.

The reef crest described by Blanchon (2010) is the one developed during the last sea level highstand. When compared with the deposition model of Pomar and Ward (1995) and the hypothetical cross section shown in figure 3.9, it is reasonable to assume that older reef layers exist below present groundwater level but they have not been characterized yet.

Corals are *animals* that secrete calcium carbonate while coralline algae are organisms that induce carbonate precipitation by extracting carbon dioxide from water to use it for photosynthesis. Algae cell walls get covered by precipitated carbonate minerals. The common characteristic of corals and coralline algae is that they thrive in seawater. In the study area there are other organisms that precipitate carbonate minerals at large scale but they thrive

on freshwater lagoons. Gischler et al. (2008) observed a microbialite of more than 10 km of total length in Bacalar, a freshwater lagoon 200 km south of the study area in the eastern coast of Yucatan Peninsula. Microbialites are microbial mats that form sedimentary structures of low magnesium calcite precipitated by cyanobacteria doing photosynthesis. Figure 3.12 show a core drilling of a relic microbialite carbonate deposits in Bacalar lagoon and the top layer containing active cyanobacteria. The thickness of microbialite carbonate deposits in Bacalar are between 0.3 and 1.5 meter and are dated between today and 9000 yr before present.

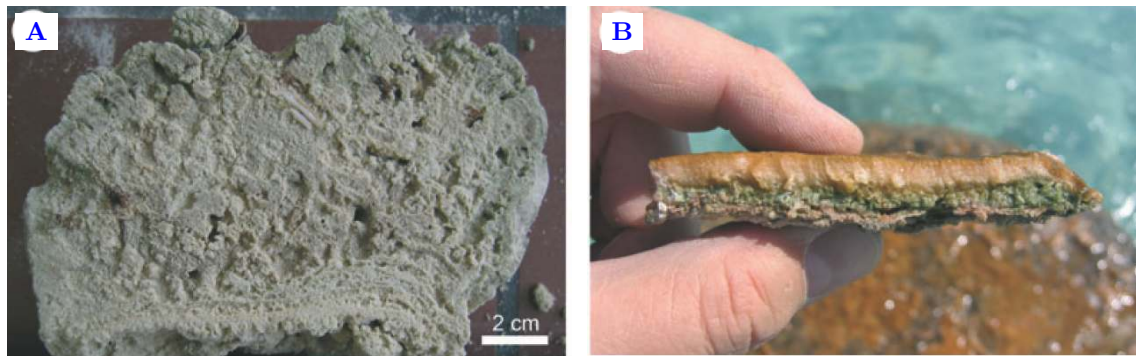


Figure 3.12: A) 15 cm core of a microbialite, B) sample of living microbialite, living organisms are mainly on the top layer of the mat, from Gischler et al. (2008)

Near the study area, active microbialite crusts have been identified in the Chunyanxché lagoon 12 km southwest of the Ox Bel Ha karst network (Centeno et al., 2012). These microbialite crusts extend horizontally on the lagoon bottom. It can be concluded that freshwater microbialites may be significant from the hydrogeological point of view because they induce carbonate deposition at a significant rate and their horizontal and vertical extents are comparable to coral reefs. It is an area of opportunity for research to look for relic microbialites in the stratigraphic sequence of the study area and assess their role in speleogenesis. Also, no research has been done on the porosity and permeability of microbialite deposits, but the general trend is that biogenic limestones are very permeable. Due to microbialite growth pattern, they can develop large and well connected carbonate strata.

Figure 3.13 shows the surface geology map of the study area and a plot of the explored conduits of Ox Bel Ha karst system represented by red lines. The oldest exposed stratigraphic unit is Pliocene limestone, between 5.3 and 2.6 million years before present, represented in yellow and denoted by the code Tmp1 Cz-Cq. Above Pliocene, there is Pleistocene sandstone

with bioclasts represented in green with code **Qpt(?)**. The Holocene is composed by 3 different unconsolidated sediments. Lagoon sediments composed of clay, calcareous silt and silt with high organic content are shown in pink with code **Qhola**. Wetland sediments composed of clay and silt with organic are shown in green and code **Qhopa**. A narrow strip of littoral sediments is shown with code **Qholi**. These stratigraphic units have not undergone significant deformation, but a lineament found in aerial images was interpreted as a normal fault in NE-SW direction (SGM, 2006). Freshwater lagoons at approximately 10 km are located along the fault line.

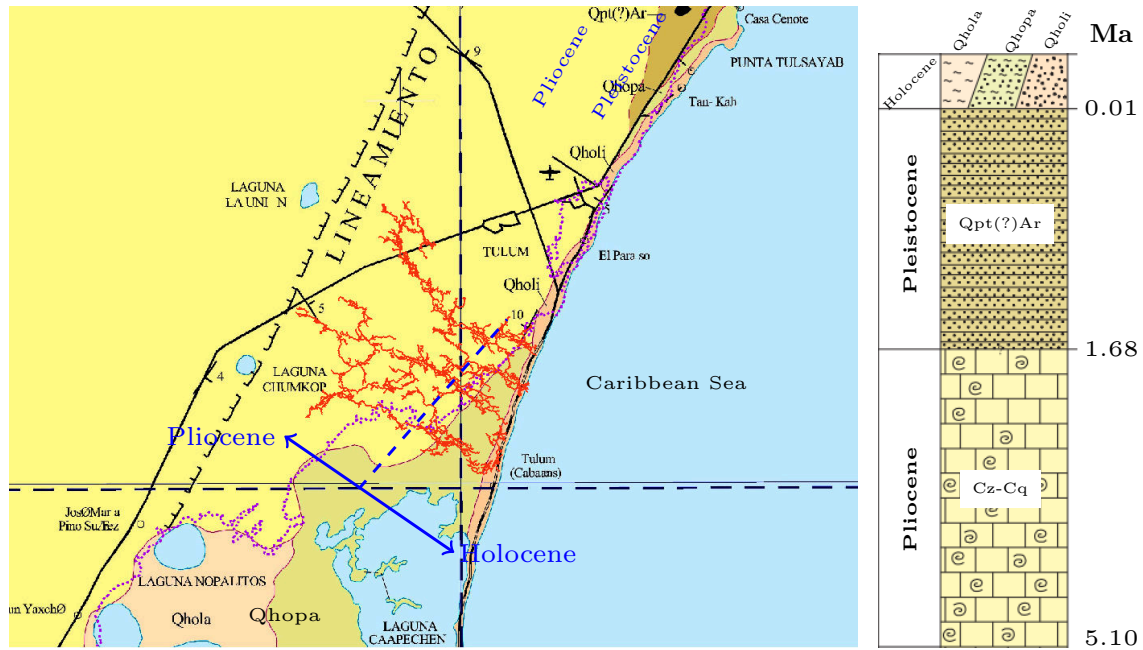


Figure 3.13: Ox Bel Ha karst system location (QRSS, 2013) shown by red lines over geological map of the study area (SGM, 2006). An normal fault runs parallel to the present coastline

Based on the geological evolution of the Yucatan platform it would be expected to find the sequence Pliocene-Pleistocene-Holocene found on the north extreme of the map in figure 3.13. However, in the zone where the karst system is located there are no outcrops of Pleistocene limestones.

This lack of continuity can be explained in two ways. The first one is to consider that Pleistocene sediments are just located below Holocene ones in the study area and not visible in the map. The second explanation may be related to the quality of the geologic map. The geological map has been designed at a scale of 1 : 250,000, thus small features are not represented. Also, it is worth considering that the geological map was constructed using

aerial photos and limited ground verification because the area is jungle and swamps.

The Pleistocene outcrop north of Ox Bel Ha is between 0 and 13 m above sea level. The elevation of this outcrop is consistent with the elevations observed by Blanchon (2010) 50 km north of Ox Bel Ha karst system. The upper limit of the grainstone body described by Ward and Brady (1979) is between 6 and 8 m above sea level. The purple dashed line on figure 3.13 shows the elevation contour with elevation 6 m above sea level, it is expected that Pleistocene limestone should be found at this elevation. Whatever the explanation is for the missing Pleistocene limestone on the geological map, the Ox Bel Ha karst system should pass through the 3 main stratigraphic units: Pliocene, Pleistocene and Holocene.

Previous published research on the study area assumes the aquifer as having homogeneous properties because no regional-scale fractures are found in the study area besides the fault parallel to the coast, see figure 3.13. This assumption may be appropriate for Pliocene limestone that was deposited in open sea conditions. However, the Pleistocene sediments deposited in a reef barrier environment are more heterogeneous in their spatial distribution and hydrogeological properties. The carbonate facies with larger grain size or coral skeletal remains have higher porosity and permeability, therefore they provide a preferential path for groundwater flow and may be related to the development of karst conduits.

3.4 The Ox Bel Ha Karst system

3.4.1 Position in the sedimentary sequence

Using the karst conduit network map and information provided by Quintana Roo Speleological Survey (QRSS, 2013), the position of Ox Bel Ha conduits within the sedimentary sequence was analyzed.

Cave divers use groundwater level as a reference for underwater topography. They assume that groundwater level on the karst system is equivalent to sea level because water flow velocity in conduits is slow enough most of time to be perceived. The estimated hydraulic gradient for the study area is 20 cm km^{-1} , thus the assumption from cave divers is a reasonable approximation considering the tools available for cave topography. Figure 3.14 shows the average elevation of karst conduits relative to groundwater level. Karst conduits are represented with lines and elevations of points defining the lines are averaged and assumed

to represent conduit elevation.

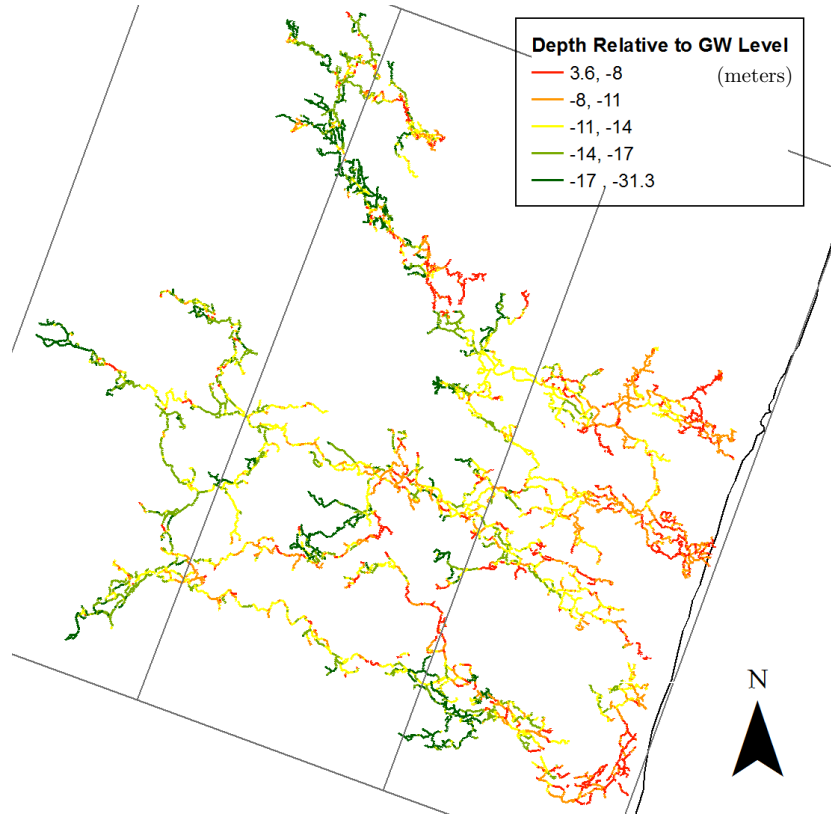


Figure 3.14: Average elevation of karst conduits relative to groundwater level. The black line in NE-SW orientation is the present shoreline

The conduit map of the Ox Bel Ha karst system has been analyzed using statistical metrics by Collon et al. (2017). One of these metrics is orientation entropy as a measure of disorder in karst conduit direction in the horizontal projection of orientations. Karst networks with lower orientation entropy values express a preferential direction of development that can be caused by regional hydraulic gradients or the orientation of fractures in limestone. The Ox Bel Ha system has a higher orientation entropy value meaning conduits in all directions are almost equally found in the network.

In addition to these previous results, we observe that conduits are shallower close to the shoreline and deeper in the upstream part of the network. The conduit farthest from the ocean is approximately 10 km from the shoreline. The network can be divided in three main zones (upstream, middle, downstream) the average depth for every zone is: -15.74 m, -12.73 m and -10.45 m respectively.

The analysis of the conduit depth, inclination and dip angle distribution were done during the author. Figure 3.15 shows the length of the conduits found at depth intervals of 1 m. 90%

of explored conduits are found between -6 and -20 m below groundwater level. Figure 3.16 shows the distribution of conduit inclination in the karst network calculated with reference to an horizontal plane. The length of conduits with inclination above 45 degrees is negligible. 90% of accumulated conduit length has an inclination between 0 and 10 degrees while 15% of conduit length was mapped as horizontal.

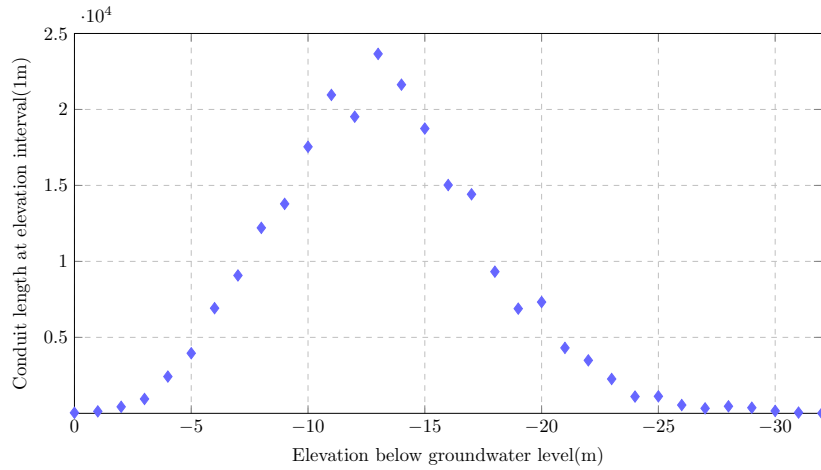


Figure 3.15: Elevation distribution of conduit length in the karst network. Accumulated length was computed at 1 m intervals.

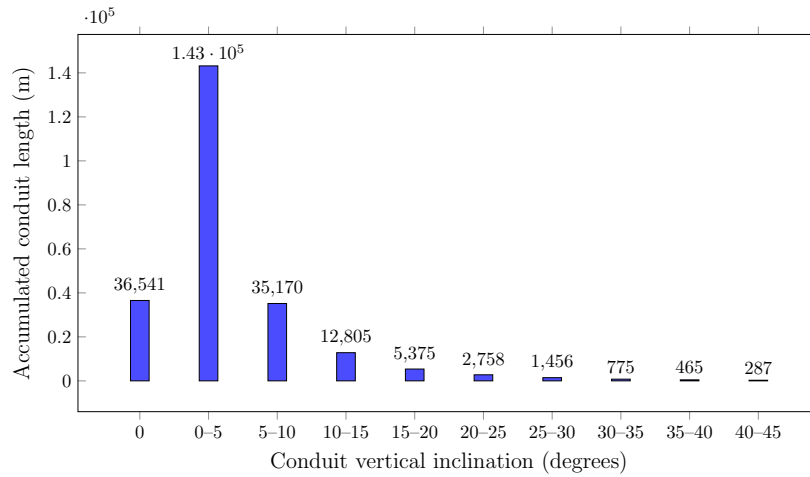


Figure 3.16: Conduit inclination distribution in the karst network. Accumulated length was computed at 5 degrees intervals.

The conduit inclination on figure 3.16 was calculated with reference to the horizontal plane. However, it does not provide information on the dip angle of conduits. To calculate dip a reference vertical plane parallel to the shoreline is set and then angles between conduits and the reference plane are computed as shown in figure 3.17.

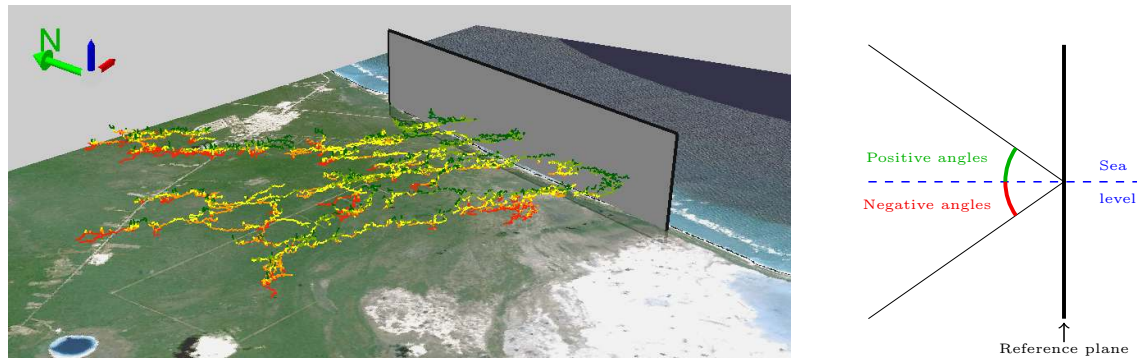


Figure 3.17: Conduit inclination angle measured from a reference vertical plane parallel to the shoreline.

In figure 3.18 negative angles mean conduits become shallower in the shoreline direction. Positive angles mean conduits get deeper when closer to the ocean. 45% of conduit length is in conduits that become shallow in the shoreline direction, 15% is horizontal conduits and 40% is conduits that dip into the ocean side.

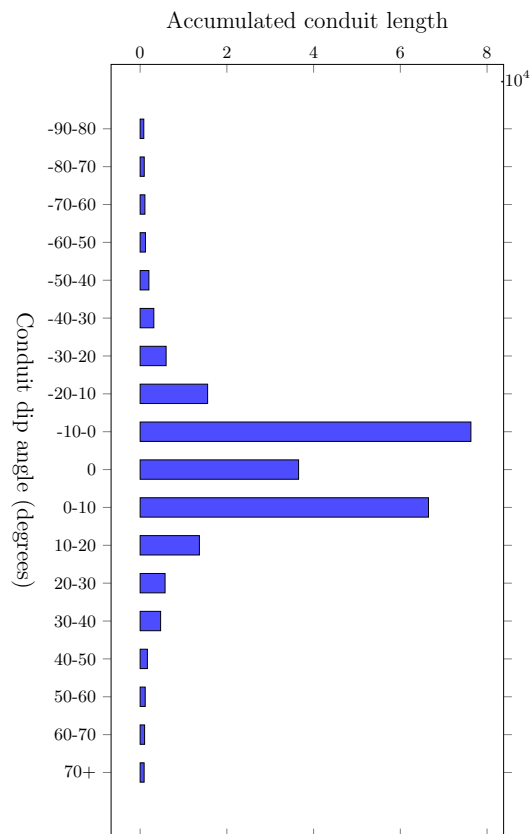


Figure 3.18: Conduit dip angle measured from a vertical reference plane. Accumulated length was computed at 10 degrees intervals.

The karst network has a vertical preferential orientation expressed in the average depth

and conduit dip angle. Conduits are closer to the surface near to the shoreline and deeper in the upstream part of the network. The dip angle of conduits correlates with the shape of the mixing zone between freshwater and saltwater influx from the ocean in the aquifer. As shown in figure 3.19 the mixing zone becomes deeper far from the shoreline. It is possible that conduit dip angle is related to this source of reactivity for mineral dissolution.

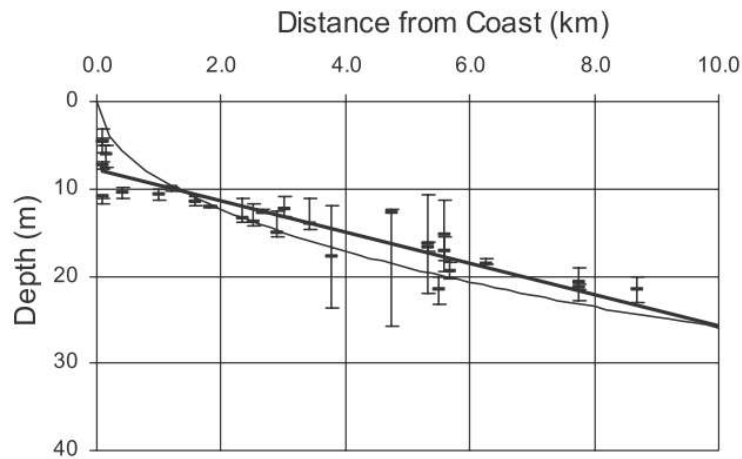


Figure 3.19: Depth of the mixing zone on Ox Bel Ha based on salinity profiles, the bars show top, middle, and base of the mixing zone (Smart et al., 2006).

Figure 3.20 summarizes the conclusions made based on all the previously presented information. The upstream part of the Ox Bel Ha karst network (at least 5 km from the coast) developed on the Miocene and Pleistocene limestones deposited on open sea conditions. The Pleistocene limestones deposited in a carbonate platform with a reef environment after the Yucatan platform emerged should be at least 10 – 15 m as inferred from the works of Ward and Brady (1979) and Blanchon (2010). However the total thickness of the Pleistocene limestones is unknown. If the Pleistocene limestones are 30 m thick, half of the karst network would have developed on limestones with high porosity and permeability due to their biogenic origin.

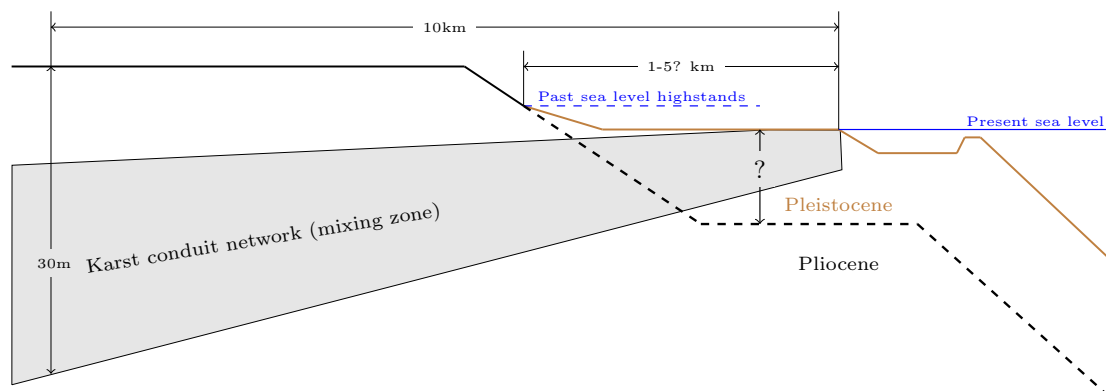


Figure 3.20: Probable position of the karst conduit network on the stratigraphic sequence.

It would be of high interest to conduct a drilling campaign and core analysis to determine the extent and properties of Pleistocene sediments in this area because the development of this large karst network system is probably related to young and permeable biogenic limestones.

3.4.2 When did speleogenesis occur?

Speleogenesis occurs after carbonate sediments deposited. The upstream part of the karst network developed on Pliocene limestones, then conduits can be up to 5 Ma old. The downstream section of the network developed in Pleistocene limestones indicates a lower bound of 2.58 Ma (<http://www.stratigraphy.org>). However, Pleistocene limestones from a reef environment deposited only until the Yucatan platform emerged due to glaciations around 800,000 yr before present (during the Pleistocene). Thus, conduits in back-reef lagoon and reef facies are certainly younger than 800,000 yr.

Another precondition for the speleogenesis is the existence of groundwater flow of reactive water through the limestone to cause dissolution. Thus, freshwater undersaturated with minerals needs to flow through the limestone layers. Groundwater flow is dependent on the altitude of the sea level, thus the development of the karst network is expected to be episodic. During a marine transgression, the sea level rises and the deposition of sediments can lead to the progradation of the shoreline seaward. During a marine regression, the sea level is lowered, and the flow of reactive groundwater through the limestone leads to the development of conduits within the sediments deposited during the previous marine transgression. If there were 5 glaciation cycles in the last 500,000 yr as shown in figure 3.5,

there should be 5 corresponding cycles of sediment deposition during marine transgression and conduit development during marine regression. It is also expected that conduits formed during a previous cycle will be reused for groundwater flow during the next cycle if they were not filled by sediments and clogged in the meantime.

3.4.3 Ox Bel Ha system during sea level changes

Today, the regional groundwater flow direction is perpendicular to the shoreline in NW-SE direction. However, sea level has fluctuated several times in the last half million years as shown in figure 3.5. The effect of sea level changes on the evolution of the system is assessed using terrain elevation data and the karst conduit network map provided by Quintana Roo Speleological Survey. Figure 3.21 shows the probable regional groundwater flow directions when sea level was lower during glaciations. Unconsolidated sediment accumulation on present day sea floor may mask the real profile of the carbonate platform but it can be considered as a reasonable approximation of past groundwater flow. Regional groundwater direction flow with lower sea level would have been deviated to the south when compared with present direction.

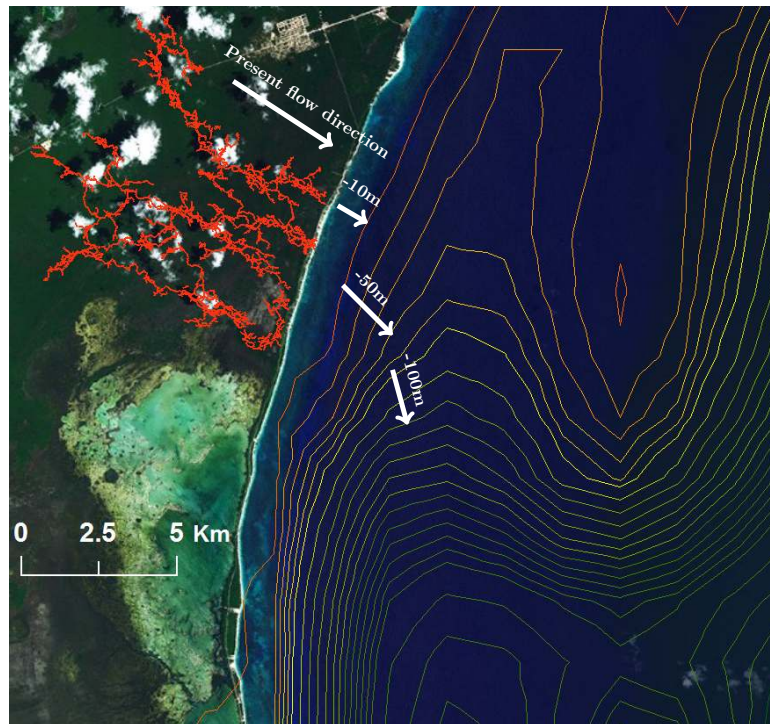


Figure 3.21: Probable regional groundwater flow directions during past glaciations when sea level was up to 100 m lower. Depth contour map elaborated with data from Amante and Eakins (2009)

Figure 3.22 shows the elevation contours of 1 and 6 m above present sea level. Terrain elevation data was obtained from NASA Shuttle Radar Topography Mission (Jarvis et al., 2008). Elevation data reveals an important feature of the evolution of Ox Bel Ha system. It is probable that higher sea levels induces a different regional groundwater flow direction. Instead of flowing NW-SE, groundwater could reach a closer ancient shoreline flowing in N-S direction.

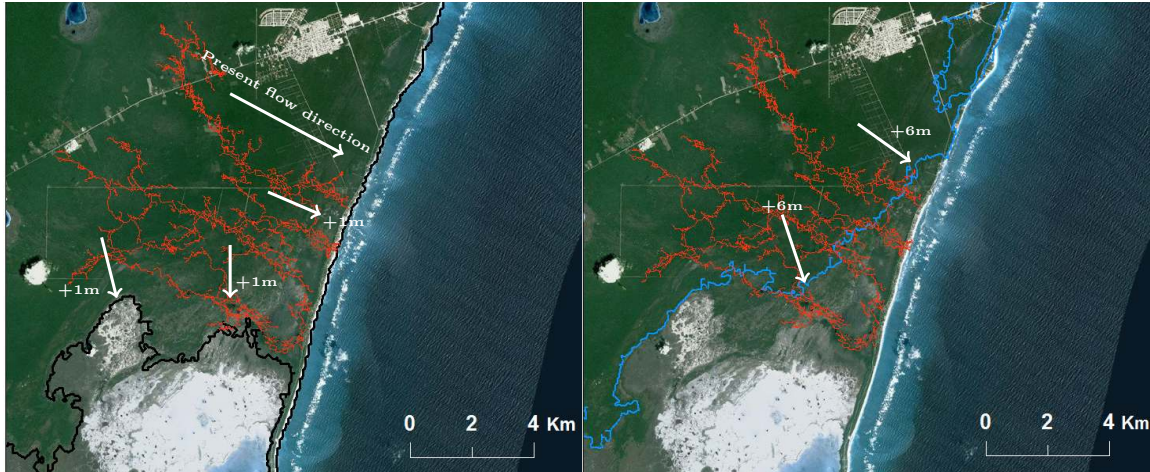


Figure 3.22: Probable regional groundwater flow directions when sea level was 1 and 6 m above present level. Contour map elaborated with data from Jarvis et al. (2008)

Figure 3.23 shows the probable position of the coastline if sea level were 10 m above present sea level as estimated for 400,000 years before present. A bay is formed upstream of Ox Bel Ha system where two freshwater lagoons exist today. Then, the terrain above the karst system becomes a peninsula. The effect on groundwater flow would be a reduction of recharge, flow rate and a reversal of flow direction for the upstream part of the system.

Changes in sea level alter shoreline position and thus the flow direction in the karst network system. The absence of a preferential orientation of conduits in the Ox Bel Ha karst network could be explained by varying flow groundwater flow directions controlled by the shoreline position depending on sea level. Thus, the complexity of the network geometry could be explained by varying hydraulic boundary conditions instead of fracturing or the deformation of limestone layer caused by tectonics.

3.5 Available data about geochemistry and groundwater flow

The aim of this section is to review what is known about the mineralogical properties of the limestones in the study area and the geochemical composition of groundwater to establish sources of reactivity for mineral dissolution.

3.5.1 Mineral composition

Mineral composition is important to study speleogenesis because dissolution reaction kinetics depends on it. The main carbonate mineral deposited by living organisms are: aragonite, low-magnesium calcite, high-magnesium calcite, and calcite and silica (Flügel, 2010). Cyanobacteria deposit low-magnesium calcite and aragonite, corals and sponges precipitate low-magnesium calcite, mollusks precipitate mainly aragonite.

Aragonite is a metastable phase of calcium carbonate precipitated by living organisms. Usually, aragonite dissolves and precipitates again in the same place as calcite. (Pittman, 1974a) measured porosity and permeability of plugs drilled in coral fossils in Barbados Island. The *Acropora palmata* coral precipitates aragonite while living, then when the coral dies aragonite is replaced by calcite. This coral species is also found in the study area. The interesting part of the process is that the overall porosity decreases because calcite precip-

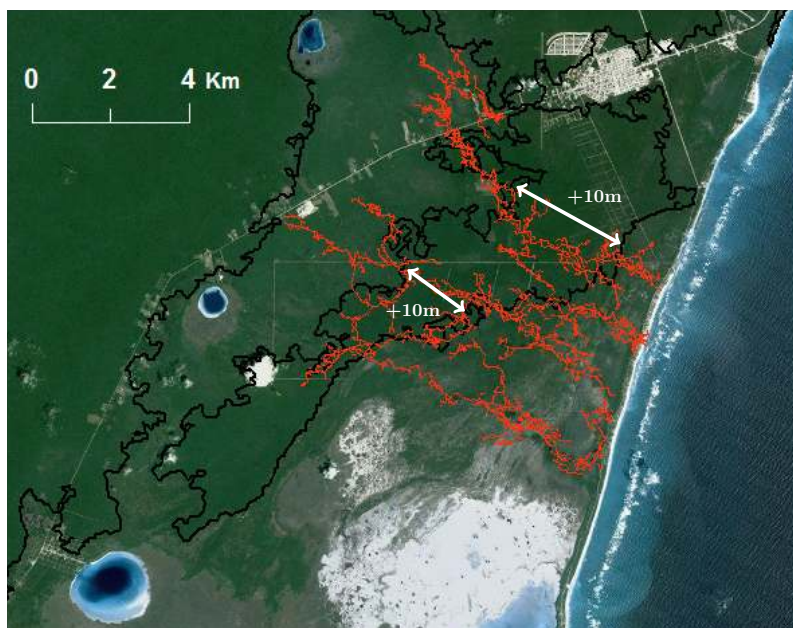


Figure 3.23: Probable regional groundwater flow directions when sea level was 10 m above present level.

itates in pores but permeability increases because of an increase of aperture in pores that remain open.

Ward and Halley (1985) analyzed the mineral composition of Pleistocene rocks in the study area. Most of limestone is composed by aragonite and calcite. In these young limestones the transition of metastable aragonite to calcite has not occurred. Also, dolomite is found in some patches of reefal limestone. On average, the dolomitized limestone contains 20% dolomite and the rest is low-magnesium calcite. In the most dolomitized zone, limestone dolomite content is up to 50%.

Smith (2004) analyzed the mineral composition of rock samples from conduit walls of Ox Bel Ha karst system (cenote Escondido/Maya Blue) using X-ray diffraction and the results were $93.8\% \pm 8.03$ of calcite content.

3.5.2 Groundwater chemistry

Limestone dissolution only occurs if groundwater is reactive to it and groundwater recharge is strong enough to replenish the aquifer with reactive water and flush away saturated water. As explained in chapter 2, the most common sources of reactivity for limestone dissolution are high dissolved carbon dioxide in solution and mixing corrosion.

Back et al. (1979) assessed the potential of limestone dissolution caused by the mixing of aquifer freshwater and saline water from the sea in a coastal lagoon 20 km north of Ox Bel Ha karst system. They described a thin layer of fast flowing freshwater overlaying a much slower saline groundwater similar to ocean water chemical composition. Between them, there is a mixing zone a few meters thick. When freshwater and saline water mix, the resulting solution is undersaturated with calcite. However, limestone dissolution takes place only when the mixing occurs underground. If the mixing occurs at the surface carbon dioxide outgasses or it is consumed by photosynthetical organisms. Results of their mixing calculations show that as much as 1mmol of calcium carbonate can be dissolved by 1 kg of water. They also observed some reactive water samples with high dissolved carbon dioxide concentration whose origin was attributed to water flowing through mangrove with CO₂ producing bacteria.

Another possible source of water reactivity is sulfate reduction and sulfide oxidation. Stoessell et al. (1993) described limestone dissolution caused by sulfide oxidation of one

sinkhole in the study area. However, this process is not spread in the karst system. Apparently, one precondition for sulfate reduction is the accumulation of organic matter in the sinkhole bottom. This occurs only in a few sinkholes surrounded by trees and deep enough to reach the saline layer of the aquifer.

Another study of geochemical composition of the study area aquifer was conducted by Smith (2004). Extensive sampling and the analysis of fresh, mixing zone and saline waters allowed her to make the following conclusions:

- Freshwater is rich in calcium ion ($\text{Ca}^{2+} = 2.19 \pm 0.55 \text{ mmol L}^{-1}$, $n=77$). This calcium concentration can not be explained by saline water intrusion.
- Most of calcite dissolution (61%), caused by freshwater flow, occurs in the vadose zone. Thus, freshwater probably arrives to the phreatic level already saturated with calcite.
- Freshwater contains organic matter and additional dissolved carbon dioxide is generated in the freshwater lens.
- Limestone dissolution potential exists in the fresh-salt water mixing zone but mixing corrosion alone can not explain calcite undersaturation. There should be also bacterial activity at and below the mixing zone.

Geochemical data from Smith (2004) is used in following chapters as input for dissolution simulations.

The origin of water reactivity in the study area is relatively simple. It is either organic matter decomposing bacteria, mixing corrosion or a superposition of both processes. However, the spatial distribution of these reactivity sources is far more difficult to establish. Mixing corrosion is limited to the mixing zone between fresh and saline water in the aquifer. The thickness of the mixing zone is controlled by the groundwater hydraulic gradient, karst conduit geometry and sea tide influence. Figure 3.24 shows a plot of in situ measurements of water electrical conductivity in the study area (Smith, 2004). The geometry of the mixing zone can be inferred from this plot. The freshwater layer becomes thicker with increasing distance from the sea, thus the mixing zone becomes deeper inland. On average the mixing zone is 3 m thick.

Thus, mixing corrosion is occurring in a layer of a few meters thick parallel to the coast with a negative dip in the inland direction. Mixing is stronger near the coast compared to far

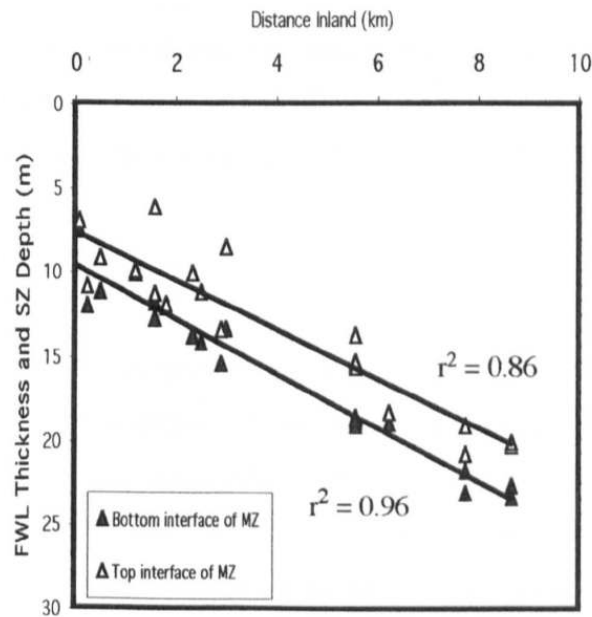


Figure 3.24: Electrical conductivity of groundwater in the study area as a function of distance from the sea, from (Smith, 2004). FWL stands for freshwater layer, SZ for saline zone and MZ for mixing zone.

away from the ocean. In contrast, the distribution of dissolved carbon dioxide originating bacterial activity is far more heterogeneous. Gulley et al. (2014) measured over a year geochemical data in a cave in Florida in an eogenetic karst aquifer similar to the study area. They observed a seasonal variation of dissolved carbon dioxide in groundwater. Seasonal ventilation and groundwater flow patterns could explain the heterogeneous distribution of dissolution potential in the cave. In another study in San Salvador Bahamas, Gulley et al. (2015) observed changes in dissolved carbon dioxide from $\log P_{\text{CO}_2} = -2$ to $\log P_{\text{CO}_2} = -1$ over a distance of 30 m. Carbon dioxide's heterogeneous distribution in groundwater was attributed to heterogeneous inputs of vadose CO_{2g} to infiltrating water and spatially variable production of dissolved carbon dioxide by bacteria. The vadose zone thickness and heterogeneity in vadose permeability control the former processes. For example, preferential paths of vadose flow could be related to increased organic matter content in groundwater and then carbon dioxide produced by bacteria. Gulley et al. (2015) estimated local and very concentrated sources of dissolved carbon dioxide could dissolve as much as 10 times more calcite than mixing corrosion.

3.5.3 Groundwater flow velocity

It was established that the aquifer is composed of three main regions: a freshwater layer on top flowing mainly toward the ocean, a saline layer that can flow either from the ocean toward inland or in the opposite direction and a mixing zone between them. Table 3.1 shows a compilation of measured flow velocities in the study area from different sources. The general trend is that groundwater flow velocity is higher near the shoreline for both freshwater and saline layers. In measurement locations near the ocean, the flow direction is reversed by the influence of sea tides. 5 km inland, the groundwater flow velocity is just slowed down by the tides but no flow direction reversal is observed. Groundwater flow velocity in conduits is in the order of thousands of meters per day. In general conduit flow velocity is two orders of magnitude greater than matrix flow.

3.5.4 Aquifer Recharge

Bauer-Gottwein et al. (2011) made the most recent estimate of groundwater recharge for the study area. In the study area and most of the Yucatan Peninsula there are no rivers. Thus, rainfall water leaves the area either by evapotranspiration or groundwater flow. The average groundwater recharge rate was estimated at 17% of annual precipitation. The same authors provided an estimate of coastal outflow between 0.3 and $0.4 \text{ m}^3 \text{ km}^{-1} \text{ s}^{-1}$. This metric refers to the average volume of water leaving the aquifer for each kilometer of coastline.

A storm that occurred on September 16th 2013 provides an unique opportunity to study the properties of the karst aquifer at the regional scale. Over 300 mm of precipitation were recorded on a rainfall measuring station located near the coastline in Tulum. The precipitation was associated to tropical storm Ingrid, these kinds of precipitation events are regional and homogeneous. The rainfall measurement was punctual, it can not be assumed that 300 mm of rainfall occurred on the whole study area, but still a significant amount of rainfall and recharge occurred on that date.

Figure 3.25 shows the location of pressure loggers installed in the aquifer by Mexico's government agency CONAGUA. Loggers are almost perpendicular to the coastline at 13 (GPS 01), 23 (GPS 02), 33 (GPS 03), 45 (GPS 04) and 43 (GPS 05) km from the coastline.

Figure 3.26 present the piezometric head in the pressure loggers shown in figure 3.25. After the storm rainfall on September 16th 2013, the piezometric head increased between

Reference	Location	Season	FW vel. (m/day)	SW vel. (m/day)	FW depth (m)	SW depth(m)	Method
Moore et al 1992	Borehole in matrix	November	-18.14	-70.8	6.1	16.1	Point dilution
Moore et al 1992	Cenote Car Wash (8.3 km)	November	-864	-	0 - 5	-	Marsh-McBirney 201 flowmeter
Moore et al 1992	Maya Blue (5.5 km)	November	-1, 728	-	0 - 4	-	Marsh-McBirney 201 flowmeter
Moore et al 1992	Yalku (0 km)	November	max -10, 368	-	0 - 3	-	Marsh-McBirney 201 flowmeter
Moore et al 1992	Tancah (0 km)	November	max -10, 368	-	0 - 3	-	Marsh-McBirney 201 flowmeter
Beddows 2004	Heaven's Gate, conduit (3.2 km)	November	max -2, 332	-	-	-	Aandera RCM9 flowmeter
Beddows 2004	Heaven's Gate, conduit (3.2 km)	April	max -864	-	-	-	Aandera RCM9 flowmeter
Beddows 2004	Casa Cenote, conduit (0 km)	Feb-Nov	-4, 760/ + 4, 501	-	4	-	Aandera RCM9 flowmeter
Beddows 2004	Xel-Ha, conduit (0 km)	Feb-Nov	-887/ + 1, 141	-	3	-	Aandera RCM9 flowmeter
Beddows 2004	Cenote Eden, conduit (1.5 km)	July	-1, 210	-	15	-	Uranine tracer test
Beddows 2004	Cenote Eden, conduit (1.5 km)	July	-5, 356/ + 5, 356	-778/ + 691	15	20	OTT Nautilus flowmeter
Beddows 2004	Yalku, brackish conduit (0 km)	Aug-Oct	-2004	-	3.65	-	Aandera RCM9 flowmeter
Beddows 2004	Yalku, SW conduit (0 km)	Aug-Nov	-	743	-	9.05	InterOcean S4 electromagnetic
Beddows 2004	Maya Blue, conduit (5.8 km)	Mar-Apr	2522 $\pm$ 86.4	-	-	24	FSI doppler 2D
Beddows 2004	The Pit, conduit (5.6)	April	1434 $\pm$ 77.8	-	-	60	FSI doppler 2D
Beddows 2007	Conduit (8.7 km)	April	-590	-	11	-	Uranine tracer test

Table 3.1: Flow measurements in the study area or near karst zones. Negative velocities indicate flow toward the sea and positive velocities indicate inland flow. FW stands for Fresh Water while SW stands for Salt Water. The data come from Moore et al. (1992) and Beddows (2004).

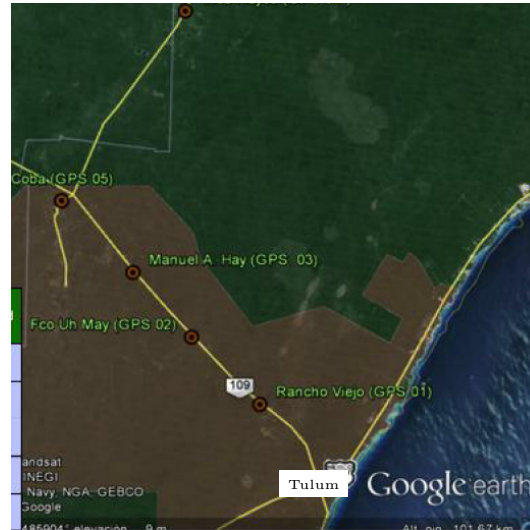


Figure 3.25: Location of pressure loggers installed by CONAGUA-OCPY (2013).

1 and 3 meters in all pressure logger. However, in the two loggers closer to the coastline the water level descended to levels before the storm in two weeks. In the 3 loggers at more than 33 km from the ocean the piezometric head did not descend a month after the storm. The difference in behavior can be explained by two causes: a significantly lower hydraulic conductivity farther away from the coastline, or that the region far from the ocean is part of another hydrogeologic unit. It is necessary to do further research on this event to establish the cause of the difference in hydraulic head between the two regions.

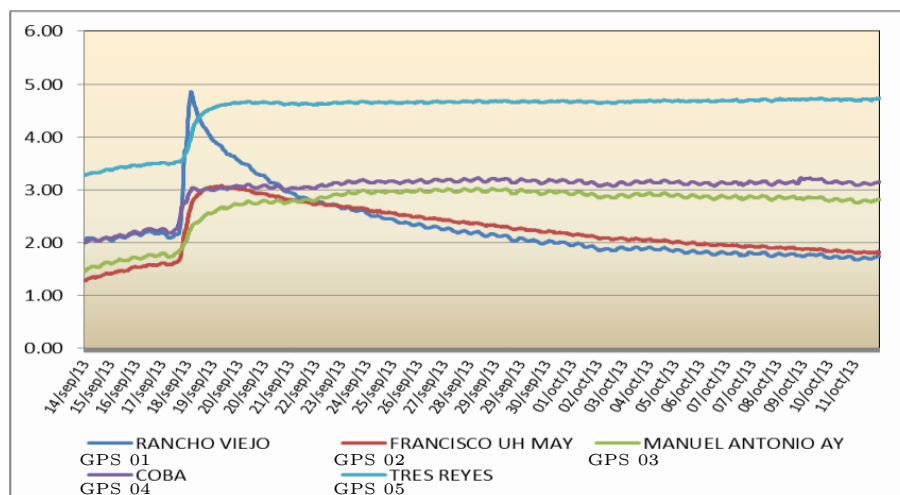


Figure 3.26: Piezometric head referenced to sea level in 5 pressure loggers (CONAGUA-OCPY, 2013).

3.5.5 Preferential dissolution

The sources of water reactivity have been described. Groundwater flow velocity ensures products of the limestone dissolution reaction are flushed out of the aquifer and the dissolution reaction can still occur. If mineral dissolution occurred homogeneously in the aquifer, the observed effect would be a porous limestone matrix with increased porosity and permeability. However, karst conduits are the evidence of preferential dissolution in the limestone aquifer and a self-organization process. Some fraction of the rock is dissolved to form conduits while other fraction of the rock remains in the form of porous matrix composing the conduit wall.

Back et al. (1986) observed preferential dissolution in Pleistocene reef deposits near the study area. Coral fossils originally composed by aragonite transitioned to calcite but the sediments around them have been dissolved. Thus, different mineral facies have different dissolution kinetics. The dissolution of a more soluble sedimentary layer can lead to the formation of a conduit.

Conduits may also develop due to the heterogeneous distribution of dissolved carbon dioxide in the aquifer. Preferential flow paths such as fractures can rapidly transport organic matter into the phreatic zone where bacteria produces CO_2 and thus water reactivity (Gulley et al., 2015).

In conclusion, the emergence of conduits results from a self-reinforcing process. Fractures in more soluble mineral facies capture flow and become larger due to mineral dissolution. Enlarged fractures make possible the transport of organic matter into the phreatic zone producing more mineral dissolution. Enlarged fractures also facilitate the mixing of the fresh and saltwater in the aquifer, thus mixing zone reactivity concentrates into enlarged fractures. Finally, enlarged fractures are also preferential flow paths to flush dissolved limestones out of the aquifers.

3.6 Data acquired from CHYN team field work

Between 2013 and 2016, a team of researchers from the Center of Hydrogeology of the University of Neuchâtel (CHYN) conducted field work in the study area in collaboration with the Geological Survey of Austria (GSA) and the local environmental conservation NGO

Amigos de Sian Ka'an. The CHYN team included Martin Hendrick, Cécile Vuilleumier, Grégory Kaeser, Philippe Renard and this PhD student. This work aimed to complement the observations made by previous researchers: piezometric monitoring, sea tide propagation into the karst aquifer, groundwater geochemistry, rock sampling and tracer tests.

3.6.1 Tides

We installed pressure loggers in sinkholes connected to the Ox Bel Ha karst network between 2013 and 2015 to measure water level every 15 minutes. A pressure logger was installed in the Xibalba Dive Center in Tulum to record the variations in atmospheric pressure. Additionally, three loggers were installed in the sea to measure tides but no data could be retrieved from them due to logger failure, except for 13 days of measurements. Sea level records from a station located in Puerto Morelos (100 km north east of study area) were used to complement measurements on the study area.

Kaeser (2016) conducted the analysis of pressure logger data. First the time drift of loggers was corrected, then the atmospheric pressure was removed, and next the data was filtered using a Butterworth filter. Then, the data from the sea level station at Puerto Morelos was analyzed using Fourier spectrum analysis. The main tidal constituents were found to be the main semidiurnal tide $M2$ and the main solar semidiurnal $S2$. They have frequencies of 1.9322 1/d and 2.001099 1/d respectively. Figure 3.27 shows all tidal constituents amplitude and frequency in the sea level station in Puerto Morelos.

Figure 3.28A shows the location of the pressure loggers in sinkholes of the karst network and figure 3.28B shows the amplitude of the main semidiurnal tide $M2$ constituent at each location. The amplitude reduction of the $M2$ tidal constituent of every location is correlated to the distance from the ocean. Closer to the ocean, the tidal variations are larger compared to the inland sinkholes. Loggers G and H correspond to Union and Kaan Luum lagoons respectively both at 10km from the ocean. The $M2$ tidal constituent is still observed at Kaan Luum (H) while it is not observed at Union lagoon (G). It can be assumed that Kaan Luum is connected to the ocean by a network of still unmapped karst conduits. For the Union lagoon, the results do not allow to conclude anything, several outcomes are possible: a) Union lagoon is not connected to the main karst network, b) the tidal signal amplitude was damped below observable levels by the karst network, or c) the pressure sensors did not

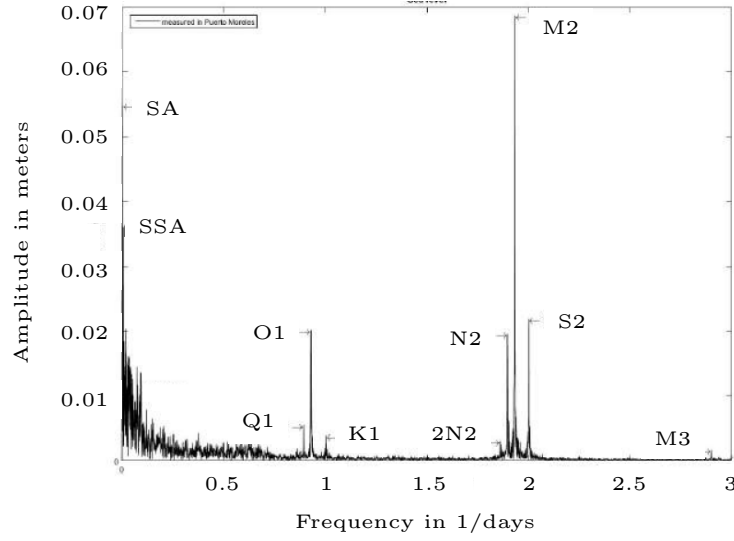


Figure 3.27: Harmonic components of tide in Puerto Morelos sea level station, from (Kaesler, 2016).

measure the signal properly.

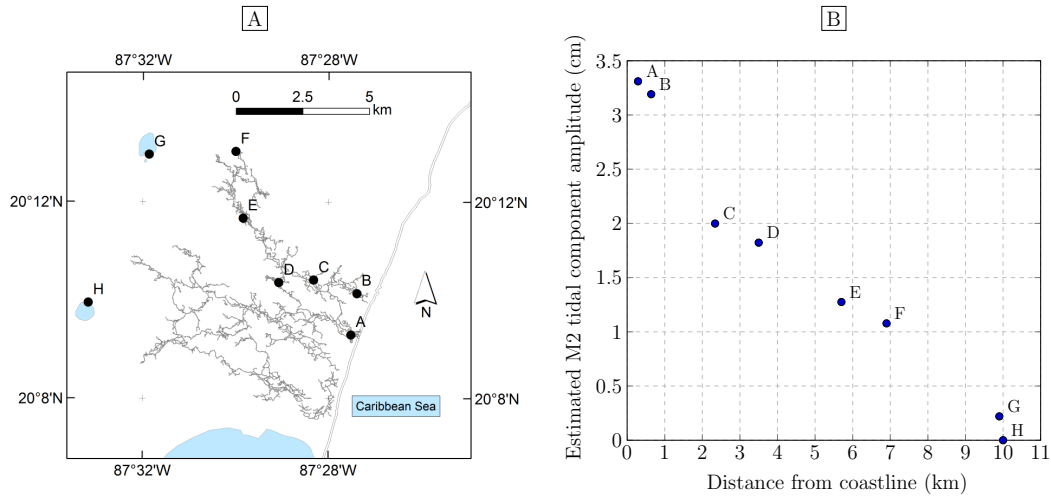


Figure 3.28: Harmonic components of tide in Puerto Morelos sea level station, from Kaesler (2016).

The following conclusions can be made from the analysis of water levels in sinkholes along the Ox Bel Ha network:

- The karst network allows the propagation of the tidal signal along the karst network up to a location 10km from the ocean.
- Hydraulic head variations related to tides and the eogenetic nature of the aquifer can induce exchange of water between karst features and the limestone matrix around them

described as tidal pumping in chapter 5.

3.6.2 Geochemistry

Seawater and groundwater samples from the freshwater and saline layers from the karst system were analyzed for anions and cations. The samples were taken using a bottom pump sent to the desired depth to bring water to the surface and measure pH and conductivity using a flow cell. Water samples were filtrated later the same day and the samples for cations were immediately acidified after filtration. Figure 3.29 shows the location of groundwater sampling sites and in red the location of the Ox Bel Ha karst network. Jailhouse 25M is a 25 m deep well drilled during the 2014 CHYN field campaign. The well is protected from collapse with a PVC screen with perforations over the whole well extension. It is located 5km from the ocean. Well TU8 is 6.6km and CAPA 30M is 8.1km from the ocean and both were constructed in the same manner as Jailhouse 25M by the GSA and Tulum Water company respectively.

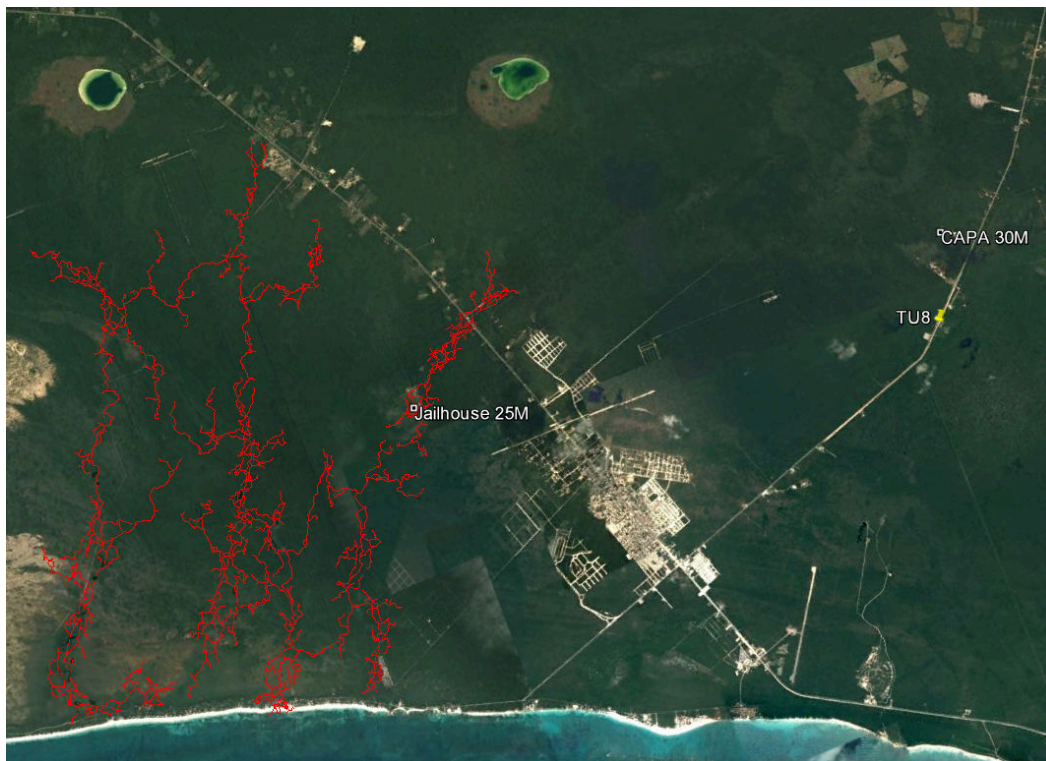


Figure 3.29: Location of groundwater sampling sites during the 2014 field campaign. In red the location of the Ox Bel Ha karst network Both fresh and saline water layers were sample at the same site.

Figure 3.30 shows the conductivity profiles at each sampling site. Only in the CAPA

Sample	Conductivity	pH	Temp	Depth	Easting	Northing
	$\mu\text{S}/\text{cm}$		$^{\circ}\text{C}$	meters		
CAPA 30M	54000	7.21	25.9	30	449436	2241200
CAPA 5M	554	6.93	26.0	5	449436	2241200
Jailhouse 23M	52900	6.85	28.1	23	448775	2232351
Jailhouse 5M	4400	7.28	26.0	5	448775	2232351
Seawater	41200	7.82	24.3	1	453309	2230911
TU8 29M	43000	7.09	26.0	29	450692	2240445
TU8 UP	4000 (*)	6.85	20.0 (*)	7.5	450692	2240445

Table 3.2: Physical properties measured on site and location (UTM-WGS84-16N of water sampling sites, (*) measured in laboratory

Anions in mg/Liter					
Sample	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^-
CAPA 30M	145.18	0.63	18428.3	6.23	2831.9
CAPA 5M	219.6	0	59.1	0	5.3
Jailhouse 23M	159.82	0.59	19024.8	5.40	2701.3
Jailhouse 5M	368.44	0	1224.6	5.31	183.7
Seawater	219.6	0.58	14965.7	41.02	2028.9
TU8 29M	219.6	0.57	15834.6	6.99	2298.8
TU8 UP	275.72	0	1230.2	10.73	188.3

Table 3.3: Anions in groundwater samples in mg/L

30M well the mixing zone is clearly observable and it is approximately 5m thick. In the other two sampling sites, conductivity increases before reaching the mixing zone where it is also 5m thick. The mixing, high conductivity in the freshwater layer, is probably influenced by near karst conduits.

Table 3.2 shows the physical properties of water. Samples named CAPA were taken in the same borehole but at different depth. One sample near to the freshwater surface and the second sample the deepest possible in the saline zone. The same for Jailhouse and TU8 boreholes.

Total alkalinity analysis of water samples was done in Mexico to avoid transporting 14 kilos of water, in spite of only 7 collected water samples. Cation/Anion analysis were conducted at CHYN laboratory using Ion Chromatography methodology. Results are shown in tables 3.3 and 3.4 and the ion charge balance results on table 3.5. Depths at which the sample was collected are indicated with M symbol after the depth. Calcite saturation index was estimate using PHREEQC.

There is not clear trend in calcite saturation. Freshwater is unsaturated in CAPA and

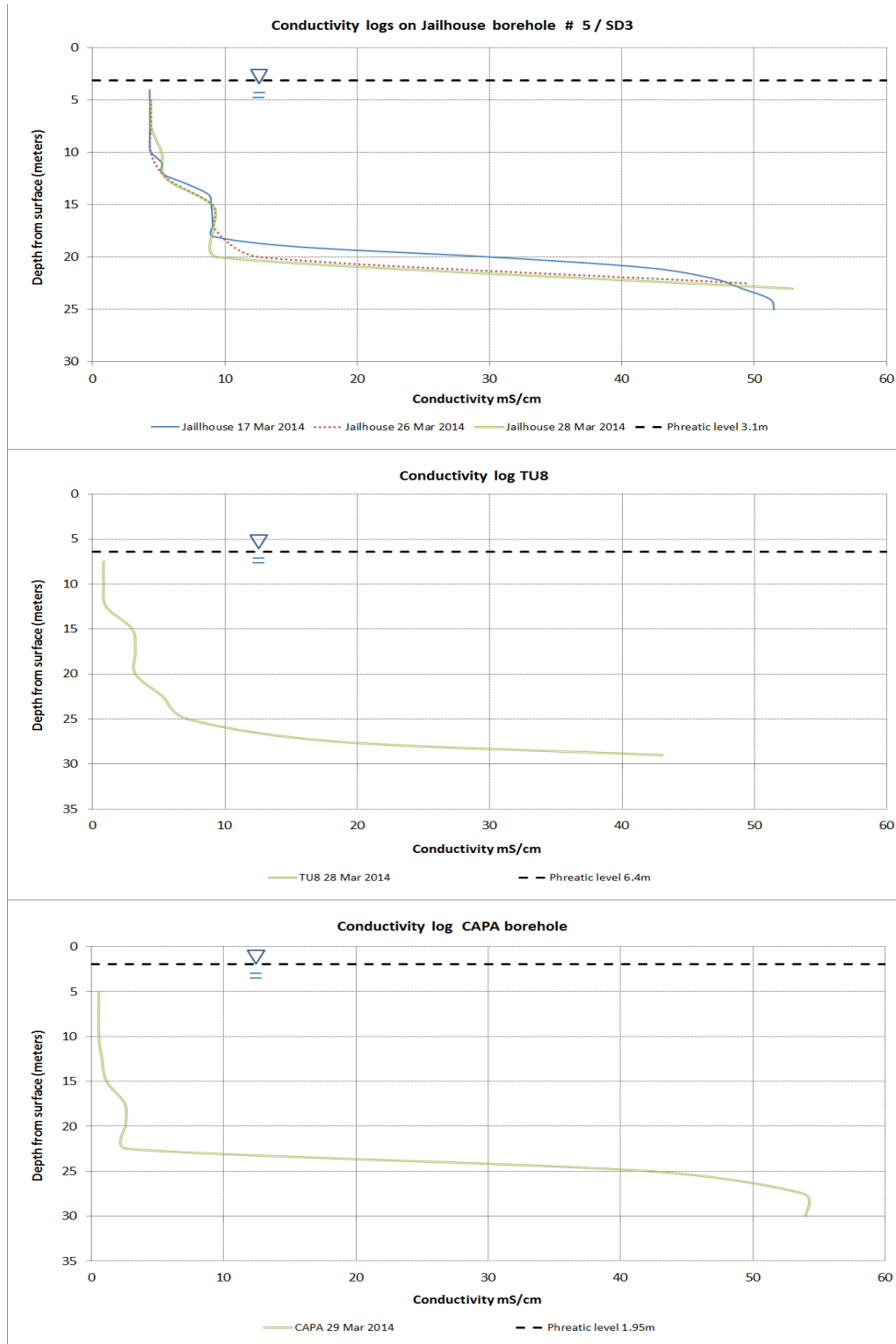


Figure 3.30: Conductivity profiles at each sampling site, March 2014

TU8 wells but saturated in Jailhouse well. In contrast, saline water is unsaturated with calcite in the 3 sampling sites. However, the estimated dissolved carbon dioxide concentration (P_{CO_2}) shows a clear trend. P_{CO_2} of saline water is 10 times the concentration of water in

Cations in mg/Liter						
Sample	Li ⁺	Na ⁺	K ⁺	Mg ₂ ⁺	Ca ₂ ⁺	Sr ₂ ⁺
CAPA 30M	0.37	9749.1	381.71	1210.96	502.26	5.2
CAPA 5M	-	31.60	2.85	5.85	73.57	0.7
Jailhouse 23M	0.27	10545.3	368.95	1244.52	425.48	5.0
Jailhouse 5M	-	652.8	20.20	90.51	151.10	2.8
Seawater	0.41	7825.2	276.37	938.29	313.56	2.1
TU8 29M	0.28	8536.5	317.78	1046.07	427.68	4.6
TU8 UP	-	689.58	25.67	87.73	118.87	1.19

Table 3.4: Cations in groundwater samples

Sample	Ion charge balance
CAPA 30M	-1.97
CAPA 5M	+2.21
Jailhouse 23M	-0.30
Jailhouse 5M	-0.50
Seawater	-3.04
TU8 29M	-1.13
TU8 UP	+0.80

Table 3.5: Ion balance in each sample

contact with the atmosphere. Freshwater P_{CO_2} is 100 times the concentration of water in contact with the atmosphere. These results are consistent with the data presented by Smith (2004), the origin of dissolved carbon dioxide is probably bacterial decomposition of dissolved organic matter.

3.6.3 Drillings, tracer tests, flux imager

A tracer test was conducted between cenotes Cristal and Escondido in the Ox Bel Ha karst network with the support of C. Vuilleumier and M. Hendrick. 300 g of uranine were injected by a diver at the entrance of an conduit with observable flow on the 26th of March 2013 at 17h15 at a depth of 2.5 m. Figure 3.31 shows the sampling points in cenote Sunhole and cenote Escondido. Continuous water sampling has been carried out in cenotes Sunhole and Escondido for 36 hours following the injection. In Sunhole, a bottom pump installed by a diver at a depth of 11.5 m was used to sample every 30 minutes. In Escondido, two conduit entrances at 5 m depth were monitored, one with a GGUN-FL30 field fluorometer and the other with an automatic water sampler (ISCO Model 6712) at a rate of one sample per hour. The collected water samples have been analysed with a Perkin Elmer LS50B

spectrofluorometer at the CHYN. Figure 3.31 shows the tracer breakthrough curve. Uranine fluorescent peak (around 490 nm) was detected first in a sample taken 31 hours after the injection (March 28 at 00:15). Concentration rises until hour 35 (March 28 at 04:20) where it reaches a maximum of 0.044 ppb. The two subsequent samples show decreasing concentrations. Sampling was stopped at 36 hours, hence it is not possible to state if the maximum observed concentration at hour 35 is the peak of the tracer breakthrough. The field fluorometer did not record any uranine concentrations during the sampling survey. Likewise, none of the samples taken at cenote Escondido by the automatic sampler showed anomalous fluorescence.

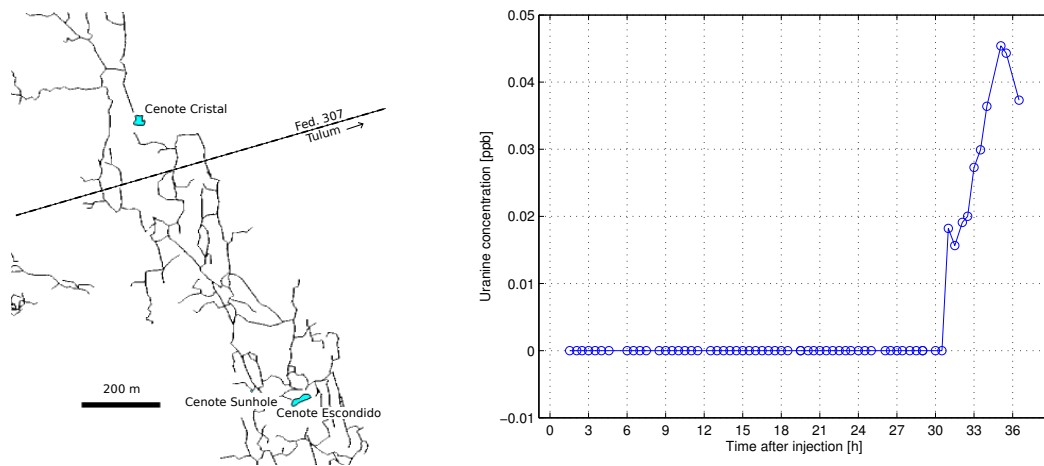


Figure 3.31: Location of injection and sampling sites for 2013 tracer test. The distance between injection and sampling sites is approximately 800m

Tracer arrival at hour 31 in cenote Sunhole suggests a maximum water velocity around 580 m d^{-1} . From the peak concentration observed at hour 35, the dominant water velocity is 514 m d^{-1} . The observed velocity of 580 m d^{-1} is in the range of the velocities reported in table 3.1 for conduits between 3 and 5 km from the coast. A proper assessment of the tracer test can not be done since the tracer concentration peak could not be established because the sampling period was too short. It is not possible to know if the peak observed at hour 31 is effectively the peak or a higher concentration arrived later.

The tracer was injected at a depth of 2.5 m and observed at 11.5 m depth 11.5 m downstream. This suggests strong mixing in the karst system. One probable explanation is that the conduits that connect injection and sampling points are not always on the freshwater layer. Some conduits of the network are in the freshwater layer and other conduits are in the

saline water zone. Thus, the tracer in the freshwater layer should travel in karst conduits and also in some sections of limestone matrix producing the high apparent vertical dispersion in the tracer plume.

In 2014, a drilling campaign was done on the study area to explore the characteristics of the karst network. A sector of the Ox Bel Ha network was selected because it was accessible to the drilling machine and considered safe to install measurement equipment for long term monitoring. The site is known as cenote Jailhouse and it is located 4.75 km from the shoreline. The area has also been carefully mapped by cave divers. 6 drillings were made with a rotary-percussion drill powered by compressed air, two of them reaching a karst conduit. In addition of a map of nodes and connecting line, measurements of the conduit diameter have been done by the GSA team to produce a 2D map of the conduit network. Figure 3.32 shows the relative positions of drillings to karst conduits and the position of geoelectrical profiles conducted by the Geological Survey .

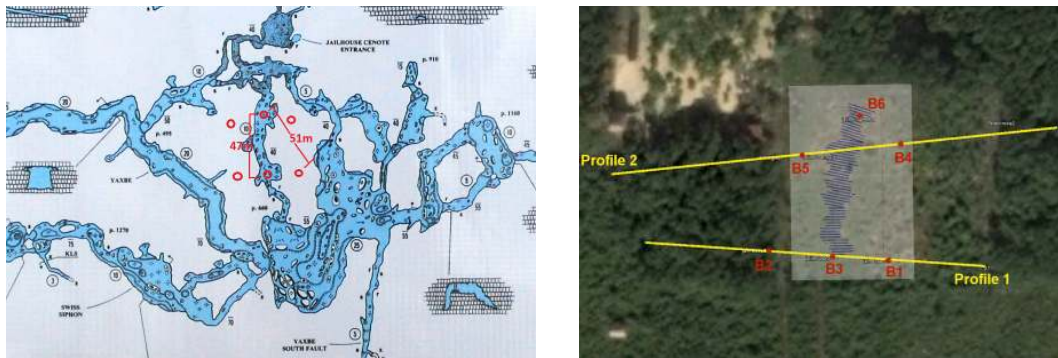


Figure 3.32: Position of drillings relative to karst conduits and resistivity imaging profiles.

Figure 3.33 shows the results of the geoelectrical profile 1. The interpretation of the ground geophysical surveys were the following: A) the water table did not produce a distinct horizontal resistivity signal, this suggests a smooth water saturation gradient in the limestone matrix; B) the structure of the karst conduit is not clear in the images, this may be caused by material heterogeneity in limestone matrix. For more information refer to Schiller (2014).

Tracer tests were conducted by M. Hendrick and A. Maqueda in this area in March 2014. The first test was done in a karst conduit reached by boreholes B6 and B3, see figure 3.32. 350g of uranine in solution were injected on March 27th at 16h44 and the injection lasted 7 minutes. The injection was done at borehole B6 at 11.5m from the surface, 1m from the conduit ceiling, 2 m from the conduit bottom and 6.5m above the mixing zone. The

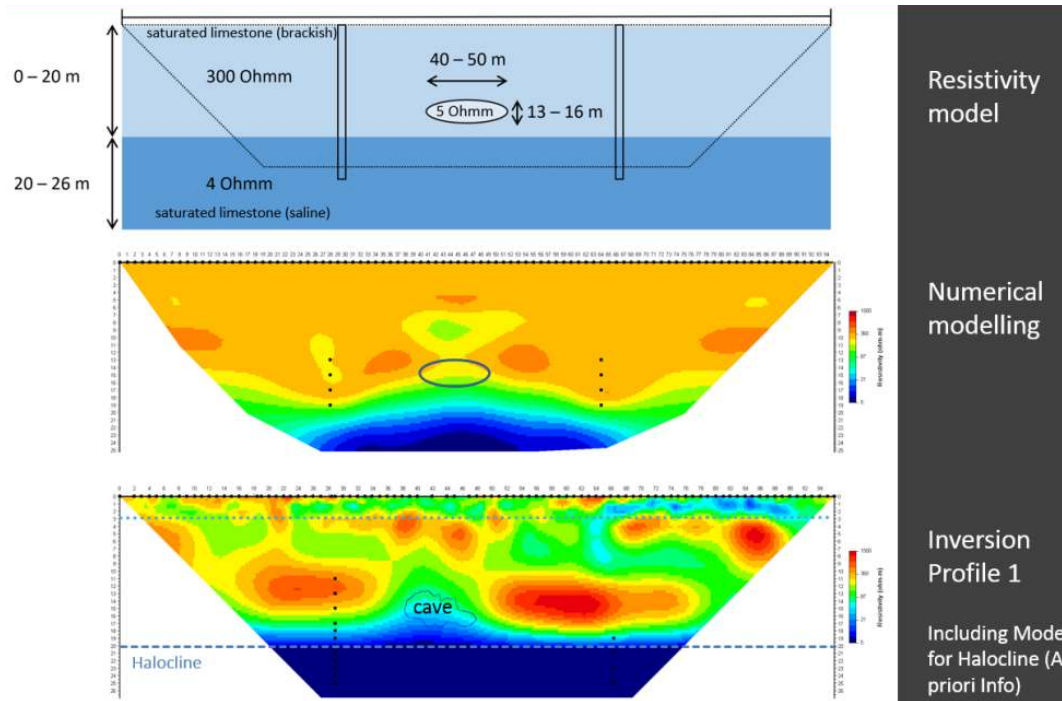


Figure 3.33: Geoelectrical profile 1 from figure 3.32. From top to bottom: water resistivity model, geoelectrical modelling and data-inversion, from Schiller (2014).

sampling was done at borehole B3 drilled in the same conduit using a borehole fluorometer installed at 14m depth. The first tracer peak arrived at 17h37m54s and a second peak was observed at 17h58m54s. The maximum observed concentration was 100 mg L^{-1} of uranine. The second tracer test was done on March 29th at 16h23 and the injection lasted 3 minutes at same borehole and depth as the first test. The sampling point was on borehole B1 at 2 m depth. The first arrival of tracer was observed at 16h52m40s. The maximum observed concentration of uranine was 140 mg L^{-1} . Figure 3.34 shows both tracer tests, the start of injection time corresponds to 0 minutes.

Flow velocity estimations based on tracer tests are shown in table 3.6. Flow velocity estimates are similar for both tracer tests. In the first tracer test, the fluorometer was installed in a mapped conduit. In the second tracer test, the borehole was supposed to be drilled in the matrix and is located about 20m on the side of the main conduit. However a cavity of 1 meter diameter was found during drilling. This cavity has not been mapped by cave divers but it is apparently well connected to the main conduit. Based on flow velocity estimates, the tracer arrived faster to the non-mapped smaller cavity compared to the larger conduit having a diameter of 2 m.

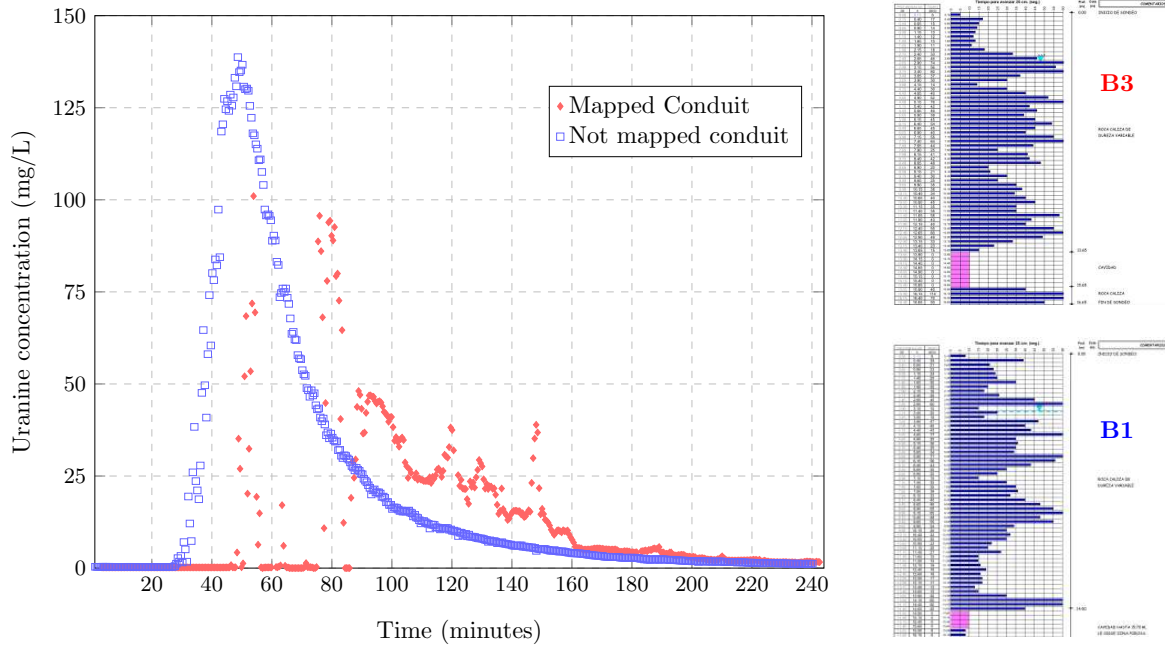


Figure 3.34: Superposition of both tracer tests. *Mapped Conduit* indicates the fluorometer installed in borehole B3 , while *Not mapped conduit* is the fluorometer installed in borehole B1. To the left, drilling velocities logs for both boreholes show the cavities found at 15m depth.

Four of the drilling logs show conduits or cavities larger than 1 m at 15 m depth. The other 2 logs show porosity at the vug scale at the same depth. These results can be interpreted by inferring the presence of a layer where preferential dissolution occurred. Even if those cavities are not large enough to be explored by cave divers, the groundwater flow velocity seems to be comparable or even higher than in large conduits.

Flow measurements were collected later in the same karst conduit between March and September 2015. The measurements were done using a new *flux imager* developed by A. Schiller from the Geological Service of Austria. Figure 3.35 shows the operating principle of the flux imager measurement device. A laser source illuminates a series of parallel planes within the karst conduit. A camera records a movie of the scene. Any moving particle flowing in the conduit is illuminated by the different laser planes and blinks as it advances through the device. The analysis of the movie can allow to retrieve the position of the particles in time and estimate velocity without disturbing the flow in the conduit. The flow measurement range spans between 0.01 and 1000 cm s^{-1} .

Figure 3.36 shows 115 flow velocity measurements in the karst conduit where the flux imager was installed. Measurement frequency is 1 day. It is the same conduit where tracer

	Conduit 1st test	Matrix 2nd test
Injection start	16:44:00	16:23:00
Injection time	00:07:20	00:03:00
Injection end	16:51:20	16:26:00
1st trace arrival	17:32:54	16:52:40
Peak Arrival	17:37:54	17:11:40
1st tracer delay (1st arrival - injection start)	00:48:54	00:29:40
1st peak delay (peak time - injection start)	00:53:54	00:48:40
2nd peak arrival	17:58:54	-
2nd peak delay	1:14:54	-
Approximate distance from injection	46.4m	50.5m
First arrival vel.	1365.6 m/day 1.58 cm/sec	8830.08 m/day 2.83 cm/sec
Peak vel.	1238.4 m/day 1.44 cm/sec	1492.8 m/day 1.72 cm/sec

Table 3.6: Flow velocity estimates from tracer tests

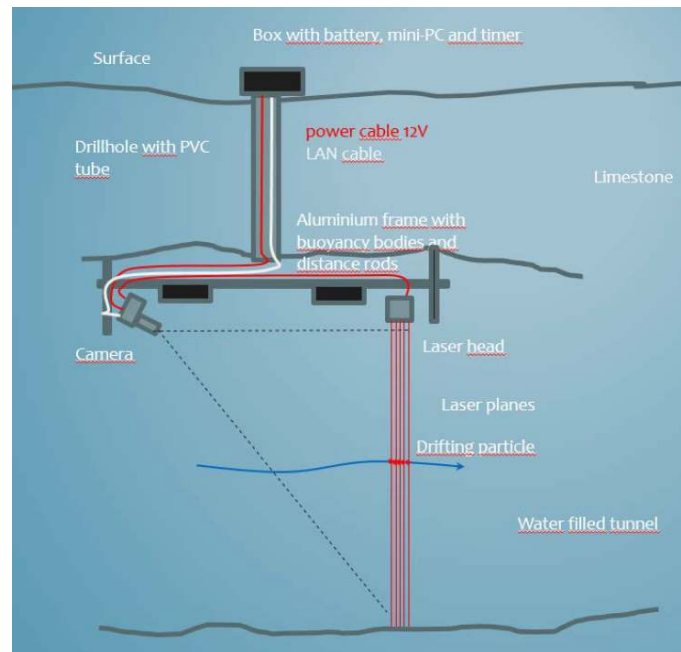


Figure 3.35: Operating principle of flux imager, (Schiller, 2014)

test was done a year earlier. The maximum flow velocity is 3.73, the minimum 0.55 and the average 1.61 cm s^{-1} . Flow velocity measurements are similar to the estimates made from the tracer tests. However, continuous measurements show flow velocity fluctuations. Future analysis of flow velocity data will allow to establish the cause of the fluctuations: either sea tides or recharge events of the aquifer.

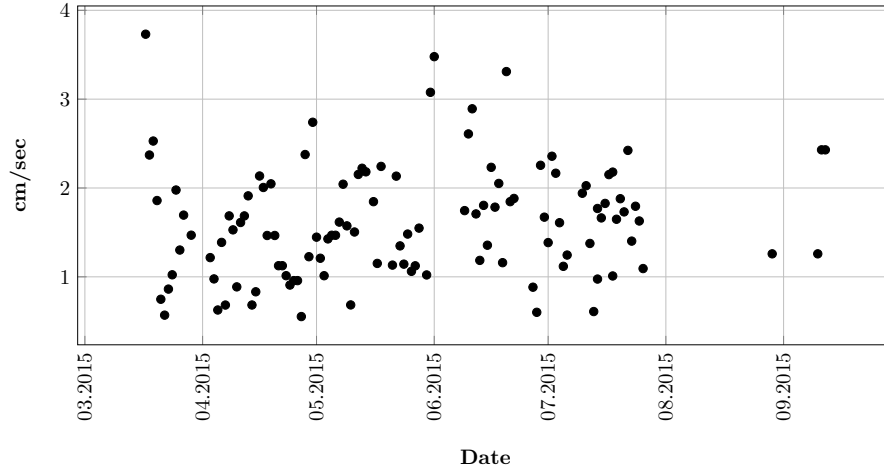


Figure 3.36: Flow velocities measured in conduit near Cenote Jailhouse between March and September 2015. Personal communication, Arnulf Schiller, April 2017

3.6.4 Limestone physical properties

In 2014, T. Hossler participated to the field campaign and collected rock samples and data focusing on the collapse mechanism of karst cavities formed by dissolution in the study area.

Hossler (2015) measured the compressive strength of limestone samples from the study area using triaxial tests. Dry rock samples have a compressive strength between 25 and 40 MPa while water saturated samples have compressive strength between 10 and 20 MPa. As comparison, concrete used in constructions has a strength of 25 MPa. However, this test reflects the properties of the rock at the scale of samples that were cylinders of 80 by 25 mm. At this scale, it is possible to have a sample without fractures or dissolution cavities, however at the conduit scale mechanical resistance should be lower because limestone is fractured or has dissolution voids. Another factor related to mechanical resistance is the bedding thickness. In the analyzed core drillings, the thinnest layer was approximately 10cm and the thickest one was 50 cm. It is expected that at every bedding plane there is a discontinuity in mechanical resistance of fracture. Thus, compression tests provide the upper limit of limestone compressive strength.

Hossler (2015) also measured porosity and permeability. For 14 samples, the minimum porosity was 0.04, the maximum 0.48 and the average 0.30. The porosity in samples followed the trend of higher porosity for higher grain size. For limestone texture following the Dunham classification porosity values were the following: mudstone (0.123), wackestone (0.32), packstone (0.345), grainstone (0.26) and floatstone (0.38). Permeability was measured in 3

samples, the results were $59.41 \text{ mD} = 0.05 \text{ m d}^{-1}$ for a sample with porosity = 0.38, $136.27 \text{ mD} = 0.114 \text{ m d}^{-1}$ for a sample with porosity = 0.44 and $58.5 \text{ mD} = 0.049 \text{ m d}^{-1}$ for a sample with porosity = 0.39. Figure 3.37 shows some limestone samples from the study area and thin sections prepared by Hossler. Thin section *c* shows ooids and the connected pores around them. Thin section *d* shows bioclasts (shells) being partially dissolved.

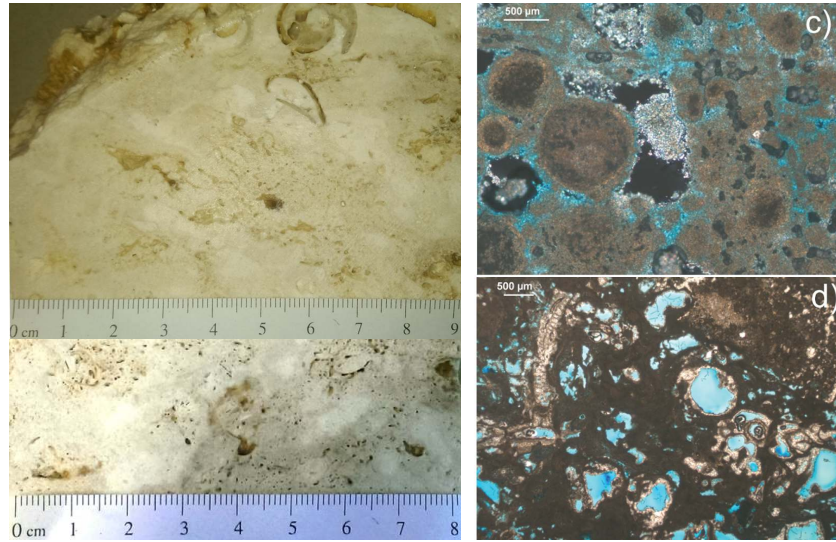


Figure 3.37: Porous limestone from the study area, bioclasts are observed. In both thin sections the porosity and connectivity is observed (Hossler, 2015).

3.7 Conclusion

After assessing the geographical and geological setting, as well as the limestone properties in the study area, we conclude that the Ox Bel Ha karst network fits well the definition of *eogenetic* karst presented on chapter 2. The Miocene-Pliocene and Pleistocene limestones which contain the karst network were never buried at depth and have not underwent mechanical and chemical compaction. Thus, the limestones in the study area have a high primary porosity and permeability. In eogenetic karst aquifers, the exchange of water between the conduits and the matrix is possible if there is a hydraulic gradient that induces the exchange. We also observed that the variations in the orientation of the position of the coastline relate to sea level changes in relation with glaciations may explain the lack of orientation of the channel conduits at a local scale.

Chapter 4

Speleogenesis models

4.1 Introduction

The previous chapters have shown that speleogenesis in the region of Tulum may occur both in the porous matrix and along discontinuities such as fractures or conduits. To investigate these processes, two simulation modules were developed.

The first module allows to couple the changes in porous medium physical properties induced by mineral dissolution undergoing flow and transport processes. The simulated hydraulic properties are porosity, hydraulic conductivity and specific storage. The simulation uses the FEFLOW software to calculate flow, mass transport and reaction in porous medium. Then, the module retrieves at the same time the solute concentrations and uses them as input for mineral dissolution calculations and to compute the evolution of the hydraulic properties.

The second module considers the evolution of aperture and cross section area of fractures after mineral dissolution occurs. Fracture growth causes a reduction of the resistance to flow (friction) in the fracture system. FEFLOW is used to calculate flow, mass transport and reaction in fractures or discrete elements in a finite element mesh model. The module retrieves the solution concentration which is used to calculate wall retreat, which is then used to update the fracture dimensions.

Groundwater flow, dissolution reaction and evolution of the hydraulic properties of the rock are processes occurring simultaneously. However, the time scales of each process is different. Groundwater has residence times in aquifers from hours to thousands of years. Equilibrium between groundwater and calcite in natural conditions takes from hours to

days (Langmuir and Mahoney, 1984). A significant increase of porosity or enlargement of fractures is the consequence of mineral dissolution occurring for long periods of time. Thus, the simulation of these processes needs a conceptual model that reconciles dissimilar time scales.

Lichtner (1988) proposed the quasi-stationary state approximation model to simulate groundwater flow and fluid-rock reactions over geologically significant time periods. The evolution of a geochemical system (porous or fractured media) can be represented by a sequence of *stationary states*. Each stationary state describes the solute concentration and dissolution rates at all positions in the system corresponding to a particular state of evolution of the system (porosity or fracture aperture). Reaction fronts remain stationary unless significant changes in surface area, porosity and permeability occur to alter stationarity.

In this conceptual model, flow, mass transport and reaction are calculated in the appropriate time frame of hours. Then, the solute concentration is used to calculate the rate of alteration of the rock and this rate is applied for periods in the scale of years. Lichtner (1988) demonstrated with finite differences that this approximation is valid if the mineral surface area, porosity and permeability change slowly compared to the time needed to establish a stationary state. The time required to reach a stationary state is the period the reaction takes to achieve a new constant solute concentration condition ($\frac{\partial C}{\partial t} \approx 0$) in the whole simulation domain after the rock properties have changed. It will be shown later that due to the residence times and calcite dissolution kinetics, the time needed to establish a stationary state is much shorter than the time needed to simulate porosity evolution, thus the approximation is valid.

A detailed description of the simulation modules and the assumptions behind them is presented in the following sections.

4.2 Evolution of porous media hydraulic properties after mineral dissolution

Mineral dissolution by groundwater is a process where a rock mass becomes dissolved solids in water. The mass removed from the rock by dissolution occupied a solid volume proportional to the rock density or molar volume. Once this solid volume is removed by dissolution, the

radius of the pores enlarges or the connectivity between the pores in the rock increases. Larger or better connected pores will cause an increase in permeability at the Darcy scale. Increases in pore volume are related also to increases in specific storage.

The relationships between dissolved mass, porosity, permeability and storage provide the framework for the simulation module that was coded.

4.2.1 Governing equations

As mentioned in the Introduction section of this chapter, flow, mass transport and dissolution reaction are solved using FEFLOW. In equation (4.1) ε is porosity, C reactive solute concentration, D molecular diffusion, Q the non-reactive bulk production term and R the reaction rate. The non-reactive bulk production term, or sink/source, is not used for mineral dissolution simulations. Reaction rate R can be a linear or higher order reactions described in chapter 2.

$$\frac{\partial}{\partial t}(\varepsilon \cdot C) - \nabla(D \cdot \nabla C) + \nabla(q \cdot C) - Q = R \quad (4.1)$$

Darcy flux q in equation (4.1) needs to be calculated. Equation (4.2) shows the implementation of Darcy's law in FEFLOW. It takes into account variably saturated media (by using a relative hydraulic conductivity $-K_r(s)$) and buoyancy (χ) due to variable fluid density to estimate the groundwater flux q .

$$q = -K_r(s)K(\nabla h + \chi e) \quad (4.2)$$

In this work, the flow simulations are conducted in 1 and 2 dimensional models of fully saturated media with no density driven flow and isotropic conductivity. Then the Darcy equation simplifies ($K_r(s) = 1$ and $\chi = 0$) into equation (4.3) where K is hydraulic conductivity and dh/dx is the hydraulic gradient.

$$q = -K \frac{\partial h}{\partial x} \quad (4.3)$$

Up to this simulation stage all equations are already implemented in FEFLOW. To conduct a simulation, it is only necessary to create a finite element mesh (FEM), attribute porous media properties to the elements and prescribe the flow initial and boundary condi-

tions (BCs). As described in detail in chapter 2, calcite dissolution kinetics can be modeled either by a 1st order reaction or a higher order model. Equation (4.4) shows the 1st order dissolution kinetics model for calcite where k is the reaction constant, C the calcium concentration in solution and C_{eq} the calcium ion equilibrium concentration. Dissolution rate R is expressed in mass per area per unit time, the specific units used in the analysis being $\text{mmol cm}^{-2} \text{s}^{-1}$. Equation (4.4) is implemented in the FEFLOW *Reaction Kinetics Expression Editor*.

$$R = \varepsilon k (C_{eq} - C) \quad (4.4)$$

Calcite dissolution can also be simulated by applying the coupling of FEFLOW and PHREEQC. PHREEQC implements the PWP equation for calcite dissolution kinetics presented in Chapter 2. The PWP equation requires 4 inputs and PHREEQC requires FEFLOW simulating the transport of 6 solute species to represent the dissolution of calcite. The porosity evolution simulations conducted with FEFLOW and PHREEQC required a significantly longer computation time and do not produce different results compared to using equation (4.4) to represent mineral dissolution.

Once the reaction kinetics are included in the model, a reactive transport simulation can be conducted. The evolution of porous media properties described by the following conceptual models and equations was coded as an additional module coupled to the reactive transport simulation.

In order to simulate the evolution of the physical properties of the porous media, the rate needs to be integrated over a discrete area and a discrete period of time. The result is the amount of dissolved mass. The amount of dissolved mass is then converted to volume which is added to the initial porosity to obtain a new porosity value. These concepts are formulated in the model proposed by Rezaei et al. (2005) and shown in equation (4.5) where $\varepsilon(t + \Delta t)$ is the porosity at calculation time $t + \Delta t$, $\varepsilon(t)$ is the porosity in the previous time-step, ε_0 is initial porosity, R is the reaction rate from equation (4.4), V_m is the porous medium molar volume and Δt is the dissolution calculation time-step.

$$\varepsilon(t + \Delta t) = \varepsilon(t) + \varepsilon_0 R V_m \Delta t \quad (4.5)$$

The permeability and specific storage are also updated. Previous research has expressed these variables as a function of porosity. The relationship between porosity and permeability chosen for this work is the one formulated by Bernabé et al. (2003) shown in equation (4.6) where K_0 is the initial hydraulic conductivity and γ is an exponent depending on the process altering the porous media. For mineral dissolution, Bernabé et al. (2003) suggested using a value of 3.

$$K = K_0 \left(\frac{\varepsilon}{\varepsilon_0} \right)^\gamma \quad (4.6)$$

The specific storage S_s has also been related to the porous media porosity. The relationship between porosity and specific storage is given by equation (4.7) (De Marsily, 1986) where C_B and C_F are the bulk porous medium and fluid compressibility, ρ is the fluid density and g the gravitational constant.

$$S_s = \rho g [(1 - \varepsilon) C_B + \varepsilon C_F] \quad (4.7)$$

4.2.2 Numerical implementation

Figure 4.1 shows a flowchart showing how the equations and the quasi-stationary approximation are implemented. There are two loops, one for reactive transport and one for dissolution and porous medium properties evolution.

Equations (4.1), (4.3) and (4.4) are part of the reactive transport loop. The simulation runs with an automatic time step between 1 and 10 days until a stationary state ($\partial C / \partial t \approx 0$) is achieved in the whole simulation domain. Stationary states are achieved between 100 and 1000 days of simulation starting from a fully unsaturated initial condition. The time to reach a stationary state t_{stat} depends on the dissolution reaction constant and flow and mass boundary conditions of the simulation. The first loop ends when the reactive transport simulation time t_{sim} is larger than the time to reach a stationary state t_{stat} .

Then, the module loops through every FEM element to perform the following actions: 1) retrieve solute concentration from the reactive transport simulation, 2) estimate dissolution rate, and 3) calculate porosity increase based on dissolution rate R and the given time step Δt . Since dissolution reaction in typical groundwaters are relatively slow, the time step for porosity increase can be several orders of magnitude larger, i.e. $\Delta t = 10,000$ days.

At this point there is a second conditional evaluation. The simulation may end if the maximum porosity value ε_{max} is reached. ε_{max} is defined before starting the simulation and it represents the maximum porosity before the porous medium is assumed to be fully dissolved. If the calculated new porosity is less than ε_{max} the calculation continues. Based on porosity new values of hydraulic conductivity K and specific storage S_s are estimated. The last action of the module is to set new values of ε , K and S_s for every element of the FEM mesh.

After the new properties have been set, the module ends and the reactive transport simulation resumes. Since, the properties of the FEM elements were modified the 1st loop will run until a new stationary state is achieved and the new properties update can be done.

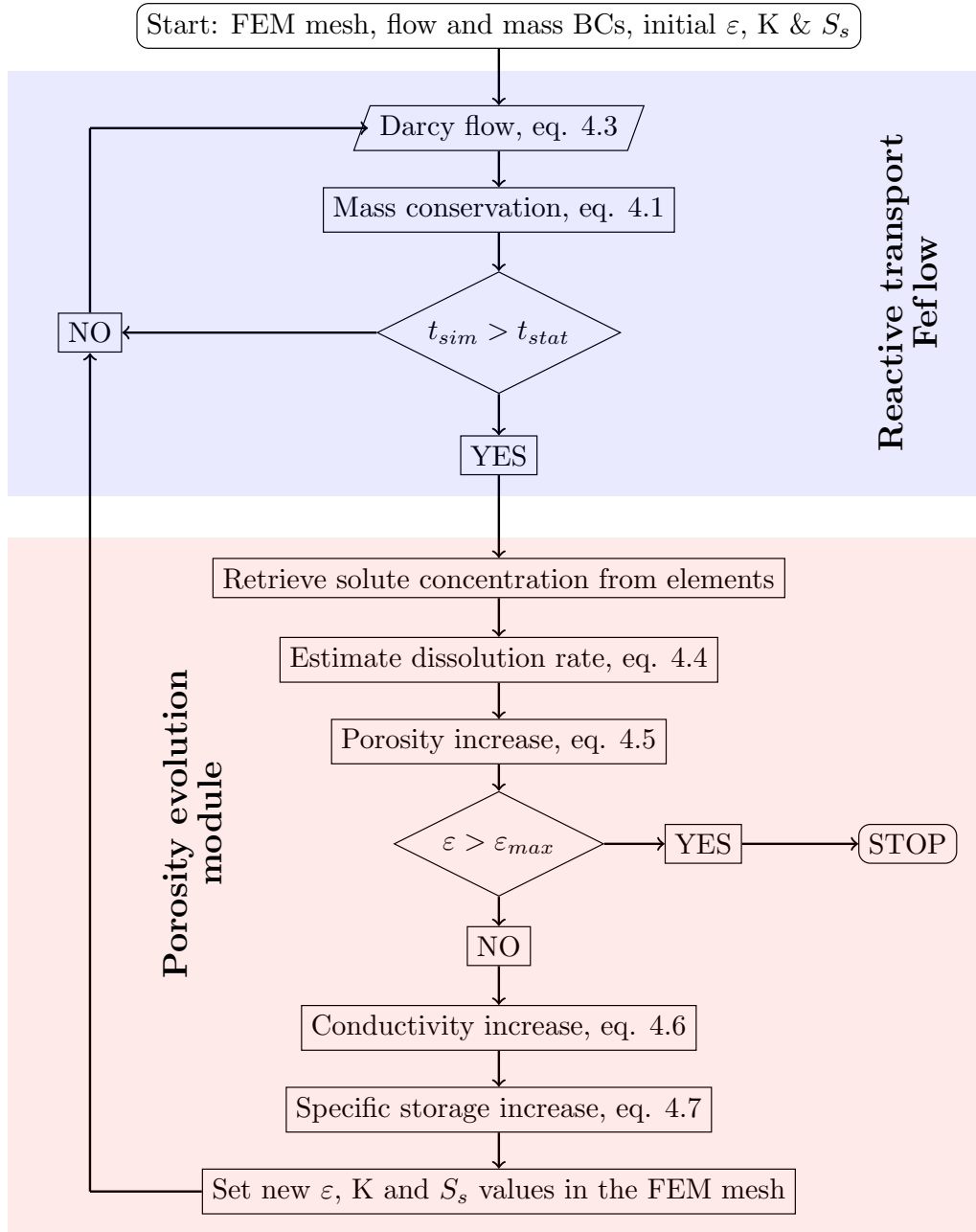


Figure 4.1: Flowchart of dissolution simulation and evolution of porous media properties with quasy-stationary state approximation approach for dissolution.

4.2.3 Analytical solution and model validation

An analytical simulation of reactive transport and porosity evolution was developed for a simplified 1D model. The results of the analytical solution were used to validate the numerical code and its coupling to reactive transport simulation in FEFLOW. The details on the analytical solution and the validation are shown in Chapter 5.

The module for porous medium evolution has the capability to represent 2D and 3D simulations. The module was applied to replicate the results of porous media evolution presented by Sanford Ward E. (1989). In these simulations flow is driven by density difference and the objective was to explore the effect of mineral dissolution by mixing corrosion in a coastal aquifer. The spatial distribution of porosity in the simulations conducted with the module developed for this work and the results of Konikow are similar. Thus, the porosity evolution module is considered as reliable.

4.3 Dissolution in fractures

FEFLOW has the capability to simulate flow in discrete elements to represent fractures. Flow in fractures can be described by using Darcy's law, Hagen-Poiseuille's law (laminar flow) or Manning-Strickler's law (turbulent flow). The principle for the simulation of mineral dissolution in fractures is similar to porous media. Flow, mass transport, and reactions are calculated in FEFLOW. The module calculates the volume occupied by the dissolved mass and converts it to *wall retreat* instead of porosity increase. If fractures are rectangular, the wall retreat is added to the aperture and width to estimate the new fracture geometry. If the fracture is assumed cylindrical, wall retreat is equal to the radius increase. Larger fractures reduce the resistance to flow of the simulated fracture network. The following sections present the relationships between dissolved mass and fracture growth.

Conceptual model

The conceptual model used in fracture evolution simulations is the one formulated by Dreybrodt et al. (2005c). Water with a certain reactivity flows through a uniform planar fracture with known width w , aperture b . Dreybrodt produced an analytical approximation for flow, mass transport, reaction and fracture evolution for this model. The numerical implementation of this model is validated using the results of the analytical approximation.

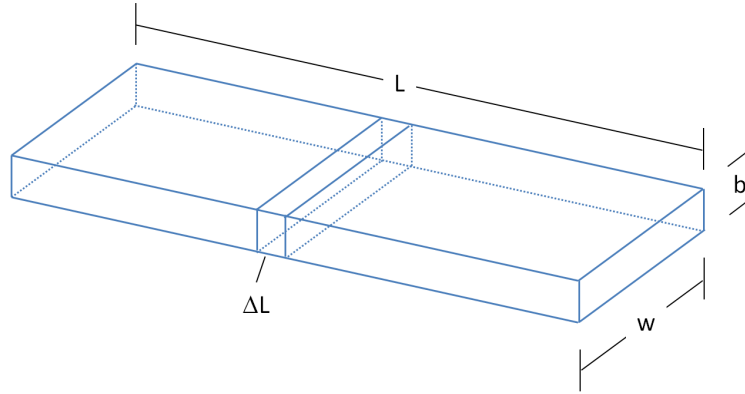


Figure 4.2: Fracture enlargement conceptual model

4.3.1 Governing equations

The mass conservation equation (4.1) is the same for fractures and porous media but fluid flow velocity u has to be calculated in a different manner.

Laminar flow in fractures is described by the Hagen-Poiseuille's equation shown in equation (4.8).

$$u = -\frac{b^2}{12\mu} \left(\frac{\partial p}{\partial x} - \rho g_x \right) \quad (4.8)$$

However, FEFLOW uses a *reduced data set* as input for fracture geometry. The friction loss in laminar and turbulent flow due to fracture geometry is converted into a *standard hydraulic conductivity* compatible with Darcy's law $q = -K\nabla h$. The standard hydraulic conductivity K for the Hagen-Poiseuille law is shown in equation (4.9) where ρ is fluid density, μ is fluid viscosity, g the gravitational constant and r_{hydr} the hydraulic radius. Constant a is equal to 3 for planar cross sections, and 2 for axisymmetric cross sections (i.e. circle). Hydraulic radius r_{hydr} is defined by the two parameters fracture aperture b and fracture cross sectional area A . To simulate flow in different cross section geometries, such as rectangles or circles, fracture aperture b is modified according to the information presented in Diersch (2013a).

$$K = \frac{r_{hydr}^2}{a} \frac{\rho g}{\mu} \quad (4.9)$$

A similar treatment is given to the Manning-Stricker's law which is also converted to hydraulic conductivity K as shown in equation (4.10) for 1D discrete elements where M

is the Manning roughness coefficient. To simulate different cross sectional geometries, the coefficient M is modified according to tables 9.12 and 9.13 in Diersch (2013a).

$$K = Mr_{hydr}^{2/3} \frac{1}{\sqrt[4]{|\nabla h|^2}} \quad (4.10)$$

The conceptual model of calcite dissolution in fractures proposed by Dreybrodt et al. (2005c) establishes that the reaction rate is different for laminar and turbulent flow and that the reaction order depends on calcium concentration in solution.

If flow is laminar, and C is far from equilibrium the reaction is 1st order (eq. 4.11). The dissolution kinetics model represents the effect of imperfect mixing in the fracture, meaning that the concentration of the bulk solution flowing in the fracture centroid is different from the concentration near the fracture wall. As the fracture grows, aperture b is larger and the overall rate slows down.

$$R_l = \frac{k_1}{1 + \frac{k_1 b}{3DC_{eq}}} \left(1 - \frac{C}{C_{eq}}\right) \quad (4.11)$$

In Dreybrodt's model, at solute concentrations $C/C_{eq} = 0.9$ the reaction becomes 4th order as shown in equation (4.12)

$$R_n = k_n \left(1 - \frac{C}{C_{eq}}\right)^4 \quad (4.12)$$

For turbulent flow, the dissolution rate for solute concentrations far from equilibrium is linear. For turbulent flow and close to equilibrium the dissolution rate is equal to equation (4.13).

$$R_t = k_t \left(1 - \frac{C}{C_{eq}}\right) \quad (4.13)$$

Equations (4.11), (4.12) and (4.13) can be implemented in the FEFLOW *Reaction Kinetics Expression Editor* according to the flow conditions of the simulated network.

PHREEQC for FEFLOW can also be used to represent mineral dissolution in fractures. However, computation time increases because 6 solute species are included in the model compared to 1 species required to apply equations (4.11, 4.12 and 4.13). Additionally, PHREEQC implements the PWP equation for mineral dissolution. As presented in Chapter

2, the PWP equation represents dissolution of a calcite surface where the transport rate of ions between the mineral surface and the bulk solution do not limits the overall dissolution rate. In the experiment that resulted in the PWP equation the solution was stirred strongly. Equations (4.11, 4.12 and 4.13) account for the mass transport limit to overall dissolution rate that may occur in the relatively slow flow speed in fractures in a limestone aquifer.

Once the solute distribution is known, the computation of the wall retreat is shown in equation (4.14). The volume of dissolved mineral is equal of the product of reaction rate R , reaction surface area A , computation time step Δt and molar volume V_m . To compute wall retreat, the dissolved volume is divided by the fracture surface area A which is equal to reaction surface area, thus they cancel each other and wall retreat is equal to the product of reaction rate, computation time step and molar volume.

$$r_{wall} = \frac{\text{dissolved mineral volume}}{\text{fracture surface area}} = \frac{R A \Delta t V_m}{A} = R \Delta t V_m \quad (4.14)$$

4.3.2 Numerical implementation

The implementation of the fracture evolution module works for 2D simulations where fractures are represented by 1D elements connecting the nodes. The simulation of the fracture size evolution requires three specific calculations in FEFLOW.

The first calculation deals with the reduced data set that describes fractures. The initial *real* geometry of a fracture is converted to aperture b and cross section area A . Then the reactive transport simulation is executed. When the wall retreat calculation is done, the reduced input needs to be converted back into the *real* fracture geometry, apply wall retreat, and convert the fracture geometry once again into the reduced input to set new fracture properties in the FEM model. These geometry conversions are easy implemented in the module coded for fracture evolution.

The second calculation is required to represent the dissolution reaction as a homogeneous reaction (liquid phase) when in reality it is a heterogeneous reaction (liquid-solid phase). In a homogeneous reaction, the rate constant $ML^{-3}T^{-1}$ is applied to the fluid volume L^3 to obtain a result in mass per time units MT^{-1} . In a heterogeneous reaction, the rate constant $ML^{-2}T^{-1}$ is applied to the surface reaction rate L^2 to obtain the output in MT^{-1} units. The objective of transforming the heterogeneous reaction into a homogeneous one is to be

able to do the computation in FEFLOW. Equation (4.15) shows how the mass change rate calculation for a homogeneous reaction, where J is the dissolution rate, V is the fluid volume and k_{hom} the homogeneous reaction constant.

$$R = V \cdot J = V k_{hom} \left(1 - \frac{C}{C_{eq}} \right) \quad (4.15)$$

Equation (4.16) shows the representation of a heterogeneous reaction as homogeneous. Fluid volume V is multiplied to by the area to volume ratio A/V of the fracture to the right output units. The ratio A/V is computed by the module and incorporated into the simulation by modifying the reaction rate of the solute.

$$R = V \cdot J = V \frac{A}{V} k_{het} \left(1 - \frac{C}{C_{eq}} \right) \quad (4.16)$$

The third calculation is required to prevent artificial fracture growth by using inadequate solute concentrations to estimate the dissolution rate. Solute concentration is known at the nodes that define every fracture. The simplest solution is to assume that solute concentration is the average of the concentrations in both end nodes. However, this assumption does not apply for all cases. Figure 4.3 shows the confluence of two fractures: A and B. The input flow of fracture A has a lower concentration of solute $C_1 = 0.1 C_{eq}$ compared to the input flow of fracture B ($C_3 = 0.99 C_{eq}$). Where the two fractures join there is a concentration of solute $C_2 = 0.12 C_{eq}$. This concentration can be explained by a much larger fluid flow rate in fracture A compared to fracture B. The average of C_1 and C_2 is a reasonable approximation of the solute concentration in fracture A. However, the average of C_3 and C_2 is not representative of concentration in fracture B. The average would produce a lower concentration than the input concentration, an unreasonable outcome. This lower concentration would result in an inadequate dissolution rate. The fracture grows in spite of fluid being almost saturated. A more reasonable approximation for fracture B is to assume that C_3 represents the solute concentration in the whole fracture.

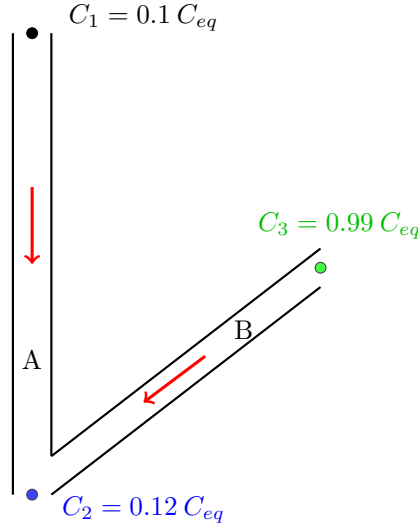


Figure 4.3: Confluence of two fractures

Figure 4.4 shows the assumed rules to estimate solute concentration C_f in fractures defined by 2 nodes. FEFLOW uses two nodes with indexes 0 and 1, the module gets the hydraulic head at both nodes and estimates flow velocity from 0 to 1. Positive velocities are cases A and C, while negative velocities are cases B and D. Cases A and B represent situations where solute concentration at node 0 is less than concentration at node 1, $C[0] < C[1]$. Cases C and D represent situations where solute concentration at node 0 is greater than concentration at node 1, $C[0] > C[1]$. Averaging of both concentrations is done only when the water flows from a lower concentration node to a higher concentration one, cases A and D. In case B and D only the upstream concentration is used to estimate solute concentration in the fracture. These four situations account for all possible combinations of flow direction and concentration inequalities using as reference the node indexing of 0 and 1.

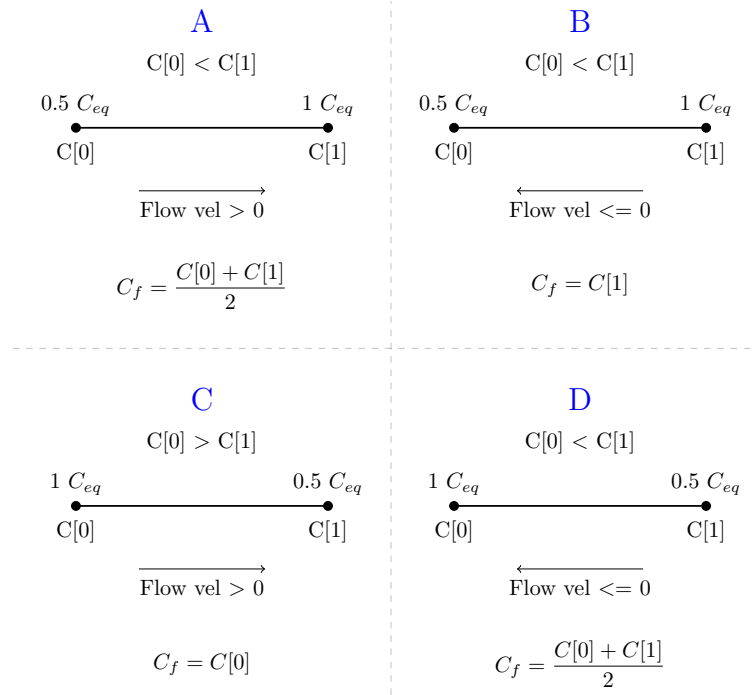


Figure 4.4: Rules to estimate solute concentration in fracture

The quasi-stationary approximation also applies to simulation of dissolution and enlargement of fracture networks. Figure 4.5 is a flowchart presenting the fracture evolution sequence. There are also two loops to implement the quasi-stationary approximation, one loop for reactive transport simulation and one for dissolution and fracture enlargement. The process starts by converting the *real* fracture geometry to reduce FEFLOW input and converting the heterogeneous reaction rate to a homogeneous one. Then the reactive transport simulation loop starts until an stationary state $\partial C / \partial t \approx 0$ is attained in the simulation domain. Then, the second loop starts and the module visits every fracture. Fracture reduced input is retrieved, converted back to real geometry and the Reynolds number is calculated. Figure 4.5 is an example for laminar flow conditions, if Reynolds number is higher than 2500 in a fracture, the simulation stops. If not, the solute concentration is estimated based on the rules shown in figure 4.4. A wall retreat is estimated, new real geometry, surface reaction area and ratio A/V are calculated. The reaction surface area and ratio A/V are updated by modifying the solute decay rate. Finally, all new fracture parameters are set in the model and the reactive transport simulation is run until a new stationary state is achieved.

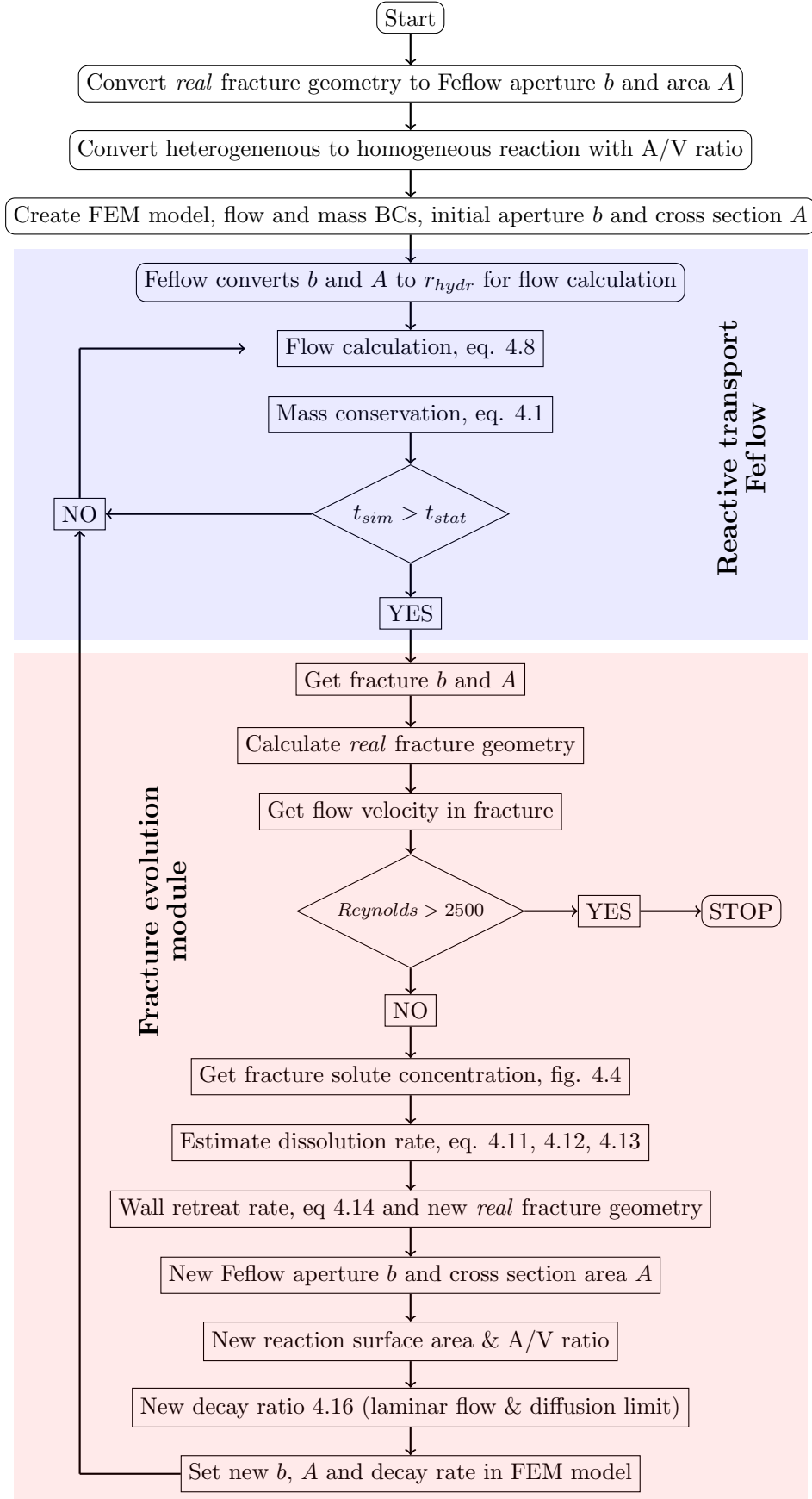


Figure 4.5: Flowchart of dissolution simulation and evolution of fractures and fracture networks

4.3.3 Model validation

The first test of the numerical implementation is to validate the reaction rate transformation. This was done by solving analytically the reaction rate for a fracture (i.e. equation 4.11) to get the amount of dissolved mass per unit of time. This result was compared with the mass budget for a fracture node in FEFLOW simulation and the result was satisfactory.

Then, the whole simulation module was used to replicate the evolution of a single fracture for which Dreybrodt et al. (2005c) provided a numerical model and an analytical approximation of the breakthrough time. The model consists in a planar fracture with an aperture $b = 0.0002$ m, a width $w = 1$ m and a length of 1000 m. The fracture was discretized into 996 elements with an exponential distribution in length. The fracture element in the inlet point was 0.02 m long while the element at the fracture outlet was approximately 5.5 m long. This element distribution was recommended by Dreybrodt to minimize numerical errors in the zone where stronger dissolution reaction occurs.

The flow boundary condition is a constant hydraulic head of 50 m on the inlet and 0 m on the outlet. The mass BC is water fully unsaturated with calcite at the fracture inlet. Figure 4.6 shows the FEFLOW model of a single fracture. Hydraulic aperture b is 0.0002095 after being corrected for fracture geometry reduced input and viscosity. Due to 4th order dissolution kinetics, the saturation concentration C_{eq} is not attained in the simulation. In this implementation, mmol L^{-1} are equivalent to mg L^{-1} .

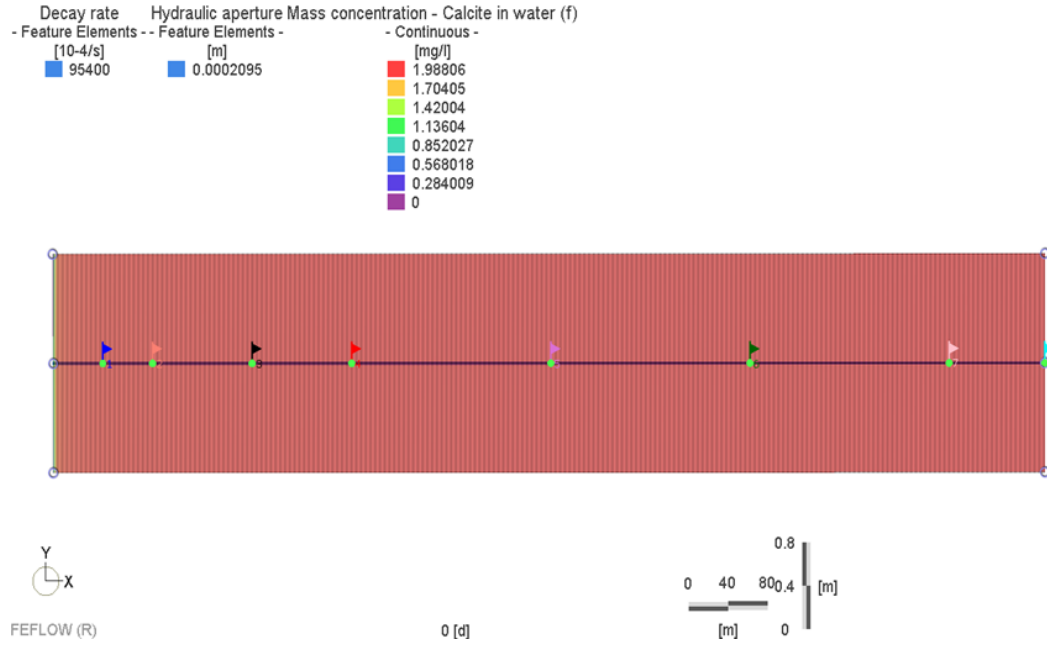


Figure 4.6: FEFLOW model of evolution of a single fracture

Figure 4.7 shows a superposition of the fracture aperture profile obtained by Dreybrodt et al. (2005c) and the aperture obtained from simulation results using FEFLOW and the fracture evolution module. Results are very close. The transition from laminar to turbulent flow (Reynolds number > 2500) occurs at 18700 yr in the FEFLOW simulation and at 19010 yr in the original results from Dreybrodt et al. (2005c). The fracture aperture distribution along the 1000 m of fracture length is not exactly identical but similar in the two simulation results.

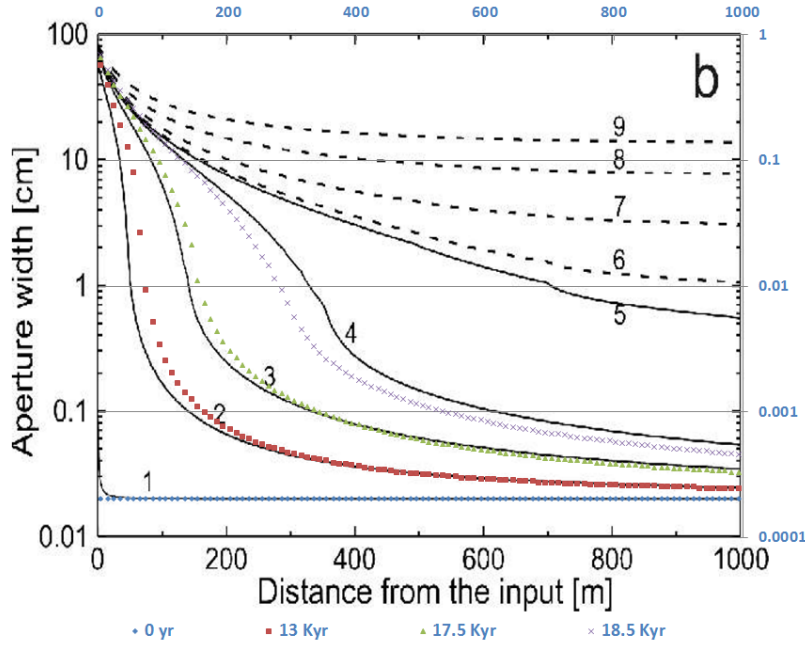


Figure 4.7: Evolution of a single fracture, analytical results by Dreybrodt et al. (2005c) in black and simulation results from this work in colored symbols. The numbers above the curves correspond to the time steps: 1 = 0 yr, 2 = 13.1 Kyr, 3 = 17.8 Kyr, 4 = 18.85 Kyr, 5 = 19.01 Kyr.

The discretization used by Dreybrodt et al. (2005c) is unknown. Three simulations were done with FEFLOW and with different element sizes to test the sensitivity of the results. The difference among the three models is the number of elements used to discretize the 1000m long fracture: 100, 1000, and 10000 elements. Figure 4.8 shows a comparison of the three simulations. The evolution of the fracture aperture is similar for the three runs. The model with larger elements (10 m) yields a faster fracture development. The reaction rate is faster at the inlet, the concentration gradients between contiguous elements are higher, thus a finer discretization is required to produce more precise results.

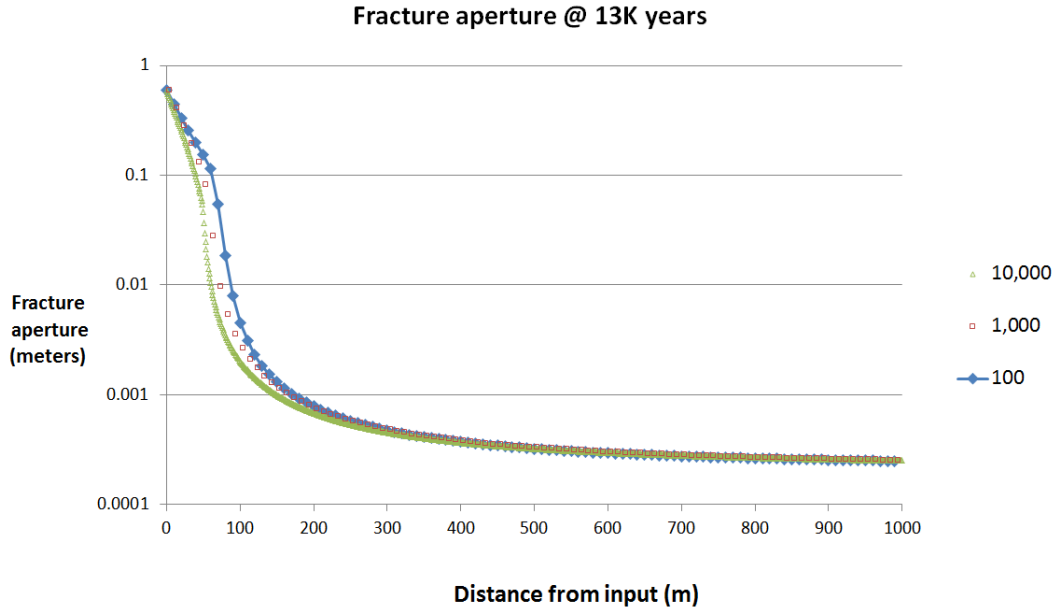


Figure 4.8: Comparison of three models of the single fracture evolution simulation at 13,000 yr. The fracture total length is discretized in 100, 1000, and 10000 elements.

4.4 Conclusion

To conclude this chapter, two modules have been implemented in FEFLOW to simulate calcite dissolution. One considers the limestone as a porous media and simulates the evolution of its porosity, permeability and specific storage. The other module considers instead that the dissolution occurs preferentially within discrete features which concentrate most of the flow. These features are maybe fractures or conduits. For both cases, we use all the capabilities of the finite element code FEFLOW to model the flow and transport processes. The update of the physical properties of the rock after the dissolution are computed by the modules. Both modules have been compared to previously published solutions and show a reasonable agreement with these results. Some discrepancies are still visible and could be due to differences in the numerical and discretization schemes.

Chapter 5

Dissolution front development around karst features due to tidal pumping in eastern Yucatan Peninsula coast

Adapted from Maqueda, A., Renard, P., Cornaton, F. (2016) *Dissolution front development around karst features due to tidal pumping in eastern Yucatan Peninsula coast* submitted to journal *Water Resources Research* on 3 March 2017.

5.1 Introduction

The dissolution of limestone by flowing reactive water develops caves. This process is also known as speleogenesis. Conceptual models include groundwater flow and a dissolution reaction to explain speleogenesis. Conceptual models are mainly based on a specific type of limestone which underwent deep burial diagenesis that reduced its porosity and permeability. However, limestones are carbonate rocks that display a great variety in physical properties. We observed high porosity and permeability in a limestone aquifer in the region of Tulum (Mexico). Our work focuses on developing a new conceptual model for karst growth accounting for high porosity and permeability in a coastal aquifer with tidal variations of hydraulic head. The distinction made based on limestone properties is important because the behav-

ior of groundwater flow depends on rock properties. Vacher and Mylroie (2002) studied the diagenesis of limestone aquifers where karst features develop and proposed a classification between *telogetic* and *eogenic* karst. Telogetic is applied to limestones that underwent burial diagenesis which causes compaction and a significant reduction of the original sediments porosity and permeability. In telogetic karst, stress or bedding plane fractures are preferential flow paths. Eogenic describes limestones that did not undergo physical and chemical compaction during diagenesis and have much higher porosity and permeability compared to telogetic ones. In eogenic karst, the limestone matrix pores also contribute to permeability, thus significant groundwater flow can occur in both fractures and the matrix.

Conceptual models for the development of karst features published in literature account for the flow conditions observed in telogetic karst. For example, Dreybrodt et al. (2005a) formulated a model to estimate the rate of enlargement of conduits, which depends on the magnitude of chemical disequilibrium between a well-mixed conduit water and the mineral that compose the conduit wall. The implicit assumption in this conceptual model is that mineral dissolution occurs only at the conduit wall macroscopic surface.

However, karst features in eogenic aquifers have permeable wall surfaces. Moore et al. (2010) observed periodic water exchange between conduits and matrix in the Santa Fe underground river in the Florida Peninsula. The river flows through a network of karst conduits for a few kilometers. Water saturated with Calcium flows from the matrix into the conduit during baseline flow conditions driven by distributed aquifer recharge. When river storm runoff causes a higher hydraulic level in the conduits compared to the matrix, the flow direction is inversed and water unsaturated with calcium flows into the matrix. Conduit enlargement can only occur when unsaturated conduit water is in contact with the conduit wall rock, thus the conduit enlargement process is episodic. Moore et al. (2010) proposed that the largest amount of dissolution should occur close to the conduit wall surface forming a friable halo of enhanced porosity around the conduit. In the same study area in Florida, Meyerhoff et al. (2014) conducted a time-lapse electrical resistivity tomographic imaging to study the mixing of conduit and matrix waters. Resistivity anomalies were observed when low conductivity river water flows into the porous rock matrix that composes the conduit wall.

Martin et al. (2012) reported water exchange between sinkholes and the porous matrix around them in San Salvador island in the Bahamas. The exchange was inferred from

periodic changes, corresponding to the tidal period, in sinkhole water pH and electrical conductivity. Tide measurements conducted on the sea shore and in two sinkholes showed that the sinkholes could be connected to the ocean by a well-developed conduit network because the tidal wave could propagate into the aquifer with minimal hydraulic head loss. The tidal propagation causes periodic changes in hydraulic head gradients between sinkholes and the porous rock matrix around them. During high tide, water level rises faster in the conduit compared to the porous matrix causing sinkhole water to enter the matrix. During low tide the process reverses and water flows from the matrix into the sinkhole. Gulley et al. (2015) described this periodic water exchange as tidal pumping, which is presented in Figure 5.1.

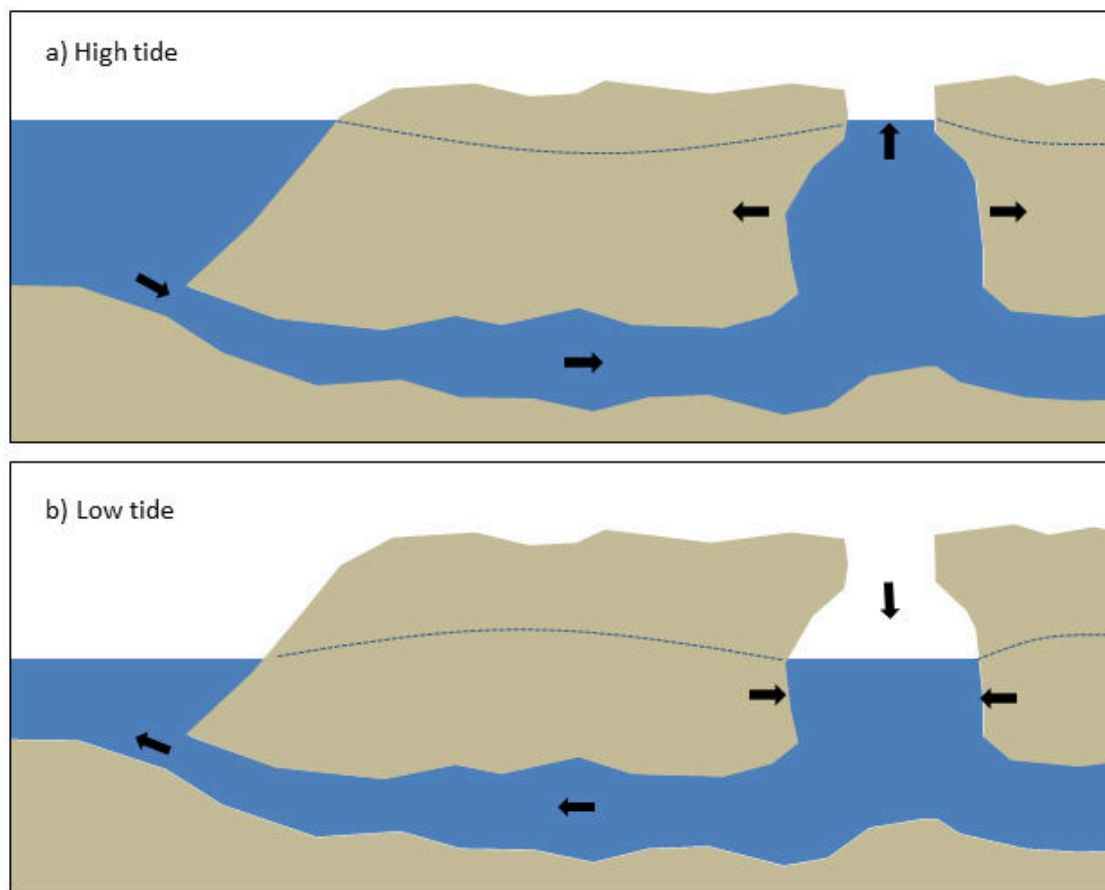


Figure 5.1: Water exchange, or tidal pumping, between karst features and porous matrix driven by hydraulic gradients generated by sea tides as inferred by Gulley et al. (2015). During high tide the hydraulic head of the ocean propagates into the aquifer and causes conduit and sinkhole water flow into the limestone matrix. During low tide the flow direction reverses.

Our study area is located in the Yucatan Peninsula in Mexico. The limestones in this area

have not experienced severe compaction due to burial during diagenesis. They have relatively high porosity and permeability fitting the definition of eogenetic karst as proposed by (Vacher and Mylroie, 2002). Porosity in limestones is between 30 and 45%, hydraulic conductivity has been reported between 0.05 m d^{-1} and up to 1 m d^{-1} (Hossler, 2015). The study area in the Yucatan Peninsula is comparable to Florida Peninsula and the Bahamas islands because limestones have a similar diagenesis and petrophysical properties. Additionally, aquifers are located in coastal plains exposed to tidal forces. We assumed the tidal pumping observed on the Bahamas could also occur in the Yucatan Peninsula coastal aquifer.

To our knowledge, no conceptual model of karst development has been formulated to account for the groundwater flow conditions observed in eogenetic karst and tidal pumping conditions. If tidal pumping occurs, the water transported into the matrix reacts with minerals yielding dissolution and a change in the matrix porosity. The objectives of our work are: a) formulate a conceptual model of karst development that accounts for the flow conditions of eogenetic karst, b) apply this model to assess karst development in our study area in the Yucatan Peninsula in Mexico, and c) assess the effect of tidal pumping on karst feature enlargement rates.

5.2 Study area

Over 1000 km of underwater karst conduits have been mapped by cave divers in the Eastern coastal plain of the Yucatan Peninsula (Kambesis and Coke, 2013). Sistema Ox Bel Ha (S-OBH) is a 258 km long underwater cave system located in this area. Most of the conduits are oriented perpendicular to the present coastline and located in a 12 km wide strip parallel to the coastline (QRSS, 2016), see Figure 5.3A.

5.2.1 Geological setting

The Yucatan Peninsula is a carbonate platform with at least 1500 m thickness of carbonate rocks from Cretaceous to Pleistocene overlaying a basement of igneous rocks. The total area of the Yucatan platform is approximately $300,000 \text{ km}^2$ and at present sea level $165,000 \text{ km}^2$ are emerged (Bauer-Gottwein et al., 2011). Dating of fossil corals in the study area shows that sea level was at least 5–6 m above the present level about 122,000 yr ago (Szabo et al., 1978). Reconstructions of Pleistocene sea level of the last 500,000 yr show that it was at

least 20 m higher and 120 m lower (Spratt and Lisiecki, 2016). The contemporary coastline is carved on the Pliocene-Pleistocene shelf margin and reefal limestones deposited during the last sea level highstand (Kambesis and Coke, 2013). The shoreline has been displaced inland and seaward periodically by sea level changes, thus the zone influenced by tidal pumping is wider compared to the zone influenced by tides at the present time.

5.2.2 Aquifer characteristics

The aquifer where S-OBH developed is formed by a porous limestone matrix that contains an extensive network of connected conduits assumed to be generated by mineral dissolution. According to Kambesis and Coke (2013), groundwater flow occurs preferentially in conduits and the rock matrix functions as storage. Bauer-Gottwein et al. (2011) estimated groundwater hydraulic gradient between 1 and 10 cm km⁻¹. Kambesis and Coke (2013) reported that 84% of coastal tidal amplitude is observed at 1 km inland and 39% at 6 km inland. In the study area aquifer there is a saline water intrusion wedge. Supper et al. (2009) estimated that the mixing zone between fresh and saline waters was 4 m below ground level (bgl) close to the sea (phreatic level 1 m bgl), and descending slowly to 20 m bgl at 7 km from the ocean (phreatic level 6 m bgl). Smith (2004) conducted mineralogical analysis of rock samples from conduits wall in the study area, the calcite fraction in limestone was reported between 92 and 100% . Calcite limestones in the study area have been dated from Miocene to Holocene. Their texture varies between packstone, grainstone (oolites) and boundstone (bioclasts, bivalves and gastropod shells) (Hossler, 2015). Figure 5.2 shows a scatter plot of porosity versus permeability of limestone samples from the study area and similar samples in the Caribbean region. Samples include: oolites from Southern Florida and Bahamas dated between Recent and Pleistocene (Robinson, 1967), reefal aragonite and calcite limestones from Barbados dated as Pleistocene (Pittman, 1974b), grainstones from West-Central Florida dated as Paleogene (Budd, 2002) and limestones from the study area Hossler (2015). We assume in this work that the initial value of porosity of limestone is 0.3 and for hydraulic conductivity K is 1198 millidarcy or 1 m d⁻¹ and it is represented by the red dot in Figure 5.2.

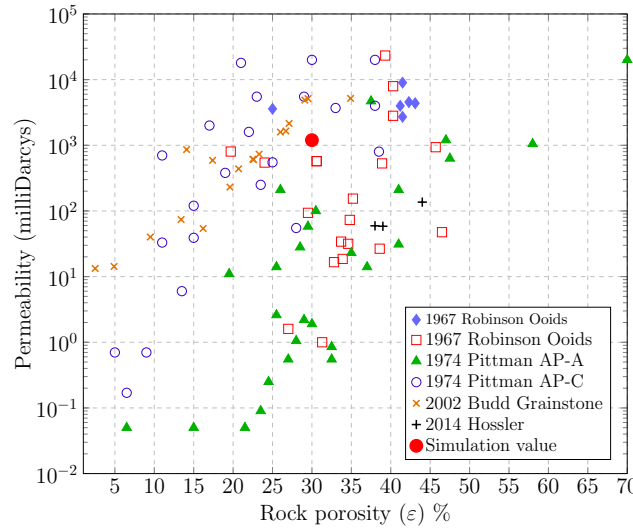


Figure 5.2: Porosity-permeability relationship in millidarcy units for limestone samples from Yucatan and Florida peninsulas and the Bahamas dated from Paleogene to Pleistocene.

5.3 Methods

5.3.1 Tide measurement

We set a network of pressure loggers to measure the propagation of the tidal wave into the karst aquifer. Loggers recorded the groundwater level every 15 minutes between March 2013 and March 2015. Loggers were placed in sinkholes along a perpendicular line to the coastline between 290 m and 10 km from the ocean, see Figure 5.3A. Pressure data logs were analyzed using Fourier analysis to decompose the tidal wave into its constituents (Kaeser, 2016). Figure 5.3B shows the tidal amplitude corresponding to the principal lunar semi-diurnal or M2 constituent. The tidal wave propagates over several kilometers into the aquifer, thus tidal pumping is likely to occur in the study area.

5.3.2 Reactivity sources for mineral dissolution

Calcite dissolution in the study area is controlled on the one hand by dissolved carbon dioxide in the freshwater layer coming from organic matter decomposition, and on the other hand by the mixing of fresh and saline waters. The water geochemical data we used in this work originates from previously published data and sampling conducted for this work. Water samples were taken in sinkholes and wells between 100 m and 9 km from the shoreline. Ion-pairing analysis was done with PHREEQC (Parkhurst and Appelo, 2013) assuming rock is 100% calcite. We used groundwater chemistry data from Smith (2004) and samples collected

during our field work. The first reactivity source is freshwater which has an average $P_{\text{CO}_2} \approx -1.63$ and temperature of 26°C . These conditions yield a calcite concentration of $2.452 \text{ mmol L}^{-1}$ and a saturation index $SI = -0.033$. Water is slightly unsaturated, the saturation concentration is $C_{eq} = 2.6089 \text{ mmol L}^{-1}$ with a dissolution reaction constant $k = 1.9 \times 10^{-4} \text{ s}^{-1}$. The second reactivity source is mixing corrosion between fresh and saline waters in the coastal aquifer. The mixture of two solutions, which are both saturated with Ca^{2+} , becomes under-saturated if mixing solutions are at different temperatures, or have different P_{CO_2} or ionic strength (Appelo and Postma, 2010).

The highest calcite under-saturation, $SI = -0.21$, occurs at a mixture of 0.7 freshwater and 0.3 saline water where $C/C_{eq} = 0.965$. In this area of the mixing zone calcium concentration is higher at $5.815 \text{ mmol L}^{-1}$ with a saturation concentration $C_{eq} = 6.0258 \text{ mmol L}^{-1}$ and a dissolution reaction constant $k = 1.7 \times 10^{-4} \text{ s}^{-1}$.

A C/C_{eq} ratio of 1 means chemical equilibrium. Values lower than 1 means water reactivity to calcite, the lowest the value the more reactive.

5.3.3 Conceptual model of porosity development

The first objective of this paper is to formulate a development conceptual model that accounts for groundwater flow conditions in eogenetic karst under tidal pumping conditions. Groundwater flow normal to the surface of the porous wall of a karst conduit can be described

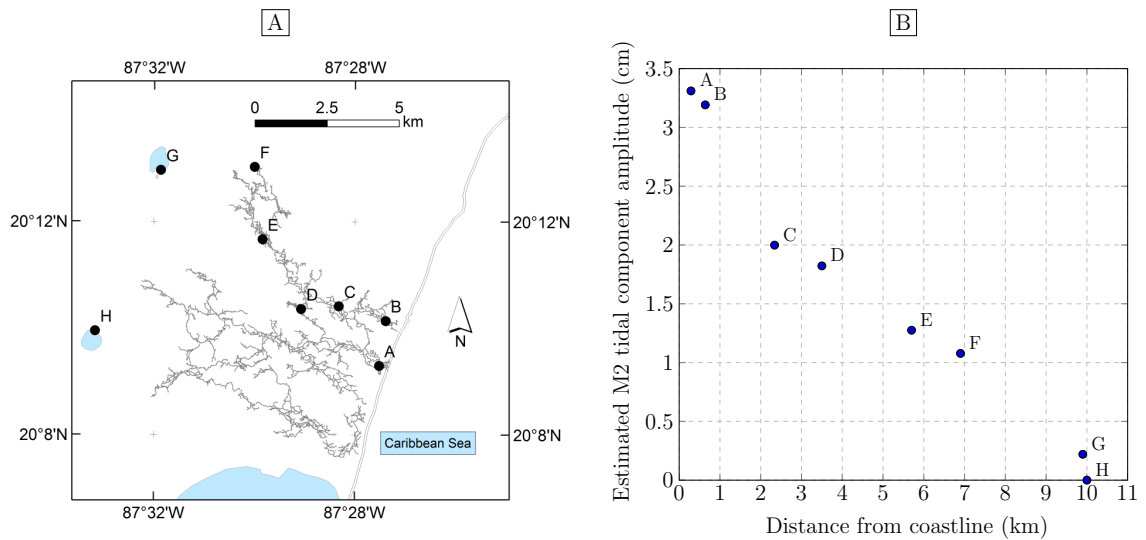


Figure 5.3: A) Solid gray lines represent the connected caves of Ox Bel Ha System (QRSS, 2016). Black circles represent the location of pressure sensors for tidal amplitude measurement, B) Estimated M2 tidal constituent amplitudes in sinkholes (Kaesler, 2016).

by a 1-dimensional domain shown in Figures 5.4 and 5.5. The boundary at $x = 0$ represents the location of the conduit wall and the position where the tidal hydraulic boundary condition is applied. The model domain is semi-infinite with length L large enough to fully damp hydraulic head fluctuations caused by tides, thus the boundary condition at $x = L$ is a prescribed hydraulic head equal to zero. The hydraulic BC will cause that during half of the tidal period the flow goes to the right and during the other half it goes to the left.

The solute BC is Ca^{2+} concentration C at $x = 0$ and water fully saturated with Ca^{2+} or

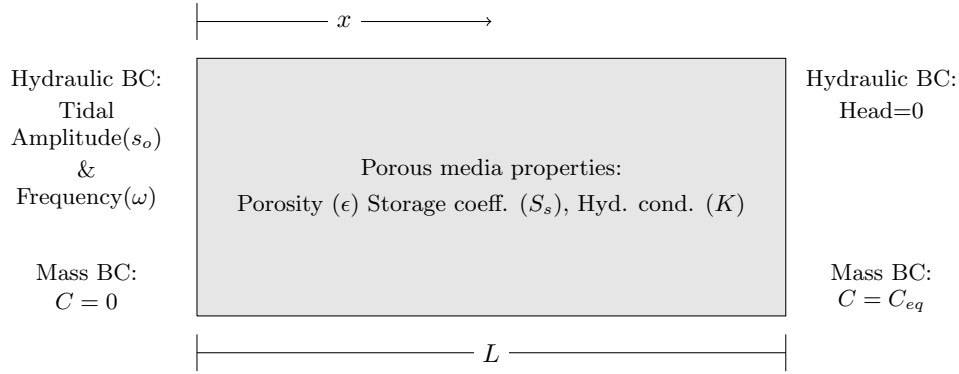


Figure 5.4: Porosity evolution under tidal pumping model

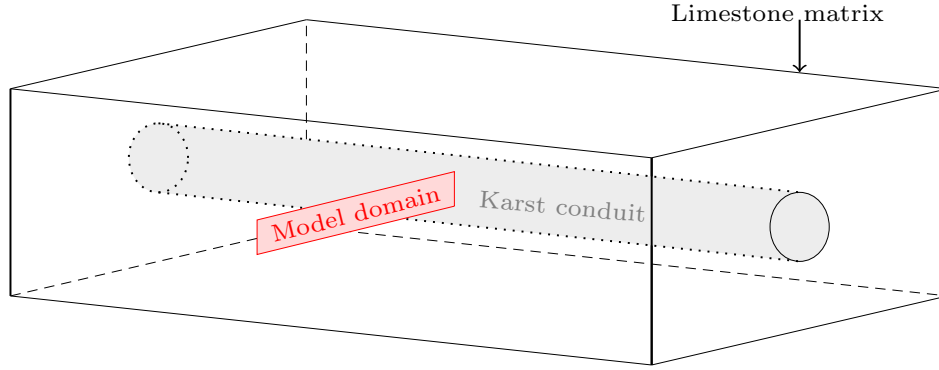


Figure 5.5: The simulated 1D domain is normal to the karst feature wall surface.

$C = C_{eq}$ at $x = L$. Water at $x = 0$ is assumed to be well mixed in a karst cavity, this implies that independently of the water flow direction due to tidal pumping, concentration remains constant. When water flows to the left in the model, the concentration at $x = 0$ is not strictly C , but this is a reasonable approximation if the water in the conduit is well-mixed.

The porous medium is assumed to be composed entirely of calcite grains. The system is assumed to behave as a closed system for carbon dioxide, meaning that the source of dissolution potential is in the conduit water and no additional carbon dioxide is generated

in the water inside the porous medium domain.

5.3.4 Governing equations

Solute transport

The conceptual model considers flow of water, and transport and reaction of a solute which is calcium ion in a porous media domain. The general advective-dispersive solute-transport equation for flow in 1 dimension is shown in equation (5.1) where v is Darcy velocity, D is the hydrodynamic dispersion and R the dissolution reaction rate:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x} - R \quad (5.1)$$

Pore water velocity v calculated with equation (5.2) is used for both for the advective term and for the computation of hydrodynamic dispersion. In equation (5.2) K is hydraulic conductivity, $\partial h / \partial x$ is the hydraulic gradient and ε is material porosity.

$$v = -\frac{K}{\varepsilon} \frac{\partial h}{\partial x} \quad (5.2)$$

Dissolution kinetics

Calcite dissolution kinetics depends on the concentration of dissolved carbon dioxide in water, the amount of Ca^{2+} in solution and solution temperature (Appelo and Postma, 2010). The rate of calcite dissolution reaction R can also be approximated by a first order reaction using the amount of solute Ca^{2+} as the only input variable. Buhmann and Dreybrodt (1985), Baumann et al. (1985) proposed the model shown in equation (5.3) where k is the reaction constant and C_{eq} is the thermodynamic equilibrium concentration of Ca^{2+} and it is a function of temperature, pCO_2 , and the effects of complexation and activity coefficients due to ionic strength in a solution. Constant k is the product of two variables, the experimental constant β and A/V which is the ratio of reaction surface area to volume of porous medium. In this work, we assume the ratio A/V as constant along the increase of porosity ε . We estimated the reaction constant k considering freshwater samples from the study area applying the following methodology: 1) use PHREEQC for ion-pairing simulation of a system closed to CO_2 and obtain the calcite dissolution non-linear reaction rate R , 2) then fit the Buhmann

and Dreybrodt (1985) linear model to the reaction rate data by manipulating the value of constant k .

$$R = \varepsilon k (C - C_{eq}) \quad (5.3)$$

Mixing corrosion dissolution is described by a second order reaction rate. However, we assumed that the mixing of fresh and saline waters occurs only in the conduit water. If the mixing effects between water in model boundary ($x = 0$) and water in the porous medium domain ($x > 0$) are neglected, the reaction can be described too by the linear model of equation (5.3).

Porosity evolution

The concentration distribution depends on the porous medium porosity, conductivity and storage properties. The evolution of the model can be represented a sequence of stationary states, where each state represents the physical properties of the porous medium. This method is described as the *quasi-stationary* state approximation by Lichtner (1985). This approach considers solving the the problem in two steps. In the first step the reactive transport problem is solved, while on the second one the changes on porous medium physical properties are calculated. The method is applicable as long as the liquid phase composition and dissolution reaction rates adjust quasi-statically to changes in the porous medium (Lichtner, 1988). In simpler terms, the reaction rate needs to be much faster than the characteristic dissolution time which is the period required for the system to achieve an stationary state where $(\partial C / \partial t = 0)$.

The concentration distribution C in the model domain can be approximated by a steady-state solution $(\partial C / \partial t = 0)$ of equation (5.1). The steady-state approach should give a result close to the solution of the transient problem after a very long simulation time. The reaction rate R can be calculated for any position x in the model according to equation (5.3). Then, the porosity evolution due to mineral dissolution was estimated with equation (5.4) (Rezaei et al., 2005), where $\varepsilon(t + \Delta t)$ is porosity at calculation time $t + \Delta t$, $\varepsilon(t)$ is porosity at the previous time-step, ε_0 is the initial porosity, V_m is the porous medium molar volume and Δt is the dissolution calculation time-step.

$$\varepsilon(t + \Delta t) = \varepsilon(t) + \varepsilon_0 R V_m \Delta t \quad (5.4)$$

Hydraulic conductivity also evolves when the porosity increases, the relationship between them is assumed to follow equation (5.5) where K_0 is the initial hydraulic conductivity and γ is an exponent depending on the altering process. For mineral dissolution Bernabé et al. (2003) suggest to use a value of 3:

$$K = K_0 \left(\frac{\varepsilon}{\varepsilon_0} \right)^\gamma \quad (5.5)$$

An increase of porosity is also followed by an increase of storage capacity. The relationship between porosity and specific storage is given by equation (5.6) (De Marsily, 1986) where C_B and C_F are bulk porous medium and fluid compressibility, ρ is the fluid density and g the gravitational constant. :

$$S_s = \rho g (C_B + \varepsilon C_F) \quad (5.6)$$

The relationship between porosity and hydraulic conductivity is of third order (equation 5.5) while the relationship between porosity and storage is first order (equation 5.6). As porosity increases, it is expected that the porous medium diffusivity will increase.

5.3.5 Simulation of dissolution and porosity evolution

The problem defined can be solved with different approaches. Solution 1 is a transient numerical simulation implemented in the FEFLOW modeling environment (Diersch, 2013b) with tidal induced changes in hydraulic head as boundary condition. Calcite dissolution reaction (eq. 5.3) was implemented using FEFLOW Reactions Kinetics Expression Editor. A custom FEFLOW plug-in developed by the authors updates porous medium properties based on dissolution estimates. The plug-in retrieves solute concentration at every mesh element and applies equations (5.3 , 5.4 , 5.5, and 5.6) to produce a new stationary state of the system.

Solution 1 while feasible requires a long calculation time and there is uncertainty on the results accuracy. To gain insight on how the system works and to verify solution 1 results, we derived an analytical approximation. The analytical approximation, solution 2, is obtained

by formulating a pure diffusive transport problem equivalent to the advective transport problem (equation 5.1). The derivation of the approximation is presented in the next section. Additionally, the analytical approximation allows to implement a simplified numerical simulation (solution 3) where tidal transport is approximated by a position dependent dispersion coefficient.

Analytical approximation of reactive transport under alternating flow

The analysis of the propagation of a sinusoidal wave into a porous medium is based on the solution derived by Ferris (1952) shown in equation (5.7). The wave amplitude and flow velocity depend on the tidal wave frequency ω and the initial amplitude s_0 , the hydraulic conductivity K , specific storage S_s , and the distance x from the boundary.

$$h(x, t) = s_0 \exp \left(-x \sqrt{\frac{\omega S_s}{2K}} \right) \sin \left(\omega t - x \sqrt{\frac{\omega S_s}{2K}} \right) \quad (5.7)$$

Over a tidal cycle, flow velocity is both positive and negative. Water is at the same position at the start and end of the cycle, therefore the advection contribution to mass transport is zero. However, the alternating flow causes hydrodynamic dispersion of the solute. The instantaneous pore velocity was calculated by substituting equation (5.2) into equation (5.7) and calculating the derivative with respect position x which yields equation (5.8).

$$u(x, t) = -\frac{K s_0}{\varepsilon} \frac{\partial \left[\exp \left(-x \sqrt{\frac{\omega S_s}{2K}} \right) \sin \left(\omega t - x \sqrt{\frac{\omega S_s}{2K}} \right) \right]}{\partial x} \quad (5.8)$$

If the problem is analyzed over multiples tidal cycles until $\partial C / \partial t \approx 0$, the alternating flow contribution to dispersion depends on the absolute long-term average pore velocity. This velocity was calculated by integrating equation (5.8) with respect to time over half of the tidal cycle and dividing by half period which yields equation (5.9).

$$\overline{|u(x)|} = \frac{2 s_0 \sqrt{\omega S_s K}}{\varepsilon \pi} \exp \left(-x \sqrt{\frac{\omega S_s}{2K}} \right) \quad (5.9)$$

Mechanical dispersion is the product of the absolute average pore velocity $\overline{|u(x)|}$ and dispersivity α_L . Mechanical dispersion was substituted into equation (5.10) (Scheidegger,

1961) to calculate hydrodynamic dispersion $D(x)$ which is distance-dependent.

$$D(x) = D_d + \overline{|u(x)|} \cdot \alpha_L \quad (5.10)$$

The solute transport equation (5.1) is adapted to the problem. The advection contribution to transport is assumed as zero, therefore removed from the solution. The equation is solved for steady-state in reaction, thus $\partial c/\partial t = 0$. Finally, the reaction rate shown in equation (5.3) substitutes R and the hydrodynamic dispersion $D(x)$ (eq. 5.10) substitutes D . The result is the solute transport equation (5.11) with distance-dependent dispersivity.

$$0 = \frac{\partial}{\partial x} \left(\left[D_d + \overline{|u(x)|} \cdot \alpha_L \right] \frac{\partial C}{\partial x} \right) - k (C - C_{eq}) \quad (5.11)$$

The analytical solution for the solute transport problem is to solve the differential equation (5.11) with the following boundary conditions: $C/C_{eq}(0) = 0, C/C_{eq}(\infty) = 1, x > 0, k > 0$. Zhou and Selim (2003) reviewed analytical solutions, for similar solute transport problems with distance-dependent dispersion, which common feature is that they are usually expressed as Bessel or hypergeometric functions. These special functions require numerical evaluation which, in the context of our work, defeats the purpose of obtaining an analytical solution.

The alternative to produce a simple solution was to derivate an approximation. The approximation was based on the assumption that hydrodynamic dispersion in equation (5.11) is constant. Then, it was solved with the boundary conditions for the problem and the result is shown in equation (5.12).

$$\frac{C(x)}{C_{eq}} = 1 - \exp \left(-x \sqrt{\frac{k}{D}} \right) \quad (5.12)$$

The constant hydrodynamic dispersion was calculated at position $x = 0$ with equations (5.9 and 5.10). The following step is to assess for which cases the approximation (eq. 5.12) represents the full transport problem (eq. 5.11). Then, saturation length x_{eq} was defined as the position x at which the reaction reaches equilibrium $C(x)/C_{eq} \approx 1$. x_{eq} was calculated by assuming by assuming $C/C_{eq} = 0.999999$ and constant dispersion equivalent at dispersion $D(x) = D(0)$, then substituting both assumptions into equation (5.12) and solved for x .

$$x_{eq} = -\frac{\ln(1 \times 10^{-6})}{\sqrt{k/D(0)}} \quad (5.13)$$

To validate the assumption of constant dispersion, saturation length was calculated for an several ratios of reaction rate k 1/day to hydrodynamic dispersion at origin $D(0)$ (m d^{-2}). Then, the hydrodynamic dispersion at saturation length $D(x_{eq})$ was calculated and compared to hydrodynamic dispersion at origin $D(0)$. Figure 5.6 shows a plot with the reaction to transport rate ratio $k/D(0)$ in the horizontal axis and a ratio of dispersion rate at saturation length to dispersion rate at origin $D(x_{eq})/D(0)$ in the vertical axis. If the reaction rate is relatively fast when compared to transport rate $k/D(0) > 100$, the ratio $D(x_{eq})/D(0)$ is 0.97. A ratio of $D(x_{eq})/D(0)$ close to unity means saturation is achieved at a position x_{eq} where the tidal wave amplitude is practically the same as the wave amplitude at $x = 0$. Therefore, the assumption of constant dispersion is valid for cases where $k/D(0) > 100$ and the solute transport problem can be solved accurately with the analytical approximation.

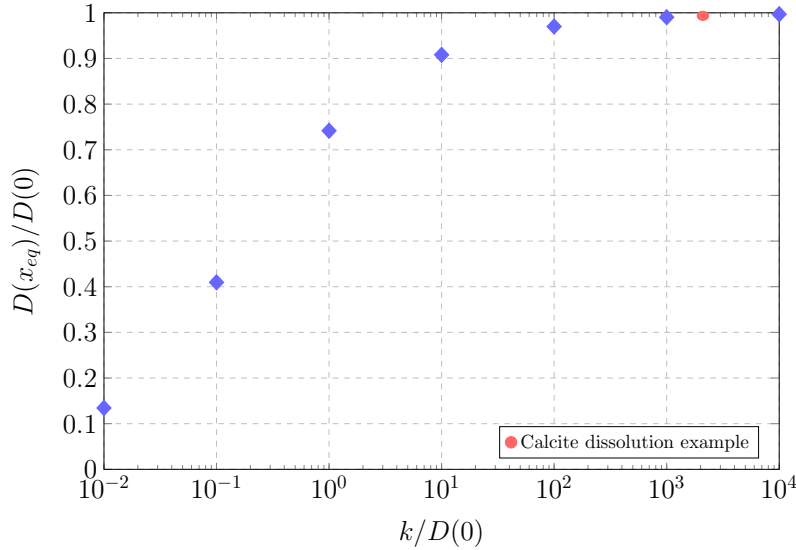


Figure 5.6: Validity assessment of analytical approximation (eq.5.12) to represent distance-dependent dispersion caused by tidal pumping. The approximation is valid for cases where the reaction to transport rate ratio $k/D(0) > 100$. The red circle shows a case for calcite dissolution for reaction constant $k = 1.73 \text{ d}^{-1}$, tidal amplitude $s_0 = 0.1 \text{ m}$, conductivity $K = 1 \text{ m d}^{-1}$ and $S_s = 1 \times 10^{-4} \text{ m}^{-1}$.

Both sides of the solute transport equation (5.12) are dimensionless. Figure (5.7) shows a plot of the solute transport equation where the left-hand side of equation is represented on the vertical axis and the right-hand side of the equation $x\sqrt{k/D}$ is plotted on the horizontal axis.

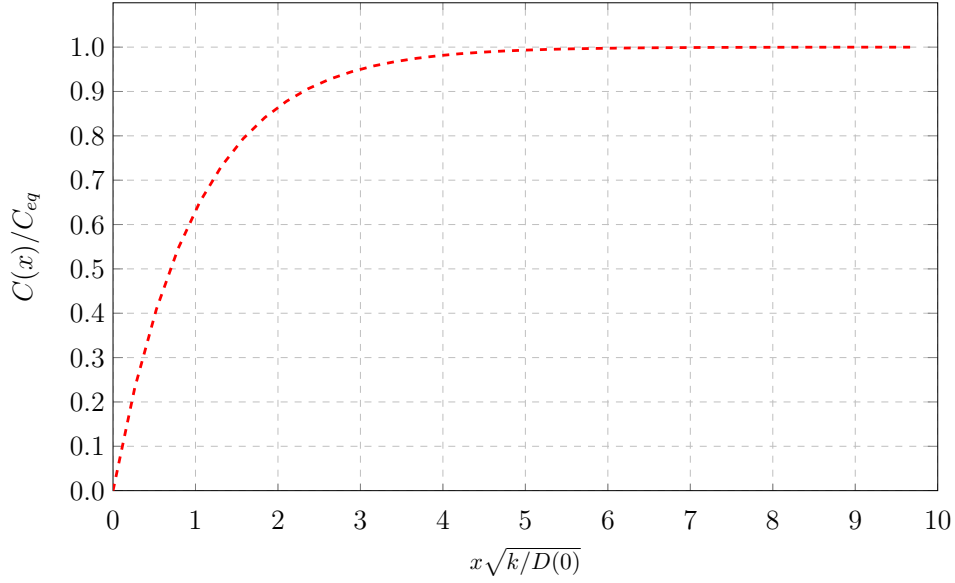


Figure 5.7: Dimensionless plot of the analytical approximation (eq. 5.12).

Equation (5.12) is a solution for the boundary $C(0)/C_{eq} = 0$. If the mass BC is not zero, equation (5.12) was manipulated to find the translation x' corresponding to the $C(x)/C_{eq}$ value to be used as mass BC. In this way the desired mass BC value of C/C_{eq} is set at $x = 0$. The result is equation (5.14a) which provides the translation x' that should be applied to equation (5.12) when the mass BC is not zero, resulting in equation (5.14b):

$$x' = -\ln \left(1 - \frac{C(x)}{C_{eq}} \sqrt{\frac{k}{D(0)}} \right) \quad (5.14a)$$

$$\frac{C(x)}{C_{eq}} = 1 - \exp \left(-(x + x') \sqrt{\frac{k}{D(0)}} \right) \quad (5.14b)$$

Once the concentration profile $C(x)$ is known in the model domain, equations (5.3, 5.4, 5.5, 5.6) are applied to update the physical properties of the porous medium.

Characteristic dissolution time

Equations (5.3, 5.12) were substituted into equation (5.4) to estimate the characteristic dissolution time τ shown in equation (5.15). τ represents the maximum time required for full dissolution of porous medium at position $x = 0$. ε_0 and ε_f represent initial and final porosities. We assumed that porosity increases with dissolution, but conductivity K and specific storage S_s remain constant until full dissolution. Equation (5.15) overestimates

dissolution time because reaction rate R increases along porosity.

$$\tau = -\frac{\varepsilon_f - \varepsilon_0}{\varepsilon_0} \frac{1}{V_m k C_{eq} \exp\left(-(x + x')\sqrt{k/D(0)}\right)} \quad (5.15)$$

Numerical simulation with pure diffusive transport

The analytical approximation provides an accurate result when hydraulic conductivity is homogeneous on the model domain, but solution 2 is not valid once K is updated after dissolution then a new solution was implemented. Solution 3 is a numerical simulation where equations (5.9 and 5.10) were applied to calculate analytically hydrodynamic dispersion for each element in the model. Dispersion was used as molecular diffusion in the numerical simulation. This simplification allowed longer simulation time-steps, which reduced calculation time significantly.

5.3.6 Parameters for porosity evolution simulations

Based on data from Ox-Bel-Ha karst network, we used the parameters shown in Table 5.1 in simulations. The tidal amplitude is of the same magnitude as the tides in the study area. The tidal period (12.42 hours) is equal to the M2 semi-diurnal Lunar tides. Equation (5.7) allowed to calculate at which position the tidal wave is almost completely damped $x \approx 600$ m. Therefore, this is the extent of the 1D model domain in numerical simulations. Additionally,

Variable	Description	Symbol	Value	Units
1	Tide amplitude	s_0	0.1	m
2	Tide frequency	ω	12.15	rad d ⁻¹
3	Molecular diffusion	D_d	8.64×10^{-5}	m ² d ⁻¹
4	Longitudinal dispersivity	α_L	0.1	m
5	Initial porosity	ε	0.3	
6	Hydraulic conductivity	K	1	m d ⁻¹
7	Specific storage	S_s	1×10^{-4}	m ⁻¹
8	Calcite Molar volume	V_m	0.0369	L mol ⁻¹

Table 5.1: Parameters used for porosity evolution simulations

the values of the water isothermal compressibility at 20 °C is taken as 4.5×10^{-10} m s² kg⁻¹ (Lide, 2004). Compressibility being the inverse of bulk modulus, limestones with 25% porosity have bulk modulus of approximately 16 GPa, therefore we assumed a compressibility of 6×10^{-11} m s² kg⁻¹ (Palaz and Marfurt, 1997).

5.4 Results

5.4.1 Validation of numerical solution results

The validation of the porosity evolution numerical solution comprises two tests. The first one is the comparison of the concentration profile obtained from the analytical approximation with the profiles resulting from solution 1 (tidal BC) and solution 2 (pure diffusive transport). The second test aims at validating the use of the quasi-stationary state approximation in the problem. The validation was done assuming reaction constant $k = 2 \times 10^{-5} \text{ s}^{-1}$, water with a $C_{eq} = 2.4051 \text{ mmol L}^{-1}$ and as inflow concentration $C/C_{eq} = 0.94$. Both transient numerical simulations produce C/C_{eq} results very close to the steady-state $dC/dt = 0$ analytical approximation with differences smaller than 1%. We conclude that the pure diffusive transport approach (simulation 3) accurately resolves the mass balance equation (5.11) formulated for the conceptual model. The formulation of the equivalent problem (solution 3) was needed because the calculation time for the pure diffusive transport is less than 1 minute, while it takes about 30 min for the full simulation that represents tidal pumping (solution 1). The application of the quasi-stationary state approximation is valid if

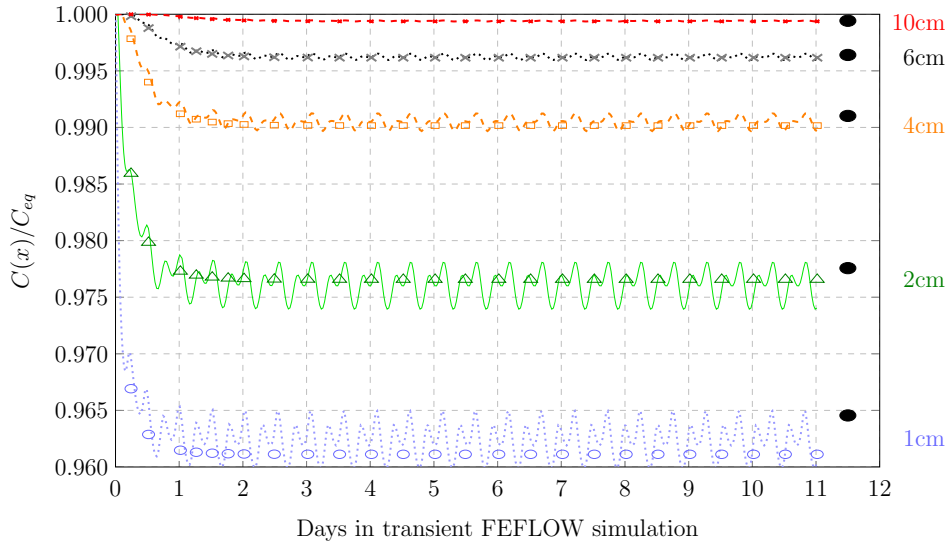


Figure 5.8: Temporal evolution of the normalized concentration $C(x)/C_{eq}$ in transient numerical simulations at position x indicated by labels. Lines represent the results of the full simulation of tides (solution 1) and symbols the pure diffusive transport (solution 3). The black dots represent the $C(x)/C_{eq}$ obtained with the analytical approximation.

the time required for full porous medium dissolution is much greater than the time required for water to equilibrate with porous medium minerals. Figure 5.9 shows the characteristic

dissolution time (eq. 5.15) in years assuming the final $\varepsilon = 0.95$. Reaction rate becomes slower when the solution is closer to equilibrium. The time to reach a stationary state $\partial c/\partial t$ is approximately 10 days (Fig. 5.8, while the period for full dissolution, $\tau = 645$ yr, is much greater. Therefore, the application of the quasi-stationary state approximation is considered valid.

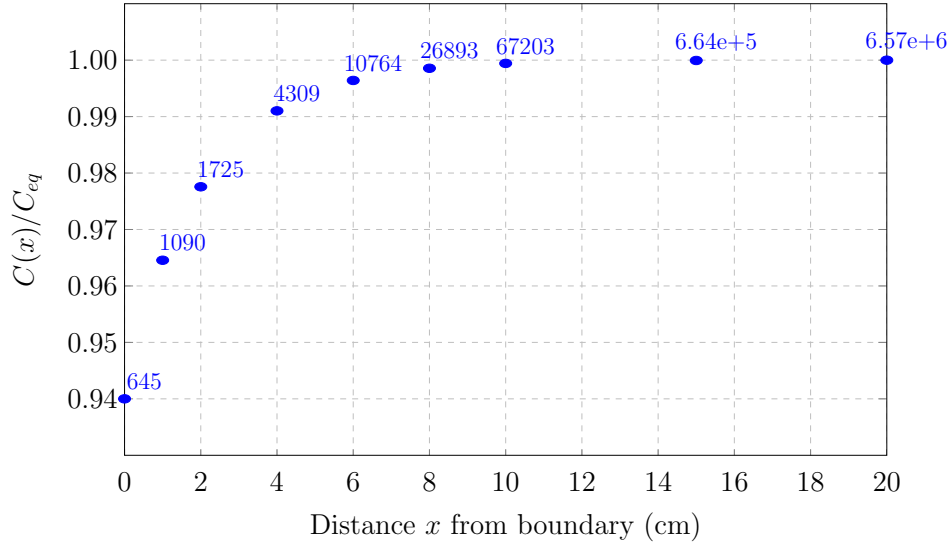


Figure 5.9: Left vertical axis: $C(x)/C_{eq}$, right vertical axis: time τ for full dissolution of porous medium. Regions where solute concentration is closer to equilibrium take more time to dissolve.

5.4.2 Porosity evolution simulations

The objective of simulations is to assess the effect of diffusivity increase on porosity evolution.

Porosity evolution in freshwater environment

In the first simulation, freshwater was assumed as boundary condition: ($C_{eq} = 2.6089$) mmol L^{-1} , $C(0) = 2.452 \text{ mmol L}^{-1}$, $k = 1.9 \times 10^{-4} \text{ s}^{-1}$. The tidal amplitude was 0.1 m and initial $K = 1 \text{ m d}^{-1}$. Figure 5.10 shows normalized concentration C/C_{eq} in the left vertical axis and porosity in the right vertical axis. The area where porosity was altered by dissolution is named dissolution front and it is approximately 5 cm wide. The plot shows 3 simulation times, the initial $t = 0$, $t = 36.5$ and $t = 72$ yr. In this simulation porosity, permeability and specific storage were updated after dissolution. The concentration profile displaces along porosity evolution because because diffusivity increases. However, the concentration profile

is almost at the same position at the start and end of simulation. The effect of porosity change in transport exists, but it is minimal for the ratio of reaction to transport rate in this simulation. Therefore, the initial concentration profile gives a reasonable approximation of the longitudinal extent of the final dissolution front.

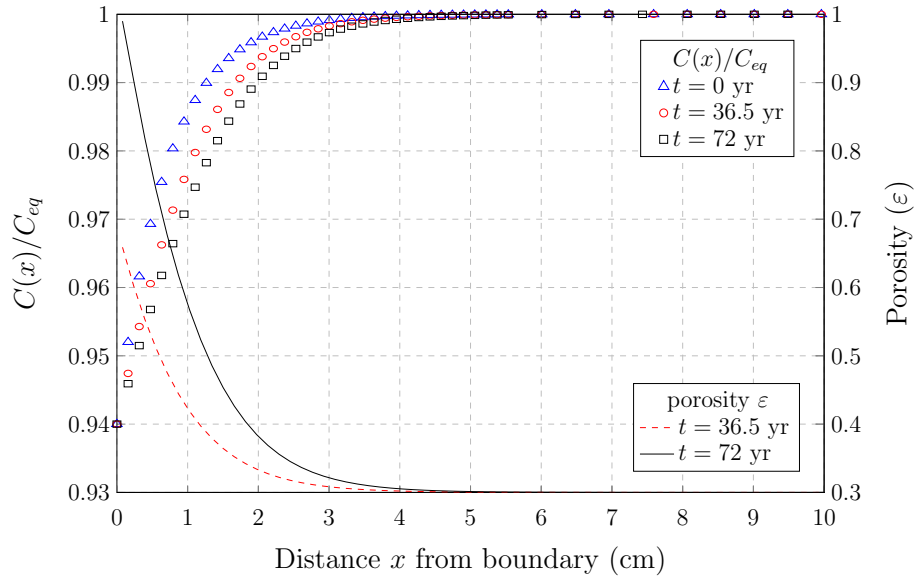


Figure 5.10: Simulation of porosity increase using study area freshwater. Symbols represent the normalized concentration while lines represent porosity for three simulation times: $t = 0$, $t = 36.5$ and $t = 72$ yr.

Porosity evolution in mixing-zone environment.

In a second simulation, water from the mixing-zone was assumed as boundary condition: ($C_{eq} = 6.026$) mmol L^{-1} , $C(0) = 5.815$ mmol L^{-1} , $k = 1.7 \times 10^{-4} \text{ s}^{-1}$. The tidal amplitude was 0.1 m and initial $K = 1 \text{ m d}^{-1}$. Figure 5.11 shows the evolution of concentration profile as porosity increases. The dissolution front extent is similar to the one developed by freshwater (Fig 5.10).

Wall-retreat rates

Figure 5.12 compares the evolution of porosity for simulations using fresh and mixing-zone water for the same tidal amplitude. Different saturation concentrations and dissolution reaction constants have a small effect on the extent of the developed dissolution front. The main observed difference is in the time period dissolution takes to develop a dissolution front. The increase of porosity from 0.3 to a theoretical 0.99 takes 72 yr for freshwater and 59.2

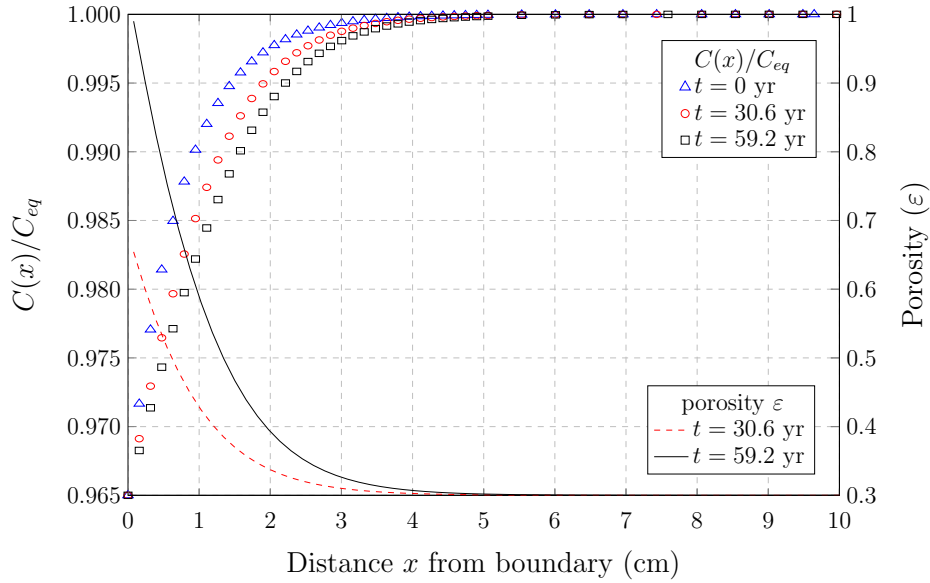


Figure 5.11: Simulation of porosity increase using water with mixing-zone properties. Symbols represent the normalized concentration while lines represent porosity for three simulation times: $t = 0$, $t = 30.6$ and $t = 59.2$ yr.

yr for mixing-zone water. Figure 5.12 also shows the assumption made to estimate wall-retreat rates. In the simulation porosity increased up to 0.65 and elements with porosity above 0.60 were assumed as fully dissolved. Wall retreat rate was calculated, 0.065 and 0.078 mm yr^{-1} for fresh and mixing-zone water respectively. A second assumption was made where the simulation continued with a porosity increase up to 0.99 and all elements with porosity above 0.95 were fully dissolved. A second wall retreat rate was calculated, 0.033 and 0.04 mm yr^{-1} for fresh and mixing-zone water respectively. Two wall retreats were calculated because it is not known at which porosity increase limestone disintegrates, further comment on these assumptions is done on the discussion section.

Effect of tidal pumping on dissolution front growth

The objective of the following simulations is to assess the effect of tidal amplitude in the development of dissolution fronts. All simulations were performed using mixing-zone water as inflow and the same initial porosity and conductivity. The variable was the tidal amplitude, from 0 (pure diffusion) up to 1 m. Figure (5.13) shows that larger tidal amplitudes contribute to a significantly larger extent of the dissolution front. Following the assumption that porosities over 0.6 represent limestone disintegration, the following rates were calculated: 0.021.

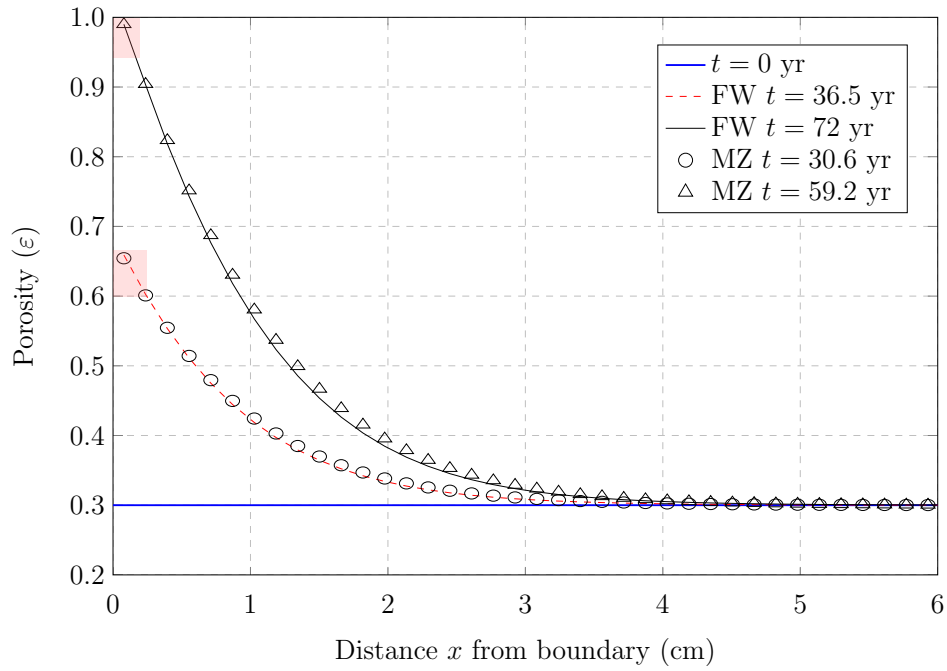


Figure 5.12: Comparison of porosity evolution for fresh (FW) and mixing-zone (MZ) water. The shaded area to the left represents the assumption made to estimate wall-retreat rates.

0.078, 0.080, 0.136, 0.190 mm yr^{-1} for tides with amplitude 0, 0.1, 0.2, 0.5 and 1 m. The dissolution front and the wall-retreat rate caused by the 1 m tide is 9 times larger than the dissolution front generated by no tides where the only transport mechanism is molecular diffusion. We conclude from this numerical experiment that mass transport caused by tidal pumping contributes largely to the extent of dissolution fronts.

5.5 Discussion

The validation tests showed that the numerical model represents accurately the conceptual model of eogenetic karst development. The numerical approximation was applied using data from the study area in the Yucatan peninsula. Simulation results are now discussed in the context of speleogenesis and field measurements. The discussion is divided into two sections: a) effect of mass transport and the effect of inflow water characteristics on dissolution front development, and b) wall-retreat rate.

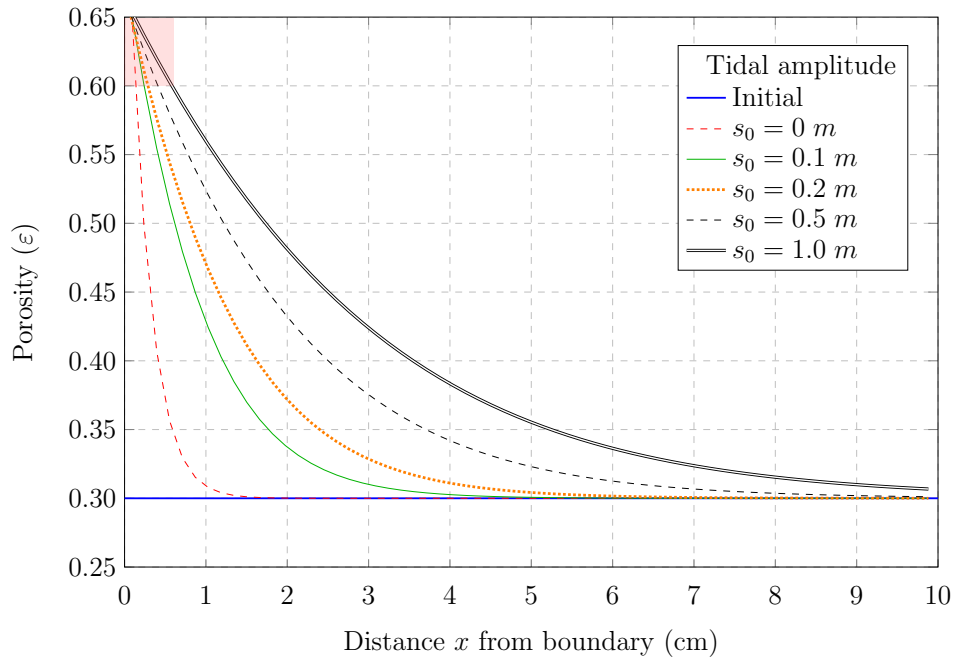


Figure 5.13: Dissolution fronts for different tidal amplitude scenarios with mixing-zone water as source of reactivity. The larger the tidal amplitude, the stronger the transport rate and extent of dissolution front.

5.5.1 Mass transport and inflow water type effect on dissolution front development

Mass transport is enhanced by tidal pumping. As shown in Figure 5.13, a larger tide will produce a larger dissolution front if water reactive to calcite is present. Moore et al. (2010) hypothesized that the exchange of reactive water between a conduit and the porous rock would produce a halo of friable rock around a conduit. This hypothesis is confirmed by the dissolution fronts obtained in our simulations and shown in Figures (5.10, 5.11 and 5.13). Furthermore, permeability measurements in cave walls in West-Central Florida show a permeability difference of an order of magnitude between the measurement close to the wall surface (3 cm depth) compared to 10 cm depth (Florea, 2006). The horizontal extent of the permeability gradient observed in caves in the scale of centimeters is comparable to the dissolution front ones observed in our simulations. A confirmation of our results and of the proposed conceptual model could be obtained by obtaining core samples of cave walls or conducting laboratory dissolution experiments under tidal pumping boundary conditions. The dissolution reaction rate depends on the degree of calcium ion under-saturation in water. As shown in Figures (5.10 and 5.11) different reaction constants k and different saturation

ratios C/C_{eq} have a small effect on the geometry of the dissolution front. Differences in water characteristics control the dissolution front development rate and therefore the wall-retreat rate. Additionally, Gulley et al. (2015) found that the spatial distribution of dissolved carbon dioxide in aquifers is highly heterogeneous. They discussed as possible causes of CO_2 heterogeneity: the thickness of vadose zone, organic matter transported from the surface into conduits yielding higher microbial CO_2 production and soil CO_2 spatial variability. If CO_2 spatial distribution is heterogeneous, reactivity and wall-retreat rate are also spatially heterogeneous.

5.5.2 Estimations of wall-retreat rate

The estimated wall-retreat rate in our work varies between 0.065 and 0.078 mm yr^{-1} for 10 cm tides for fresh and mixing-zone water from the study area. Dreybrodt et al. (2005a) calculated a wall retreat rate of 10 mm yr^{-1} for turbulent flow in telogenetic karst. Moore et al. (2010) estimated 14 mm yr^{-1} in eogenetic karst in Florida. Our wall-retreat rate estimate is smaller but it describes a process additional to the dissolution reaction at the limestone surface. Therefore, the wall-retreat rate caused by dissolution front development should be added to the surface reaction rate, yielding a larger overall karst growth rate.

The wall-retreat rate estimation depends on the porosity increase at which limestone disintegrates. Limestones from the study area are composed by grains (oolites, bioclasts) of several sizes kept together by calcite cement. Since the cement is the first material to be dissolved, limestone may disintegrate well before dissolution increases porosity above 0.95. Apparent limestone disintegration in the study area has been reported by cave divers when exhaust bubbles detach rock fragments from cave ceilings near the mixing-zone (Smart et al., 2006). Rock disintegration observed by divers implies very low mechanical resistance of limestone. To our knowledge, there are no published experimental results for limestone dissolution and mechanical resistance tests. The development of dissolution fronts may lead to the loss of mechanical resistance of unexposed limestone in the interior of a karst conduit wall. That is the reason we used two porosity thresholds (0.65 and 0.95) to estimate wall-retreat, 0.95 for full dissolution and 0.65 to simulate limestone disintegration before full dissolution. The initial hydraulic conductivity also controls the development of dissolution fronts. However, simulation results showed that concentration profiles at initial porosity are

similar to concentration profiles after a dissolution front has developed. This outcome can be explained because of the combination of parameters used in our simulations where the reaction constant k is relatively larger compared to the transport rate D caused by tidal pumping and rock properties.

5.6 Conclusions

In the coastal aquifer of Tulum (Yucatan peninsula, Mexico), the ocean tides propagate up to 10 km inland through the karst conduit network. The high porosity of the limestone matrix and the alternating hydraulic head gradients between the karst conduits and the surrounding matrix are likely to produce tidal pumping. A conceptual model for based on this environment was formulated to assess the effect of tidal pumping on karst development. An analytical approximation was developed to validate numerical solutions. Then numerical simulations were conducted using data from the study area to estimate the extent of dissolution fronts and wall-retreat rate. These were our conclusions:

1. Simulation results shows porosity increases that develop a dissolution front, which is similar to the friable halo hypothesis developed by Moore et al. (2010).
2. Tidal pumping contributes significantly to mass transport and therefore to the development of dissolution fronts.
3. Tidal pumping is the main factor that controls the extent of the dissolution front developing in the karst conduit wall.
4. The estimated wall-retreat rates driven by a tide of 0.1 m are the order of 0.065 to 0.078 mm yr⁻¹. These rates are smaller compared to other published results Dreybrodt et al. (2005a) and Moore et al. (2010). However our estimates account for a dissolution process that has not been quantified before. Therefore, karst growth can be driven by a superposition of dissolution front and surface dissolution which may explain why the conduit network in the study area is one of the largest explored cave systems in the world.
5. Our wall-retreat estimate depends on one critical assumption: the porosity increase at which limestone disintegrates. Further research in this area can help to produce better

wall-retreat estimates.

As a final note, in our simulations, we considered only one component of the tidal signal. But in reality, the head variations in the conduit are influenced by the superposition of several components including also daily, seasonal, or even long-term climate fluctuations (sea level changes for example). All those components interact and should be considered simultaneously. This was not done in this paper to keep the analysis simple, but it is reasonable to expect that the combination of these different oscillations having different wavelengths and amplitudes play a role in the karstification process.

Chapter 6

Evolution of fracture networks

6.1 Introduction

The behavior of karst aquifers is of great interest for the management of water resources. Groundwater flow through a karst conduit network is controlled by its geometry and topology. The physics of conduit flow, mass transport and reaction are known. In contrast, the geometry of karst networks is often unknown or, at best, only partially known because of speleological surveys. The limit to cave exploration is the human size, conduits of less than 40 cm diameter remain unmapped. Thus, the modeling of groundwater flow in karst networks is done today with incomplete information caused by lack of explorations or exploration physical limitations.

An alternative to bridge this gap in karst geometry data is to generate artificial networks or complete partially explored ones using simulations. Different techniques can be used that include some geometrical and statistical approaches (Jaquet et al., 2004; Pardo-Iguzquiza et al., 2012; Borghi et al., 2012; Hendrick, 2016). However, it is necessary to characterize quantitatively natural networks and then assess the properties of artificial ones. Pardo-Iguzquiza et al. (2011) proposed several indexes to quantify the conduit cross sections and spatial variability and connectivity of karst networks. It was found that width and height of conduits follow a log-normal distribution and that conduit size has a significant correlation length. Collon et al. (2017) proposed another set of parameters to quantify the geometry and topology of karst networks. Networks are described as graphs, which are a set of nodes and links between them.

Hendrick (2016) characterized the karst networks in the Yucatan Peninsula in Mexico. He found that their properties correspond to fractal objects with a specific fractal dimension and he proposed a technique to generate random artificial networks based on subnetworks of percolation clusters. These artificial networks have the same fractal parameters as the natural ones, however those artificial networks provide only the regional scale geometrical and topological information. The information about the dimensions of the conduit cross sectional geometry is not simulated. This problem is shared for most of the techniques listed above.

In summary, the topological characteristics of natural karst networks can be quantified and it is possible to generate artificial networks that have the same properties. But, those artificial statistical networks lack information on the conduit cross section geometry which is very important because it controls the hydraulic head loss of flow in a conduit. When one has to use those techniques to model groundwater flow, then one has to assume or identify the conduit diameters from indirect data such hydraulic head and flow rate measurements. This was done for example by assuming a hierarchical distribution of the conduit sizes in form of a power law of the order of the conduit (analog to Horton's law in hydrology) and calibrating the exponents to reproduce the observed head gradient in the region of Tulum by Vuilleumier et al. (2013). But all conduits having the same order had exactly the same diameter. This model was assumed based on a rather arbitrary concept and was not based on field measurements nor on the base on an analysis of speleogenesis processes.

The aim of this chapter is to initiate an analysis of the diameters of the conduit based on numerical simulations of the evolution of fractures by mineral dissolution and to compare the resulting observations with natural karst networks. The simulations are done by using the toolset for fracture development presented in chapter 4. The overall and general aim of that part of the research is to provide the basis for recommendations to allow modelers to better constrain the models of karst conduit diameters when they build a regional model of a karst system.

6.2 Examples of cave geometry

Among all the karst network data that were collected for the study related to the characterization of karst network geometry and topology (Collon et al., 2017), only three networks

were not hypogenic and had a rather complete cross section information available: Shuanghe in China, Sieben Hengste in Switzerland and Wakulla Springs in Florida, USA. The cross sectional data available for these karst networks is measurements of width and height at every cave survey station. Based on these measurements, we estimated an equivalent radius for a conduit who would have a similar cross sectional area. This calculation is obviously an approximation and a simplification of the reality.

Shuanghe is a 100 km long conduit network that developed in a block of dolomite and dolomitic limestone from Cambrian and Ordovician periods with embedded gypsum layers (Zhang et al., 2017). The system outlet is at 670 m above sea level. Speleogenesis is attributed to the preferential dissolution of gypsum layers and limestone weathering due to gypsum recrystallization in fractures. Sieben Hengste is a 140 km long network in Switzerland developed on Barremian and Aptian limestone with an outlet at 500 m above sea level (Jeannin, 1996). Wakulla Spring is a 19 km long network in Florida that developed in Lower Oligocene limestones (am Ende, 2012). Wakulla Springs conduits are on average 90 m below the phreatic level.

Figure 6.1 shows the geometry and the distribution of the radius in the conduits in these three karst networks. On these data sets, the conduit diameter follows a rather well defined log-normal distribution. However, conduits smaller than 0.2 m in radius are not possible to explore due to the limit of human size, thus the distribution is truncated for smaller conduits. In Shuanghe, the largest conduit has 100 m radius while in Wakulla and Sieben Hengste the maximum conduit radius is approximately 10 m. We also observe that the spatial distribution of the conduit radius is not random. Some branches have systematically larger conduit sizes while others are narrower. We also observe that there is no clear trend of larger conduits found upstream or downstream in the network. The hierarchical model assumed in Vuilleumier et al. (2013) does not seem to hold for those networks.

6.3 Fracture network evolution simulations

Simulations of dissolution on fracture enlargement by dissolution were done to explore how conduit cross section size is distributed on a network. The FEFLOW simulations were done using the module for fracture evolution described on Chapter 4. Mineral dissolution is simulated using the model from Dreybrodt et al. (2005b) for laminar flow presented in

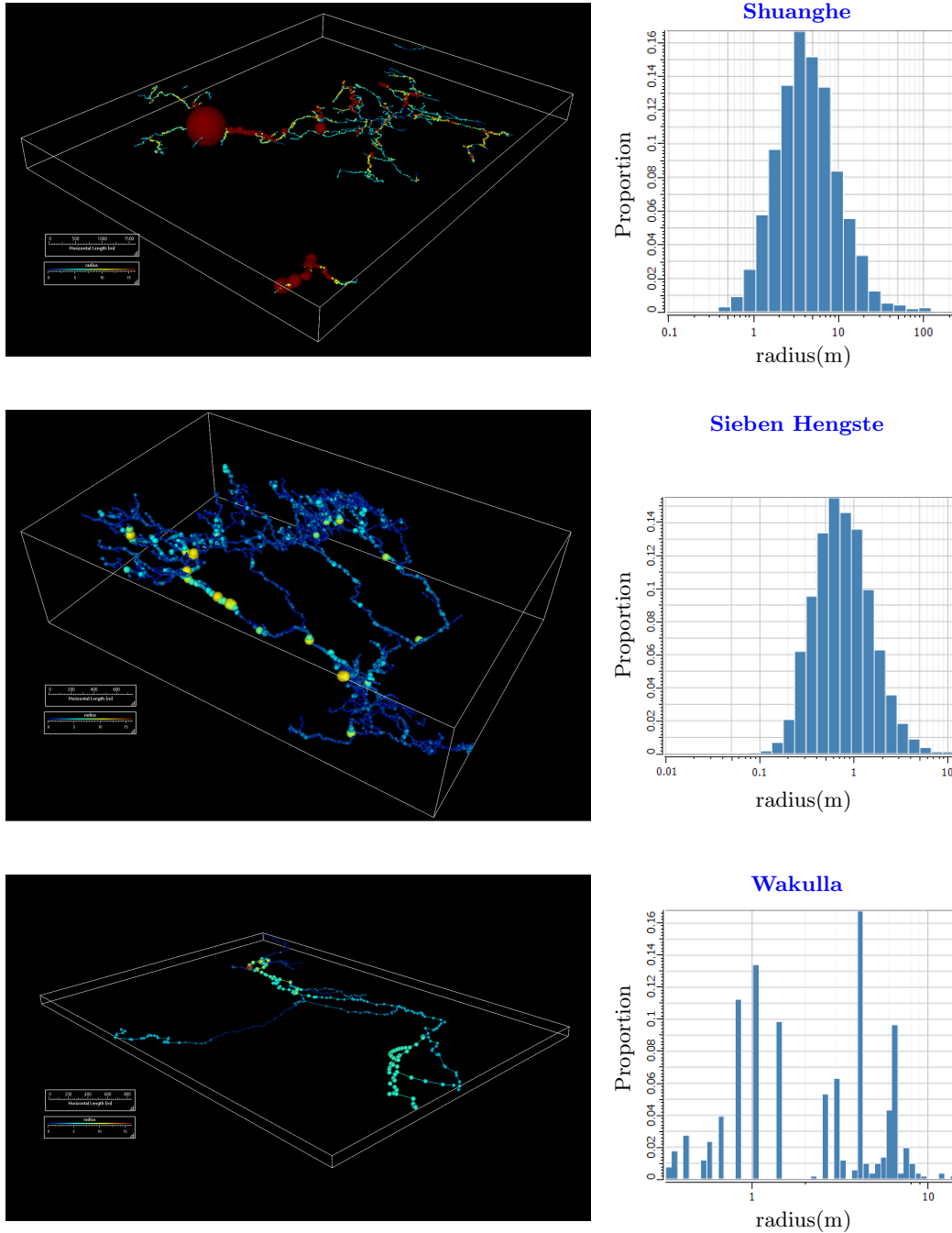


Figure 6.1: Geometries and distribution of conduit radius in three mapped karst systems.

Chapter 4 and that accounts both for 1st and 4th order dissolution kinetics. Equilibrium concentration is assumed as 2 mmol L^{-1} represented as 2 mg L^{-1} in FEFLOW.

Figure 6.2 presents the first simulation. The model is a fracture network of rectangular cross section with homogeneous distribution of initial aperture equal to $4 \times 10^{-4} \text{ m}$ and 1 m width. The fractures are created on the element boundaries of a FEM mesh generated by Delaunay triangulation. The hydraulic boundary condition is constant recharge of 50

$\text{m}^3 \text{d}^{-1}$ on the top boundary and constant head on the bottom of the simulation domain. Mesh elements have a high transmissivity on the top of the model to distribute flow evenly in fracture and a transmissivity several orders of magnitude less than fractures in the rest of the model. The mass boundary condition is fully unsaturated water at the injection nodes. The dissolution kinetics rate is assumed to be the same in all fractures representing homogeneous mineral composition. The simulation domain extent is 500×500 m. Fractures were not created in the model boundaries because boundaries are the path with less resistance to flow between the injection points and the outlets. If fractures were set in the boundaries, these fractures would be the only ones that develop after the simulation starts. The number of simulated fractures is 2000.

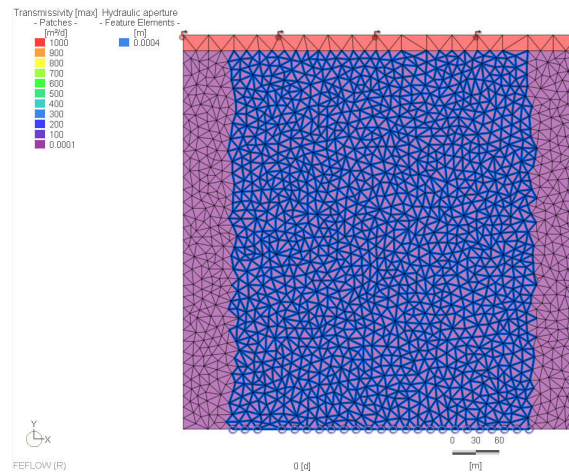


Figure 6.2: Geometry of simulated fracture network evolution and initial fracture aperture. The edges of triangles in 2D mesh represent fractures.

Figure 6.3 presents the results of the first model after a simulation time of 17,000 yr. Since fracture distribution is homogeneous, dissolved fractures do not resemble a cave. The development of fracture aperture after dissolution resembles more the geometry of wormholes developed by dissolution porous media (Petrus and Szymczak, 2016). The histogram shows the accumulated length of fractures of a certain aperture. The homogeneous distribution of apertures evolved into an exponential distribution.

A second simulation was done after setting the initial fracture apertures to an exponential distribution with mean $\mu = 4 \times 10^{-4}$ m. The exponential distribution is defined as $y = f(x|\mu) = 1/\mu \exp(-x/\mu)$. Figure 6.4 shows that the exponential distribution of aperture is randomly located in space.

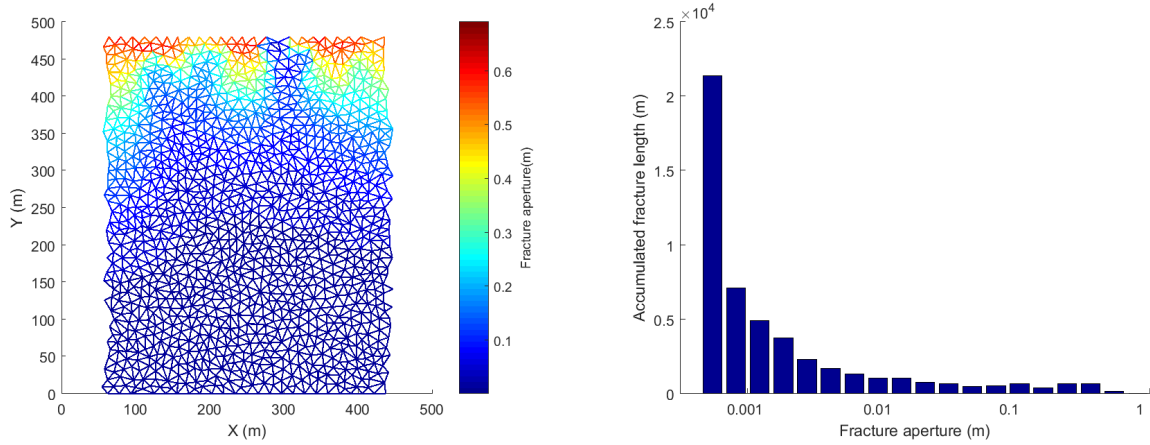


Figure 6.3: Fracture network geometry after dissolution at simulation time $t = 17,000$ yr.

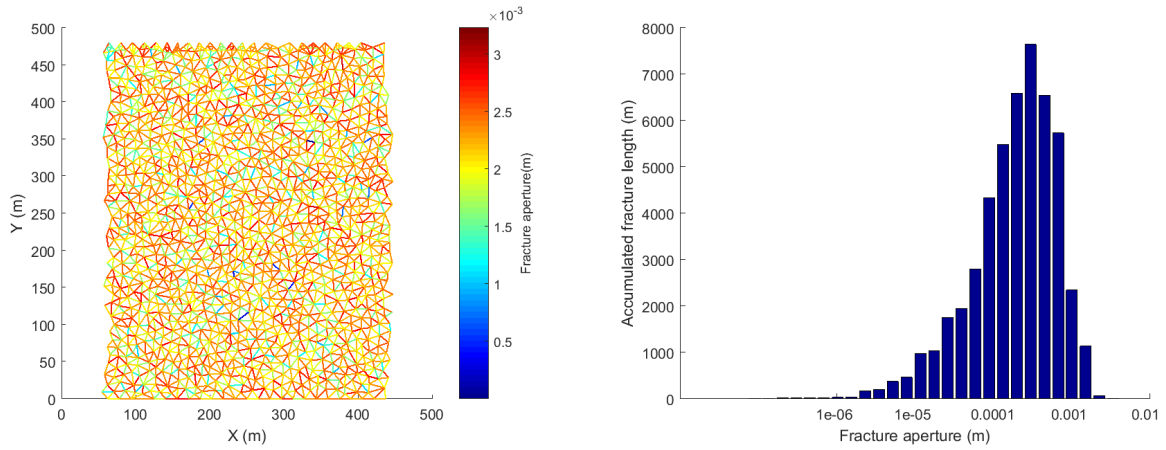


Figure 6.4: Initial fracture aperture with exponential distribution at simulation time $t = 0$.

Figure 6.5 shows the geometry of the network after 19,600 yr of simulated dissolution. The initial distribution of aperture apparently had no effect on the geometry of the resulting network. The developed fractures also resemble a wormhole geometry. The distribution of fracture aperture evolved into a log-normal distribution with two peaks: one for the initial aperture and one for the developed fractures.

Figure 6.6 presents the third simulation with the initial fracture aperture set to a log-normal distribution with mean $\mu = \log(4 \times 10^{-4})$ m and standard deviation $\sigma = 0.8$. The aperture was set randomly in the space.

Figure 6.7 shows results after 26,000 yr of simulated dissolution in the network with initial aperture with log-normal distribution. Developed geometries resemble wormholes and the distribution aperture also has two peaks.

The last results show that simulating dissolution in a randomly spatially distributed

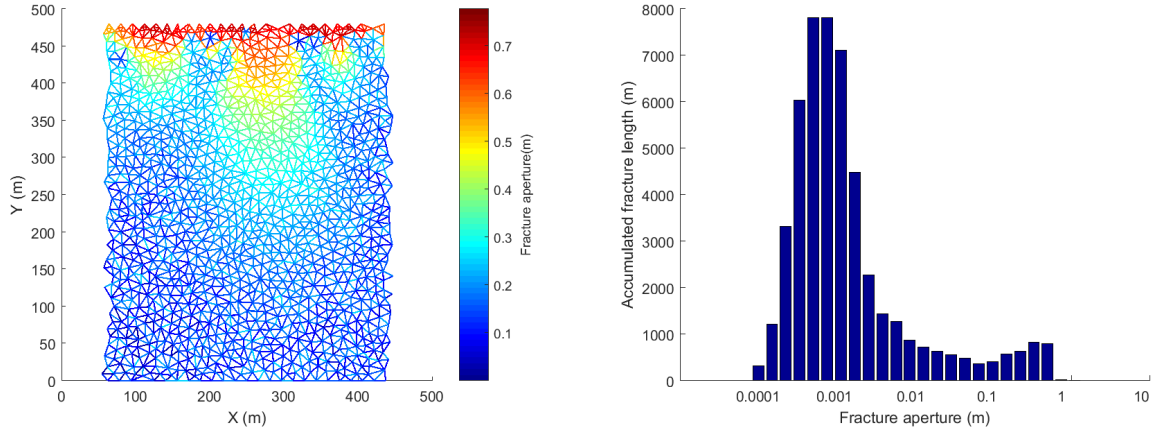


Figure 6.5: Final fracture aperture of network with initial exponential distribution at simulation time $t = 19,000$ yr.

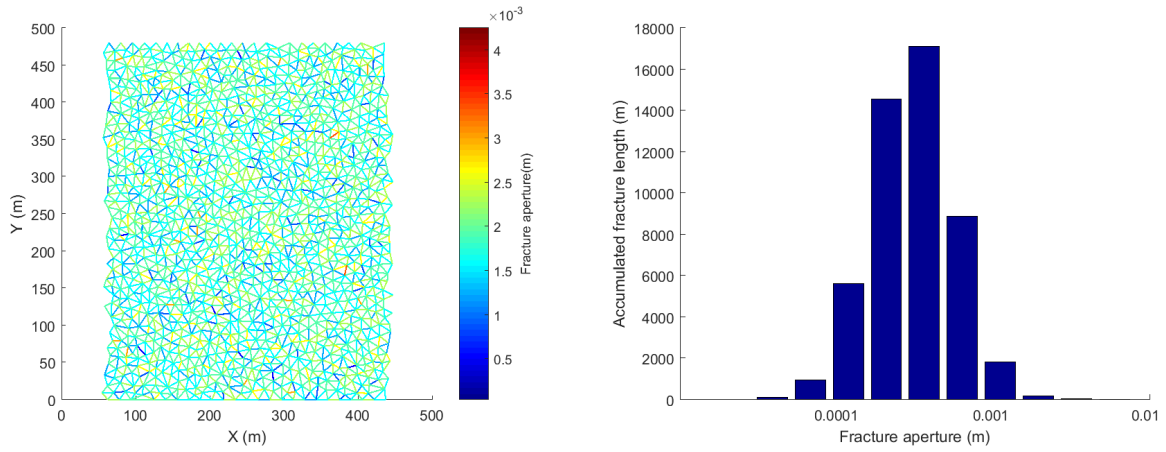


Figure 6.6: Initial fracture aperture with log-normal distribution

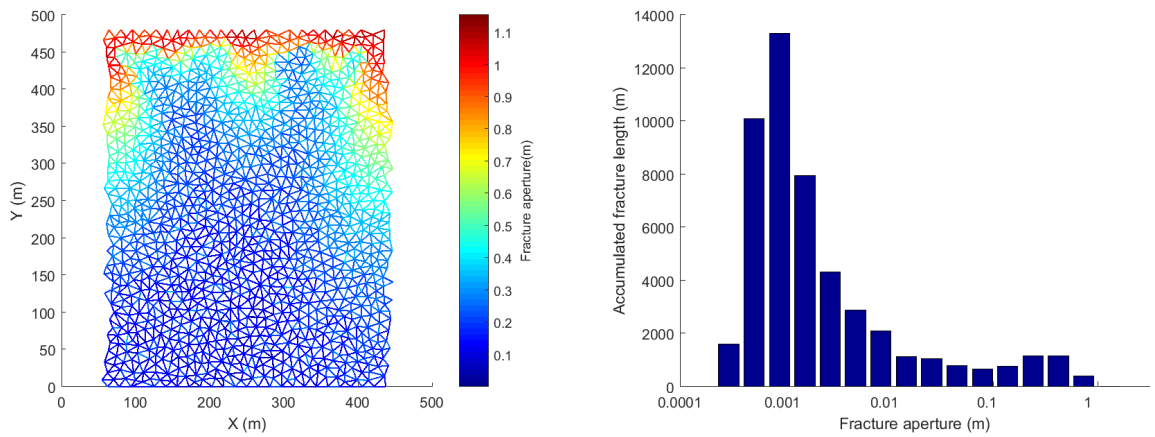


Figure 6.7: Final fracture aperture of network after simulation time $t = 27,000$ yr. with initial log-normal distribution.

network does not produce geometries that resemble cave geometries as the real measured ones in figure 6.1. Two of the simulated networks had heterogeneity in fracture aperture. However

the connectivity of fractures was evenly distributed and this may be a factor contributing to wormhole geometry development.

Another alternative to generate artificial networks is applying percolation theory. Percolation models were used by Hendrick and Renard (2016) to study the fractal properties of karst networks in the study area. Percolation models are pure geometric models to study connected clusters in disordered media. Percolation models have 1 parameter which is the probability p of a site being occupied. The size of connected clusters diverges for a certain value which is the critical point. At the critical point there is a non-zero probability that a site in the model domain belongs to a cluster that connects the model boundaries. Probability p is the order parameter of the system. A model in the disordered phase has a zero probability of having clusters that connect the system boundaries. Models in the ordered phase have a non-zero probability of connecting model boundaries with a cluster. The critical point is the transition point between ordered and disordered phases.

To build a percolation model the first step is to build a mesh which is the substrate. Then a probability of being occupied is assigned to mesh edges. This generates several clusters. When working with the critical probability, the largest cluster connects the substrate (mesh) boundaries. The largest cluster is selected among the many generated clusters to study flow across the mesh (Hendrick, 2016) .

A percolation model scaled to dimensions (1000x800 m) relevant for calcite dissolution was used as initial fracture geometry of a fourth simulation. This percolation model has an occupation probability at the critical point: the largest cluster connects all the model boundaries. Figure 6.8 shows the initial fracture aperture and flow boundary conditions which are 7 injection points with equal maximum hydraulic heads of 50 m and maximum flow rate of $10 \text{ m}^3 \text{ d}^{-1}$. Figure 6.8 also presents the initial concentration of solute before dissolution. Injection points in the bottom have larger plumes because they are closer to the outlet boundary. They have less resistance to flow, then advective transport is stronger compared to injection point farther from the outlet. As the first simulations, the dissolution rate accounts for both the 1st and 4th order dissolution kinetics. Reaction rate is assumed as homogeneous in the model domain. The number of simulated fractures is 79,000.

Figure 6.9 shows the fracture network geometry and aperture distribution after all injection points are connected with the outlet boundary by enlarged fractures. The resulting

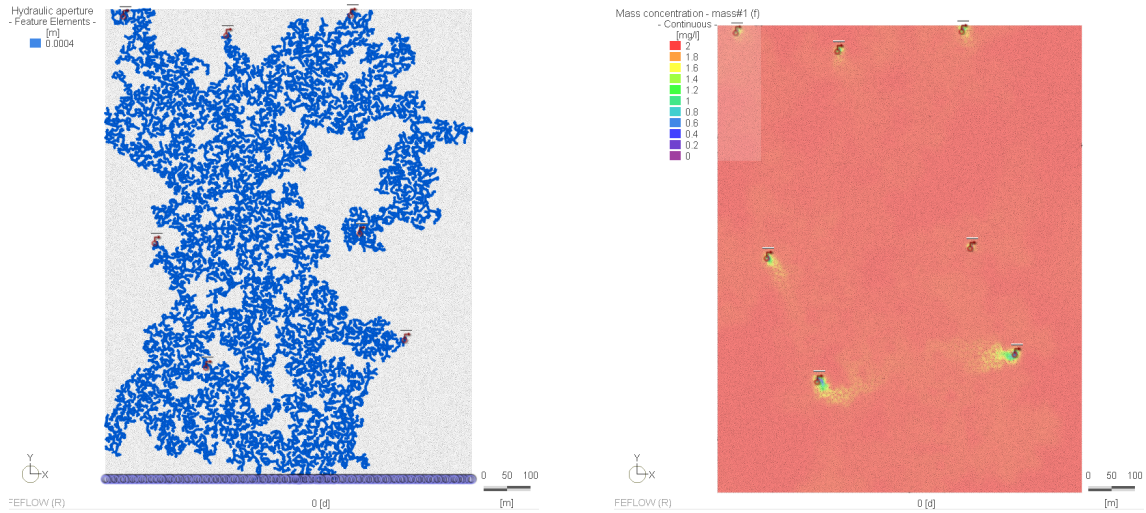


Figure 6.8: Percolation cluster representing initial conditions of fracture network.

network after simulation time of $t =$ resembles the cave topology like the ones presented on figure 6.1. This results is influenced by the properties of the percolation cluster where there are preferential flow paths. Some fractures are dead ends with no flow, thus they do not enlarge. The distribution of aperture has also two peaks, the first one represents the initial aperture of 0.0004 m and the second one the *cave*. The fractures near to the outlet boundary are larger, meaning that they developed faster compared to fractures farther from the outlet. Along each fracture, the aperture is distributed from a maximum at the injection point and a minimum at the outlet boundary or at the intersection with other enlarged fractures. Along a fracture the aperture is almost homogeneous, heterogeneity in aperture developed only at intersections of developing fractures and dead ends where diffusion is the only available mechanism for mass transport. Flow in a preferential path and homogeneous dissolution rate will tend to homogenize conduits cross sections along the preferential flow path. This behavior is not observed in real caves where large cross sections are contiguous to smaller ones.

A fifth simulation was done assuming heterogeneity in the dissolution kinetics. In the study area there is heterogeneity in limestone properties according to the the origin of sediments. The spatial distribution of limestone properties is related to the depositional history described in Chapter 3. Reefal limestone has a different texture and thus dissolution rate compared to backreef lagoon sediments with finer grain size. Both limestones are near 100% calcite, and have the same equilibrium concentration corresponding to the carbon dioxide

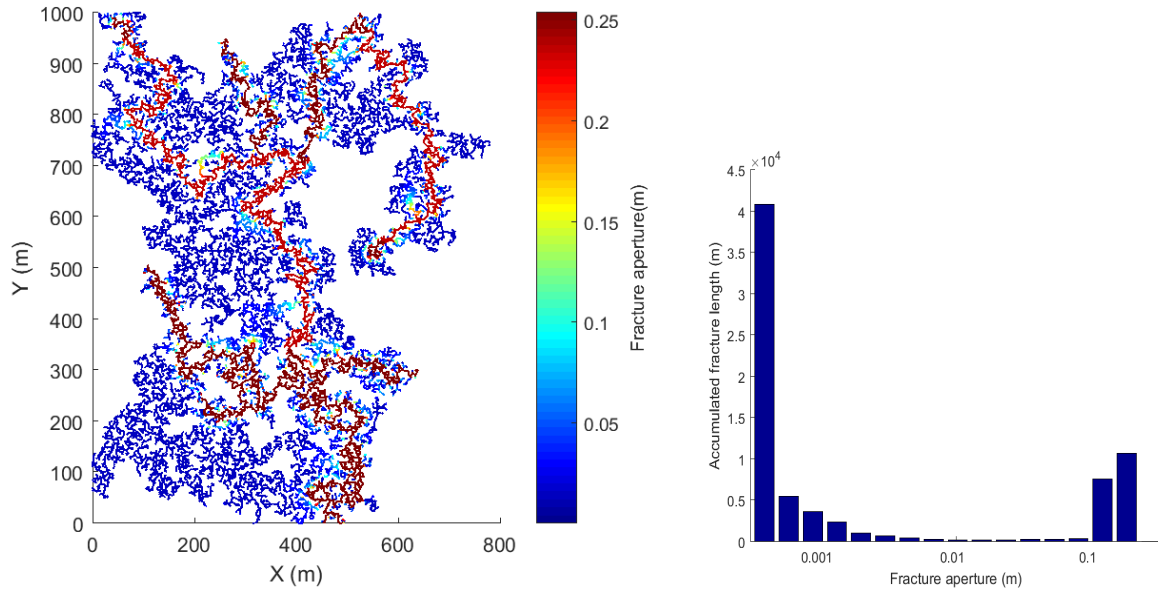


Figure 6.9: Fracture network geometry after dissolution time $t = 1,200$ yr. and aperture distribution of simulation 4. Initial percolation cluster is shown in figure 6.8.

in solution. However, differences in grain size, meaning different reaction surface area will result in different dissolution rates. The fifth simulation assumes reaction rate spatially distributed in 50 m thick highly reactive bands intercalated among 150 m less reactive bands. The reaction rate is 10 times faster in the highly reactive bands.

Figure 6.11 presents the results of fracture evolution assuming heterogeneity in reaction rate. Flow and mass boundary conditions are equal to simulation 4. Heterogeneity in reaction rate produces heterogeneity in fracture aperture. Large apertures are followed downstream by smaller apertures and then larger apertures once again. This behavior is similar to real caves presented in figure 6.1. But, the most interesting feature of simulation 5 is that the geometry of the developed cave system is different.

Figure 6.12 present the differences between simulation 4 with homogeneous reaction rate and simulation 5 with heterogeneous reaction rate. In simulation 4, the fracture that developed was the closer to the outlet in terms of resistance to flow. Since initial fracture aperture was the same for all fracture in simulation 4, the path with less resistance to flow was the shortest one. However, in simulation 5 the fracture that developed is not the shortest one. The fracture that developed is located in the lower dissolution reaction rate. The intuitive result is that faster dissolution rate is a preferential flow path for fractures. This is true at the injection point where a higher dissolution rate creates larger fractures,

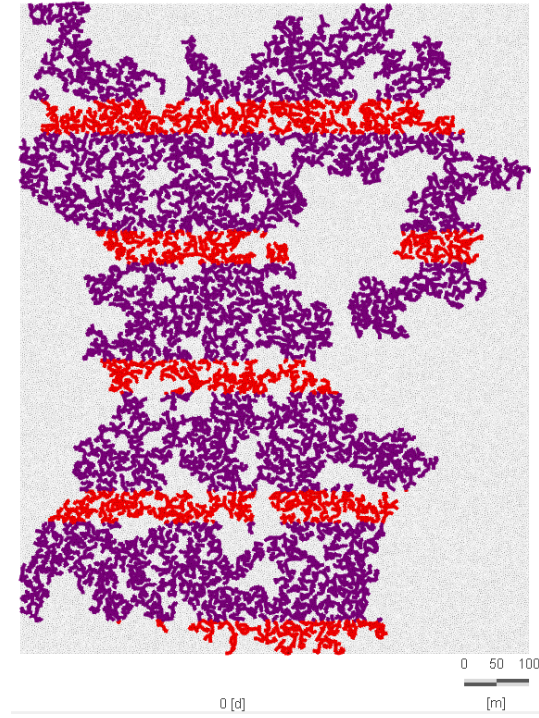


Figure 6.10: Assumed heterogeneity in reaction rate in simulation 5. 50 m thick highly reactive bands (red), intercalated among 150 m less reactive bands (purple).

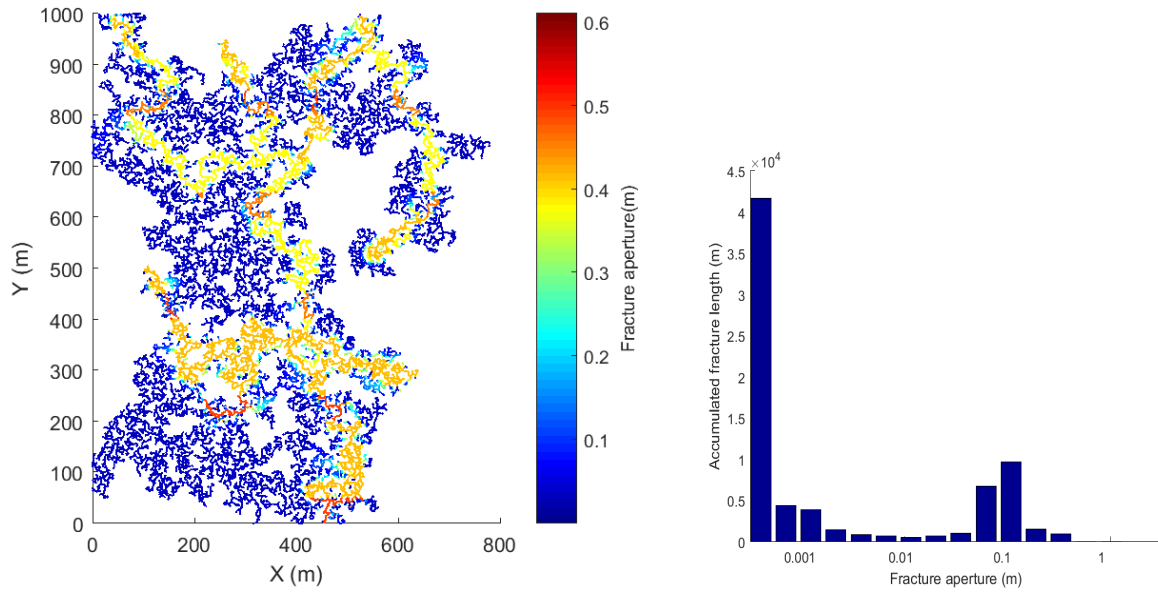


Figure 6.11: Fracture network geometry after dissolution time $t = 1,650$ yr. and aperture distribution of simulation 5. Heterogeneity in reaction rate in contrast to results presented in figure 6.9.

but only near the injection point. The fracture enlarged in simulation 5 has less resistance to flow because it developed farther away from the injection point because water less saturated could travel further into the fracture network. Thus, development of fractures is controlled

by the enlargement of the whole fracture from the injection point to the outlet. This can be explained by the use of Hagen-Poiseuille linear law for flow. As fractures grow their contribution to friction is less important and the largest fraction of resistance to flow is caused by the fractures that have the initial aperture. Thus, higher reaction yields *larger* fracture cross sections where reactive water enters the system, but lower reaction rates control the development of *longer* fractures that connect the injection point with the outlets.

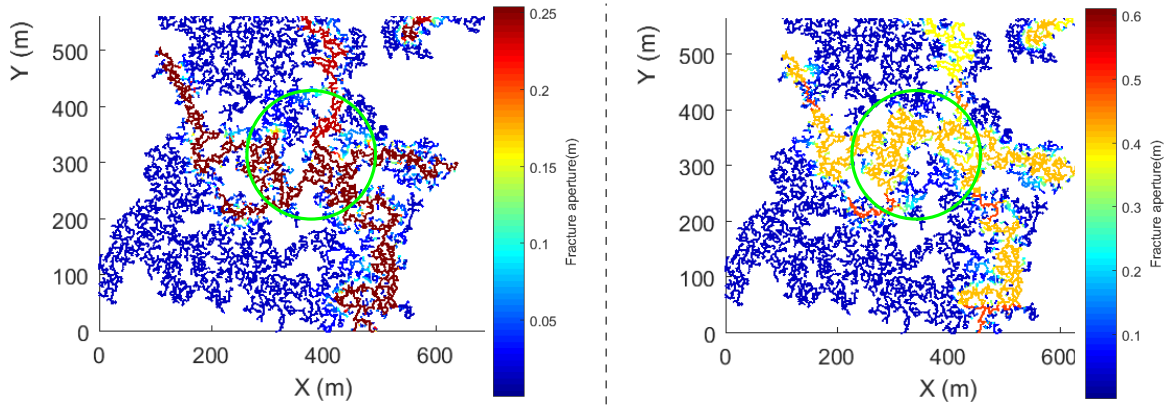


Figure 6.12: Differences in developed network geometry between simulations 4 and 5.

6.4 Discussion and conclusion

Results of the simulation of the evolution of fracture networks show that fracture networks with homogeneous spatial fracture distribution yield fracture development resembling worm-holes in porous media.

The application of percolation clusters as initial fracture networks allows to develop networks that resemble the topology of real caves. However, flow and dissolution tend to homogenize fracture cross sections along the developed fracture.

Simulating heterogeneity in dissolution rates produces a more heterogeneous distribution of fracture cross sections geometry. An unexpected result is that heterogeneity in dissolution rates control the fractures that are enlarged by dissolution. Fractures with lower reaction rate are enlarged before fractures with higher reaction rate because water can travel longer into the fracture network without getting saturated and then connecting the injection points with the outlet. The fractures that control the development of the geometry are at the end of the dissolution front, the maximum distance measured from the injection point at which water still can dissolve and enlarge fractures.

All simulations showed that fracture aperture after dissolution tends to a bi-modal distribution. The second mode represents the enlarged fractures and it could be an exponential or a log-normal distribution similar to the one of real caves shown in figure 6.1. What has been surveyed in caves could be the second peak. The first peak is impossible to survey because fractures caused by stresses on the rock are too small to explore but might contribute significantly to flow.

Results show that adding more initial information to the simulations, such as reaction rate heterogeneity, yields more realistic networks. However, the initial problem is precisely the lack of information about the system, either stratigraphical data, fracture network geometry or flow rates. Thus, the simulation of fracture enlargement can produce meaningful results only if some reliable information is known for the system.

The results presented in this chapter are only a first attempt to investigate the statistical and spatial distribution of conduit diameters in a karstic network. Further work is still needed to characterize in a systematic manner the networks and cross sections obtained by simulating mineral dissolution. The role of the geological history of a site with the evolution of the boundary conditions and accounting for a reasonable model of the heterogeneity of the sediments is still to be investigated.

Chapter 7

Conclusions

7.1 Main results

In this work, we applied the concepts of reactive transport and calcite dissolution kinetics to develop simulations tools to explore the development of caves in the study area. The main questions were: why large karst systems developed in the study area? and, what can we learn from these caves to understand other caves?

The following is a summary of the results discussed in the context of the main questions of the thesis. Also, possible future developments are proposed for theoretical speleogenesis research and interpretation of data available from the study area.

Why large karst systems developed in the eastern coast of the Yucatan Peninsula?

In chapter 3, the particular characteristics of the study area were presented in detail and are enumerated here:

1. The karst aquifer in the area of Tulum has a high primary porosity and permeability resulting from its geological history which is described as eogenetic.
2. High primary and porosity are related to Pleistocene sediments deposited in prograding coastline reef-rimmed environment. However, the horizontal and vertical extent of Pleistocene sediments is not known in detail. It is possible that most of the karst system is located in the porous and friable limestones.

3. The low relief topography of the Yucatan platform combined with sea level fluctuations due to glaciations have caused displacement of the coastline in the scale of kilometers. A moving coastline implies displacement of flow outlet of the karst system, displacement of the mixing zone between the freshwater and saline layers in the aquifer and variability in the groundwater flow direction in the conduit network. The combined effect of these processes may contribute to the apparent lack of order or preferential development of direction of the karst network.
4. It was observed that the largest karst network of the study area is located near an area where sea level drops to 300 meters in a relatively short horizontal distance. Under lower sea level conditions, this relief provides stronger hydraulic gradient compared to neighboring zones with gentler carbonate platform slopes.

The main novel result of this thesis is the conceptual model of karst conduit development by tidal pumping presented in chapter 5. It was shown that exchange of reactive water between a karst feature and the porous rock matrix around it, can produce dissolution relevant to the development of karst networks. Tidal pumping is stronger closer to the coast, but the coastline has been moving over the whole study area due to sea level changes.

To further investigate the theory of karst development by tidal pumping, it would be worth obtaining and analyzing a set of rock samples from the field. If a dissolution front is developing due to tidal pumping, differences of porosity should be observed between a sample near the cave wall surface and samples deeper on the wall. Drilling underwater is a complicated task, but there are also dry caves in the study area that developed in underwater conditions. Core drillings could also be done in other coastal karst networks where the conditions for tidal pumping are met.

Are existing conceptual models of speleogenesis adequate to describe karst networks on the study area?

The study area is different to other regions because limestone is quite permeable at the pore scale. Thus, groundwater flow occurs in karst conduits and if hydraulic conditions are met, water exchange can occur between the karst conduit and the porous wall around it. This exchange, known as tidal pumping, dissolves limestone not only at the conduit wall surface but also at the interior of the wall.

Based on these observations from the study area a conceptual framework and a simulation tool were produced to simulate dissolution by tidal pumping. Simulation results show that the action of tidal pumping combined with rock properties and groundwater chemistry from the study can lead to significant conduit enlargement rates. The simulation results contribute to explain the development of large karst cavities found in the study area.

What can we learn from these caves to understand other caves?

This question aims to respond to the initial problem of information gaps on cave geometry. Exploring and surveying karst networks is a challenging task if not impossible. A simulation tool was developed to explore the evolution of fracture networks driven by mineral dissolution. Results of the simulations are networks with topological and geometrical properties that can be compared to the properties of real networks.

The work done during the time frame of the thesis generated more questions than answers. We observed that the combined action of groundwater flow and dissolution can produce a statistical distribution of fracture apertures (conduit cross section size) that shares some characteristics with the one observed in real karst networks. However, flow and dissolution are not sufficient to generate the spatial distribution of fracture aperture if we assume a simple setup. Instead, it is necessary to supply more information to the model such as heterogeneity in dissolution rates to be able to generate networks having a spatial distribution of aperture closer to real networks. However, this is a paradoxical situation because the purpose of simulating speleogenesis was to bridge gaps on karst network data. If reliable structural geology, stratigraphical and mineralogy data is available, a reliable simulation of speleogenesis can be done.

7.2 Future developments

7.2.1 For conceptual development

The statistical analysis applied to the networks generated by dissolution could be extended into metrics of spatial variability of topological analysis. This development could help to improve the simulation of speleogenesis as a tool to complement information on unexplored karst systems.

7.2.2 For the study area

Data on the study area was collected during the field campaigns. Additional data on the study area has been generated by the Geological Survey of Austria. A fraction of this information was not analyzed in this thesis work and is a promising area of research. The following is a list of suggested analysis for existing data and sampling work to generate more information on the study area:

1. Geophysical measurements were conducted on the boreholes presented in Chapter 3. Borehole geophysics data could be used to generate stratigraphical information.
2. The geological Survey of Austria conducted airborne electromagnetic measurements. One of the products is the depth of the mixing zone in the aquifer. Assuming constant flux in the freshwater layer of the aquifer, a thinner freshwater layer could be interpreted as a higher hydraulic conductivity zone. Higher hydraulic conductivity can be interpreted as karst conduits.
3. There are estimates of aquifer coastal outflow for the study area. However, the recharge basin area has not been established yet. Knowing the recharge area is important for the management of groundwater quality resources. As presented in Chapter 3 Section Recharge, there may be a groundwater divide between 23 and 33 km from the coast. It is worth studying the causes of the differences in hydraulic head for piezometers after storm precipitation.
4. The Geological Survey of Austria conducted continuous measurements of flow speed at Jailhouse site. If data is appropriate, a Fourier analysis can be applied to look for the influence of sea tides in groundwater flow speed in the karst system. This analysis can provide insight into the transport processes occurring in the aquifer which is a requisite to understand pollution dispersion.
5. The stratigraphic knowledge of the study area is minimal. It is not known precisely if the karst systems developed entirely on Pleistocene sediments corresponding to a prograding coastline or if the karst system also developed on older sediments deposited in shallow sea conditions. A drilling campaign and analysis of drilling cores could help to determinate the extent and properties of Pleistocene sediments in the study area.

Appendix A

Code developed for the thesis

The code developed for this thesis work is mainly plug-ins for FEFLOW software. These plug-ins retrieved solute transport data from the reactive transport simulation. Then calculate changes on model properties accounting for the effects chemical reaction.

For porous medium models, the modified properties are:

- Porosity
- Hydraulic conductivity
- Specific storage

For discrete element representing fractures or conduits, the modified properties are:

- Hydraulic aperture
- Cross-section area

The compiled FEFLOW plug-ins and source code are available at the GitHub repository the Centre for Hydrogeology and Geothermics of the University of Neuchâtel. Additional code developed for this thesis is also available at the group repository.

<https://github.com/UniNE-CHYN>

For any inquiries about the code or its functionalities please address to:

axa.maqueda@protonmail.ch

Bibliography

- am Ende, B. A. (2012). Wakulla Spring underwater cave system, Florida. In White, W. B. and Culver, D. C., editors, *Encyclopedia of Caves (Second Edition)*, pages 875 – 881. Academic Press, Amsterdam, second edition edition.
- Amante, C. and Eakins, B. W. (2009). ETOPO1 1 Arc-Minute Global Relief Model: Procedures, Data Sources and Analysis. NOAA Technical Memorandum NESDIS NGDC-24.
- Angeles, F. J. (2006). Monografía petrolera de la zona marina. *Boletín de la Asociación Mexicana de Geólogos Petroleros*, 77:16–30.
- Appelo, C. A. J. and Postma, D. (2010). *Geochemistry, Groundwater and Pollution*, chapter 5. Carbonates and Carbon Dioxide, pages 175–232. CRC Press.
- Back, W., Hanshaw, B. B., Herman, J. S., and Van Driel, J. N. (1986). Differential dissolution of a Pleistocene reef in the ground-water mixing zone of coastal Yucatan, Mexico. *Geology*, 14(2):137–140.
- Back, W., Hanshaw, B. B., Pyle, T. E., Plummer, L. N., and Weidie, A. E. (1979). Geochemical significance of groundwater discharge and carbonate solution to the formation of Caleta Xel Ha, Quintana Roo, Mexico. *Water Resources Research*, 15(6):1521–1535.
- Bauer-Gottwein, P., Gondwe, B. R. N., Charvet, G., Marín, L. E., Rebolledo-Vieyra, M., and Merediz-Alonso, G. (2011). Review: The Yucatán Peninsula karst aquifer, Mexico. *Hydrogeology Journal*, 19(3):507–524.
- Baumann, J., Buhmann, D., Dreybrodt, W., and Schulz, H. (1985). Calcite dissolution kinetics in porous media. *Chemical Geology*, 53(3):219 – 228.

- Beddows, P. A. (2004). Groundwater hydrology of a coastal conduit carbonate aquifer: Caribbean coast of the Yucatan Peninsula, Mexico. PhD Thesis, Department of Earth Sciences, University of Bristol.
- Bernabé, Y., Mok, U., and Evans, B. (2003). Permeability-porosity relationships in rocks subjected to various evolution processes. *Pure and Applied Geophysics*, 160(5):937–960.
- Bjørlykke, K. (2010). *Petroleum Geoscience: From Sedimentary Environments to Rock Physics*, chapter 2. Introduction to Sedimentology, pages 72–74. Springer Science.
- Blanchon, P. (2010). Reef demise and back-stepping during the last interglacial, northeast Yucatan. *Coral Reefs*, 29(2):481–498.
- Bögli, A. (1964). Corrosion par mélange des eaux. *International Journal of Speleology*, 1:61–73.
- Borghi, A., Renard, P., and Jenni, S. (2012). A pseudo-genetic stochastic model to generate karstic networks. *Journal of Hydrology*, 414-415(1):516–529.
- Budd, D. A. (2002). The relative roles of compaction and early cementation in the destruction of permeability in carbonate grainstones: A case study from the Paleogene of West-Central Florida, U.S.A. *Journal of Sedimentary Research*, 72(1):116–128.
- Buhmann, D. and Dreybrodt, W. (1985). The kinetics of calcite dissolution and precipitation in geologically relevant situations of karst areas, 2. Closed System. *Chemical Geology*, 53(1):109 – 124.
- Centeno, C. M., Legendre, P., Beltrán, Y., Alcántara-Hernández, R. J., Lidström, U. E., Ashby, M. N., and Falcón, L. I. (2012). Microbialite genetic diversity and composition relate to environmental variables. *FEMS microbiology ecology*, 82(3):724–735.
- Collon, P., Bernasconi, D., Vuilleumier, C., and Renard, P. (2017). Statistical metrics for the characterization of karst network geometry and topology. *Geomorphology*, 283:122 – 142.
- CONABIO (2016). Relieve Submarino del Ecosistema Arrecifal Coralino del Caribe Mexicano: Punta Nizuc-Santa Rosa, escala: 1:20000. edición: 1.

- CONAGUA-OCOPY (2013). Estudio de reactivació de la red piezométrica en el acuífero península de de Yucatán (COBA-TULUM) en la region costera norte del estado de Quintana Roo.
- Cunningham, K. J., Renken, R. A., Wacker, M. A., Zygnerski, M. R., Robinson, E., Shapiro, A. M., and Wingard, G. L. (2006). Application of carbonate cyclostratigraphy and borehole geophysics to delineate porosity and preferential flow in the karst limestone of the Biscayne aquifer, SE Florida. *Geological Society of America Special Papers*, 404:191–208.
- De Marsily, G. (1986). *Quantitative Hydrogeology*. Academic Press.
- Del Castillo, L. and Vivas, A. (1973). Esquema tectónico del borde de la Placa del Caribe Al Este de Yucatan. *Boletín de la Asociación Mexicana de Geólogos Petroleros*, 25:160–187.
- Denis, A., Durville, J.-L., Massieu, E., and Robert, T. (1987). Problèmes posés par un calcaire très poreux dans l'étude de la stabilité d'une carrière souterraine. *Bulletin de liason des Laboratoires des Ponts et Chausses*, 152:69–74.
- Diersch, H.-J. (2013a). *FEFLOW - White papers vol. I*, pages 194–197. WASY Ltd., Berlin.
- Diersch, H.-J. (2013b). *FEFLOW: finite element modeling of flow, mass and heat transport in porous and fractured media*. Springer Science & Business Media.
- Dreybrodt, W., Gabrovšek, F., and Romanov, D. (2005a). *Processes of a Speleogenesis: A Modeling Approach*, volume 4. Založba ZRC.
- Dreybrodt, W., Gabrovšek, F., and Romanov, D. (2005b). *Processes of Speleogenesis: A Modeling Approach*, chapter 2. Equilibrium Chemistry and Dissolution Kinetics of Limestone in $\text{H}_2\text{O} - \text{CO}_2 - \text{CaCO}_3$ Solutions. Založba ZRC.
- Dreybrodt, W., Gabrovšek, F., and Romanov, D. (2005c). *Processes of Speleogenesis: A Modeling Approach*, chapter 3. The Evolution of a Single Fracture. Založba ZRC.
- Dubliansky, Y. V. (2000). *Speleogenesis, Evolution of Karst Aquifers*, chapter 4.1.5 Dissolution of Carbonates by Geothermal Waters, pages 158–159. National Speleological Society.
- Ehrenberg, S. N., Eberli, G. P., and Baechle, G. (2006). Porosity-permeability relationships in Miocene carbonate platforms and slopes seaward of the Great Barrier Reef, Australia (ODP Leg 194, Marion Plateau). *Sedimentology*, 53(6):1289–1318.

- Eisenlohr, L., Meteva, K., Gabrovšek, F., and Dreybrodt, W. (1999). The inhibiting action of intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in aqueous $\text{H}_2\text{O} - \text{CO}_2$ solutions. *Geochimica et Cosmochimica Acta*, 63(7–8):989 – 1001.
- Ferris, J. G. (1952). Cyclic fluctuations of water level as a basis for determining aquifer transmissibility. Technical report, US Geological Survey.
- Fleming, K., Johnston, P., Zwartz, D., Yokoyama, Y., Lambeck, K., and Chappell, J. (1998). Refining the eustatic sea-level curve since the Last Glacial Maximum using far- and intermediate-field sites. *Earth and Planetary Science Letters*, 163(1–4):327 – 342.
- Florea, L. J. (2006). The karst of West-Central Florida. Ph.D. Thesis, Department of Geology, University of South Florida.
- Flügel, E. (2010). *Microfacies of Carbonate Rocks*, chapter 3. Microfacies Analysis, page 103. Springer Science.
- Ford, D. and Williams, P. (2007). *Karst Hydrogeology and Geomorphology*, chapter 1. Introduction to Karst, page 1. John Wiley & Sons.
- Garrels, R. M. and Christ, C. L. (1965). *Solutions, Minerals, and Equilibria*, chapter Carbonate Equilibria, pages 74–92. Harper and Row.
- Gischler, E., Gibson, M. A., and Oschmann, W. (2008). Giant holocene freshwater microbialites, laguna bacalar, quintana roo, mexico. *Sedimentology*, 55(5):1293–1309.
- Gouze, P. and Luquot, L. (2011). X-ray microtomography characterization of porosity, permeability and reactive surface changes during dissolution. *Journal of Contaminant Hydrology*, 120:45–55.
- Greenfield, R. and Baker, G. (1920). Relationship of hydrogen-ion concentration of natural waters to carbon dioxide content. *The Journal of Industrial and Engineering Chemistry*, 12(10):989–991.
- Gulley, J., Martin, J., and Moore, P. (2014). Vadose CO_2 gas drives dissolution at water tables in eogenetic karst aquifers more than mixing dissolution. *Earth Surface Processes and Landforms*, 39(13):1833–1846. ESP-13-0294.R2.

- Gulley, J. D., Martin, J. B., Moore, P. J., Brown, A., Spellman, P. D., and Ezell, J. (2015). Heterogeneous distributions of CO₂ may be more important for dissolution and karstification in coastal eogenetic limestone than mixing dissolution. *Earth Surface Processes and Landforms*, 40(8):1057–1071.
- Hanshaw, B. B. and Back, W. (1979). Major geochemical processes in the evolution of carbonate aquifer systems. *Journal of Hydrology*, 43(1):287 – 312.
- Hatzor, Y. H., Wainshtein, I., and Mazor, D. B. (2010). Stability of shallow karstic caverns in blocky rock masses. *International Journal of Rock Mechanics and Mining Sciences*, 47(8):1289–1303.
- Hendrick, M. (2016). Scaling behaviors of karst networks around Tulum, Mexico: characterization, model and application. PhD Thesis, Université de Neuchâtel, Switzerland.
- Hendrick, M. and Renard, P. (2016). Fractal dimension, walk dimension and conductivity exponent of karst networks around tulum. *Frontiers in Physics*, 4:27.
- Hiatt, E. and Kyser, T. (2000). *Fluids and Basin Evolution*, chapter 4. Links between Depositional and Diagenetic Processes in Basin Analysis: Porosity and Permeability Evolution in Sedimentary Rocks, pages 63–92. Mineralogical Association of Canada.
- Hossler, T. (2015). Towards the integration of rock mechanics in the simulation of karstogenesis. Master’s Thesis, Université Pierre et Marie Curie, MinesParisTech and AgroParisTech.
- Howard, A. D. (1966). Verification of the ”mischungskorrosion” effect. *Cave Notes*, 8(2):9–12.
- Jaquet, O., Siegel, P., Klubertanz, G., and Benabderrhamane, H. (2004). Stochastic discrete model of karstic networks. *Advances in Water Resources*, 27(7):751–760. Times Cited: 14
- Jaquet, O Siegel, P Klubertanz, G Benabderrhamane, H.
- Jarvis, A., Reuter, H. I., Nelson, A., and E., G. (2008). Hole-filled seamless SRTM data V4, scenes 19-08 and 19-09. <http://srtm.csi.cgiar.org>.
- Jeannin, P.-Y. (1996). Structure et comportement hydraulique des aquifères karstiques. PhD Thesis, Université de Neuchâtel, Switzerland.
- Kaesler, G. (2016). Groundwater flow and solute transport modeling in the karst system Ox Bel Ha, Tulum, Mexico. Master’s Thesis, Université de Neuchâtel, Switzerland.

- Kambesis, P. N. and Coke, J. G. (2013). *Coastal Karst Landforms*, chapter Overview of the controls on eogenetic cave and karst development in Quintana Roo, Mexico, pages 347–373. Springer Netherlands.
- Klimchouk, A. B., Ford, D. C., Palmer, A. N., and Dreybrodt, W. (2000). *Speleogenesis, Evolution of Karst Aquifers*, chapter 2. Historical Perspective. National Speleological Society.
- Lambeck, K., Esat, T. M., and Potter, E.-K. (2002). Links between climate and sea levels for the past three million years. *Nature*, 419(6903):199–206.
- Langmuir, D. (1971). The geochemistry of some carbonate ground waters in central Pennsylvania. *Geochimica et Cosmochimica Acta*, 35:1023–1045.
- Langmuir, D. (1984). *Guide to the hydrology of carbonate rocks*, chapter Physical and chemical characteristics of carbonate water, pages 69–130. UNESCO.
- Langmuir, D. and Mahoney, J. (1984). *Practical Applications of Ground Water Geochemistry*, chapter Chemical Equilibrium and Kinetics of Geochemical Processes in Grounwater Studies. National Water Well Association.
- Lichtner, P. C. (1985). Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems. *Geochimica et Cosmochimica Acta*, 49(3):779 – 800.
- Lichtner, P. C. (1988). The quasi-stationary state approximation to coupled mass transport and fluid-rock interaction in a porous medium. *Geochimica et Cosmochimica Acta*, 52(1):143 – 165.
- Lide, D. R. (2004). *CRC Handbook of Chemistry and Physics*. CRC Press.
- Lopez Ramos, E. (1973). Estudio geológico sobre la Península de Yucatán. *Boletín de la Asociación Mexicana de Geólogos Petroleros*, 25:25–76.
- Martin, J. B., Gulley, J., and Spellman, P. (2012). Tidal pumping of water between Bahamian blue holes, aquifers, and the ocean. *Journal of Hydrology*, 416–417:28 – 38.
- Menke, H. P., Bijeljic, B., Andrew, M. G., and Blunt, M. J. (2015). Dynamic three-dimensional pore-scale imaging of reaction in a carbonate at reservoir conditions. *Environmental Science & Technology*, 49(7):4407–4414.

- Meyerhoff, S. B., Maxwell, R. M., Revil, A., Martin, J. B., Karaoulis, M., and Graham, W. D. (2014). Characterization of groundwater and surface water mixing in a semiconfined karst aquifer using time-lapse electrical resistivity tomography. *Water Resources Research*, 50(3):2566–2585.
- Moore, P. J., Martin, J. B., Screaton, E. J., and Neuhoﬀ, P. S. (2010). Conduit enlargement in an eogenetic karst aquifer. *Journal of Hydrology*, 393(3–4):143 – 155.
- Moore, Y. H., Stoessell, R. K., and Easley, D. H. (1992). Fresh-water/sea-water relationship within a ground-water flow system, northeastern coast of the yucatan peninsula. *Ground Water*, 30(3):343–350.
- Morse, J. W., Arvidson, R. S., and Lüttge, A. (2007). Calcium carbonate formation and dissolution. *Chemical Reviews*, 107(2):342–381.
- Murray, J. W. (2004). Activity scales and activity correction. Lecture notes on Chemical Oceanography.
- Myroie, J. R. and Myroie, J. E. (2007). Development of the carbonate island karst model. *Journal of Cave and Karst Studies*, 69(1):59–75.
- Nogues, J. P., Fitts, J. P., Celia, M. A., and Peters, C. A. (2013). Permeability evolution due to dissolution and precipitation of carbonates using reactive transport modeling in pore networks. *Water Resources Research*, 49(9):6006–6021.
- Noiriel, C., Luquot, L., Madé, B., Raimbault, L., Gouze, P., and van der Lee, J. (2009). Changes in reactive surface area during limestone dissolution: An experimental and modelling study. *Chemical Geology*, 265(1–2):160 – 170.
- Palaz, I. and Marfurt, K. (1997). *Carbonate Seismology*. Society of Exploration Geophysicists.
- Pardo-Iguzquiza, E., Dowd, P. A., Xu, C. S., and Duran-Valsero, J. J. (2012). Stochastic simulation of karst conduit networks. *Advances in Water Resources*, 35:141–150.
- Pardo-Iguzquiza, E., Durán-Valsero, J. J., and Rodríguez-Galiano, V. (2011). Morphometric analysis of three-dimensional networks of karst conduits. *Geomorphology*, 132(1–2):17 – 28.

- Parise, M. and Lollino, P. (2011). A preliminary analysis of failure mechanisms in karst and man-made underground caves in southern Italy. *Geomorphology*, 134(1–2):132 – 143.
- Parkhurst, D. L. and Appelo, C. A. J. (2013). Description of input and examples for PHREEQC version 3 . A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey Techniques and Methods book 6. chapter A43 497 p.
- Petrus, K. and Szymczak, P. (2016). Influence of layering on the formation and growth of solution pipes. *Frontiers in Physics*, 3:92.
- Pittman, E. D. (1974a). Porosity and permeability changes during diagenesis of Pleistocene corals, Barbados, West Indies. *GSA Bulletin*, 85(11):1811–1820.
- Pittman, E. D. (1974b). Porosity and permeability changes during diagenesis of Pleistocene corals, Barbados, West Indies. *GSA Bulletin*, 85(11):1811–1820.
- Plummer, L. N. and Wigley, T. M. L. (1976). The dissolution of calcite in CO₂-saturated solutions at 25 °C and 1 atmosphere total pressure. *Geochimica et Cosmochimica Acta*, 40:191–202.
- Plummer, L. N., Wigley, T. M. L., and L., P. D. (1978). The kinetics of calcite dissolution in CO₂-water systems at 5°C to 60 °C and 0.0 to 1.0 ATM CO₂. *American Journal of Science*, 278:179–216.
- Pomar, L. and Ward, W. C. (1995). *Sequence Stratigraphy and Depositional Response to Eustatic, Tectonic and Climatic Forcing*, chapter Sea-Level Changes, Carbonate Production and Platform Architecture: The Lluçmajor Platform, Mallorca, Spain, pages 87–112. Springer Netherlands.
- QRSS (2013). Map of explored conduits in Ox Bel Ha karst system until year 2012.
- QRSS (2016). List of long underwater caves in Quintana Roo Mexico. <https://caves.org/project/qrss/qrlong.htm>. Accessed: 2016-07-19.
- Rezaei, M., Sanz, E., Raeisi, E., Ayora, C., Vázquez-Suñé, E., and Carrera, J. (2005). Reactive transport modeling of calcite dissolution in the fresh-salt water mixing zone. *Journal of Hydrology*, 311(1–4):282 – 298.

- Robinson, R. B. (1967). Diagenesis and porosity development in Recent and Pleistocene oolites from southern Florida and the Bahamas. *Journal of Sedimentary Research*, 37(2):355–364.
- Rohling, E. J., Fenton, M., Jorissen, F. J., Bertrand, P., Ganssen, G., and Caulet, J. P. (1998). Magnitudes of sea-level lowstands of the past 500,000 years. *Nature*, 394(6689):162–165.
- Sanford Ward E., K. L. F. (1989). Simulation of calcite dissolution and porosity changes in saltwater mixing zones in coastal aquifers. *Water Resources Research*, 25:655–667.
- Scheidegger, A. E. (1961). General theory of dispersion in porous media. *Journal of Geophysical Research*, 66(10):3273–3278.
- Schiller, A. (2014). Internal report on the Tulum field campaign 2014 of the Geological Survey of Austria (GSA) . Collaboration with University of Neuchâtel in course of the joint project XIBALBA, financed by Austrian and Swiss Science Fund within the D-A-CH-programme. .
- SGM (2006). Carta geológico-minera cozumel f16-11. SGM = Servicio Geológico Mexicano.
- Shaw, T. R., Lowe, D. J., and White, W. B. (2000). *Speleogenesis, Evolution of Karst Aquifers*, chapter 2. Historical Perspective, pages 20–43. National Speleological Society.
- Smart, P. L., Beddows, P. A., Coke, J., Doerr, S., Smith, S., and Whitaker, F. F. (2006). Cave development on the Caribbean coast of the Yucatan Peninsula, Quintana Roo, Mexico. *Geological Society of America Special Papers*, 404:105–128.
- Smith, S. L. (2004). The geochemistry and geomicrobiology of a salinity-stratified coastal carbonate aquifer: Yucatan Peninsula, Mexico. PhD Thesis, Department of Earth Sciences, University of Bristol.
- Spratt, R. M. and Lisiecki, L. E. (2016). A late Pleistocene sea level stack. *Climate of the Past*, 12(4):1079–1092.
- Stoessell, R. K., Moore, Y. H., and Coke, J. G. (1993). The occurrence and effect of sulfate reduction and sulfide oxidation on coastal limestone dissolution in yucatan cenotes. *Ground Water*, 31(4):566–575.

- Sukop, M. C., Huang, H., Alvarez, P. F., Variano, E. A., and Cunningham, K. J. (2013). Evaluation of permeability and non-darcy flow in vuggy macroporous limestone aquifer samples with lattice boltzmann methods. *Water Resources Research*, 49(1):216–230.
- Supper, R., Motschka, K., Ahl, A., Bauer-Gottwein, P., Gondwe, B., Alonso, G. M., Romer, A., Ottowitz, D., and Kinzelbach, W. (2009). Spatial mapping of submerged cave systems by means of airborne electromagnetics: an emerging technology to support protection of endangered karst aquifers. *Near Surface Geophysics*, 7(5-6):613–627.
- Szabo, B. J., Ward, W. C., Weidie, A. E., and Brady, M. J. (1978). Age and magnitude of the late Pleistocene sea-level rise on the eastern Yucatan Peninsula. *Geology*, 6(12):713–715.
- Tiab, D. and Donaldson, E. C. (2004). *Petrophysics: Theory and Practice of Measuring Reservoir Rock and Fluid Transport Properties*, chapter 3. Porosity and Permeability. Gulf professional publishing.
- Vacher, H. L. and Mylroie, J. E. (2002). Eogenetic karst from the perspective of an equivalent porous medium. *Carbonates and Evaporites*, 17(2):182–196.
- Vuilleumier, C., Borghi, A., Renard, P., Ottowitz, D., Schiller, A., Supper, R., and Cornaton, F. (2013). A method for the stochastic modeling of karstic systems accounting for geophysical data: an example of application in the region of Tulum, Yucatan Peninsula (Mexico). *Hydrogeology Journal*, 21(3):529–544.
- Ward, W. and Halley, R. B. (1985). Dolomitization in a mixing zone of near-seawater composition, late Pleistocene, northeastern Yucatan Peninsula. *Journal of Sedimentary Research*, 55(3).
- Ward, W. C. and Brady, M. J. (1979). Strandline sedimentation of carbonate grainstones, upper Pleistocene, Yucatan Peninsula, Mexico. *AAPG Bulletin*, 63(3):362–369.
- White, W. B. (2002). Karst hydrology: recent developments and open questions. *Engineering Geology*, 65(2–3):85 – 105.
- Wigley, T. M. L. and Plummer, L. N. (1976). Mixing of carbonate waters. *Geochimica et Cosmochimica Acta*, 40:989–995.

- Zehender, F., Stumm, W., and Fischer, H. (1956). Freie kohlensäure und pH von wasser in calciumkarbonat-löslichkeitsgleichgewicht. *Bulletin Mensual Société Suisse de la Industrie du Gaz et des Eaux*, 36(11):269–275.
- Zhang, Jie and Zhou, Z., Cao, M., and Pan, Y. (2017). *Characteristics and Environmental Significance and Physical and Chemical Properties of Karst Cave Water in Shuanghe Cave, Guizhou Province (in China)*, pages 563–571. Springer Singapore, Singapore.
- Zhou, L. and Selim, H. (2003). Scale-dependent dispersion in soils: An overview. *Advances in Agronomy*, 80:223 – 263.