PERIÓDICO TCHÊ QUÍMICA
ARTIGO ORIGINAL

ESPECIAÇÃO GEOQUÍMICA E SIMULAÇÃO DE MODO BATCH NOS AMBIENTES DEPOSICIONAIS DE CARBONATOS

GEOCHEMICAL SPECIATION AND BATCH MODE SIMULATION IN THE CARBONATE DEPOSITIONAL ENVIRONMENTS

KLUNK, Marcos Antônio[1]*; DASGUPTA, Sudipta[2]; DAS, Mohuli[2]; WANDER, Paulo Roberto[1]; DI CAPUA, Andrea[3,4]

[1] University of Vale do Rio dos Sinos, Department of Mechanical Engineering, São Leopoldo, RS, Brazil

[2] Indian Institute of Technology Bombay (IIT Bombay), Department of Earth Sciences, Powai, Mumbai, India.

[3] CNR- Istituto per la Dinamica dei Processi Ambientali-Sezione di Milano, Via Mangiagalli, Milano, Italy

[4] Università Degli Studi di Milano-Bicocca, Piazza della Scienza, Milano, Italy

** Correspondence author*
e-mail: marcosak@edu.unisinos.br

Received 12 August 2019; received in revised form 30 October 2019; accepted 14 November 2019

RESUMO

A modelagem geoquímica tem sido freqüentemente usada para entender e interpretar interações água-rocha em bacias sedimentares. Dados termodinâmicos, parâmetros cinéticos, métodos numéricos, histórico e condições de contorno são fatores que afetam qualquer sistema de modelagem geoquímica. No presente estudo, tentamos estabelecer um modelo de especiação geoquímica comparando a interação da água de formação e da rocha carbonática nos ambientes deposicionais carbonáticos das sucessões cambrianas da área de Bachu e Tarim. Um estudo comparativo da especiação geoquímica foi realizado usando quatro softwares diferentes: PHREEQC™, GWB™, TOUGHREACT™ e GEODELING. GEODELING é um simulador geoquímico onde os detalhes são apresentados mais adiante neste trabalho. Todo o software foi analisado minuciosamente, considerando a distribuição, mobilidade e disponibilidade de espécies químicas em ambientes geológicos. Resultados muito semelhantes na especiação são observados ao trabalhar com sistemas de baixa temperatura. Uma discrepância pode ser observada nos resultados ao trabalhar com altas temperaturas. No entanto, uma formulação completa de Newton-Raphson, o dimensionamento de equações algébricas e a troca de espécies principais ajudam a reduzir a possibilidade de falhas do método numérico usado no PHREEQC™.

Palavras-chave: *Simulação Numérica; Diagênese; GWB™, PHREEQC™, TOUGHREACT™.*

ABSTRACT

Geochemical modeling has been frequently used to understand and interpret water-rock interactions in sedimentary basins. Thermodynamic data, kinetic parameters, numerical methods, boundary history, and boundary conditions are factors affecting any geochemical modeling system. In the present study, we have attempted to establish a geochemical speciation model by comparing the interaction of formation water and carbonate rock in the carbonate depositional settings of Cambrian successions of Bachu and Tarim area. A comparative study of geochemical speciation has been performed using four different software: PHREEQC™, GWB™, TOUGHREACT™, and GEODELING. GEODELING is a geochemical code simulator that we have developed, and the details are presented further in this work. All the software has been analyzed minutely, considering the distribution, mobility, and availability of chemical species in geological environments. Very similar results in speciation are observed while working with low-temperature systems. A discrepancy can be observed in the results while working with high temperatures. However, a thorough Newton-Raphson formulation, scaling of algebraic equations and master-species switching helps to reduce the possibility of failures of the numerical method used in PHREEQC™.

Keywords: Numerical Simulation; Diagenesis; GWB™, PHREEQC™, TOUGHREACT™.

DOI: 10.52571/PTQ.v16.n33.2019.751_Periodico33_pgs_736_748.pdf

1. INTRODUCTION

The scientific community has progressed in geochemical modeling for both natural and hypothetical environments (Manoj *et al.,* 2019; Johnson *et al.,* 2018; Fowler *et al.,* 2018; Somasekhar *et al.,* 2018; Singh *et al.,* 2017). These developments are associated with numerical techniques, which are capable of solving complex mathematical problems, along with incorporating improvements in evaluating capability of computers (Singh *et al.,* 2017). Geochemical modeling studies evolved during the 1960's after the works of Helgeson and James (1968), Helgesson (1967a, 1967b) and Garrels and Mackenzie (1967) made remarkable progress in this field (Apollaro *et al.,* 2019; Eppner *et al.,* 2017). The first simulations were initially studied for understanding the chemical reactions in aquatic environments in order to solve water pollution hazards. These simulations also assessed the diagenetic processes such as natural formation and alteration of rocks (Lai *et al.,* 2018; Limarino *et al.,* 2017; Crémière *et al.,* 2016; Klunk *et al.,* 2015; Udchachon *et al.,* 2011). It is impossible to reproduce the exact behavior of most geochemical systems in the laboratory due to the complexity and diversity in time scale of the reactions in geological environments (Klunk *et al.,* 2018).

It is important to take care of our defined goals and expectations of what the modeling will reveal while producing a geochemical model (Lassin *et al.,* 2018). Our defined goals were to focus on the major issues and to identify the processes which control the geochemical system (Buccianti *et al.,* 2018; Osorno *et al.,* 2015; Mason *et al.,* 2015; Verma, 2012; Bernhard, 1999). These processes might reveal the kind of modeling which is most appropriate for the research of geological environment. Generally, the processes involved in geochemical systems are not simple (Guseva and Kopylova, 2013; Wang *et al.,* 2010; Fritz *et al.,* 2010; Spiteri *et al.,* 2007).

Hence, it can be advantageous to choose simpler models with lesser details as it will provide more results for analysis. In this paper, a comparative study of geochemical speciation using PHREEQC™, TOUGHREACT™, Geochemist's Workbench™ (GWB), and GEODELING has been performed (Alvarez *et al.,* 2018; Klajmon *et al.,* 2017; De Lucia and Kühn 2013; Wolf *et al.,* 2017; Shevalier *et al.,* 2014; Xu *et al.,* 2011; Shabani *et al.,* 2019; Cleverley and Bastrakov 2005; Kong *et al.,* 2013; Sellerino *et al.,* 2019; Bethke 2008, 2002; Parkhurst and Appelo 1999; Xu and Pruess 1998). GEODELING is a software that have developed to fulfill this purpose (Klunk *et al.,* 2017). In this comparative study, the distribution, mobility, and availability of chemical species in geological environments have been verified (Baccar and Fritz, 1993). The efficiency and accuracy of GEODELING software have also been established. The chemical behavior of mineral compounds from the North Sea (Morad *et al.,* 1990) has been modeled in this particular study.

2. MATERIALS AND METHODS

2.1. Geochemical speciation modeling

The concept of speciation is applied to several chemical systems and is most commonly applied in the case of aqueous solutions (Klunk *et al.,* 2017; Batley *et al.,* 2009). These aqueous solutions typically include natural water systems viz., sea, river, lake, and ground waters. The natural water systems are multi-component solutions where a network of interactions is established (Klunk *et al.,* 2017). This leads to the formation of chemical species which have different thermodynamic stability (Ball and Nordstrom, 1991). The diverse chemical behavior of ions that are present in the medium leads to a different quantitative distribution of species, which further depends on the kinetics of the process (Dutta *et al.,* 2010; Peng, 2009; Drever, 1997). Chemical speciation is used to evaluate the distribution of certain chemical species with different chemical forms and oxidation states (Purkait and Mukherjee, 2008; De Stefano *et al.,* 1999; Foti *et al.,* 2000). A geochemical modeling system attempts to map all the reactions and events of the modeled environment (Klunk *et al.* 2018; Chidambaram *et al.,* 2011a). These events include complexation, oxidation, reduction, precipitation, and dissolution. The geochemical model system is also influenced by environmental conditions such as temperature, pH and surface properties (Wu *et al.,* 2015; Foti *et al.* 2004). To fulfill the purpose of our study, a code simulator called GEODELING is being developed. Its functionalities and features have been further explained in this paper.

2.1.1. GEODELING - Speciation Model

GEODELING has been developed from the thermodynamic model based on the numerical method of DISSOL™ (Fritz, 1975, 1981). The mentioned thermodynamic code was expanded through the introduction of kinetic laws governing the geochemical speciation for making numerical

simulations possible in time functions (Lasaga, 1984; Helgeson and James, 1968). Therefore, in the kinetic and thermodynamic model of the GEODELING code, the molecular diffusion of the aqueous phase and a porous layer formed by the dissolution or precipitation of minerals control the mineral reaction rates. The speciation code has been applied in the form of the physical, a chemical, aqueous, and geochemical tool with intuitive and interactive interface (Klunk *et al.,* 2017). The language chosen for GEODELING is C++. It is a well-known programming language that has a bias towards programming of the system. It also supports efficient low-level computation, generic programming, object-oriented programming and data abstraction (Dale and Weems, 2014). It also provides impactful and flexible mechanisms for “abstraction” i.e., construction of the language, which allows the programmer to introduce and implement contemporary objects matching the required concepts of an application.

2.1.2. Geochemist's Workbench™ – GWB

Department of Geology in the University of Illinois at Urbana-Champaign developed GWB™ in 1978. GWB™ uses modules SpecE8 in React mode as a speciation model (Bethke, 2008, 2002). An initial geochemical system is set in order to attain thermodynamic equilibrium (Kong *et al.,* 2013). This software automatically installs a specific quantity of water (1 kg) in the system, followed by setting a specific quantity of solutes. During this period, the GWB™ starts calculating and interacting, which further leads to the speciation model. The output data is generated when GWB™ finishes the simulation (Klunk *et al.,* 2018). The information of the output files includes temperature, pressure, ionic strength, pH, solution density, water activity, ionic strength, the mass of solvent, ionic strength, and mass of the rock (Cleverley and Bastrakov, 2005).

An aqueous species index has been generated with the solutes of the simulation. GWB™. solved a particular set of nonlinear algebraic equations (Sellerino *et al.,* 2019). These equations were formulated using the mass action equation and the equilibrium constant. It is also correspondent to aqueous species like minerals or gas from the database simultaneously. GWB™ solves the mass action equation by resolving the system’s mass balance. GWB™ software solves such equations with the aid of Newton-Raphson method (Klunk *et al.,* 2015).

2.1.3. PHREEQC™

PHREEQC™ is a software that has been designed for performing a broad range of geochemical calculations (Klunk *et al.,* 2017; Parkhurst and Appelo, 1999). It is written using programming languages C and C++ (Alvarez *et al.,* 2018; Klajmon *et al.,* 2017). PHREEQC™ is competent for the following functions: (1) calculation of the speciation and saturation index; (2) calculation of the reactions in "batch model" and one-dimensional (1D) transportation; (3) utilization of the Pitzer model for high salinity water outside the application range of the Debye-Huckel theory (Klunk *et al.,* 2015; De Lucia and Kühn, 2013; Pitzer, 1991). The software operates an integral numerical method and allows the solution of standard differential equations to be discerned for reconstructing the three-dimensional (3D) trajectories (Klunk *et al.,* 2018; Parkhurst and Plummer, 1993).

2.1.3. TOUGHREACT™

Xu and Pruess (1998) developed the first version of TOUGHREACT™, which introduces reactive geochemistry heat flow along with multi-phase fluid in TOUGH2™. TOUGHREACT™ requires 64-bit arithmetic for the implementation to be successful (Wolf *et al.,* 2017; Klunk *et al.,* 2015; Zhang, 2013). The code requires understanding of the fundamental equations of fluid flow and non-isothermal multiphase transport occurring within geological environment (Shabani *et al.,* 2019; Klunk *et al.,* 2017; Jin, 2007). It also needs a fundamental knowledge of the numerical solution of the equations which are used to describe similar geological processes (Klunk *et al.,* 2018; Shevalier *et al.,* 2014; Xu *et al.,* 2011; Xu and Pruess, 1998). The simulator has an application in one-dimensional, two-dimensional, or three-dimensional geologic domains, respectively. These domains are comprised of heterogeneous physical and chemical components. Hence, the results can be used for a wide range of geological conditions (Wolf *et al.,* 2017; Pruess *et al.,* 1999). A data base module that employs the thermodynamic equation of state (EOS) monitors the temperature and pressure. The code computes the speciation of the constituent solutes of formation water and marine connate water, which acts as a function of temperature and pressure (Shabani *et al.,* 2019; Pruess, 1991). For discretization, the numerical methods with geometrical parameters are used, which are resolved using the Newton - Raphson method (Xu *et al.,* 2011; Pruess, 1991).

2.2. Initial conditions of the water speciation and batch mode simulation

A numerical simulation study was carried out with GWB™, PHREEQC™, and TOUGHREACT™ software, which predicted the geochemical speciation of formation water (from Nordstrom *et al.,* 1994). The deciphered results were compared with our own developed code (GEODELING). The optimum temperatures used for simulations are 25°, 40°, 60°, 80°, 100°, 120°, 140°, 150°, and 160°C, respectively. Baccar and Fritz (1993) studied several interactions between the rock and formation water in different temperatures. The composition of formation water was assembled from Nordstrom *et al.* (1994). The major elements of the chemical composition of formation water are exhibited in Table 1.

Table 1. Composition of the formation water with pH 8.22.

Chemical Species	Composition (mM/L)
K^+	10.45
Na^+	479.32
Ca^{2+}	10.53
Mg^{2+}	54.39
SO_4^{2-}	28.89
Cl^-	559.5

The initial conditions of simulation using the GEODELING have the combination of the chemical species as its starting point. The logarithmic activity of ionic species calculates and represents the contemporary concentrations (Sahu *et al.,* 2016). The effect of interaction between the ions of the solution is eliminated by the activity concentration (Saxena *et al.,* 2012). Modeling of a carbonate rock system was proposed to complement the tests of our own code. In this work, the core samples of Well Batan-5 from the Lower Cambrian Xiaoerbulak Formation in Bachu area (Peng *et al.,* 2018), and that of Well Mabei-1 from the Middle Cambrian Shayilik Formation in North Tarim area have been studied. Dissolution fluids of carbonate rock comprise of meteoric fresh water (mainly consisting of CO_2) and acid fluid (mainly consisting of CO_2 and organic acid) (Chidambaram *et al.,* 2011b). These are related to thermal maturity of organic matter associated with deep hydrothermal fluid (mainly with CO_2) and burial condition (Srivastava 2013; Ponomarev *et al.* 2017b; Moore 1989; Mazzullo and Harris 1992).

Initial conditions have partial pressure amounting to 2.0 MPa of the CO_2 solution (at pH value of about 5.0). The experimental temperatures were set with respect to the burial heat evolution of the Cambrian sedimentary succession in the Bachu Area and the North Tarim Area (Peng *et al.,* 2018). In Bachu Area, the succession is closer to the surface with the highest temperature of 144°C, whereas in the North Tarim Area, the Cambrian succession is buried at greater depth with temperature of about 234°C. The hydrostatic pressure was set at the particular depths, which were correspondent to the temperatures of the strata (slightly adjusted).

The samples are shown to be dolomitic limestone from the section authentication. X-diffraction (Peng *et al.,* 2018) reveals that the dolomitic limestone sample shows calcite concentration of 52.49% and dolomite concentration of 44.18%, respectively.

3. RESULTS AND DISCUSSION

Events that are predicted by numeric simulation between 25° and 160°C with the aid of GWB™, PHREEQC™, and TOUGHREACT™ software as compared to GEODELING, are summarized in Figure 1. Analyzing the trend of simulations, we observed two significant episodes: 1) events developing at low temperatures (25°–100°C) and 2) events developing at high temperatures (120°–160°C). The logarithm of ion activity is dependent on the temperature of the reaction system. We observe similar behavior of the software at low temperatures. The numerical method of software attributes to the unique characteristics at higher temperature, thus causing discrepancy in the results.

We observed the similarity in low-temperature events while correlating the results of GEODELING with the other software. GEODELING reproduces the logarithm of the activity of Mg^{2+}, Ca^{2+}, K^+, and SO_4^{2-} ions for their speciation. Again, the ions like Na+ and Cl- when correlated with GWB™, PHREEQC™, and TOUGHREACT™ software, shows diverse behavior at high temperatures. The saturation index event to carbonate rock shows similar behavior in all the four software. The geochemical modeling predicts the dissolution of calcite and dolomite from the acids fluids found in meteoric fresh water and acid fluid (Fig. 2).

Figure 3a and Figure 3b show the dissolution of calcite and dolomite. It can also be noted that the anhydrite does not get dissolved with its saturation index in the region of precipitation. In the generated models, this mineral did not suffer due to acidic action of the fluid. Such

behavior can be seen by the micrograph of Figure 3a.

GEODELING code was built to predict the different species of a geological environment. The simulations of this study permitted a comparative study of GEODELING behavior with speciation of other commercial software (Fig. 1). The results revealed different results for different codes during the modeling of two temperature events. The convergence of outcomes is less evident at high temperatures than at low temperatures. Usually, at low temperatures, the results of the simulation exhibit similar behavior as each software applies identical numerical methods for solving various sets of reactions. At low temperatures (T < 100°C), the similarity of the code results can be observed because of the involvement of low kinetic energy in the reactions. Each simulator possesses its algorithms established on the numerical methods which depend on kinetic and thermodynamic parameters contained in the database.

For higher temperature reactions (120°–160°C), the kinetic energy increases, thereby generating different results irrespective of the model. Accordingly, the GEODELING system produces dissimilar results for sodium and chloride ions. However, when compared to GEODELING, other software such as GWBTM, PHREEQC™, and TOUGHREACT™ have similar approaches while operating with high temperatures. This particular behavior was also observed in calcium and magnesium ions. Generally, GWB™ and TOUGHREACT™ reproduce a similar behavior from 120°C.

These equations depend on kinetic as well as thermodynamic data, thereby directly affecting the medium of the reaction. In the case of temperatures above 120°C, the thermodynamic and kinetic conditions acquire an anomalous behavior assuming constant values of “500” in numeric treatment. The appearance of “500” value is a reference approach to indicate that no value has been calculated. This comparative study revealed two episodes, depending on the temperature. The first and second stage are correspondent to the temperature range of 25°–100°C and 120°–160°C respectively. The first stage verifies the convergence of the results, and the second stage confirms a peculiarity in the numerical method. Users should be cautious while selecting a geochemical speciation software based on the temperature range, as various systems can generate discrepant behaviors.

Batch mode simulations were executed at 25°C, and software packages like GWB™, PHREEQC™, TOUGHREACT™, and GEODELING were employed. These batch mode simulations react in a closed system without flux. Typically, carbonate rock buried at very low depth, and temperature rises slowly. The fluid flow rates are also quite low, limiting the migration of elements en-masse through the rocks. However, over the years, carbonate-rock interactions tend to attain chemical equilibria. The batch mode focuses on achieving that particular steady state. Due to changes in temperature and fluid flow, the water contained in the pores cannot be in chemical equilibrium with its enclosing mineral phases. Therefore, the carbonate reactions are the result of this gradual tendency towards a state of progressive equilibrium, which never accomplishes a finite state. Hence, a condition approximated to a "steady state" is more suitable to describe the chemical state of rocks.

Figure 2 provides the progress of carbonate reactions for different simulations in batch mode. The minerals are initially observed to be far away from equilibrium. Gradually, the minerals achieve the "steady-state" condition. The four geochemical modeling packages manifest similar behavior in the dissolution of dolomite and calcite minerals. We also observed the phenomenon of intense nucleation with the carbonates.

The geochemical results reveal that the dolomitic limestone with calcite concentration of 52.49% has a higher dissolution rate at a particular pressure and temperature than the residual sand. The fine-grained crystalline dolomite with no calcite indicates that dissolution ability of calcite is higher than dolomite under both near-surface and deep burial conditions. Places where calcite and dolomite coexists, also demonstrates that acidic fluid dissolves calcite before dolomite. Therefore, irrespective of rock types, transitional carbonate rocks with higher calcite concentration in burial state are more susceptible to dissolution and henceforth, form high quality reservoirs.

For the residual sand with fine-grained dolomite crystals, observations with the aid of a polarizing microscope and CT scan images demonstrate that the smaller pores expand and integrate, forming bigger pores or caves comprising smooth dissolution edges, after dissolution (thin section images in Figs. 3a – 3b). When observed with the aid of polarizing microscope, the sample consisting of a small proportion of anhydrite showed cracks developing in contact with pores before dissolution, but the trace of dissolution along the cracks cannot be identified after the occurrence of dissolution (thin

section images in Fig. 3c). There is a minute variation in the models produced by TOUGHREACT™ as a result of using the numerical method for simulation of the reactions. However, GWB™, PHREEQC™, and GEODELING using almost identical numerical methods at particular range of temperatures reveal similar plots.

4. CONCLUSIONS

The present study of geochemical speciation and batch mode using the application of GWB™, PHREEQC™, and TOUGHREACT™ codes along with GEODELING for the simulating the formation of water and carbonate rocks provides the following conclusions:

1) The reactions at low temperatures (from 25°C to 100°C) consisting of multiple simulators produce similar behaviors. At such temperature range, involving low energy, the thermodynamic parameters, and reaction kinetics behave in accordance with the particularities of each code. GWB™, PHREEQC™, TOUGHREACT™ and GEODELING software used the numerical methods which can attain only limited convergence of results, with high precision in case of reactions involving geological environments at low-temperature.

2) From 120°C to 160°C temperature range with higher kinetic energy and greater intensity of the reactions, the simulations with all the four software generate diverse results. This diversity is due to the utilization of different mass balance equations for calculating chemical speciation by the different software.

3) In this temperature range, the simulators use several mathematical interpolations that are less stable and produce a lower convergence of results. Thereby, each simulator pursues its own ideal set of numerical solutions for achieving the equilibrium.

4) The geochemical speciation was pursued to compare the results of different simulators for predicting the various chemical species of a geological environment. The application of GEODELING allows correlation of results with other software such as GWB™, PHREEQC™, TOUGHREACT™ possessing a high degree of acceptance for low temperatures. Near high temperatures, users need to be cautious while choosing the appropriate geochemical modeling software. The user should undertake a precursory study utilizing the temperature information with the available codes for verifying the convergence.

5) In batch mode simulation at low temperatures (around 25°C), various simulators proliferate altogether divergent behaviors. In this particular range of temperatures with low energy, the thermodynamic parameters and reaction kinetics are treated with respect to the particularities of each code. The numerical methods of GWB™, PHREEQC™ TOUGHREACT™, and GEODELING software have achieved limited convergence of results, with low precision expected for reactions involving carbonate rocks at low-temperature geological environments. Consequently, each simulator perceives its best set of numerical solutions for attaining the equilibrium.

6) Users should be careful while selecting a specific geochemical modeling software because the knowledge of the temperature range is an important factor for choosing a simulator. With the temperature information, the user should commence with a preliminary study of the available codes in order to verify the convergence of the observed results in the formation of water and carbonate rocks.

5. ACKNOWLEDGMENTS

The authors acknowledge the Brazilian agencies CNPq (National Council of Technological and Scientific Development – Brasília, DF, Brazil), CAPES (Coordination for the Improvement of Higher Education Personnel) for the research funding, and the generous assistance of all the people from the company who granted us access to their database and perception information.

6. REFERENCES

1. Manoj, S., Thirumurugan, M., Elango, L. Hydrogeochemical modelling to understand the surface water–groundwater interaction around a proposed uranium mining site. Journal of Earth System Science, **2019**, 128(49), 1-14.
2. Johnson, L. M., Rezaee, R., Kadkhodaie A., Smith, G., Yu, H. Geochemical property modelling of a potential shale reservoir in the Canning Basin (Western Australia), using Artificial Neural Networks and Geostatistical tools; Computers & Geosciences, **2018**, 120, 73-81.
3. Fowler, A. P. G., Ferguson, C., Cantwell, C. A., Zierenberg, R. A., McClain, J., Spycher, N., Dobson, P. A conceptual geochemical model of the geothermal system at Surprise Valley, C. A. Journal of

Volcanology and Geothermal Research, **2018**, 353, 132-148.
4. Somasekhar, V., Ramanaiah, S., Sarma, D. S. Geochemical characterization of the siliciclastic rocks of Chitravati Group, Cuddapah Supergroup: Implications for provenance and depositional environment. Journal of Earth System Science, **2018**, 127-154.
5. Singh, C. K., Kumar, A., Shashtri, S., Kumar, A., Kumar, P., Mallick, J. Multivariate statistical analysis and geochemical modeling for geochemical assessment of groundwater of Delhi, India. Journal of Geochemical Exploration, **2017**, 175 59-71.
6. Helgeson, H. C., James, W. R. Activity coefficients in concentrated electrolyte solutions of elevated temperatures. Journal of the American Chemical Society, **1968**, S 130.
7. Helgeson, H. C. Thermodynamics of complex dissociation in aqueous solutions at. elevated temperatures. Journal of Physical Chemistry, **1967a**, 71, 3121-3136.
8. Helgeson, H. C. Solution chemistry and metamorphism. In: Abelson P.H. (ed.) Researches in Geochemistry, v. II, New York, Wiley, **1967b**, 362-404.
9. Garrels, R. M., Mackenzie, F. T. Origin of the chemical compositions of some springs and lakes. Equilibrium concepts in natural water systems. American Chemical Society, **1967**, 67, 222-242.
10. Apollaro, C., Perri, F., Le Pera, E., Fuoco, I., Critelli, T. Chemical and minero-petrographical changes on granulite rocks affected by weathering processes. Frontiers in Earth Science, **2019**, 13(2), 247-261.
11. Eppner, F., Pasquier, P., Baudron, P. A coupled thermo-hydro-geochemical model for standing column well subject to CO_2 degassing and installed in fractured calcareous aquifers. Geomechanics for Energy and the Environment, **2017**, 11, 14-27.
12. Lai, J., Wang, G., Wang, S., Cao, J., Li, M., Pang, X., Qin, Z. Review of diagenetic facies in tight sandstones: Diagenesis, diagenetic minerals, and prediction via well logs. Earth-Science Reviews, **2018**, 185, 234-258.
13. Limarino, C. O., Giordano, S. R., Rodriguez Albertani, R. J. Diagenetic model of the Bajo Barreal formation (Cretaceous) in the southwestern flank of the Golfo de San Jorge Basin (Patagonia, Argentina), Marine and Petroleum Geology, **2017**, 88, 907-931.
14. Crémière, A., Lepland, A., Chand, S., Sahy, D., Kirsimäe, K., Bau, M., Brunstad, H. Fluid source and methane-related diagenetic processes recorded in cold seep carbonates from the Alvheim channel, central North Sea. Chemical Geology, **2016**, 432, 16-33.
15. Klunk, M. A., Damiani, L. H., Feller, G., Rey, M. F., Conceiçao, R. V., Abel, M., De Ros, L. F. Geochemical modeling of diagenetic reactions in Snorre Field reservoir sandstones: a comparative study of computer codes. Brazilian Journal of Geology, **2015**, 45, 29-40.
16. Udchachon, M., Thassanapak, H., Feng, Q., Chonglakmani, C. Geochemical constraints on the depositional environment of Upper Devonian radiolarian cherts from Loei, north-eastern Thailand. Frontiers in Earth Science, **2011**, 5(2), 178-190.
17. Klunk, M. A., Dasgupta, S., Conceiçao, R. V. Computerized geochemical modeling of burial diagenesis of the Eocene turbidite reservoir elements: Urucutuca Formation, Espírito Santo Basin, southeastern Brazil passive margin. Journal of Palaeogeography, **2018**, 7, 12-26.
18. Lassin, A., André, L., Devau, N., Lach, A., Beuvier, T., Gibaud, A., Azaroual, M. Dynamics of calcium carbonate formation: geochemical modeling of a two-step mechanism. Geochimica et Cosmochimica Acta, **2018**, 240, 236-254.
19. Buccianti, A., Lima, A., Albanese, S., De Vivo, B. Measuring the change under compositional data analysis (CoDA): Insight on the dynamics of geochemical systems. Journal of Geochemical Exploration, **2018**, 189, 100-108.
20. Osorno, J., Rangel, A. Geochemical assessment and petroleum systems in the Sinú-San Jacinto Basin, northwestern Colombia. Marine and Petroleum Geology, **2015**, 65, 217-231.
21. Mason, S. E., Corum, K. W., Ramadugu, S. K. Fundamental insights about environmental interface reactivity from DFT calculations of geochemical model systems. Surface Science, **2015**, 631, 48-56.
22. Verma, M. P. GeoSys.Chem: Estimate of reservoir fluid characteristics as first step in

geochemical modeling of geothermal systems. Computers & Geosciences, **2012**, 49, 29-37.
23. Bernhard, M. Quality control and reference materials in speciation analysis. Fresenius Journal of Analytical Chemistry, **1999**, 363, 439-445.
24. Guseva, N., Kopylova, Y. Geochemical Mobility of Chemical Elements in Saline Lake Systems in Khakassia (Russia). Procedia Earth and Planetary Science, **2013**, 7, 325-329.
25. Wang, P., Anderko, A., Springer, R. D., Kosinski, J. J., Lencka, M. M. Modeling chemical and phase equilibria in geochemical systems using a speciation-based model. Journal of Geochemical Exploration, **2010**, 106(1-3), 219-225.
26. Fritz, B., Jacquot, E., Jacquemont, B., Baldeyrou-Bailly, A., Rosener, M., Vidal, O. Geochemical modelling of fluid–rock interactions in the context of the Soultz-sous-Forêts geothermal system. Comptes Rendus Geoscience, **2010**, 342(7-8), 653-667.
27. Spiteri, C., Slomp, C. P., Regnier, P., Meile, C., Van Cappellen, P. Modelling the geochemical fate and transport of wastewater-derived phosphorus in contrasting groundwater systems. Journal of Contaminant Hydrology, **2007**, 92(1-2), 87-108.
28. Alvarez, A. C., Blom, T., Lambert, W. J., Bruining, J., Marchesin, D. Analytical and numerical validation of a model for flooding by saline carbonated water. Journal of Petroleum Science and Engineering, **2018**, 167, 900-917.
29. Klajmon, M., Havlová, V., Červinka, R., Mendoza, A., Franců, J., Berenblyum, R., Arild, Ø. REPP-CO_2: Equilibrium Modelling of CO_2-Rock-Brine Systems. Energy Procedia, **2017**, 114, 3364-3373.
30. De Lucia, M., Kühn, M. Coupling R and PHREEQC: Efficient Programming of Geochemical Models. Energy Procedia, **2013**, 40, 464-471.
31. Wolf, J. L., Fischer, S., Rütters, H., Rebscher, D. Reactive Transport Simulations of Impure CO_2 Injection into Saline Aquifers Using Different Modelling Approaches Provided by TOUGHREACT V3.0-OMP. Procedia Earth and Planetary Science, **2017**, 17, 480-483.
32. Shevalier, M., Dalkhaa, C., Humez, P., Mayer, B., Becker, V., Nightingale, M., Zhang, G. Coupling of TOUGHREACT-Geochemist Workbench (GWB) for Modeling Changes in the Isotopic Composition of CO_2 Leaking from a CCS Storage Reservoir. Energy Procedia, **2014**, 63 3751-3760.
33. Xu, T., Spycher, N., Sonnenthal, E., Zhang, G., Zheng, L., Pruess, K. TOUGHREACT Version 2.0: A simulator for subsurface reactive transport under non-isothermal multiphase flow conditions. Computers & Geosciences, **2011**, 37(6), 763-774.
34. Shabani, B., Vilcáez, J. TOUGHREACT-CO_2Bio – a new module to simulate geological carbon storage under biotic conditions (Part 1): the multiphase flow of CO_2-CH_4-H_2-H_2S gas mixtures. Journal of Natural Gas Science and Engineering, **2019**, 63, 85-94.
35. Cleverley, J. S., Bastrakov, E. N. K2GWB: Utility for generating thermodynamic data files for The Geochemist's WorkbenchTM at 0–1000°C and 1–5000 bar from UT2K and the UNITHERM database. Computers & Geosciences, **2005**, 31(6), 756-767.
36. Kong, X-Z., Tutolo, B. M., Saar, M. O. DBCreate: A SUPCRT92-based program for producing EQ3/6, TOUGHREACT, and GWB thermodynamic databases at user-defined T and P. Computers & Geosciences, **2013**, 51, 415-417.
37. Sellerino, M., Forte, G., Ducci, D. Identification of the natural background levels in the Phlaegrean fields groundwater body (Southern Italy). Journal of Geochemical Exploration, **2019**, 200, 181-192.
38. Bethke, C. M. GWB Reaction Modeling Guide-A User's Guide to React and Gtplot. University of Illinois, Urbana, IL, **2008**, 74p.
39. Bethke, C. M. The Geochemists Workbench Version 4.0: A User's Guide. University of Illinois, Urbana, IL, **2002**, 224p.
40. Parkhurst, D. L., Appelo, C. A. J. User's guide to PHREEQC-a computer program for speciation, batchreaction, one-dimensional transport, and inverse geochemical calculations.Water-Resources Investigations Report 99-4259. Reston, Virginia: U.S. Geological Survey, **1999**, 312.
41. Xu, T., Pruess, K. Coupled modeling of non-isothermal multiphase flow, solute transport and reactive chemistry in porous and fractured media: 1. Model development and validation, Lawrence

Berkeley National Laboratory Report LBNL-42050, Berkeley, California, **1998**.
42. Klunk, M. A., Ponomarev, A. A., Dasgupta, S., Das, M. Arsenic Speciation in Groundwater using the Softwares PHREEQC, GWB, and GEODELING Southern Brazilian Journal of Chemistry, **2017**, 25 30–35.
43. Baccar, M. B., Fritz, B. Geochemical modelling of sandstone diagenesis and its consequences on the evolution of porosity. Applied Geochemistry, **1993**, 8, 285-295.
44. Morad, S., Bergan, M., Knarud, R., Nystuen, J. P. Albitization of detrital plagioclase in Triassic reservoir sandstones from the snorre field, Norwegian North Sea. Journal of Sedimentary Research, **1990**, 60, 411-425.
45. Batley, G. E., Francesconi, K. A., Maher, W. A. The role of speciation in environmental chemistry and the case for quality criteria. Environmental Chemistry, **2009**, 6(4), 273-274.
46. Ball, J. W., Nordstrom, D. K. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. Open-File Report, **1991**, 91-183.
47. Dutta, S., Mallick, M., Mathews, R. P., Mann, U., Greenwood, P. F., Saxena, R. Chemical composition and palaeobotanical origin of Miocene resins from Kerala-Konkan Coast, western India. Journal of Earth System Science, **2010**, 119(5), 711-716.
48. Peng, S. Characterization of solute transport parameters in leach ore: inverse modeling based on column experiments; Frontiers of Earth Science in China, 2009, 3(2), 208-213.
49. Drever, J. I. The Geochemistry of Natural Waters (3rd ed), New Jersey, Prentice-Hall Inc, **1997**, 436p.
50. Purkait, B., Mukherjee, A. Geostatistical analysis of arsenic concentration in the groundwater of Malda district of West Bengal, India. Frontiers of Earth Science in China, **2008**, 2(3), 292-301.
51. De Stefano, C., Gianguzza, A., Piazzese, D., Sammartaus, S. Speciation of low molecular weight carboxylic ligands in natural fluids: protonation constants and association with major components of seawater of oxydiacetic and citric acids. Analytica Chimica Acta, **1999**, 398(1), 103-110.
52. Foti, C., Gianguzza, A., Piazzese, D., Trifiletti, G. Inorganic speciation of organotin (IV) cations in natural waters with particular reference to seawater. Chemical Speciation and Bioavailability, **2000**, 12(2), 41-52.
53. Chidambaram, S., Karmegam, U., Sasidhar, P., Prasanna, M. V., Manivannan, R., Arunachalam, S., Manikandan, S., Anandhan, P. Significance of saturation index of certain clay minerals in shallow coastal groundwater, in and around Kalpakkam, Tamil Nadu, India. Journal of Earth System Science, **2011a**, 120(5), 897-909.
54. Wu, Z., Wu, J., Lu, G. A one-way coupled atmospheric-hydrological modeling system with combination of high-resolution and ensemble precipitation forecasting. Frontiers of Earth Science, **2015**, 10(3), 432-443.
55. Foti, C., Gianguzza, A., Milea, D., Millero, F. J., Sammartano, S. Speciation of trialkyltin(IV) cations in natural fluids. Marine Chemistry, **2004**, 85(3-4), 157-167.
56. Fritz, B. Etude thermodynamique et simulation des réactions entre minéraux et solutions. Application a la géochimie des altérations et des eaux continentals. Sciences Géologiques – Bulletins et Mémoires, **1975**, 41, 152.
57. Fritz, B. Etude therrnodynamique et modélisation des réactions hydrothermales et diagénétiques. Sciences Géologiques – Bulletins et Mémoires, **1981**, 65, 197.
58. Lasaga, A. C. Chemical kinetics of water-rock interactions. Journal of Geophysical Research: Solid Earth, **1984**, 89(B6), 4009-4025.
59. Dale, N. B., Weems, C. Programming and problem solving with C++. Jones Bartlett Publishers, **2014**, 1068p.
60. Pitzer, K. S. Activity coefficients in electrolyte solutions. 2nd edition. C.R,C. Press. Chapter 3. Pitzer, K.S. Ion interaction approach. T D Corr., **1991**, 5-153.
61. Parkhurst, D. L., Plummer, L. N. Geochemical models. In: ALLEY, W. M. Regional ground-water quality. New York: Van Nostrand Reinhold, **1993**, 199-225.
62. Zhang, W. Effect of modeling factors on the dissolution-diffusion-convection process during CO_2 geological storage in deep saline formations. Frontiers in Earth

Science, **2013**, 7(2), 238-256.
63. 63 Jin, Y. Theory and application for retrieval and fusion of spatial and temporal quantitative information from complex natural environment. Frontiers in Earth Science, **2007**, 1(3), 284-298.
64. Pruess, K., Oldenburg, C., Moridis, G. TOUGH2 user's guide, Version 2.0, Lawrence Berkeley Laboratory Report LBL-43134, Berkeley, California, **1999**.
65. Pruess, K. TOUGH2: A general numerical simulator for multiphase fluid and heat flow, Lawrence Berkeley Laboratory Report LBL-29400, Berkeley, California, **1991**.
66. Nordstrom, D. K. On the evaluation and application of geochemical models, Appendix 2 in Proceedings of the 5th CEC Natural Analogue Working Group and Alligator Rivers Analogue Project, an international workshop held in Toledo, Spain, EUR 15176 EN, **1994**, 375-385.
67. Sahu, P., Sikdar, P. K., Chakraborty, S. Geochemical evolution of groundwater in southern Bengal Basin: The example of Rajarhat and adjoining areas, West Bengal, India. Journal of Earth System Science, **2016**, 125(1), 129-145.
68. Saxena, A., Sachan, H. K., Mukherjee, P. K., Mukhopadhya, D. K. Fluid–rock interaction across the South Tibetan Detachment, Garhwal Himalaya (India): Mineralogical and geochemical evidences. Journal of Earth System Science, **2012**, 121(1), 29-44.
69. Peng, J., Wang, X., Han, H., Yin, S., Xia, Q., Li, B. Simulation for the dissolution mechanism of Cambrian carbonate rocks in Tarim Basin, NW China. Petroleum Exploration and Development, **2018**, 45(3), 431-441.
70. Chidambaram, S., Prasanna, M. V., Karmegam, U., Singaraja, C., Pethaperumal, S., Manivannan, R., Tirumalesh, K. Significance of pCO_2 values in determining carbonate chemistry in groundwater of Pondicherry region, India. Frontiers in Earth Science, **2011b**, 5(2), 197-206.
71. Srivastava, R. K. Petrological and geochemical characteristics of Paleoproterozoic ultramafic lamprophyres and carbonatites from the Chitrangi region, Mahakoshal supracrustal belt, central India. Journal of Earth System Science, **2013**, 122(3), 759-776.
72. Ponomarev, A. A., Bubnova, A. V., Klunk, M. A. The Use of X-Ray Microtomography to Assess Changes in the Voids Structure of Rocks. Southern Brazilian Journal of Chemistry, **2017b**, 25, 12-16.
73. Moore, C. H. Carbonate diagenesis and porosity. 1st Edition, New York: Elsevier, **1989**, 337p.
74. Mazzullo, S. J., Harris, P. M. Mesogenetic dissolution: Its role in porosity development in carbonate reservoirs; AAPG Bulletin, **1992**, 76(5), 607-620.

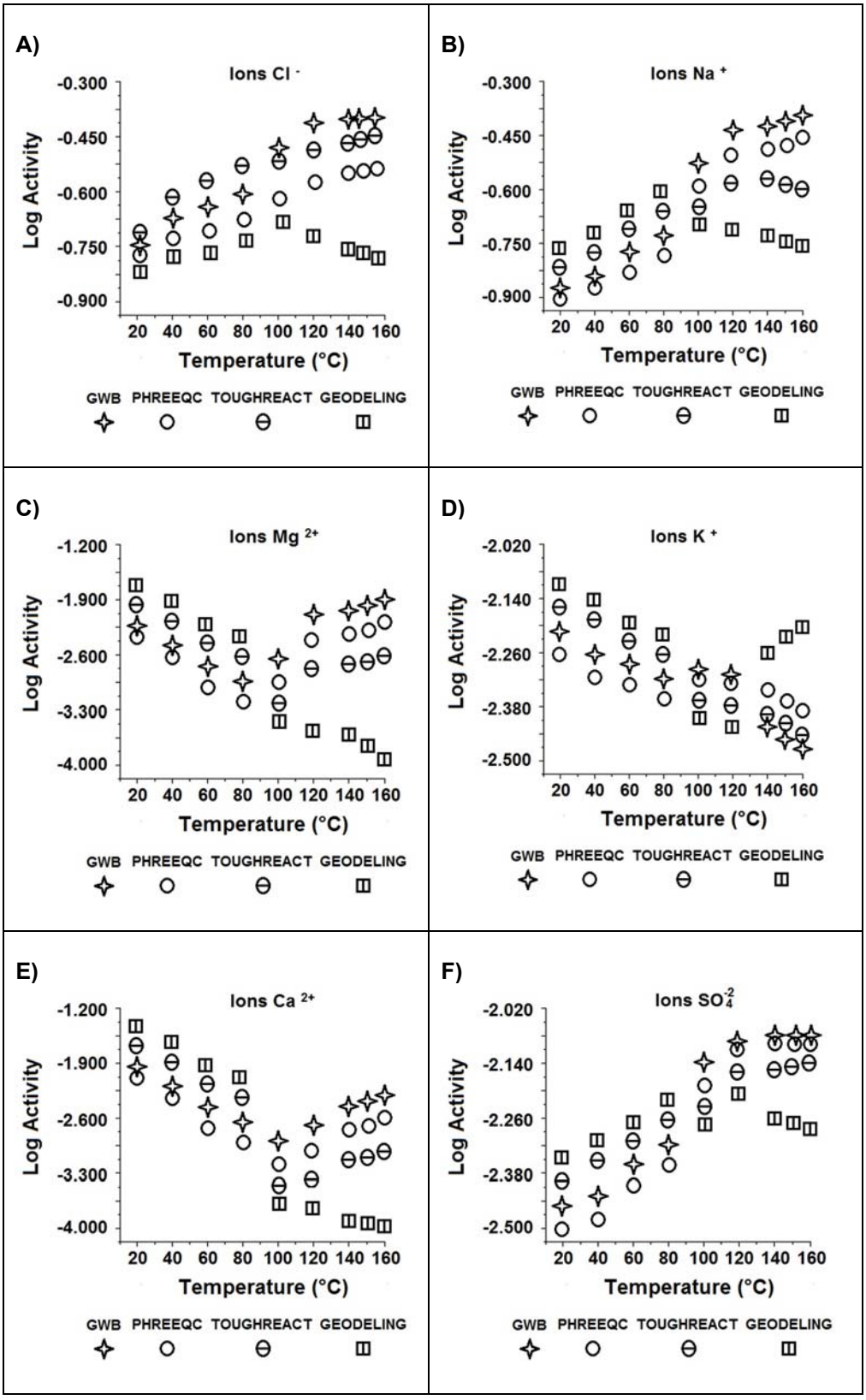

Figure 1. *Speciation model using GWBTM, PHREEQCTM, TOUGHREACTTM and GEODELING.*

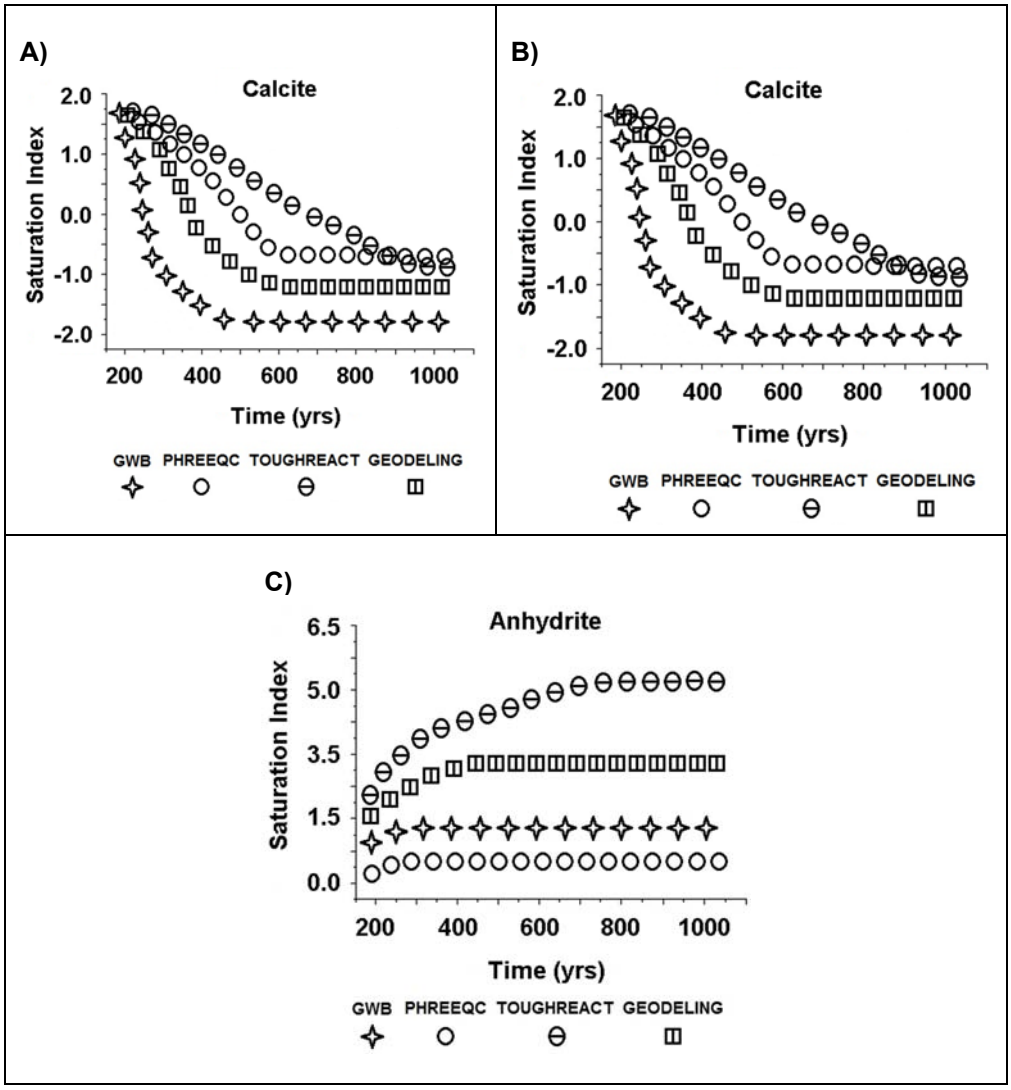

Figure 2. *Case study of a carbonate rock system model. Saturation index acquired with the aid of GWB™, PHREEQC™, TOUGHREACT™ and GEODELING.*

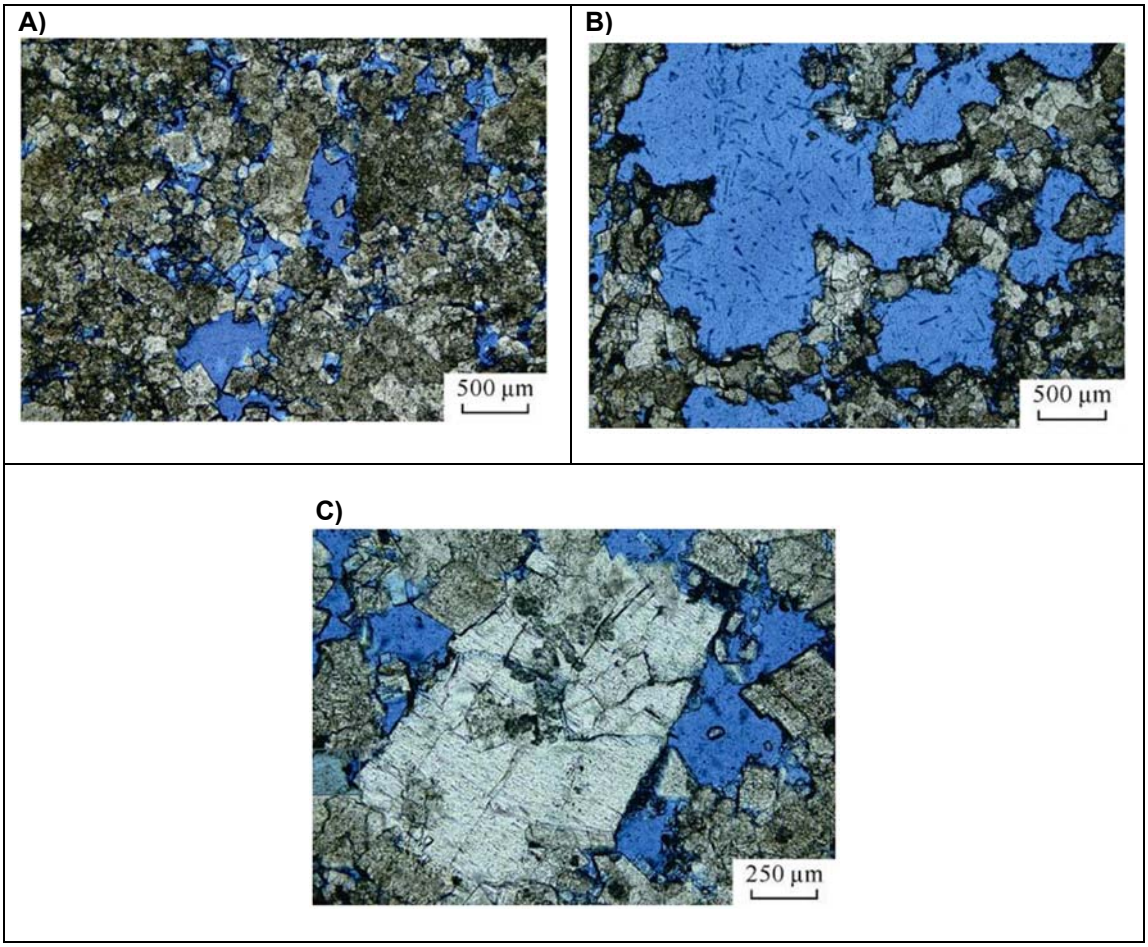

Figure 3. *The characteristics of Cambrian rock samples under microscope. a) Batan Well-5 at the depth of 5785.95m in Xiaoerbulak Formation showing residual sand fine-crystalline dolomite before the dissolution, with developed intercrystalline pores, observed, under single polarization (casting slice); b) Batan Well-5 at the depth of 5785.95m in Xiaoerbulak Formation showing residual sand fine-crystalline dolomite after the dissolution, where the intercrystalline pores are diffused into karst caves with smooth edges, under single polarization (casting slice); c) Batan Well-5 at the depth of 5785.95m in Xiaoerbulak Formation showing residual sand fine-crystalline dolomite after the dissolution where the anhydrite in the intercrystalline cavity remains uneroded, under single polarization (casting slice) (Peng et al., 2018).*