ESTUDO COMPARATIVO DA MODELAGEM GEOQUÍMICA DE ESPECIAÇÃO UTILIZANDO O SOFTWARE GEODELING

COMPARATIVE STUDY OF GEOCHEMICAL SPECIATION MODELING USING GEODELING SOFTWARE

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RESUMO

A modelagem geoquímica é usada para entender as interações água-rocha que ocorrem na bacia sedimentar. As atividades de espécies aquosas são geralmente calculadas usando a equação de Davies, a equação de Debye-Hückel, B-Dot ou Newton-Raphson. Realizamos um estudo comparativo da especiação geoquímica utilizando três softwares diferentes: PHREEQC™, Geochemist's Workbench™ (GWB) e GEODELING (código próprio). Detalhes de cada software são cuidadosamente analisados, levando em conta a distribuição, mobilidade e disponibilidade de espécies químicas em ambientes geológicos. Podemos observar resultados muito semelhantes na especiação ao trabalhar com sistemas de baixa temperatura. GWB™ e GEODELING empregam um sistema integrado para definir quando usar a equação de Davies, Debye-Huckel ou B-Dot, de acordo com o valor da força iônica da solução. A utilização do GEODELING permite comparar os resultados com o software GWB™ e PHREEQC™ com um alto grau de aceitação para baixas temperaturas. Para altas temperaturas, precisamos ser cautelosos no uso.

Palavras-chave: *Geochemist's Workbench™ (GWB), PHREEQC™, Debye-Hueckel, Simulação Numérica, Processos Diagenéticos.*

ABSTRACT

Geochemical modeling is used to understand water-rock interactions that occur in the sedimentary basin. Activities of aqueous species are usually calculated using the Davies equation, Debye-Hückel equation, B-Dot or Newton-Raphson. We perform a comparative study of geochemical speciation using three different software: PHREEQC™, Geochemist's Workbench™ (GWB) and GEODELING (own code). Details of each software are carefully analyzed, taking into account the distribution, mobility, and availability of chemical species in geological environments. We can observe very similar results in speciation when working with low-temperature systems. GWB™, GEODELING employ an integrated system to define when to use Davies, Debye-Huckel or B-Dot equation, according to the value of the solution ionic strength. The utilization of GEODELING allows comparing the results with software GWB™ and PHREEQC™ with a high degree of acceptance for low temperatures. Soon to high temperatures, we need to be cautious in their use.

Keywords: *Geochemist's Workbench™ (GWB), PHREEQC™, Debye-Hueckel, Numerical Simulation, Diagenetic Processes.*

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INTRODUCTION

The scientific community has seen progress in geochemical modeling for a natural and hypothetical environment. This development is related to numerical techniques capable of solving complex mathematical problems as well as improves the computing capacity of computers. The geochemical modeling studies and comprehension lead us back to the 60's when works as Garrels *et al.* (1967), Helgesson (1967a, 1967b) and Hengesson *et al.* (1968) started to making progress in this area. The first simulations were initially applied to understand the fundamental issues involving chemical reactions in aquatic environments. To solve problems like pollution of surface waters and assessment of diagenetic processes (involving natural formation and alteration of rocks). Due to the complexity and the timescale involved in the reactions in geological environments, it is not possible to reproduce in the laboratory the behavior of most geochemical systems.

In an attempt to create a geochemical model, it is important to keep in mind the goals and expectations that modeling will reveal. With defined goals, you can focus on the main issues and begin to identify the processes that control the geochemical system. The answers to these questions might give clues about what kind of modeling is most appropriate for the geological environment in research. In general, the processes operating in geochemical systems are complex. The choice of a simpler model with less detail can be advantageous since it will provide more results to analyze. We performed a comparative study of geochemical speciation using PHREEQCTM, Geochemist's Workbench™ (GWB) and GEODELING (own code). GEODELING is a software that we are developing. In this comparative study, we verify the distribution, mobility, and availability of chemical species in geological environments (Baccar and Fritz, 1993) as well as check the efficiency and accuracy of GEODELING. In this study, we modeled the chemical behavior of the minerals compounds known for the water from the North Sea (Morad *et al.,* 1990).

GEOCHEMICAL SPECIATION MODELING

The general concept of speciation applies to many chemical systems. It is most commonly used in the context of aqueous solutions (Batley *et al.,* 2009). Typically, such solutions include natural water systems such as sea, river, ground and lake waters. Natural waters are multi-component solutions where a network of interactions is established leading to the formation of chemical species with different thermodynamic stability. The different chemical behavior of ions in the medium leads to a different quantitative distribution of species depending on the kinetics of the process. The term chemical speciation is used to assess the distribution of a certain chemical species under different chemical forms and oxidation states (Gianguzza *et al.,* 1999; Gianguzza *et al.,* 2000). Geochemical modeling system tries to map all the reaction and processes happening in the modeled environment. As an example of the processes, we can mention complexation, oxidation, reduction, precipitation, and dissolution, just to name a few. It is natural to understand that the geochemical model system will be affected by environmental conditions such as temperature, pH, pE, oxidation and surface properties (Gianguzza *et al.,* 2004). In this context, we are developing a GEODELING code, its features and functionalities will be explained further in this study.

GEODELING – Speciation Code

The own code speciation has application in physical, chemical aqueous and geochemists useful tool with intuitive and interactive interface. GEODELING is planned as: i) speciation model – solving reaction as equilibrium reactions with the help of matrix reduction method; ii) extending options on activity correction method – Debye-Hueckel, B-dot, Pitzer and Davies and iii) adding kinetic reaction to the speciation model – recompose the speciation model to solve mineral-water interaction (Kehew, 2001; Pitzer, 1979; Pitzer, 1991).

The language chosen is C++, which is a general-purpose programming language with a bias towards system programming that supports efficient low-level computation, data abstraction, object oriented programming, and generic programming (Dale 2004; Plummer *et al.,* 1994). It provides powerful and flexible mechanisms for abstraction; that is, language constructs that allow the programmer to introduce and use new types of objects that match the concepts of an application needed. Thus, C++ supports styles of programming that rely on fairly direct manipulation of hardware resources to deliver a high degree of efficiency plus higher-level styles of programming

that rely on user-defined types to provide a model of computation that is closer to human's view of the task being performed by a computer (Parkhurst and Plummer, 1993; Plummer, 1984).

Geochemist's Workbench™ – GWB

GWB™ (was developed by the Department of Geology at the University of Illinois at Urbana-Champaign in 1978) use modules SpecE8 in React mode for speciation model (Bethke, 2008). The user set an initial geochemical system to be taken to thermodynamic equilibrium. The software automatically inserts a known quantity of water in the system (1 kg). Then, the user set the amounts of each solute present. At this time, the GWB™ start a calculation and necessary interactions that lead to speciation model. When GWB™ finished the simulation, output data is generated. The information contained in this file are temperature, pressure, pH, ionic strength, water activity, mass of solvent, dissolved solids, solution density and mass of the rock (Parkhurst and Plummer, 1993). An aqueous species list is formed with all solutes presents in the simulation. GWB™ solves simultaneously a set of nonlinear algebraic equations, composed by the equation of mass action and the equilibrium constant corresponding to aqueous species, gas or minerals that are contained in a database (Kehew, 2001). While GWB™ solves the equation of mass action, it is solving all the mass balance of the system. The GWB™ solve the equations using the Newton-Raphson method (Kehew, 2001).

PHREEQC

PHREEQC™ is software written in programming languages C and C++ designed to perform a wide range of geochemical calculations. PHREEQC™ is capable of (i) calculate the saturation index and speciation (ii) calculates the reactions in "batch mode" and transport one-dimensional (1D). Use the Pitzer model for high salinity water that is an outside range of application of the Debye-Huckel theory. The software uses a numerical method of integration allowing solution of ordinary differential equations, which can be generalized for the reconstruction of three-dimensional trajectories (Parkhurst *et al.,* 1999).

INITIAL CONDITIONS OF THE WATER SPECIATION IN SIMULATION

A numerical simulation study, predict the geochemical speciation of formation water (Nordstrom *et al.,* 1979) was carried out with GWB™ and PHREEQC™ software with the aim of comparing the results obtained with own code (GEODELING). The temperature used for simulations é 25, 40, 60, 80, 100, 120, 140, 150 and 160°C. Baccar and Fritz (1993) studies were focused in this scenario, in which there are several interactions between the rock and formation water in different temperatures. Formation water composition was compiled from Nordstrom et al. (1979), which major element composition is shown in Table 1.

Table 1. *The chemical composition of the formation water (mM/L).*

Elements	Concentration (mM/L)
K^+	10.45
Na^+	479.32
Ca^{2+}	10.53
Mg^{2+}	54.39
SO_4^{-2}	28.89
Cl^-	559.50
pH	8.22

The initial conditions of simulation using the GEODELING have as its starting point the combination of the chemical species. The new concentration is calculated and represented by the logarithm activity of ionic species. The activity concentration also known as "effective", used to eliminate the effect of the interaction between the ions in solution. The method uses GEODELING: Debye-Hueckel, B-dot, Pitzer, and Davies (Kehew, 2001).

RESULTS AND DISCUSSIONS

Events predicted by numeric simulation between 25 and 160°C using GWB™, PHREEQC™ in comparison to GEODELING, are summarized in Figure 1. Analyzing the graphs of simulations we observed two significant moments: i) events at lower temperatures (25-100°C) and events at high temperatures (120-160°C). The logarithm of the activity of ions depends on the temperature of the reaction system. At low temperatures, we observe that the software acquire similar behavior. At higher temperatures, the software's numerical method attributes unique characteristics and causing discrepancies in the

results. When comparing the results of GEODELING with other software, we observed similarity in low-temperature events. For the speciation of the ions Mg^{2+}, Ca^{2+}, K^{+} and SO_4^{2-} the GEODELING reproduces the logarithm of the activity of these ions. On the other hand, the ions Cl^{-} and Na^{+} have different behavior for high temperatures when compared with software GWB™ and PHREEQC™.

Geochemical speciation is critical for understanding the form of chemicals of interest in natural systems. It is crucial in assessing bioavailability and, ultimately, fate, transport, and risk to humans and ecosystems. Chemical speciation measures through analytical methods the amount of free ion or total concentration, used in conjunction with thermodynamically based models.

To this end, the GEODELING code itself was built to predict the species present in a geological environment. The various simulations in this study enabled a comparative study of GEODELING behavior with commercial software speciation. The results showed that the use of different codes produces different results during modeling for two events of temperature. The convergence of outcomes is more evident at low temperature than between high temperatures. Generally, at low temperatures, the simulation results show the same behavior, because each software uses similar numerical methods to solve a different set of reactions.

At low temperatures (T<100°C), it is possible to observe similarity among the results of the various codes due to the low kinetic energy involved in the reactions. Each simulator has their algorithms based on numeric methods that are dependent on kinetic and thermodynamic parameters, contained in the database. In higher temperature reactions (120 – 160°C), the kinetic energy increases and generate discrepant results, regardless of the model. Consequently, the GEODELING system produces different results in ions chloride and sodium. However, GWB™ and PHREEQC™ have same approaches while working with high temperatures when compared to the GEODELING. This behavior was observed in ions magnesium and calcium. In general, from 120°C GWB™ and PHREEQC™ reproduce the similar behavior. The numerical method of both systems uses polynomial equations of 8th grade to resolve the physical-chemical interactions in geological environments.

These equations are dependent on kinetic, and thermodynamic data are directly affecting the reaction medium. For temperatures above 120°C, these kinetic and thermodynamic data acquire an anomalous behavior, assuming constant values of 500 in numeric treatment. If the software finds the 500 value, indicate that that value has not been calculated.

This comparative study revealed two events, taking into account the temperature. The first stage corresponds to the temperature range 25–100°C and the second to the temperature range of 120-160 °C. In the first stage is possible to verify the convergence of the results. In the second stage, we can confirm a peculiarity due to the numerical method. Users must be careful when choosing a geochemical speciation software because, depending on the temperature range, different systems can produce very discrepant behaviors.

CONCLUSIONS

The present study of geochemical speciation comparing the application of GWB™ and PHREEQC™ with GEODELING codes for the simulation of water formation resulted in the following conclusions:

a) Reactions at low temperatures (25 to 100°C) with different simulators reproduce quite the same behaviors. In this temperature range, which involves low energy, the reaction kinetics, and the thermodynamic parameters behave according to the particularities of each code. The numerical methods used by GWB™, PHREEQC™ and GEODELING code can achieve only limited convergence of results, with the high precision expected for reactions at low-temperature geological environments.

b) The range of temperature from 120 to 160°C (which as a higher kinetic energy involved and greater intensity in the reactions) the simulations with all the four software generate different results. The reason for that is that they use different mass balance equations for calculation chemical speciation.

The mathematical interpolations used by simulators in this temperature range are less stable giving rise to a lower convergence of results. In this way, each simulator seeks each own best set of numerical solutions to achieve the equilibrium.

The geochemical speciation aimed to compare the results of simulators able to predict the chemical species present in a geological environment. The utilization of GEODELING allows comparing the results with software GWB™ and PHREEQC™ with a high degree of acceptance for low

temperatures. Soon to high temperatures, we need to be cautious in their use. With the temperature information, the user should do a preliminary study with the available codes for verifying the convergence.

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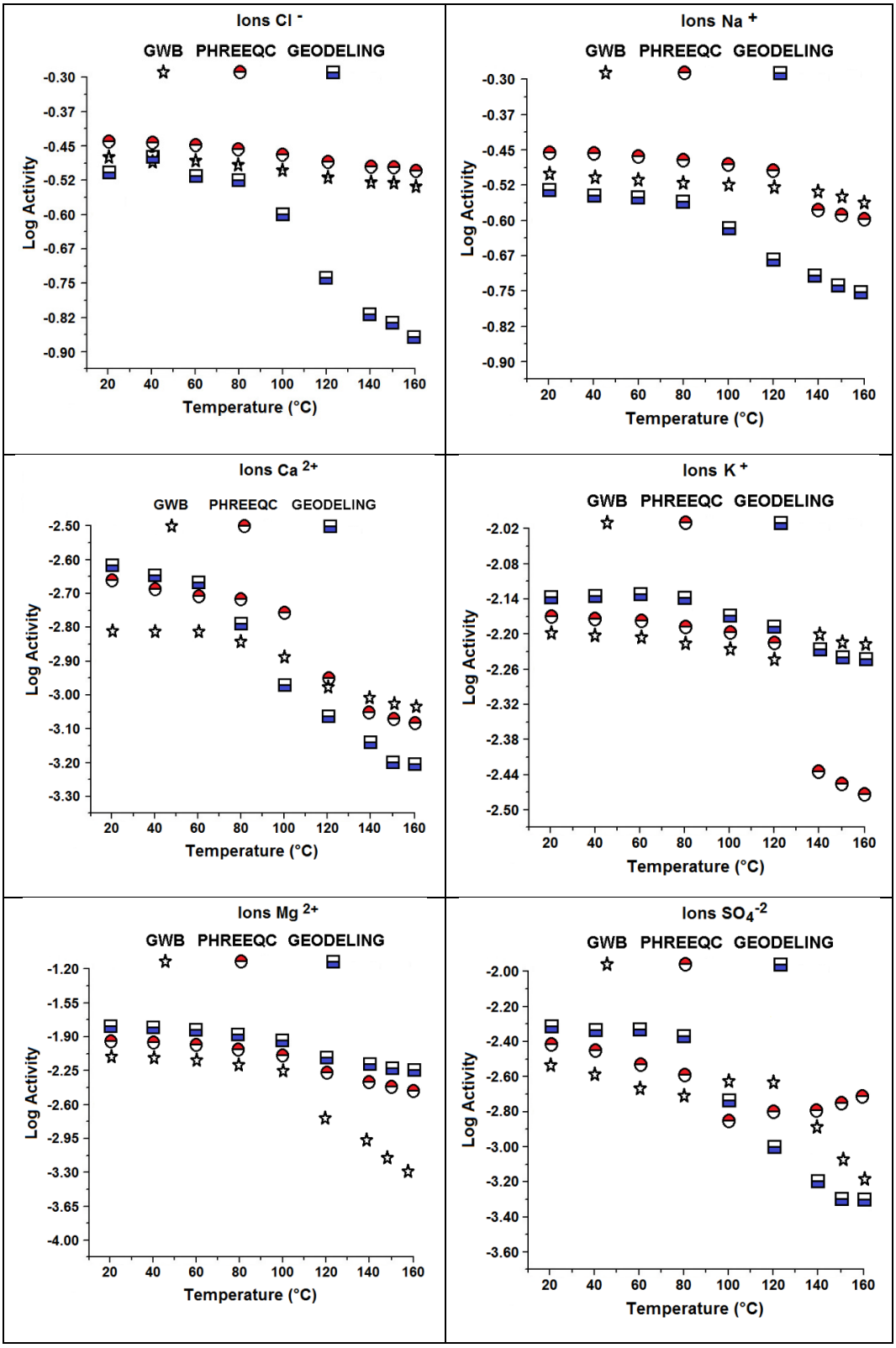

Figure 1: *Speciation model using GWB, PHREEQC and GEODELING*