Chapter 26

Aspects of the Thermodynamics and Kinetics of the System CO_2-H_2O-Carbonates in Tropical Karst Mountain of Western Cuba

J.M. Pajón and J.R. Fagundo

Abstract The chemico-physical principles, which include the thermodynamic and kinetics basis, of the classic system of chemical reactions CO_2-H_2O-$CaCO_3$, and achieve a control of the mechanism and processes of the karstification, had been fully studied by the international scientific community, with new precisions and contributions in the last decades. Some significant contributions, among others, developed in the tropical mountain karst of western Cuba are: studies about the chemico-physical behavior and the chemical evolution of the karstic waters of different hydrogeological natures; the works about the experimental chemical simulation of the water-rock interaction processes in the karst; the work of hydrogeologic, chemico-physical and isotopic monitoring of the karstic waters in different hydrodynamic zones of the karst. This work offers information and brief analyses about the above mentioned, and attention is paid to some cardinal problems, totally or partially not yet solved.

Keywords Thermodynamic • Karstification • Hydrogeology • Cuba

26.1 Introduction

The chemical and physical principles, including thermodynamic and kinetic fundamentals of the classical system of chemical reactions CO_2-H_2O-$CaCO_3$, and governing processes and mechanisms of karstification have been adequately studied

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(Garrels and Christ 1965; Back et al. 1966; Langmuir 1971; White 1977; Stumm and Morgan 1981; Boegli 1972; Roques 1964, 1973a, b; Picknett 1964, 1972, 1973; Stchouzkoy-Muxart 1972; Miserez 1973; Fagundo and Valdés 1975; Bakalowicz 1979; Ford 1988). New details and contributions have been developed in recent decades, among others, White (2000), Klimchouk et al. (2000), Dreybrodt (2000) and Plummer (2002).

Some contributions to the thermodynamic and kinetic studies of the system CO_2-H_2O-carbonates in the tropical karst mountains of western Cuba are: studies on the chemico-physical behavior and chemical evolution of waters of differing karst hydrogeology (Fagundo et al. 1981a, 1986, 1991, 1992; Fagundo and Pajón 1985; Fagundo 1986, 1990; Pajón et al. 1990); work on the experimental simulation of the processes of water-rock interaction in carbonate karst (Bermúdez et al. 1987; Pajón and Valdés 1991; Fagundo et al. 1992; González et al. 1997; González 1997; Fagundo and González 2003); work "point" monitoring of hydrogeological, chemical, physical and isotopic karst water in different areas of karst hydrodynamics (Fagundo et al. 1985; Molerio et al. 1985, 1999; Arellano et al. 1992; Molerio 1992; Pajón et al. 2009, 2010); paleoclimatic researches from high-resolution records of stable isotopes of oxygen and carbon and Th-U dating and ^{14}C-AMS on stalagmites (Pajón et al. 2006; Pajón 2007, 2009; Fensterer et al. 2010).

Despite the efforts mentioned above, some basic problems remain unresolved, in whole or in part, such as: continuing to conduct monitoring of isotopic chemical-physical, hydrological and climates suitable for hydrological cycles in loading zones stations across the hydrodynamic karst zones; performing multiparametric monitoring stations of the aeration zone of the karst (hypodermic flow), especially designed for recording rainfall and drip into the study of speleothems: palaeoclimate and palaeoenvironmental studies during the Late Pleistocene-Holocene; continuing the simulation experiments of solution chemistry in laboratory conditions in the karst lithologies under n-parametric control in open, closed and "nearly closed" systems; to study the problem of seawater intrusion in the coastal karst connected to the mountain area, related to human activity and climate change, and chemical denudation taking into account the effect of salt and water mixture on the equilibrium of carbonates; deepen the study of the relationship between the CSR (Ratio of the Calcite Saturation) and ΔpH (Tillman-Trombe Index).

26.2 Result and Discussion

26.2.1 Monitoring of the Chemical, Physical, Hydrogeologic and Isotopic Behaviour of the Karstic Waters. Paleoclimatic Researches

Fagundo et al. (1981), using thermodynamic principles, studied the behavior of the main parameters and physico-chemical indexes in 35 sites representing different types of waters of the Cuyaguateje River Basin in the Sierra de los Organos

Mountains (Pinar del Río Province, Cuba). A series of chemical and physical indices, including the relationship of water saturation with respect to calcite (CSR), dolomite (DSR) and gypsum (YSR) were calculated. The data obtained, which characterized the rainy and dry periods 1978–1989, reflected patterns of sequence variation characteristic of the different types of natural waters that occur in the region. A hydrogeochemical study (Fagundo et al. 1981b) was developed in the Fuentes Cave System (Sierra de Mesa, Sierra de los Órganos) and its surroundings, which showed the occurrence of two mechanisms of water-rock interaction. The first one mechanism include lose of CO_2 and carbonates precipitation in the form of travertine along watercourses. Pajón et al. (1990) evaluated as a first approximation, the kinetics of the precipitation of carbonates in the form of travertine along 600 m of the Mil Cumbres stream (Sierra del Rosario, Pinar del Rio, Cuba).

Arellano et al. (1992) performed an interesting study to clarify aspects of the regional flow dynamics and the origin of recharge in the area of articulation of the criptokarstic plain with karst mountain of the Sierra del Rosario (Pinar del Rio, Cuba), particularly in areas related to the Santa Cruz, San Cristobal and Taco Taco rivers. To do this, they monitored the chemical and isotopic composition and physical parameters of the karstic water springs, caves, wells and rainwater in the region, specifically in the basin and Santa Cruz River canyon.

In recent years, paleoclimatic research has been developed in Cuba that has contributed to the assessment of climatic and environmental changes that occurred during the Late Pleistocene-Holocene, from high-resolution records of stable isotopes of oxygen and carbon and Th-U and ^{14}C-AMS dating, on stalagmite representing tropical karst mountains of western Cuba. Oxygen isotope records ($\delta^{18}O–\delta^{16}O$ $^{o}/_{oo}$ PDB) and Carbon ($\delta^{13}C$ y $\delta^{12}C$ $^{o}/_{oo}$ PDB) of the studied stalagmites inside the Dos Anas cave (Sierra de San Carlos, Pinar del Rio, Cuba), indicate the following paleoclimatic behavior for the karst mountain area studied (Pajón et al. 1999, 2001a, b, 2006; Pajón 2007, 2009): the existence of large climate variability since the Last Glacial Maximum (LGM) to the present, with a general warming trend; the occurrence of a temperature difference of 8–10 ^{o}C between the Last Glacial Maximum (LGM, 18,000 years ago) and the Present Interglacial (Current), confirming the influence of the extent and magnitude of continental cooling occurred in the glacial period on the ecosystems of the tropical-subtropical, especially over the western half of Cuba; detection of abrupt climate warming occurred in the early Holocene, with a high increase of $\approx$ 6-7 ^{o}C and that lasted until about 2,000 years ago.

During the 2008–2009 hydrological years, Pajón et al. (2009) developed a bimonthly monitoring program of the karst water infiltration (hypodermic flow) aeration zone of the karst caves, Dos Anas (Majaguas-Cantera Cave System, Sierra de San Carlos) and Torch (Santo Tomás Cave System, Sierra de Quemados), to study in a preliminary way, the behavior of the main chemical-physical parameters and stable isotopes of oxygen and carbon, climate and trace elements at four sites representing these localities. Fensterer et al. (2010) studied by ^{230}Th/U a Late Holocene stalagmite in Dos Anas Cave, whose findings are part of the research program developed in the karst of the Sierra de San Carlos and Sierra de Quemados, to study, using stable isotopes and isotopic dating, the natural behavior of the past climate of Cuba.

26.2.2 Thermodynamic and Kinetic Aspects in the System CO_2-H_2O-$CaCO_3$

From the thermodynamic principles, taking into account the classic equation that represents the dissolution-precipitation of limestones, and a set of chemical reactions and their equilibrium constants, Fagundo and Valdés (1975) arrived at the following expression (Eq. 26.1) to calculate the Coefficient of the Calcite Saturation (CSC):

$$CSC = \left[Ca^{2+}\right]\left[HCO_3^-\right]10^{pK_c - 2pK_2 + pH} \tag{26.1}$$

Where: $[Ca^{2+}]$: Molal concentration of Ca^{2+}, $[HCO_3^-]$: Molal concentration of HCO_3^-, pK_C: $-\log K_C$ (solubility product of calcite), pK_2: $-\log K_2$ (Equilibrium constant for dissociation of the ion HCO_3^-), pH: $-\log [H^+]$.

As the ratio of water saturation with respect to calcite (CSR) is defined as (Eq. 26.2):

$$CSR = \log CSC \tag{26.2}$$

Equation (26.3) is:

$$CSR = \log\left[Ca^{2+}\right] - \log\left[HCO_3^-\right] + pk_c - pK_2 + pH \tag{26.3}$$

That is only the Saturation Index (SI) of Back et al. (1966), then (Eq. 26.4):

$$CSR = IS \tag{26.4}$$

Roques (1972) and Stchouzkoy-Muxart (1972) proposed equations (Eq. 26.5) relating the field measured pH (pH_m) and equilibrium pH (pH_e), to assess the status of the solution referred to the chemical balance, being defined ΔpH index as:

$$\Delta pH = pH_m - pH_e \tag{26.5}$$

The terms proposed by Stchouzkoy-Muxart (1972) and Roques (1972) are:

$$\Delta pH = pH_m - 2\log\left[Ca^{2+}\right] - p\gamma Ca^{2+} - p\gamma HCO_3^- + pK_2 - pK_c - 0.3013 \tag{26.6}$$

$$\Delta pH = pH_m - \log K_s + \log K_2 + \log\left[HCO_3^-\right] - \log\left(1 - K_5\left[SO_4^{2-}\right]\right) + C \tag{26.7}$$

Where: $p\gamma Ca^{2+}$: $-\log$ the activity coefficient of Ca^{2+}, $p\gamma HCO_3^-$: $-\log$ the activity coefficient of HCO_3^-, pK_C: $-\log K_C$ (solubility product of calcite), pK_2: $-\log K_2$ (Equilibrium constant for dissociation of the ion HCO_3^-), K_S: Equivalent to K_C (solubility product of calcite in equilibrium), K_5: Equilibrium constant for the dissociation of $CaSO_4$, $[SO_4^{2-}]$: molal concentration of SO_4^{2-}, Me: may be $[Ca^{2+}]$ o $[Mg^{2+}]$, C: Represents the contribution to the pH of the ion pairs $MgHCO_3^+$, $MgCO_3^0$, $CaHCO_3^+$ and $CaCO_3^0$, can be calculated as: (Roques 1972 en Bakalowicz 1979, 1980).

Pajón et al. (1985a) studied the correlation between the values of CSR (IS) and ΔpH (expression of Stchouzkoy-Muxart 1972) in natural waters of the karst mountains of the Sierra de los Organos (geochemical testing cycles of the Cuyaguateje River Basin during the periods of March 1979, August 1979, February 1980 and July 1980) and Pan de Guajaibón (geochemistry testing cycles for the period from January to February 1980). They found a numerical similarity between the two indices, considering or not the complex ions and ion pairs (in the calculation of CSR), although the accuracy is higher for the CSR to present them. Based on the work of Berner and Morse (1974) and through the study of carbonate aquifers waters of Pennsylvania and Kentucky, White (1977) found that the parameter ΔpH of the experiments of these authors is related to the IS of the form following:

$$\Delta pH = \frac{1}{2} IS \tag{26.8}$$

The results obtained by Pajón et al. (1985) and Pajón (1986) are consistent with the statements by Bakalowicz (1980), which concludes that the Back saturation index (SI) is equal to the ratio between the measured pH in a solution and the pH of a solution in equilibrium with a given mineral, regardless of ion-pair complexes eventually formed. Although the same author (Bakalowicz 1979) posed that the ΔpH has the same meaning as the IS Back, even if they do not exactly correspond. He thus concludes that:

$$CSR = IS = \Delta pH \tag{26.9}$$

Carbon dioxide plays a fundamental role in the dissolution of carbonates (Miserez 1973; Roques 1973a; Wigley 1973; Bakalowicz 1979; Kempe 1982). Humic and fulvic acids also play an important role in the processes of water-rock interaction of the system CO_2-H_2O-$CaCO_3$. Stchouzkoy-Muxart (1972) makes a numerical and graphical analysis where the pCO_2 is based on the ion HCO_3^- and Ca^{2+} and the equilibrium constants. Fagundo (1982) presents an empirical expression for calculating the pCO_2, which relates to the $\sqrt{I}$ and activity of ion HCO_3^- with the electrical conductivity and temperature.

$$\log pCO_2 = -\frac{A\sqrt{I}}{1 + a^0 HCO_3^- B\sqrt{I}} + \log\left(HCO_3^-\right) + pK_B + pK_1 - pH \tag{26.10}$$

Where: I: Ionic strength, a^o: Effective diameter of the ionic species I, B: Constant B of the Debye-Huckel equation, pK_1: $-\log K_1$ (Equilibrium constant for the dissociation of H_2CO_3), pK_B: $-\log K_B$

26.2.3 Experimental Simulation and Kinetic Studies of the Reaction of Carbonate Dissolution in Kars

Laboratory experimental work with controlled simulation of the processes of water-rock interaction of the system CO_2-H_2O-$CaCO_3$ developed by several authors (Weyl 1958; Picknett 1964; Curl 1965; Stchouzkoy-Muxart 1972; Roques 1973a; Berner and Morse 1974; Rauch and White 1977; Plummer et al. 1978; Richard and Sjöberg 1983; Sjoberg and Rickard 1984; Herman et al. 1986; Comton and Unwin 1990), were a source of inspiration for the early 1990s, and resulted in the first attempts to develop work of this nature with geological samples of carbonates in the Cuban karst regions. These regions develop significant karstification processes that have resulted in the occurrence of large cave systems in Cuba, as is the case of Santo Tomás Cave System, the Majaguas-Cantera Cave System and Palmarito Cave System, among others. Some excellent studies influenced by this methodology were developed by Fagundo et al. (1992), Fagundo and Gonzalez (1997), González et al. (1997) and González (1997).

Based on laboratory kinetic studies on the natural systems of the dissolution of carbonates, Pajón and Valdés (1991) designed a simple solution simulation experiment with rock samples from the formations Guajaibón (RAC-3) and Chiquita (SA-4) belonging to the mountains of the same name in the Pan de Guajaibón massif (Sierra del Rosario, Pinar del Rio, Cuba), as well as a “Tinajitas” (TIN-1), lapiaz in limestone surface of the Ancón Creek in the Pan de Guajaibón massif. The aim of this study was to compare quantitative experimental results concerning the speed and intensity of dissolution of carbonate rocks with chemical denudation estimates derived from field investigations. The experiments described here are of the “free trend” variety (Rauch and White 1977), where an initial solution of distilled water maintained as “quasi-closed” and in equilibrium with $pCO_{2,}$ reacts with carbonate rocks to a balanced approach. It was noted the purchase of ions HCO_3^- and Ca^{2+} over time, increases in the order of TIN-1 → SA-4 → RAC-3, which means an increase in the rate of dissolution in the same order. The velocity of dissolution of the Chiquita formation rocks is higher than Guajaibón formation, and in turn in the Tinajitas.

A suitable and systematic study on the kinetics and thermodynamics of the system CO_2-H_2O-Carbonate was carried out by Fagundo et al. (1992), González et al. (1997) and González (1997), which provided the basis for the work of experimental simulation of dissolution of carbonates developed by these authors (Fig. 26.1). There are various procedures and equations to estimate the rate of dissolution in the system CO_2-H_2O-$CaCO_{3,}$ which represents the variation of the concentrations of dissolved species over time, may include the equations of Plummer and Wigley (1976), Sjöberg (1976), Plummer et al. (1978), Christoffersen and Christoffersen (1979), Rickard and Sjöberg (1983), and Appelo and Postma (1993). Fagundo et al. (1996), Álvarez et al. (1996) and González et al. (1997) developed kinetic expressions of the rate of dissolution of carbonates, especially evaluated for the case of carbonate karst geological formations in western Cuba, which have unique cases of open and closed systems for CO_2 (Fagundo and González 2003). Whereas the dissolution of calcite and dolomite in the work of simulation of the water-rock interaction in the laboratory is obtained a

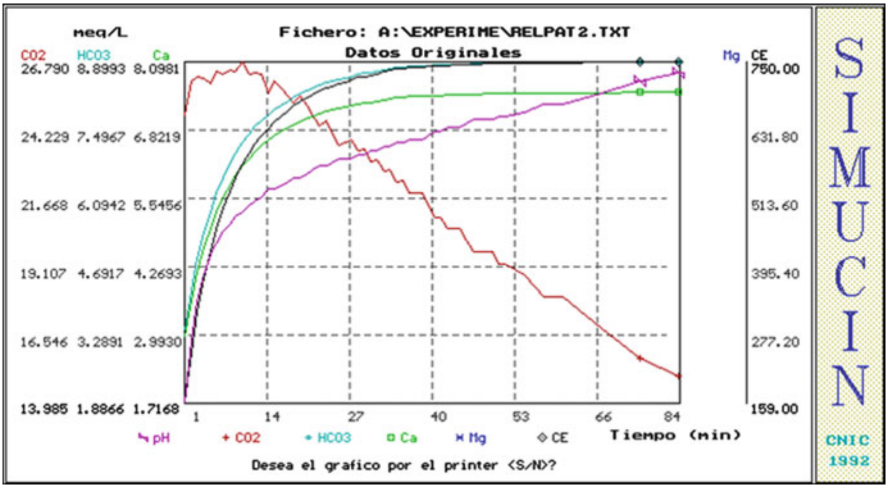

Fig. 26.1 Experimental simulation of dissolution of carbonates (Cinepat 2, limestone). The variation in the time of the pH and the composition of the ions HCO_3^-, Ca^{2+} and Mg^{2+} (González 1997; González et al. 1997; Fagundo and González 1997)

pseudo first-order equation which expresses the change in ionic concentration over time (Fagundo 1996; Álvarez et al. 1996):

$$C = C_{eq}\left(1 - e^{-kt^n}\right) \tag{26.11}$$

Where, n is an experimental coefficient takes values between 0 and 1.

Fagundo et al. (1992) used samples of the limestone formations Jaimanitas, Guasasa, Jagua and Guajaibón in a laboratory experiment, which simulated the process of dissolution of these carbonates under conditions of open and closed system with respect to CO_2. Álvarez et al. (1996) performed simulation experiments in the laboratory using carbonate rocks containing calcite and dolomite minerals in different proportions with the aim of studying the process of acquisition of the chemical composition of natural waters run at a karst aquifer. González (1997) and González et al. (1997) simulated in the laboratory the process of dissolution of carbonate (calcite and dolomite) under conditions of open and closed system for CO_2. They obtained rate expressions that describe the acquisition process of the chemical composition of natural waters that interact with the limestone and dolomite studied. They demonstrated that in closed system conditions during the kinetic process of water-carbonate rock interaction, the variation of CO_2 can be expressed by exponential equations of a specific type, while the change in open system conditions is negligible. The variation in the time of the electrical conductivity and the composition of the ions HCO_3^-, Ca^{2+} and Mg^{2+} can also be expressed with an exponential equation type. The dissolution rate of calcite was found to be higher by about five times compared to dolomite.

26.2.4 Some Problems and Approaches to the Study of Karst Processes in the Tropical Karst Mountains of Western Cuba

Molerio and Valdés (1975), in a pioneering study ahead of its time, raised some problems and cardinal prospects for the karstological and geospeleological studies in Cuba. The authors drew attention to the need to address these studies by weighting the morphogenetic criteria on morphographics and the morphologicals. Here is implied the use of thermodynamic and kinetics approach in the studies on geochemistry of karst waters and paleoclimate from speleothems records (Pajón et al. 2009).

Monitoring is needed to continue with physical, isotopic, chemical, hydrogeological and climatic stations throughout the zoning of karst hydrodynamics during hydrological cycles appropriate to characterize not only the basic “steady conditions” of karst systems, but also the conditions attached climate-hydrological events diverse and extreme. Special attention should be paid to the realization of multiparametric monitoring stations in the aeration zone of the karst (hypodermic flow), especially designed to record rainfall (drip) in the speleothems. A derivation of the monitoring of chemical characteristics and isotopy of seepage water is towards the paleoclimatic and paleoenvironmental studies covering the Late Pleistocene-Holocene.

Despite the unquestionable value of experimental studies of chemical simulation of carbonate dissolution in laboratory conditions from Cuba, it is necessary to continue this line with lithologies, which is heavy in the development of karst. These experiments will lead to a multi-control n-parametric, in open systems, closed or “nearly closed”, automated facilities that control a set of variables and parameters previously selected. In this sense the conceptual model developed by Rauch and White (1977) may be resumed, since the experimental design is based on the use of carbonate blocks with ducts simulating karst cavities or channels. The fundamentals developed by Dreybrodt (1992, 2000) can be used, who proposed a model of evolution of karst channels to simulate the dissolution of limestone from these primary cracks.

It remains to explain if a numerical difference exists between the chemical and physical indices of the saturation ratio of calcite (CSR) and Tillman-Trombe Index (ΔpH). The first has two approaches, one by the American school and another school in Cuba, while the ΔpH responds to the European school. There are similarities between the two indices if we consider the Cuban and European schools; however, to compare the rates according to American and European schools is a ½ relationship between them. This is an algorithmic error in this treatment and/or variables that make up the equations, or errors of other kinds?

Of current and capital importance is the continuation of studies related to paleoclimatic and paleoenvironmental reconstructions during the Late Pleistocene-Holocene, from natural paleo records high resolution, as is the case of speleothems.

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