

# **Chapter 25**

## **Geochemistry of Waters from Tropical Karst Mountain of Western Cuba**

**J.M. Pajón and J.R. Fagundo**

**Abstract** The studies on geochemistry of the karstic waters, especially, those related to the classic system of chemical reactions  $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$ , have been fully developed in different karstic areas around the world, many of them to disembowel the mechanism and processes of the karstification. Some significant contributions, among others, developed in the tropical mountain karst of western Cuba are: studies about the chemico-physical behavior of the karstic waters of different hydrogeological natures and their typologies; studies about the chemical evolution of the karstic waters and the empiric relations among variables, parameters and physico-chemical indexes; quantitative estimations about the chemical denudation; the “prompt” 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 pay attention to some cardinal problems, totally or partially not yet solved.

**Keywords** Karst waters • Geochemistry • Isotopic monitoring • Cuba

### **25.1 Introduction**

The researches on geochemistry of the karstic waters, especially those related to the classical system of chemical reactions  $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$  and the governing processes and mechanisms of karstification, have been adequately studied (Garrels and

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

Some contributions to the geochemistry of the karstic waters in the tropical karst mountains of western Cuba are: studies on the chemical behavior of waters of differing karst hydrogeology, the influence of geodynamic factors on the properties of the waters and its types (Fagundo et al. 1981a; Valdés et al. 1981; Molerio 1995); the studies of the chemical evolution in karst waters and the empirical relationships between variables, parameters and physico-chemical indices (Fagundo et al., 1986a; Pajón et al., 1990; Fagundo, 1990; Fagundo et al., 1991; Fagundo et al., 1992); the quantitative estimates of chemical denudation in experimental sites in karst areas (Pulina et al., 1984; Fagundo et al., 1986b; Rodríguez 1995; Rodríguez and Fagundo 1995); work “point” monitoring of hydrogeological, chemical, physical and isotopic karst water in different areas of karst hydrodynamics (Fagundo et al. 1987; Arellano et al. 1992; Molerio 1992; Pajón et al. 2009, 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 multi-parametric 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; to obtain quantitative estimates of global denudation of the karst mountain areas; 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. Some of these actions have already been identified earlier by Molerio and Valdes (1975) (“The Problem”) and Molerio (1981).

## 25.2 Results and Discussions

### 25.2.1 Monitoring Behaviors of Chemical-Physical and Hydrogeological Karst Waters

#### 25.2.1.1 Types and Characterization

Fagundo et al. (1981a, c) 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). The variables and physical-chemical parameters were determined in situ using the techniques of Markowics and Pulina (1979), which were previously implemented and adjusted to the natural water conditions in Cuba (Pajón and Fagundo

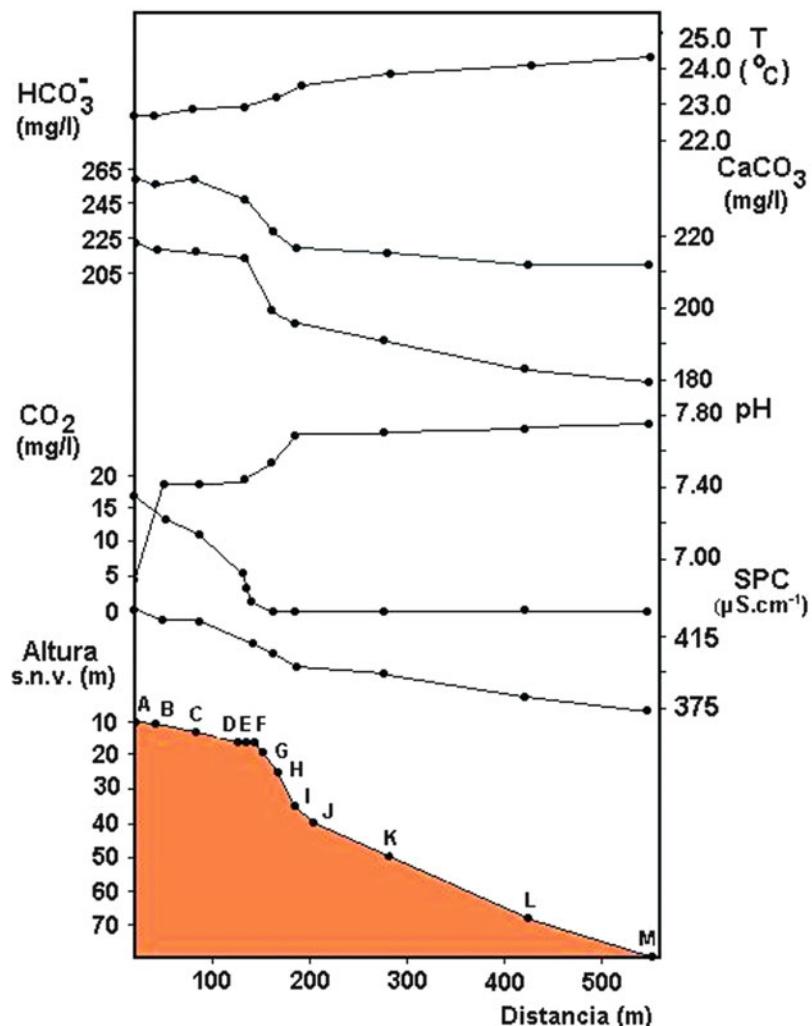
1978, 1983). The data obtained, which characterized the rainy and dry periods 1978–1989, reflected patterns of sequence variation characteristic of the different types of natural waters that occur in the region. The results were analyzed on the basis of geological and hydrogeological characteristics of the basin, which fairly represents the zoning of karst hydrodynamics.

To establish a classification of karst waters of the Cuyaguateje River Basin and to study the relationship between the type of waters, defined by geomathematics methods and those defined by geological and hydrogeological criteria, Valdés et al. (1981) applied methods of numerical classification and factor analysis to the chemical and physical data of the karstic waters for six geochemical testing cycles developed between 1978 and 1979, by sampling and characterizing the winter and summer periods for the years in question. From the analysis and interpretation of the dendrogram (Cluster Analysis), five groups of waters were defined. A Factor Analysis of the results of the karst water hydrochemistry testing of the Cuyaguateje River Basin August 1979 results were conducted. The results demonstrate that the chemical and physical properties of these waters are effectively linked to the two main geological formations in the region, the non-karst rocks (slate, sandstone, shale, etc.) and the karst rocks (limestone and dolomitized limestone).

A hydrogeochemical study (Fagundo et al. 1981b) was developed in the Fuentes Cave System (Sierra de Mesa, Sierra de los Órganos), which showed the occurrence of two mechanisms of water-rock interaction. The first mechanisms were along watercourses that lose CO<sub>2</sub> and carbonates are precipitated in the form of travertine. The second mechanism tends to dissolve these, from the rainwater and allochthonous streams not influenced by the environment karst. De la Cruz and Valdés (1985) studied karst waters of the Sierra del Pan de Guajaibón and its surroundings using mathematical methods of exploratory data analysis. Molero (1995) conducted a hydrogeochemical regionalization of groundwater in the Sierra de Quemados, Pinar del Rio, Cuba, which evaluates the patterns of movement of groundwater. Rodríguez M (2005) applied principles and methods of physical chemistry and mathematical modelling to characterize the flow system and hydrogeochemical processes that cause the chemical composition of natural and mineral waters in the Sierra del Rosario. A complete catalogue of the natural waters of Sierra del Rosario was realized by González et al. (2005). 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.

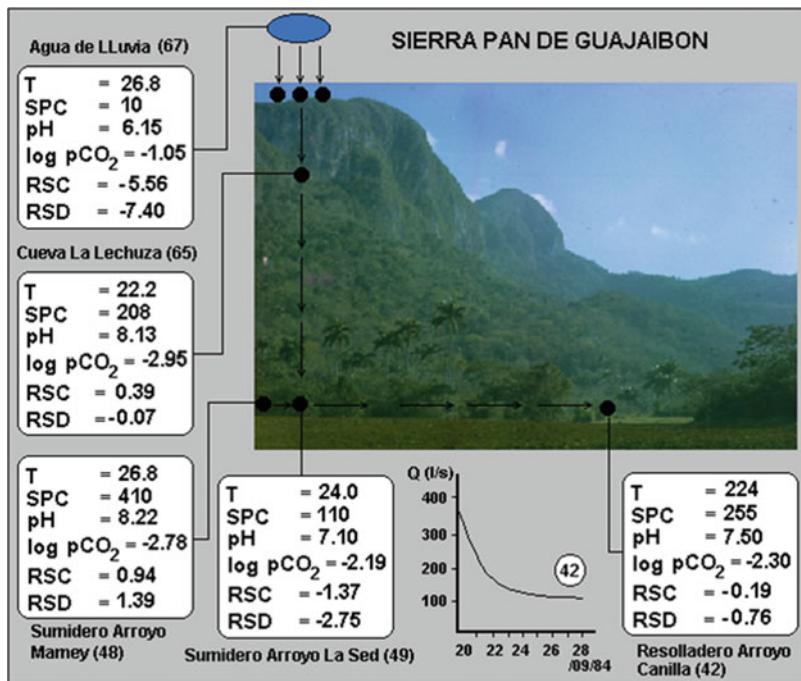
### 25.2.1.2 Chemical Evolution and Empirical Relationships in Karst Waters

The process of the dissolution of limestone by waters passing through the zone of aeration takes a certain amount of CO<sub>2</sub>, ionic and molecular species of the system CO<sub>2</sub>-H<sub>2</sub>O-CaCO<sub>3</sub> concentrations will vary depending on the time nonlinear way. The relationship between the pH or the CO<sub>2</sub> with the concentration of Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, as well



**Fig. 25.1** Variation of some parameters and physico-chemical indices of the karstic waters of the Mil Cumbres stream (Sierra del Rosario, Pinar del Río, Cuba). Sampling of the profile realized the 20.09.1985 (Pajón et al. 1990)

as the hardness (expressed as, mg/l de  $\text{CaCO}_3$ ), are not linear. To cite a few examples, this behavior is observed in the laboratory work carried out by Picknett (1964), Fagundo and Pajón (1985) and González (1997) in saturated conditions. Fagundo (1985) found that if relationships were determined between ion concentrations and electrical conductivity of waters (SPC) at  $25^\circ\text{C}$ , it is possible to automate the quality control of waters (macrocomponent) by simple measurements of in situ temperature, pH and electrical conductivity. These principles were applied in the karst waters of Pan de Guajaibón with satisfactory results (Fagundo and Pajón 1985).



**Fig. 25.2** Representative diagram of the model dissolution (spot) Guajaibón karst massif (Campaign 2 September 1984) (Pajón 1990)

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). They studied pH variation, SPC ( $25^{\circ}\text{C}$ ), the concentrations of major ionic species macrocomponent, the  $\text{CO}_2$  and  $\text{CaCO}_3$  as well as some chemical and physical indices, to experience the waters from the upwelling to the level of the valley (Fig. 25.1). Pajón (1986) presents a representative diagram of the model dissolution (spot) Guajaibón karst massif, based on the seasonal variations of parameters and physico-chemical indices of waters associated with the main entrances, inside and out sectors of the massif, which represent the areas of food, intermittent aeration and saturation (Fig. 25.2). Fagundo et al. (1991) studied using mathematical modelling, chemical evolution and the empirical relations existing in natural waters of the San Marcos River watershed, Sierra del Rosario, Pinar del Rio, Cuba.

### 25.2.2 Chemical Denudation

A comprehensive assessment of chemical denudation processes for the seasonally humid tropical karst Pan de Guajaibón can be seen in Pulina et al. (1984),

Fagundo et al. (1987) and Rodriguez (1995). The karst denudation hyperannual values for wet and dry periods, in the Ancon and Canilla karstic systems are as follows:

**Ancon System:** an average value was obtained for the hydrological cycle of  $107 \text{ m}^3/\text{km}^2 \cdot \text{year}$ , with  $37 \text{ m}^3/\text{km}^2 \cdot 181 \text{ days}$  for dry period and  $70 \text{ m}^3/\text{km}^2 \cdot 184 \text{ days}$  for the rainy season. The average values of the order of the highest recorded globally, as in the case of: Gnong Mulu, Indonesia, with  $120\text{--}200 \text{ m}^3/\text{km}^2 \cdot \text{year}$  (Tropical Climate Zone); SW Caucasus, Georgia,  $114\text{--}139 \text{ m}^3/\text{km}^2 \cdot \text{year}$  (Mediterranean climatic zone); Picos de Europa, Spain,  $148 \text{ m}^3/\text{km}^2 \cdot \text{year}$  (Temperate-Transitional Climatic Zone).

**Canilla System:** The estimated average chemical denudation for Canilla system was  $49 \text{ m}^3/\text{km}^2 \cdot \text{year}$ , with  $19 \text{ m}^3/\text{km}^2 \cdot 181 \text{ days}$  for dry period and  $37 \text{ m}^3/\text{km}^2 \cdot 184 \text{ days}$  for the rainy season. These results are consistent with those reported for other areas of tropical, Mediterranean, temperate and polar climates (Pulina 1977; Garay and Morell 1989; Rodriguez 1995).

The direct linear correlation between denudation and the rainfall has been extensively studied by various researchers for different climatic areas of the world (Pulina (1971); Garay and Morell 1989). Taking into account the values of palaeoprecipitation (up to 6,000 mm) obtained for the karst region of the Sierra de San Carlos during the Sangamon Interglacial (Pajón et al. 2001), replacing them in the equation for calculating the denudation, estimates of chemistry paleodenudation order of those found today in Papua New Guinea can be obtained, where Maire (1981) gave values of chemical denudation in the order of  $270\text{--}760 \text{ m}^3/\text{km}^2 \cdot \text{year}$ , and where ranging from 5,700 to 12,000 mm rainfall annually. Farfán (2005) makes an evaluation processes considering karstification of polycyclic and polygenic natures conducted by the analysis of the age through karstification geoindicators.

### 25.3 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. They noted, among other things, the importance of hydrochemical investigations in Cuba. Molerio (1981) also noted earlier some problems related to the hydrogeology of the karst mountains of Cuba in general, and Pinar del Rio in particular. The work carried out over several decades in the karst mountain of western Cuba, some of them mentioned in the text, providing various data and assessments that contribute to the understanding of karst processes in this region.

As was mentioned above, monitoring is needed to continue with physical-chemical, isotopical, 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. A notable example in this regard was Project PIGEK (Pulina et al. 1984). 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 and drip in the speleothems. A remaining problem is to obtain quantitative estimates of Global Denudation (DG) in the karst areas, whether mountain or other terrestrial ecosystems in karst. Although there are good estimates of chemical denudation for karst areas (e.g. Pan de Guajaibón), virtually no estimates of mechanical denudation, therefore, has not been possible to have even an estimate of the DG. Moreover, although some efforts have been made, it is important to study the chemical denudation (quantitative estimates) in the coastal karst connected to the karst mountain, taking into account the effect of saline and mixing water on the balance of the carbonate. Of current and capital importance is the continuation of studies related to paleoclimatic and paleoenvironmental reconstructions during the Late Pleistocene-Holocene, from natural paleorecords high resolution, as is the case of speleothems.

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