

Karst, cambio climático
y aguas subterráneas
Karst, changement climatique
et des eaux souterraines
Karst, climate change
and groundwater



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Hydrochemistry of karstic waters in a low-energy cave (Castañar de Ibor, Spain)

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Abstract

Castañar de Ibor (Caceres, Spain) is a low energy cave showing very high micro-environmental stability throughout the annual cycle under natural conditions. After the continuous automatic recording of climatic parameters during a whole year the annual variation is 0.09°C for the temperature and 1120 ppm for CO₂. Nine sampling campaigns were carried out from December 2003 to August 2005 for the hydrochemical characterization of the karstic waters in this stable micro-environment. A total of 58 water samples have been collected at 7 locations in the cave, such as lakes, gours and drippings. Physical-chemical features of karstic waters are mainly controlled by (a) petrologic and mineralogic composition of the host rock of the cave and (b) hydrogeologic properties of rocks that have a strong influence on the extent of water/rock interaction. The chemical composition of the karstic water is highly stable during the year, being essentially of Mg²⁺-Ca²⁺-HCO₃⁻ (calcium-magnesium bicarbonate) type as the water percolates through dolomitic limestones. A decrease of the ratio Mg²⁺/Ca²⁺ occurs during the summer probably related with evaporation and mineral precipitation processes at the exterior soil (and/or epikarst). Karstic waters are very near to equilibrium throughout the annual cycle or eventually slightly saturated in calcite and aragonite. Saturation state and mineral precipitation both are determined essentially by small differences in partial pressure of CO₂ between air and infiltration water. In low energy caves the water has a crucial role in the interchanges of matter and energy between atmosphere and karst system.

Key words: CO₂ partial pressure, karstic waters, low-energy cave, mineral saturation

Resumen

La Cueva de Castañar de Ibor (Cáceres, España) es una cueva de baja energía presentando, bajo condiciones naturales, una elevada estabilidad microambiental a lo largo del ciclo anual con una oscilación térmica anual de 0,09°C. Se realizaron nueve campañas de muestreo desde diciembre de 2003 a agosto de 2005 para la caracterización hidroquímica de las aguas kársticas en este microambiente estable. Un total de 61 muestras de agua fueron recogidas en siete puntos de la cavidad incluyendo lagos, gours y goteos. Las características fisicoquímicas de las aguas kársticas están principalmente controladas por: (a) la composición mineralógica y características petrológicas de la roca encajante de la cueva y (b) las propiedades hidrogeológicas del macizo rocoso que tienen una fuerte influencia en la tasa de interacción agua-roca. La composición química de las aguas kársticas es muy estable a lo largo de todo el año, siendo esencialmente de tipo Mg²⁺-Ca²⁺-HCO₃⁻ como consecuencia de su percolación a través de materiales dolomí-

ticos. Durante el verano se produce un descenso de la relación Mg^{2+}/Ca^{2+} vinculado a procesos de evaporación y precipitación mineral en la zona del epikarst. Todas las aguas analizadas están muy próximas al estado de saturación o sobresaturadas en calcita y aragonito. En un ambiente termohigrométricamente muy estable el estado de saturación y la tasa de precipitación mineral están controladas esencialmente por los ligeros desequilibrios entre la P_{CO_2} del aire y del agua de infiltración. En cuevas de bajo rango energético como Castañar de Ibor el agua juega un papel decisivo en los intercambios entre la atmósfera y el sistema kárstico.

Palabras clave: *aguas kársticas, cueva de baja energía, presión parcial de CO_2 , saturación mineral*

1. Introduction

The Castañar de Ibor Cave (Cáceres, Spain) develops by dissolution of dolomite strata interbedded in shales and greywackes of Precambrian Age (Alonso-Zarza *et al.*, 2005). It is a remarkable cave (natural monument) with a singular variety of calcitic and aragonitic speleothems and also moonmilk deposits composed of huntite, dolomite and minor hydromagnesite (Alonso Zarza *et al.*, 2005). After the continuous automatic recording of climatic parameters during a whole year, the mean value of the temperature and CO_2 air concentration is 16.94°C and 3680 ppm respectively. The annual oscillation is only 0.09°C for the temperature and 1120 ppm for air CO_2 . Therefore is able to define Castañar de Ibor as a "low energy cave" (Heaton, 1986) showing very high micro-environmental stability throughout the annual cycle under natural conditions. This large microclimatic stability is a basic characteristic of the karst systems and causes a high sensitivity to changes in environmental conditions, such as rainfall, temperature, vegetation and anthropic activities.

In this work, the results of a hydrochemical study carried out during the period December 2003-August 2005 are exposed. The objective was to know the type of karstic waters existing in a high-stable cave and the physical-chemical variations that suffer along the annual cycle.

2. Methods

During the study period (December 2003-August 2005) it was performed nine water sampling campaigns, at which it was taken sixty water samples at different locations of the cavity (Fig. 1). Fourteen samples were from dripping waters and 46 from lakes/gours and one sample from a dark water system of the nearby camping.

The physical-chemical properties susceptible of suffering modifications due to storage and transport of the samples, such as the temperature, the pH and the CO_2 , have been measured *in situ* with portable devices and using methods of standard titration. The samples have been transported using isothermal containers (12-13°C) to the geochemistry laboratory of MNCN/CSIC. There, the water samples were completely analysed for chemical composition using Spectroscopy of Atomic Absorption (metals), titrated (carbonates) and Electrophoresis of the Ionic Capillarity (remaining mayor elements and nitrogenated compounds).

The geochemistry an determination of speciation calculations required to know the saturation state concerning the main carbonate minerals that constitute the speleothems have been done by means of the informatic code PHREEQC-I version 2.11 (Parkhurst and Appelo, 1999). For the calculation of the saturation rates, it was used the most updated database, minteq.v4.dat, that develops the corresponding equations of temperature dependence of equilibrium. Chemical formula, decomposition in ions and solubility constant at 25°C of the main carbonate minerals are:

Aragonite:	$\text{CaCO}_3 = \text{Ca}^{+2} + \text{CO}_3^{-2}$	$\log_k = -8.3$
Calcite:	$\text{CaCO}_3 = \text{Ca}^{+2} + \text{CO}_3^{-2}$	$\log_k = -8.48$
Dolomita:	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{+2} + \text{Mg}^{+2} + 2\text{CO}_3^{-2}$	$\log_k = -17.09$
Magnesite:	$\text{MgCO}_3 = \text{Mg}^{+2} + \text{CO}_3^{-2}$	$\log_k = -7.46$
Nesquehonite:	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O} = \text{Mg}^{+2} + \text{CO}_3^{-2} + 3\text{H}_2\text{O}$	$\log_k = -4.67$
Huntite:	$\text{CaMg}_3(\text{CO}_3)_4 = 3\text{Mg}^{+2} + \text{Ca}^{+2} + 4\text{CO}_3^{-2}$	$\log_k = -29.968$
Hydromagnesite:	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} + 2\text{H}^+ = 5\text{Mg}^{+2} + 4\text{CO}_3^{-2} + 6\text{H}_2\text{O}$	$\log_k = -8.766$

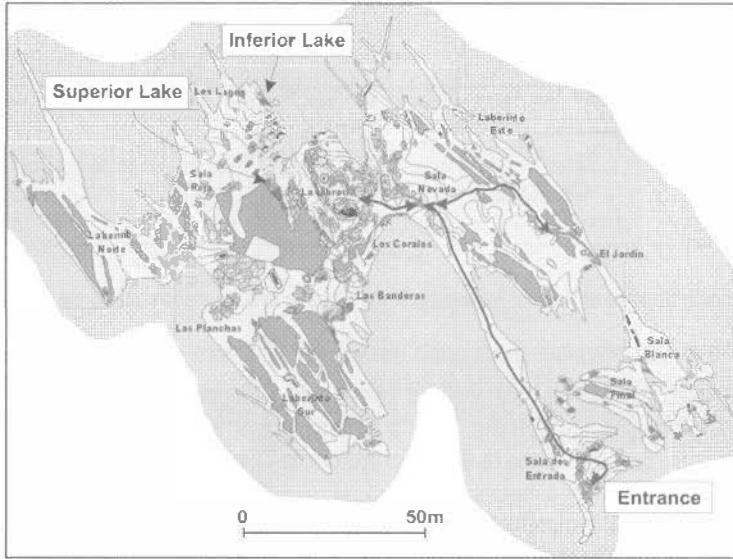


Fig. 1. Cave map with location of sampling points.

3. Results

The results of the complete analytical analysis are presented in nine tables at the end of the report. Figure 2 shows the graphic representation of the chemical composition (major elements) of the analysed samples.

The scarcity of rains at the long range has caused very low seepage rates at all the locations in the cavity, which made the sampling of the water difficult to accomplish at most of the campaigns. During the campaigns of December and April 2004 it was observed how the seepage rate varies from one location to another, both in terms of time of feedback after extreme rains (that were fast in the Galería de Salida and very slow at Jardín and the Librería), as in intensity and stability (there is drippings of low seepage rate but with high stability, as at Jardín). The area with strong seepage rate during the year is Sala de los Lagos, which appears to be superior to the others sampling places, although it is diffuse and drops dispersedly. Therefore, it was decided to have a detailed analysis of the hydrochemistry with periodic sampling from the cave guides, besides the sampling gathered from the nine sampling campaigns by the authors. However, the guides have taken some additional samples at Jardín, due to its low flux prevents to obtain sufficient sampling at the nine sampling campaigns.

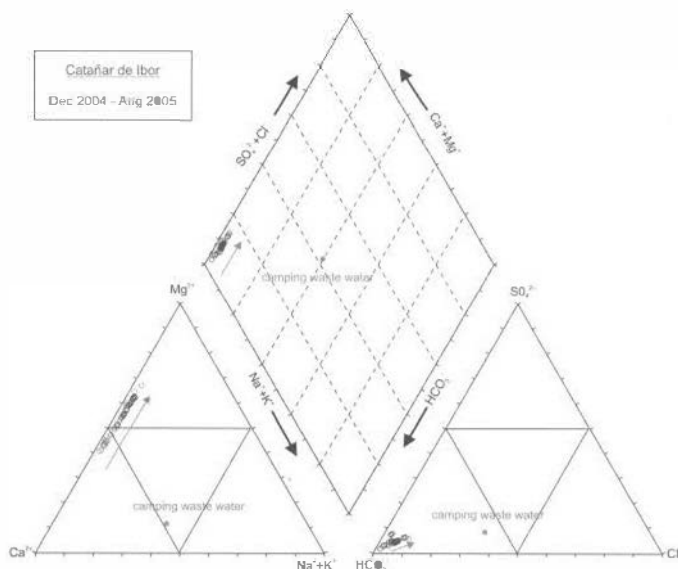


Fig. 2. Piper and triangular diagrams of the ionic relationship of the 60 water samples analysed during the campaigns of year 2004.

On the whole, results indicate that the analysed karstic waters (dripping and lakes) have moderate to high mineralization of calcium-magnesium type (Fig. 2), as a consequence of the dissolution of the dolomitic materials $[\text{CO}_3]_2\text{CaMg}$ presents in the host rock of the cavity. The proportion in Cl^- with SO_4^{2-} is always inferior to 15% from the total of anions (85% of HCO_3^-) with a maximum value of Na^+ plus K^+ of 3,3% among the cations. Generally, the results indicate that the chemical composition in the cavity shows high stability along the annual cycle.

A favorable aspect for the conservation of the cavity is the lack of the levels of contamination, as it shows the inexistence of organic compounds, such as ammonia, nitrate, phosphate and heavy elements in dissolution. In the sampling campaigns of January 2004 and May 2005, it was realized the specific analysis of heavy metals (Pb, Cs, Ni, Cr, Sc, Hg, Cu, Ti) using the Spectroscopic of Atomic Emission using induced Plasma-ICP, with results inferiores to 0,02 ppm of all the above mentioned chemical elements. It was been detected values of Si between 5 and 10 ppm and values of B, Li and Sr inferiores to 0,1 ppm. In the sample of C-61, taken in the exterior and the one from the waste water of the camping, it was detected phosphates (<0,01 ppm) caused by the use of detergents. The high degree of Cl^- indicates probably the use of clorates for the drinkable waters. The concentration of nitrate (NO_3^-) presents in the samples vary between the 0,4 to 11 ppm depending on two factors:

- (1) The season of the year, with an increase in the summer 2004 due to the fertilizer used at the external area of the cave. The fallen rains in July and October may have favoured the increase of these elements in karstic waters.
- (2) The rate of seepage with higher concentration in points with high flow due to a fast and effective dilution (Galería de Salida) and the lowest and stable levels in areas with (Jardín and Librería).

In the summer 2005, the concentration of nitrates of the karstic waters remained low due to the lack of rains. The similarity in the evolution of the NO_3^- and the SO_4^{2-} at the Superior Lake in the Sala de los Lagos (Fig. 3) indicates that the products used as fertilizers are of the nitro-sulfate type. The nitrogenate and sulphate compounds are the necessary nutrients for the development, reproduction and expansion of microbial communities in underground environments that are characterized by the scarcity of available organic mater.

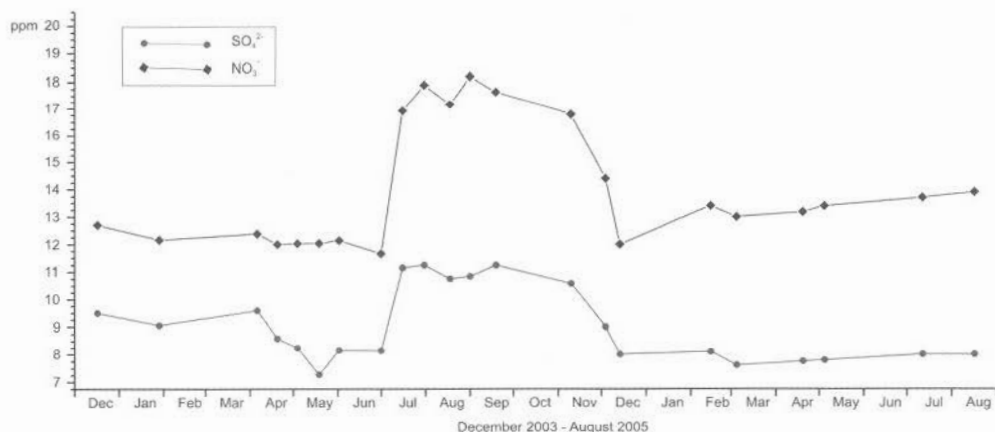


Fig. 3. Evolution of the concentration in nitrates and sulfates in the Lago Superior of the Sala de los Lagos, during the period of December 2003-August 2005.

4. Discussion

The major trends in the chemical compositional variation along the annual cycle are based both on changes in $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio and in the proportion of $\text{Cl}^- + \text{SO}_4^{2-}$ in relation to HCO_3^- (Figure 2, indicated with arrows). These variations are controlled by two main factors: (1) litological factor and (2) external meteorological conditions.

4.1. Litological factor

The texture, the fracture system and the mineral composition of the host rock in the different path of water percolation control the infiltration rate of meteoric waters to reach the cavity. The infiltration rate influences directly over the water chemical composition being decisive in the degree of mineralization of karstic waters. The dripping water of the Galería de Salida, Librería and the Sala Nevada, show a relation $\text{Ca}^{2+}/\text{Mg}^{2+} > 1$, unlike the area of Jardín and specially in Sala Blanca where the proportion of Mg^{2+} is always higher than Ca^{2+} . The litological control (proportion of calcite /dolomite in the formation of the host rock) appears to be the fundamental factor that controls the variations that occurs between the G. Salida (high flow, low concentration) and the Librería (low-moderate flow, high concentration). These differences should reflect also in the mineral composition of the speleothems in the different rooms of the cave. The amount of $\text{Cl}^- + \text{SO}_4^{2-}$ is inferior to 15% of all anions in analysed samples ($\text{HCO}_3^- \approx 85\%$)

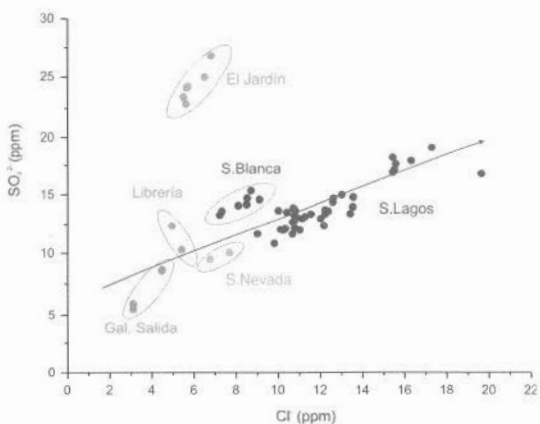


Fig. 4. $\text{SO}_4^{2-}/\text{Cl}^-$ ratio at all analysed samples.

showing a high correlation degree to each other (Fig. 4) to exception of the samples corresponding to the area of El Jardín. The importance of the lithological factor it is very clear in this area that, besides the high relation of $\text{Ca}^{2+}/\text{Mg}^{2+}$ close to 0,5, present a proportion of SO_4^{2-} different and superior to all the remaining samples. This characteristic can be related with the presence of iron sulphur (pyrites) disseminated in the route of infiltration of the water through the host metamorphic rock (mainly shales).

Moreover the velocity of seepage water flow, determined by the structural and texture of the rock, can favour the occurrence of higher content of Mg^{2+} in solution. This occurs if there is a path (network of fissures) that enables a higher water/rock interaction due to a longer time of residence. This process of Mg dissolution is due to the slower kinetic dissolution of the dolomite (Herman and White, 1985) than the one of calcite (Plummer *et al.*, 1979), which means that only the waters with a high time of contact with dolomite induce effective dissolution and the consequent increment of the Mg^{2+} in solution.

4.2. External meteorological conditions

The rainfall and the external temperature can influence directly the chemical composition and the degree of mineralization of the karstic waters as they control the amount of meteoric water available for seepage.

The transit time of water from the surface to a cave drip can vary from hours to years, with different drip sites exhibiting various hydrological behaviours (Smart and Friederich, 1986; Tooth and Fairchild, 2003) and showing considerable variation in physic and chemical characteristics depending on the transit time of waters (Roberts *et al.*, 1998).

The low rate of seepage during the studied period have caused a progressive increment of the proportions of the Cl^- and the SO_4^{2-} detected in the samples of the Superior Lake (Fig. 4). Likewise, during the periods with higher temperature takes place a decrease of the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio (Fig. 5), very common in the karstic system in the vadose zone. This decrease is related with the processes of evaporation and mineral precipitation that have occurred on the soil/rock interface during the time of seepage until reaching the cavity. Both phenomena, specially pronounced in the samples of summer 2004, indicate that there is a probable existence of light evaporation phenomena in the mentioned room (Sala de los Lagos) not detected in the micro environmental monitoring system. A very small evaporation rate favours the increase of concentration of conservative elements (such as Cl^- and SO_4^{2-}) in a very stable geochemical system and the precipitation of carbonates favours a decrease of the relationship $\text{Ca}^{2+}/\text{Mg}^{2+}$ during the year 2004 in comparison with the year 2005. The lack of rainfall during the studied period, restrain insufficient renovation and the situation evolves progressively due to insufficient water recharge renewal showing the low $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio during the last winter.

4.3. State of mineral saturation and the PCO_2

The results of the calculation of mineral saturation state and CO_2 partial pressure (PCO_2) obtained at all the analysed samples are summarized in Table 1. The analysis of the results reveals that all the analysed samples are close to saturation (± 0.25) or oversaturated (>0.25) in aragonite, calcite and dolomite. This oversaturation, indicates that at the superior and external part of the karst (epikarst) prevails the process of dissolution of carbonates (mainly dolostones) while in the interior of the cave the process of speleothems formation is active even though it is developed slowly. Regarding the magnesite, the karstic waters are found to be slightly undersaturated or near the equilibrium while are undersaturated in huntite, nesquehonite and hidromagnesite.

Concerning to mineral saturation state the whole of samples present a high homogeneity. The main variations are related to its degree of mineralization and are mainly controlled by the PCO_2 in the water, while the later depends

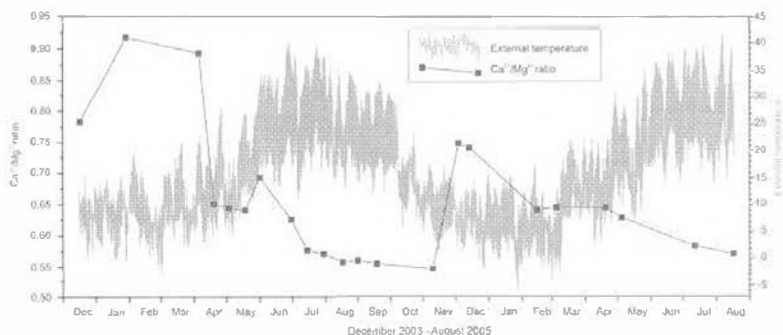


Fig. 5. External temperature and $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio on Superior Lake of Sala de los Lagos along the period of December 2003-August 2005.

on the environmental conditions (external and internal). Figure 6 shows the relationship between the mineral saturation rate of all the samples in calcium-magnesium carbonates and the value of PCO_2 dissolved in the water. It is observed that there is a high degree of correlation between both parameters, which is significantly higher in the case of the magnesium minerals compared with the calcium phases. This is due to the fact that in the cave the precipitation of dolomite and huntite is active (Alonso-Zarza *et al.*, 2005).

In the case of the water from lakes, the values and the variations of the PCO_2 depends directly and mainly on the internal environmental conditions, especially on the air PCO_2 , the three points in those has been carried out a detailed pursuit of their hydrochemistry (Superior Lake, Inferior Lake and Sala Blanca) show similar values in terms of saturation state and PCO_2 , although there is some slight variations important for performing a physical-chemical integrated modelling. For instance, the variations from the sampling of the Sala de los Lagos indicate the stratification of the air in the mentioned area. The area of the Inferior Lake it is found more cold (-0.1 to -0.2°C) and with higher concentrations of the CO_2 in the air (until 100 ppm) than the area of the Superior Lake. This phenomena of accumulation/stratification of cold and enriched CO_2 air is reflected in higher values of PCO_2 in the water of the lower

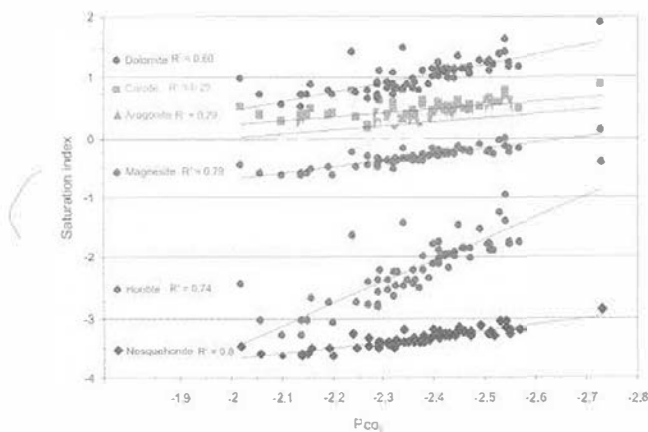


Fig. 6. Relationship between the mineral saturation respect to carbonate minerals and the value of PCO_2 in the water. The degree of linear correlation is presented (R^2).

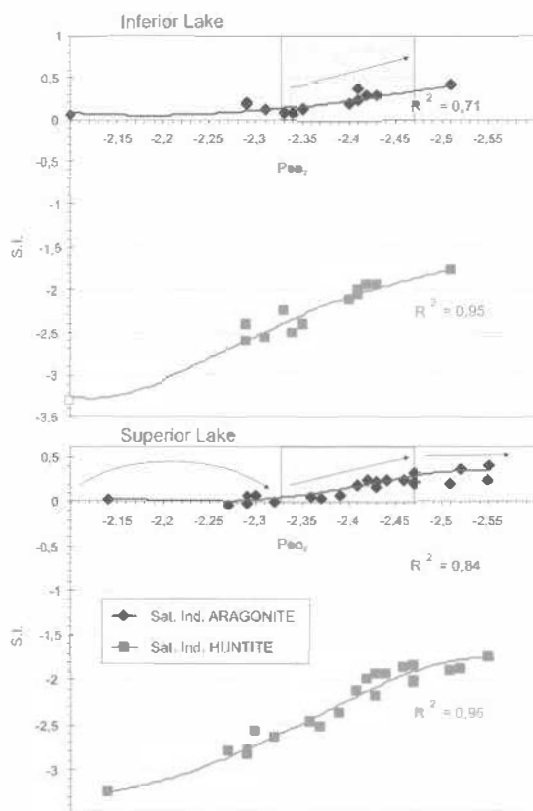


Fig. 7. Relationship between the rate of saturation, of the aragonite and huntite, and the $\log P(\text{CO}_2)$ in the superior and inferior lake (at Lake room). The degree of correlation (R^2) of the fitted curves (polynomials of degree 4) is given.

zone (average PCO_2 : $10^{-2.33}$ against $10^{-2.48}$ in the upper zone), and consequently a slightly lower degree of mineral oversaturation in aragonite and calcite. This fact indicates the possible existence of a threshold for mineral precipitation controlled by the PCO_2 .

At Figure 7 it is shown the significance of PCO_2 for the degree of mineral saturation of aragonite and huntite in the water of both lakes. From values of PCO_2 around $10^{-2.30}$ - 2.35 bar until $10^{-2.47}$ - 2.50 bar, there is a progressive gradual increase of the saturation index that indicates a minimum or low precipitation of the mineral phases calcium-carbonate (aragonite and/or calcite) and causes a decrease of the under saturation in the magnesium phase (huntite). Once the $\log (\text{PCO}_2)$ decrease below $10^{-2.47}$ bar the rate of mineral precipitation should increase, causing a new stabilizing oversaturation of the mineral. This evolution is related with the strong dependence of the kinetics of carbonate precipitation regarding the water PCO_2 . Mineral precipitation from waters with a certain degree of oversaturation can be delayed and therefore constrained according to the CO_2 in dissolution. Thus, these waters can remain oversaturated until the PCO_2 is sufficiently low so that mineral precipitation is produced. The mentioned values of PCO_2 ($10^{-2.30}$ - 2.35 bar and $10^{-2.47}$ - 2.50 bar) are thresholds of the rate of mineral precipitation, which will determines the formation of the speleothems.

Regarding the drippings, their PCO_2 is moderately higher than the air PCO_2 at the cave atmosphere throughout the annual cycle. This fact indicates that the water is the main vehicle of transport of CO_2 into the cave. The degassing of CO_2 in the drippings is caused by a slight unbalance of water/air CO_2 pressures that favours the singular slow processes of mineral precipitation taking place in this particular cave.

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