Effect of Ventilation on Karst System Equilibrium (Altamira Cave, N Spain): an Appraisal of Karst Contribution to the Global Carbon Cycle Balance

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Abstract Altamira cave air CO_2 concentration, and both cave and air $\delta^{13}C$ values seasonally vary indicating the cave behaves as a CO_2 reservoir or source in winter and summer, respectively. During the 'CO_2-reservoir phase' the $\delta^{13}C$ of the cave air is lower, because it is influenced by the infiltration of soil-derived organic carbon-rich waters. In the 'CO_2-source phase' the $\delta^{13}C$ of the cave air is heavier due to the ventilation of the cave and the mix with the air from the external atmosphere and soil. The $^{13}C/^{12}C$ analyses confirmed the importance of the external soil as the CO_2 source for the underground system as well as the effect of ventilation on system equilibrium.

1 Introduction

For the carbon present in the three principal phases of underground systems (rock, water, and air), every phase change that comes about includes isotopic fractionation processes that modify the proportions of each stable isotope. Thus, each chemical reaction implies a particular discrimination factor that bestows a characteristic isotopic signal on the newly generated phase. The characterization of this isotopic signal for each of the new phases involved in underground CO_2 transfer processes between the interior and exterior of the underground environment is useful in the evaluation of the degree to which different processes are important. Likewise, the study of the behaviour of CO_2 in karstic environments is critical because its contribution to the global carbon cycle balance (Yuan 1997; Kowalski et al. 2008).

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B. Andreo et al. (Eds.), *Advances in Research in Karst Media*
DOI 10.1007/978-3-642-12486-0, © Springer 2010

The aim of the study is to characterize the interchange processes between the underground (endokarst) and the external environment, with special emphasis on the study of exchange cycles of atmospheric CO_2.

Altamira Cave is world-famous for possessing a remarkable collection of Palaeolithic rock paintings and engravings. It is a 270 m-long downward-trending cave located in the unsaturated water zone of a tabular polygenic karst system. The depth of the cave ranges from 4 to 21 m. The climate is Atlantic and humid and the pluvial regime is moderate to high.

2 Methods

Annual microclimatic series for different sectors of the cave and exterior have been obtained. Studied climate parameters in cave atmosphere include: air temperature, rock temperature, CO_2 on air, and relative humidity. Above the cave the measured parameters also include CO_2 fluxes of the ecosystem, soil temperature and soil relative humidity. Karstic waters were monthly sampled for both geochemical analysis and infiltration rate studies. The $^{13}C/^{12}C$ isotopic analysis of air from the cave interior, soil pore space and exterior were done by the GEOTOP Isotope Laboratory (Québec, Canada). The analyses of solid (rock and speleothems) and water $^{13}C/^{12}C$ isotopic signatures were done by the Stable Isotope Analytical Service of the University of Salamanca and Zaidin Station (CSIC, Granada), respectively.

3 Results

Annual average temperature in the cave is 14°C, and relative humidity is approximately 100% the whole year. Cave air shows lower CO_2 concentration during summer when the external temperature is higher than cave air temperature (Fig. 1). In winter, CO_2 concentration in the cave is approximately eight-ten times higher than in summer, then the cave acts as a CO_2 reservoir. The underground air renewal prevails during spring-summer seasons, when the exterior air temperature is constantly above the cave air temperature. Under these dry environmental conditions the air exchange between the cave and the outer atmosphere is favoured, with an intense degasification process taking place such that the CO_2 levels drop to minimum concentrations of 1000 ppm. Degassing processes involve a net emission of CO_2 to the atmosphere. From November to May the outside temperature is frequently below the cave air temperature, and intense rainfalls and high values of atmospheric relative humidity are registered. Under these environmental conditions, the membranes covering the cave (host rock and soil) tend to a full state of water saturation; so, a limited air exchange prevails between the cave and exterior atmosphere through the network of fissures and pores. When the confined conditions are reached (especially during the rainy periods), the microfracture networks, carry diphasic infiltration (water plus air) delaying the air gaseous transfer between the cave atmosphere and the exterior. During this stage the cave behaves as a CO_2 reservoir, reaching the maximum mean levels: 5000–6000 ppm of CO_2. Therefore, recharge of CO_2 in the cave is closely related to infiltration water input after rainfall. This gravitational water percolates through the soil zone and host-rock porosity and is recharged of CO_2 due to organic activity in soil and water-rock interaction. During the summer time, the cave degasification is produced except when rainfall events occur. The main CO_2 cave recharge coincides with the beginning of the rainy season, at the end of September (Fig. 1).

The data (Table 1) invokes for a seasonal variation of the $\delta^{13}C$ in the CO_2 of the interior of the cave. During the 'CO_2-reservoir phase' the $\delta^{13}C$ of the cave air is light, because this is influenced by the soil contribution. In the 'CO_2-source phase' the $\delta^{13}C$ of the cave air is heavier due to the ventilation of the cave and the mix with the air from the external atmosphere and soil. The $\delta^{13}C$ value of the infiltration waters presents a seasonal variation, similar to that observed in the cave air (Fig. 2). The $\delta^{13}C$ of the water (averaging −12.6‰), varies according to the degree of water/rock interaction with less negative values corresponding to greater time

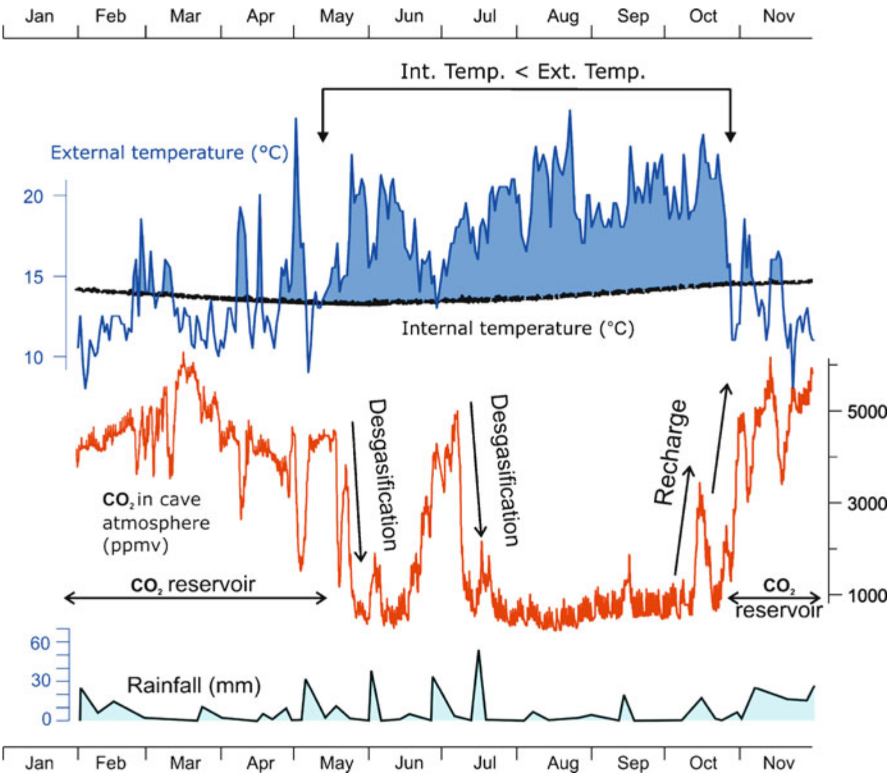

Fig. 1 Time series (*annual cycle*) of the main microclimatic parameters of Altamira cave in relation to the external atmosphere

Table 1 Isotopic signal of air (average values, 2005)

Cave environmental dynamics	CO_2 reservoir	CO_2 source
	T ext < T cave	T ext > T cave
AIR $\delta^{13}C$	MARCH	SEPTEMBER
Cave	−21.9	−18.0
Soil	−21.4	−18.7
External atmosphere	−9.7	−10.4

spent reaching the cavity due to enhanced influence of the hostrock ($\delta^{13}C = +2‰$ limestone, $+3‰$ dolomite). The mean $\delta^{13}C$ of rapidly infiltrating water (−12.9‰) corresponds to the fractionation signature (coefficient of +9.1‰ at 14°C; Emrich et al. 1970) of CO_2 dissolution and formation of HCO_3 (Fig. 3). Slow steady fluxes result from dolomite reactions and show heavier mean values ($\delta^{13}C = -11.4‰$). The speleothems show $\delta^{13}C$ values varying from −4 to −13.5‰. In detail, the currently growing speleothems show an averaged value −8.4‰.

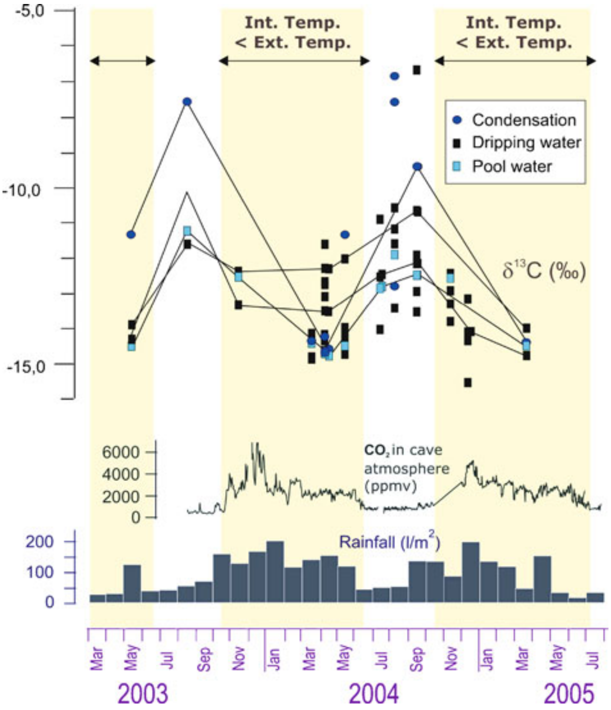

Fig. 2 Time series (*annual cycles*) of the aqueous phase $\delta^{13}C$ isotopic signatures in relation to cave air CO_2 concentration and rainfall

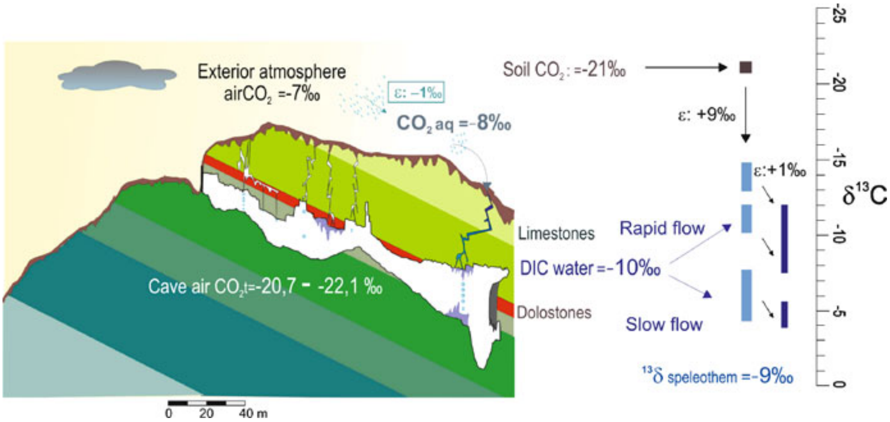

Fig. 3 $^{13}C/^{12}C$ isotopic composition of CO_2 from air (external atmosphere, soil pore space and cave atmosphere), water and solid (speleothems and host-rock)

4 Discussion and Conclusions

The $^{13}C/^{12}C$ analyses for air, water and rock/speleothem in Altamira Cave (Spain) confirm the importance of the external soil as the CO_2 source for the underground system, as well as the effect of ventilation on system equilibrium. The similarity between the typical C3 vegetation signal of the air in the soil pore space ($\delta^{13}C$ $-21‰$) (Deines et al. 1980) and the air in the different points sampled in spring inside the cave ($\delta^{13}C = -18.7$ to $-21.4‰$) reflect a clear connection within the gas phase between the exterior and the interior (Table 1). These data evidence that karst underground atmospheres accumulate carbon dioxide, which has their origin in the overlying soils, and that carbon dioxide should be considered in the annual balances of atmosphere/soil flows in different ecosystems. The cyclic variation of cave air CO_2 concentration indicating the cave behaves as a CO_2 reservoir or source in different season is clearly outstanding in Altamira cave, as, the same as in other shallow karst systems (Fernández-Cortés et al. 2009).

The annual cycle of the aqueous phase isotopic signatures (Fig. 2), in addition to the rate of water/rock interactions, presents a seasonal variation, similar to that observed in the cave air, showing the influence of the gaseous exchange between cave and exterior atmosphere. During summer, periods of enhanced ventilation and reduced CO_2 concentration are observed to coincide with heavier isotopes (enriched in $\delta^{13}C$). This suggests an increased external influence, but also that the cave water is more prone to degasification; the kinetic isotopic discrimination makes the water heavier than equilibrium isotopes. This kinetic effect is more pronounced in waters with slow infiltration rates, where water from condensation mixes with the slow drip and the time scale for interaction between cave water and air – prior to drip – is enhanced.

The isotopic signature of gaseous CO_2 inside the cave also is influenced by ventilation and degasification of the cavity, due to the invasion of isotopically heavy air from the exterior atmosphere and the fractionation (enrichment of light isotopes in the gaseous part) caused by the entrance of water laden with organic CO_2 and its subsequent gasification (Fig. 3). Consequently, the isotopic signature of the speleothems precipitated from this cave water, essentially composed of calcite, should conform to expectations from the previously mentioned mechanisms. Thus, it ought to reflect the influence of the overlying vegetative canopy – in type and dynamic – and also the importance of the ventilation process. Indeed, it is seen that the speleothems have values ($\delta^{13}C = -4$ ato $-13.5‰$) that are congruent with their precipitation in isotopic equilibrium with the interior of the cave (discrimination coefficient of $+0.4‰$ at 14°C, Labonne et al. 2002).

Acknowledgements This research was supported by CGL2006-11561/BTE project. All Altamira Cave Research Centre and Museum staff is acknowledged for their collaboration throughout the whole research period.

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