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Interpreting CO₂-SIc relationship to estimate CO₂ baseline in limestone aquifers

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Abstract

Saturation index with respect to calcite (SIc) and equilibrium CO₂ partial pressure are important parameters to study groundwater in limestone aquifers. Aside from their use in time series, CO₂ and SIc are used to estimate the baseline of CO₂ in the vadose zone. The objective of this paper is to present conceptual examples on the use of the CO₂-SIc relationship in order to have new information from usual parameters. Case study was considered as an example of use from Cussac site, a limestone aquifer in Southwest of France. The result showed that CO₂ base line in unsaturated zone is found close to 25 000±1 000 ppm.

Key words: CO₂ baseline, carbonate rock, unsaturated zone

Nomenclature

[A]	ionic activity of A species	HCO ₃ ⁻	bicarbonate
Ca ²⁺	calcium	Pco ₂	partial pressure of CO ₂
K ₀	constant of Henry for gas dissolution	Pco ₂ eq	equilibrium Pco ₂
K ₁	first ionisation constant	Pco ₂ sat	saturation Pco ₂ , a specific value of Pco ₂ eq, defining the air Pco ₂ baseline
K ₂	second ionisation constant		
K _c	calcite dissolution constant	SIc	Saturation Index with respect to calcite
γ _A	ionic activity coefficient of A species		

1 Introduction

In limestone aquifers, interactions between gas, water and rock are important processes triggering the aquifer behaviour. The CO₂ present in the rock porosity (matrix and fractures) in the unsaturated zone dissolves in the water and increase its acidity. Commonly, the equilibrium CO₂ partial pressure (named Pco₂eq in this article) is used to take account of the dissolved CO₂ and its consequences on the water total dissolved inorganic carbon.

P_{CO_2eq} had been studied to better understand the aquifer behaviour. The most common ways to use P_{CO_2eq} are: 1) in proposing an average characteristic value for water origin or flow condition, 2) in monitoring time series for temporal evolution, and 3) in assessing the degassing processes. For example, Thrailkill and Robl (1981) and Karimi *et al.* (2005) used P_{CO_2eq} to discriminate between quick and slow flows or open and closed conditions. Drake and Harmon (1973), Roberge (1989) and White (1997) characterised water type according to their origin: conduit, matrix (diffuse water), soil, run-off, river, tropical area and drip-water. Johnson *et al.* (2012) and Pasvanoghu and Gultekin (2012) showed the influence of deep sources of CO_2 in the behaviour of aquifers.

Monitoring P_{CO_2eq} evolution through time, in some researches (Vesper *et al.* 2004; Liu *et al.* 2007; Li *et al.* 2008; Zhao *et al.* 2010), estimated the contribution of different compartments during a flood event. Unger-Lindig *et al.* (2010) showed that evolution of P_{CO_2eq} can be used as an indicator of water quality following acidity neutralization activities. In the context of cave studies, Shuster and White (1972) and Troester and White (1984) made time series of P_{CO_2eq} to estimate cave air P_{CO_2} evolution along the year and Spötl *et al.* (2005) made comparisons between cave air P_{CO_2} and P_{CO_2eq} dissolved in water. Finally, effects of CO_2 degassing processes were studied (Herman and Lorah 1986; Shuster and White 1971; Liu *et al.* 1995; Bono *et al.* 2001) on water flowing along surface streams after came to surface. Sometime, degassing can also be considered as a perturbation of the water sample. In this case then, the P_{CO_2eq} calculated from samples may not exactly represent the P_{CO_2eq} of the water when it flows in the unsaturated zone.

Research studies were made to estimate the P_{CO_2eq} of the water before the effect of the degassing. Some authors computed this effect with available software. For instance, Fairchild *et al.* (2000) used Mix4 program (Plummer *et al.* 1975) to estimate what was the P_{CO_2eq} before degassing. Faimon *et al.* (2012a; 2012b) and Riechelmann *et al.* (2011) used PHREEQC software (Parkhurst 1995) to estimate the P_{CO_2eq} before degassing, using measured bicarbonate and modelled pH; adjusted until water reaches the saturation index with respect to calcite (named SIc). Another way to do this estimation is through analytical calculation based on calcium-carbonate equations (or carbonate equilibrium equations). Authors like White (1997), Tooth and Fairchild (2003), Vesper *et al.* (2004) and Matthey *et al.* (2010), calculated the air P_{CO_2} that would justify the measured concentration in calcium.

However, it appears interesting to perform the calculation of the P_{CO_2eq} before degassing using bicarbonate instead of calcium. Indeed, bicarbonate is a central component in the relationship between air, water and rock, whereas, calcium ions are, rather, involved in water and rock interactions. Subsequently, Peyraube *et*

al. (2012) proposed a calculation to estimate the P_{CO_2eq} that would justify the bicarbonate concentration, allowing an estimation of the P_{CO_2eq} before degassing and independently from pH measures. They presented the evolution of water during its flow in the unsaturated according to the different air P_{CO_2} encountered. Yet, detailed information on the interpretations of water data (P_{CO_2eq} and SIc) to estimate air P_{CO_2} values are found short in terms of presentation and full discussion.

In this line, this article focused on the use of P_{CO_2eq} and SIc in the context of limestone aquifers in an open system condition in order to: 1) estimate what was the P_{CO_2eq} before degassing processes and 2) estimate the limits for the air P_{CO_2} in contact with water. However, kinetic aspect of calco-carbonic relations and implications for speleothems growth are not discussed and may be found in the work of Dreybrodt *et al.* (1997). The main objective is to clearly expound the ways of interpretation of the CO_2 - SIc relationship and its representation in the $(-\text{Log}(P_{CO_2eq}) ; SIc)$ reference frame. These parameters might not be new but can still provide additional information on the air P_{CO_2} in the unsaturated zone. An application is presented, using the measurements on water of three springs in Cussac site (France), to provide estimations of air P_{CO_2} base line.

2 Site background

Cussac site is located in Southwest of France (Fig.1). It is a karstified aquifer composed of upper cretaceous calcareous sandstone. The width of the vadose zone can reach 70m above the small saturated zone of about 10m. The saturated zone takes place above upper cretaceous marly limestone, characterized by lower permeability than the calcareous sandstone. Finally, a discontinuous, ~20m thick, blanket of clayey sands from Eocen-Oligocen can be seen at the top of the outcrops.

The climate is temperate with an average annual temperature of 13°C, an average summer temperature between 22°C and 23°C, and an average winter temperature between 2°C and 3°C. The vegetation is composed of Oak and Chestnut trees. Average annual precipitation varies between 800 and 1000mm, and because of evapotranspiration, effective rainfall is computed ranging from 200 to 350mm per year.

The site gives access to several springs; though, only three springs are presented in this article. The three springs take place in three compartment of the aquifer: Subcutaneous spring (156m.a.s.l.), a seasonal spring located in the upper part of the unsaturated zone; Farfal spring (110m.a.s.l.) in the unsaturated zone, the main outlet of the system; and the Gutter (95m.a.s.l.), an accumulation of water seeping from saturated zone. At Subcutaneous spring, the water flows in stress-released and aerated limestone before the sampling point. At Farfal spring, water surges in a small basin and is directly accessible. At the Gutter, the spring itself is not

accessible and the water has a short flow on a cliff before the sampling point. Peyraube *et al.* 2012 presented a conceptual functioning scheme of the Cussac aquifer: rainwater flows through epikarst where it gains mineralization then it flows through the other parts of unsaturated zone where it degasses and precipitates calcite.

3 Material and methods

A bi-monthly monitoring for two years was conducted with water sampling and field measurements of conductivity, pH and temperature using WTW 340i probes. Measurements of bicarbonate concentration (HCO_3^-) using a Hach Lange field titrator was performed immediately on the site to avoid perturbation caused by late analysis. Water samples were filtered to 0.45 μm and preserved at 4°C in 60 ml HDPE flasks (one for anion, one for cation). The contents of the cation flasks were acidified with HCL. The ion concentrations (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Cl^- , NO_3^- and SO_4^{2-}) were determined by Dionex ICS900 liquid chromatography. Table 1 gives the mean values of temperature, electrical conductivity, pH and major ions concentrations for the three springs.

4 Discussion

4.1 Pco_2 – SIc relationship

In limestone environment, in the absence of dolostone, the groundwater chemistry is mainly driven by calcium and bicarbonate ions. Calcium-carbonate equations are governed by equilibrium constants dependent on the temperature. From these equations two parameters are calculated: equilibrium CO_2 partial pressure (Pco_2eq) and Saturation index with respect to calcite (SIc). Pco_2eq represents the CO_2 partial pressure that would be in gas-liquid equilibrium with water at the moment of the measure. It is a transcription in terms of partial pressure of the CO_2 dissolved in water (aqueous CO_2 and H_2CO_3). SIc has been defined by Langelier (1936) as the ability of water to precipitate (for super saturated water with $\text{SIc}>0$) or dissolve calcium carbonate (for under saturated water with $\text{SIc}<0$).

From the expressions of these parameters, Peyraube *et al.* (2012) gave an expression of SIc dependent of Pco_2eq , bicarbonate activity and temperature (equations (1)):

$$(1) \text{SIc} = -1 \cdot \text{Log}(\text{Pco}_2\text{eq}) + 3 \cdot \text{Log}[\text{HCO}_3^-] + \log \left(\frac{K_2}{K_0 \cdot K_1 \cdot K_c} \cdot \frac{\gamma_{\text{Ca}^{2+}}}{2 \cdot \gamma_{\text{HCO}_3^-}} \right)$$

K_0 , K_1 , K_2 and K_c are equilibrium constants dependent on the temperature calculated using the coefficients given by Plummer and Busenberg (1982) and the water temperature at the moment of sampling. The terms γ_{ca} and γ_{HCO_3} represent ionic activity coefficient (see nomenclature) and the term in square bracket is the

activity of the ion. This expression is limited by some assumptions: 1) groundwater is electrically neutral, 2) mineralization is dominated by Ca^{2+} and HCO_3^- in the absence of other species such as magnesium (no dolostone) or sulphates (no gypsum) in significant proportions, 3) CaCO_3 precipitates only in calcite with no aragonite, and 4) pH is only driven by dissolved CO_2 .

Subsequently, for SIc equal to zero, the Pco_2eq is called “water saturation Pco_2 ” and written Pco_2sat in equation (2):

$$(2) \text{Pco}_2\text{sat} = 10^{\left(3 \cdot \text{Log}[\text{HCO}_3^-] + \log\left(\frac{K_2}{K_0 \cdot K_1 \cdot K_c} \cdot \frac{\gamma_{\text{Ca}^{2+}}}{2 \cdot \gamma_{\text{HCO}_3^-}} \right) \right)}$$

4.2 conceptual uses of the projection in the (-Log(Pco_2eq) ; SIc) reference frame

The linear relationship between $-\text{Log}(\text{Pco}_2\text{eq})$ and SIc described in equation (1) is represented by the straight black line with a slope of 1 in the $(-\text{Log}(\text{Pco}_2\text{eq}) ; \text{SIc})$ graph presented in Fig.2. The vertical axis differentiates super saturated water, under saturated water and saturated water for SIc equal to zero with a tolerance of ± 0.1 . Above the horizontal axis corresponding to $-\text{Log}(\text{Pco}_2\text{eq})$, an indicative scale of Pco_2eq expressed as a percentage is added to help the interpretation (10 000 ppm = 1%). An indicative HCO_3^- scale in mg/l, computed for a temperature of 13°C, is displayed on the graph. In Fig.2, an example is computed for HCO_3^- equal to 220mg/L at 13°C at various Pco_2eq drawing to the black line. The specific value of Pco_2eq corresponding to the intersection of the black line and the $\text{SIc}=0$ line corresponds to Pco_2sat . In this example, Pco_2sat is equal to 0.6%, calculated from equation (2). For this particular value, the water is in equilibrium with the calcite. Then one can say that Pco_2eq represents the gas-liquid equilibrium and Pco_2sat represents the gas-liquid-solid equilibrium.

During the transit of the water in the unsaturated zone, Pco_2eq and HCO_3^- will vary through gas dissolution (gassing) and degassing processes and through calcite dissolution and precipitation processes. The variations of Pco_2eq and HCO_3^- can be simultaneous, however, gassing and degassing are rapid processes compared to dissolution and precipitation in non-turbulent flow (Ford and Williams 2007). Then, to simplify the concept of the processes, any variation of Pco_2eq and HCO_3^- is divided into a succession of two consecutive steps where one parameter varies while the other remains constant. In that case, the arrows displayed in the Fig.2 present the possible changes of water chemical characteristics for a constant water temperature. These changes correspond to: variation of Pco_2eq caused by gassing and degassing (arrow no.1) or variation in HCO_3^- concentration caused by dissolution and precipitation of calcite (arrow no.2).

Displaying the data on the $(-\text{Log}(\text{Pco}_2\text{eq}) ; \text{SIc})$ reference frame is a useful technique to display the variability of water chemistry (White 1997; Leybourn *et al.* 2009) or to assess the origin of water (Roberge 1989). This representation can also help to better understand the processes that happened during the transit of the water in the unsaturated zone, in the saturated zone and even at the sampling point. In Fig.3, several illustrations of the uses of this reference frame were presented. The proposed theoretical examples are not modelled data but rather arbitrary values of Pco_2 , temperature and HCO_3^- chosen to illustrate the use of the Pco_2 -Isc relationship.

Fig.3.a presents the perturbation caused by site effect. The term "site effect" embraces the alterations and influences on the quality of the measure caused by configuration and accessibility of the sampling point. A simple field example is an inaccessible spring where water can be sampled only after a short turbulent flow at the surface. In this case, the measure Pco_2eq is not anymore representative as the water undergone degassing before sampling. In Fig.3.a, the theoretical example talks about a water in gas-liquid equilibrium inside the unsaturated zone, with a Pco_2eq of 5% (represented in the point "b"). This water reaches the surface and undergoes degassing and, at the moment of sampling, Pco_2eq is measured at 0.1%. Despite degassing, this kind of water still provides information on the air Pco_2 of the unsaturated zone. Pco_2sat presented in point "a" is equal to 1%. It represents a minimum limit of the possible air Pco_2 values of the unsaturated zone. Indeed, the starting Pco_2eq of 5% is higher than Pco_2sat and the water in "b" is under-saturated with respect to calcite. If the water would have stayed in the unsaturated zone, dissolution processes could have occurred, and a new equilibrium between gas, liquid and solid would have been reached in "c" for a higher HCO_3^- concentration.

Fig.3.b shows the theoretical example of water flowing through two compartments characterised by two different air Pco_2 in the unsaturated zone and, finally, arriving at the earth's surface. Thus, these parts are mentioned as "second to last compartment", and "last compartment" and, finally, "external atmosphere". In this theoretical example, let's imagine an air Pco_2 higher in "the second to last compartment" than in "the last compartment". This leads the water to undergo degassing inside the unsaturated zone when it arrives in the last compartment. Then, subsequently to the degassing, the water undergoes calcite precipitation. Afterwards, the water reaches the surface and can be sampled and Pco_2eq is measured.

Air Pco_2 in the second to last compartment is supposed to be unknown and written "d?". Although, to draw the figure, a value of 5% for air Pco_2 is chosen. In the last compartment, the water degasses from value "d?" to the measured Pco_2eq (0.1%). The measured Pco_2eq may not represent the last compartment air Pco_2 , but Pco_2sat can provide information on it. The Pco_2sat in point "a" (0.3%) is the maximum limit of possible air Pco_2 that forced the water to degas and precipitate in the last compartment. Air Pco_2 in the last compartment may be

lower than measured P_{CO_2eq} (0.1%). In this case and if the water would have stayed in the last compartment in the unsaturated zone, the water would have continue to degas and precipitate until it would have reached an equilibrium with respect to calcite.

P_{CO_2sat} is a particular value of P_{CO_2eq} for SIc equal to zero, and can be accepted as a footprint of the air P_{CO_2} with which water has interacted in the unsaturated zone. P_{CO_2sat} is a maximum or a minimum value of the air P_{CO_2} in the unsaturated zone and the interpretation depends on the behaviour of the water before sampling: degassing only or degassing and precipitation.

In a given spring, P_{CO_2eq} and P_{CO_2sat} (calculated from HCO_3^- concentration) may vary over the years. Nonetheless, the natural yearly variations of P_{CO_2eq} and P_{CO_2sat} ranges between usual values characterising the spring. Then, on a $(-Log(P_{CO_2eq}) ; SIc)$ reference frame in figures 2.c and 2.d, the samples are gathered within a zone represented by the square area that takes account of the variability of the P_{CO_2eq} and the HCO_3^- concentration. Field cases of this gathering of samples are presented in Fig.3 from Cussac site measures.

Fig.3.c and 3.d specially talks about the consequences of an important increase of P_{CO_2} in the air of the unsaturated zone. Discussing the causes of the variation is not the aim of this article. To give an example, one of the causes can be a CO_2 leakage from geological storage. Limestone would probably not be used as host layer for geological CO_2 storage, however, limestone can be found above the host layer of geological CO_2 storage and be affected by leakage as CO_2 gas will move toward surface.

Fig.3.c shows the theoretical example of an increased of air P_{CO_2} on a water that does not interact for a long time with this abnormal high air P_{CO_2} . It can be possible if the water flows quickly in the unsaturated zone and reaches the surface where it is sampled. Then, gas-liquid interaction may occur and lead to an increase of P_{CO_2eq} . Yet, the interaction time is too short to lead to noticeable change in HCO_3^- concentration and P_{CO_2sat} remain unchanged. In the example, P_{CO_2eq} increases from a common value in point "a" to the measured value. The water becomes more under saturated with respect to calcite (SIc is highly negative).

Fig.3.d shows the theoretical example of an increase of air P_{CO_2} on water with a slow flow that interacts for a long time with this abnormal high air P_{CO_2} . Then, gas-liquid-solid interaction may occur, leading to an increase of P_{CO_2eq} and, in addition, carbonate dissolution may occur leading to an increase of P_{CO_2sat} . The example presents water with a given HCO_3^- concentration and a P_{CO_2eq} of 0.5% in the point "a". Then, let's imagine that the water is in contact with an air P_{CO_2} of 3.1%. Subsequently, there is gas dissolution and P_{CO_2eq} increases to reach 3.1%. As the water remains in contact with the limestone, carbonate dissolution occurs until equilibrium with respect to calcite is reached ($SIc=0$). P_{CO_2sat} increases toward a new value equal to 3.1%, the

same as air P_{CO_2} and P_{CO_2eq} . However, water can be sampled at any moment of this process. Then, the Fig.3.d shows several possible samples scattered along a vertical line with an abscissa corresponding to a P_{CO_2eq} of 3.1%. P_{CO_2sat} of the samples can have any value between 0.5 and 3.1%.

An important increase of P_{CO_2} in the air of the unsaturated zone can be detected by P_{CO_2eq} or P_{CO_2sat} according to the behaviour of the water: quick flow or slow flow. However, limitations exist as the method works only in limestone as water mineralization have to be dominated by Ca^{2+} and HCO_3^- . In addition, P_{CO_2eq} can be affected by degassing occurring before sampling as described in Fig.3.a. Then, no variations are noticeable. P_{CO_2sat} is not affected by degassing and represents an integrative measure. Indeed, P_{CO_2sat} will increase if there an increase of air P_{CO_2} occurs in whichever part of the whole volume of the unsaturated zone that contributes to drain water towards the point where water is sampled. Nonetheless, the interaction time between water and limestone has to be sufficient to lead to noticeable carbonate dissolution. As described in Fig.3.b, another limitation in the use of P_{CO_2sat} is that no precipitation should occurs in a compartment of the unsaturated zone following the last increase of P_{CO_2sat} .

5 Application

In Cussac site, P_{CO_2eq} and P_{CO_2sat} are calculated for Subcutaneous spring (n=7), Farfal spring (n=56) and for the Gutter (n=26). The aim of the present article is to focus on the uses of P_{CO_2eq} and P_{CO_2sat} to estimate air P_{CO_2} baseline line the unsaturated zone. A detailed review of the results from the measurements on these springs is available in the work of Peyraube *et al.* 2012. Table 1 gives the mean values of the measured parameters. Water chemistry is mostly represented by calcium and bicarbonate. In the absence of dolostone, magnesium concentration remains low. Fig.4 presents the projections of the samples from the 3 springs in the $(-\text{Log}(P_{CO_2eq}) ; SIc)$ reference frame. For each spring, a model was constructed. This model (see Fig.4) is not a linear regression but a constrained straight line with a slope of 1. For each sample belonging to the same spring, a modelled SIc is calculated using the sample's P_{CO_2eq} and the average SIc and $\text{Log}(P_{CO_2eq})$ of the considered spring (equation (3)).

$$(3) SIc_{\text{model}} = 1 \cdot -\text{Log}(P_{CO_2eq}) + \left(\overline{SIc} - \overline{\text{Log}(P_{CO_2eq})} \right)$$

Equation (3) is the expression of a straight line ($y=a*x+b$) where the term "b" directly comes from the equation (2) applied to the gravity centre of the samples in $(-\text{Log}(P_{CO_2eq}) ; SIc)$ reference frame. The models help to define an average P_{CO_2sat} that characterises the spring: $4.0 \pm 0.7\%$ at subcutaneous spring, $2.5 \pm 0.1\%$ at Farfal spring and $1.8 \pm 0.1\%$ at the Gutter.

Subcutaneous spring and the Gutter are good examples of the degassing presented in Fig.3.a. The configuration of the sites, or "site effect", leads to degassing before the sampling. Then, the values of P_{CO_2eq} from this water are not representatives of the air P_{CO_2} in the unsaturated zone. Otherwise, Farfal spring and the Gutter are good examples of the processes presented in Fig.3.b. Besides, Farfal spring and the Gutter are good illustration of the gathering of the samples in a square limited by usual values characterising the spring.

The interpretations of P_{CO_2sat} from the three springs follow the examples of Fig.3. Epikarst spring P_{CO_2sat} is a footprint of what was the P_{CO_2eq} before degassing (c.f. Fig.3.a); it represents the minimum value of air P_{CO_2} in the upper part of the unsaturated zone. Farfal spring P_{CO_2sat} is a footprint of what was the air P_{CO_2} in the part of the unsaturated zone where the water degassed and precipitate calcite (c.f. Fig.3.b). It represents the maximum value of the air P_{CO_2} , present in this area, that leads to degassing and precipitation towards a new equilibrium with respect to calcite, whether this equilibrium was reached or not. The Gutter P_{CO_2sat} is a footprint of what was the P_{CO_2eq} before degassing (Fig.3.a) and it represent the maximum value of the air P_{CO_2} (Fig.3.b) in this part of the unsaturated zone at the limit with the saturated zone.

Furthermore, times series of the maximum and minimum values of the air P_{CO_2} baseline can be proposed in Fig.5. From Subcutaneous spring, one estimates the air P_{CO_2} in upper part of the unsaturated zone higher than to 4.0% on average. This estimation of the lower limit is in accordance with estimation of air P_{CO_2} proposed by Peyraube *et al.* 2013 using isotopes measures and ranging from 6.2% to 11.5%. From Farfal spring, the higher limit of air P_{CO_2} ranges from 2.2% to 2.8% along the year. These stable values can be taken as an estimation of the air P_{CO_2} base line in the unsaturated zone. Then, from the Gutter one can define another air P_{CO_2} baseline corresponding to another part of the unsaturated zone closer to the limit with the saturated zone. This second baseline ranges from 1.4% to 2.0% and appears also very stable along the year. On Cussac site, the decrease of the values of the estimated base lines from upper part to lower part of the unsaturated zone shows that the air P_{CO_2} value is inversely proportional with the distance from the surface. This leads for a CO_2 originating from surface with a production from vegetation roots and soil organic matter degradation.

6 Conclusion

Natural CO_2 baseline of unsaturated zone can be estimated with water measurements and new interpretations of calco-carbonic equations. This estimation relies on saturation P_{CO_2} (P_{CO_2sat}) which is a footprint of the air P_{CO_2} in the unsaturated zone of limestone aquifer with which water has interacted. This study showed that in one hand, P_{CO_2sat} can correspond to the maximum value of air P_{CO_2} encountered in the

unsaturated zone that justify the bicarbonate concentration. On the other hand, P_{CO_2sat} can correspond to the maximum air P_{CO_2} that led the water to degas CO_2 and precipitate carbonate. Applied on Cussac site in carbonated system, the method gives good and sound results for natural CO_2 estimation.

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Figures

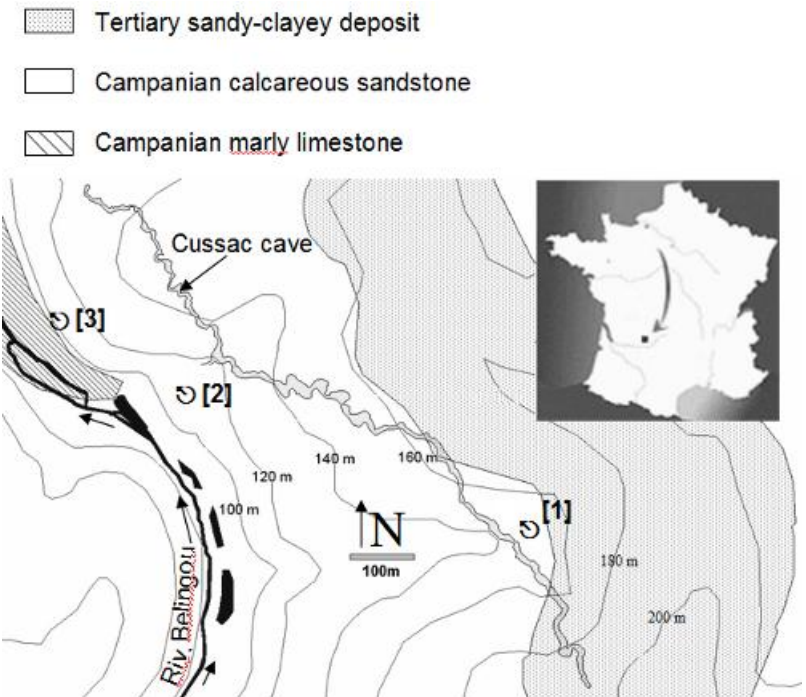


Fig.1 Location and simplified geological context of Cussac site with three of the main springs: [1] Subcutaneous spring, [2] Farfal spring and [3] the Gutter for seepage water

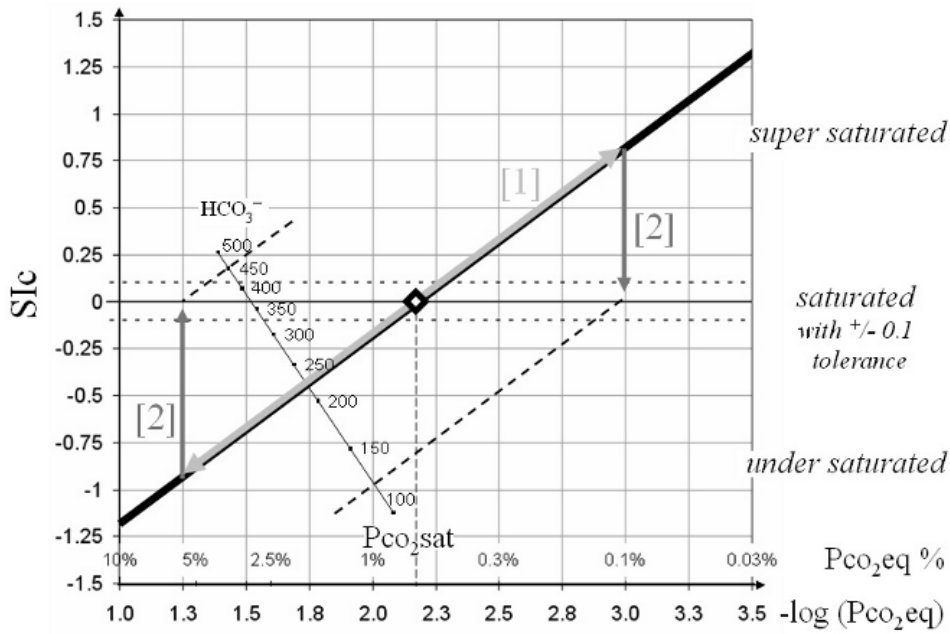


Fig.2 ($-\log(P_{CO_2,eq})$; S/c) reference frame. A scale for $P_{CO_2,eq}$ (in percent) is added above horizontal axis; a scale for HCO_3^- concentration in mg/l at 13°C is added. Black line represents a constant bicarbonate concentration. Light-grey arrow [1] corresponds to gassing and degassing for constant HCO_3^- concentration, grey arrow [2] corresponds to calcite precipitation or dissolution for constant $P_{CO_2,eq}$

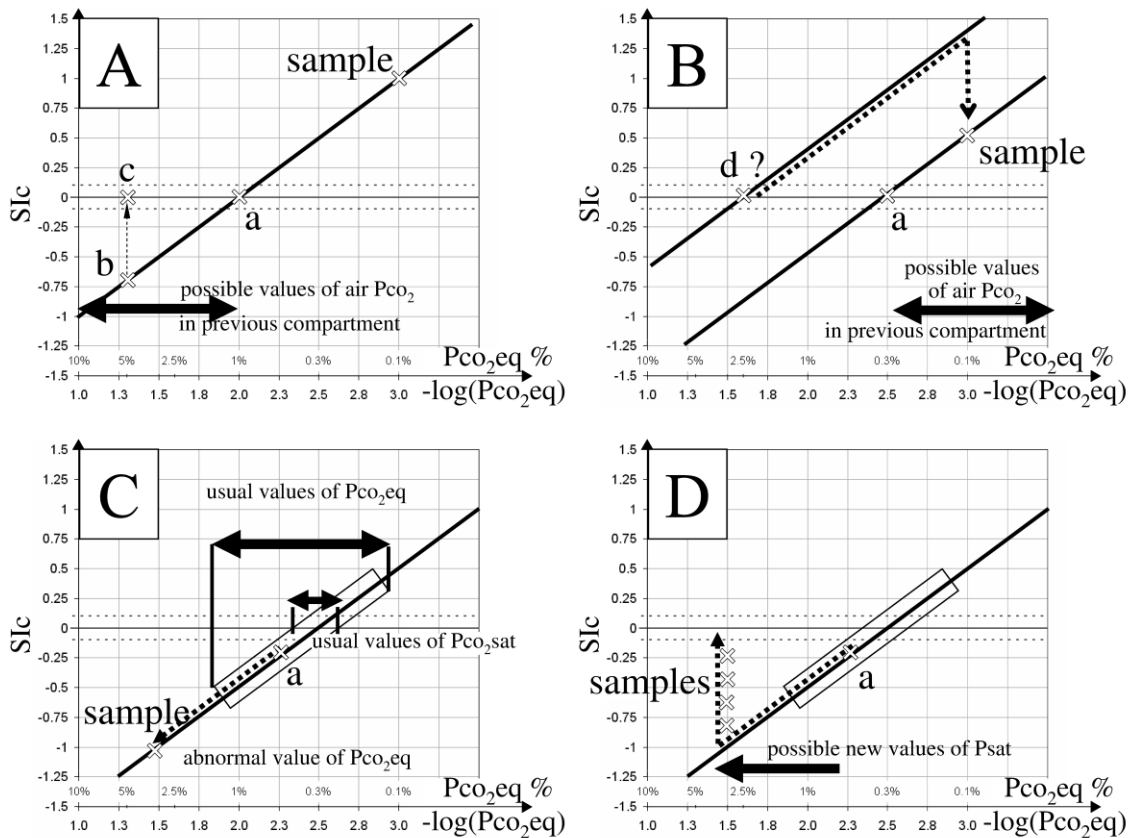


Fig.3 (a) and (b) quarters illustrate the meaning of P_{CO_2sat} as minimum and maximum for air P_{CO_2} estimation. (a) quarter corresponds to water undergoing degassing only from high value of air P_{CO_2} in “b” to P_{CO_2eq} of the sample point; P_{CO_2sat} calculated in “a” is the minimum limit of possible air P_{CO_2} in previous compartment, $P_{CO_2sat}=1\% < 5\%$ in “b”. (b) quarter corresponds to water undergoing degassing and calcite precipitation from unknown value of air P_{CO_2} in “d” to P_{CO_2eq} of the sample point; P_{CO_2sat} calculated in “a” is the maximum limit of possible air P_{CO_2} that led to degassing-precipitation in former compartment. (c) and (d) quarters illustrate the consequences of air P_{CO_2} increase in unsaturated zone on spring water; usual values of P_{CO_2eq} and P_{CO_2sat} of the water are within the symbolised square area. (c) quarter corresponds to the first consequences of air P_{CO_2} increase leading to an increase of sample P_{CO_2eq} , without carbonate dissolution (P_{CO_2sat} unchanged). (d) quarter corresponds to long term consequences of air P_{CO_2} increase with carbonate dissolution and new values of P_{CO_2sat} ; an increase of P_{CO_2sat} is an evidence of long term air P_{CO_2} increase and water sample may be measured at different SIC values for a given P_{CO_2eq} .

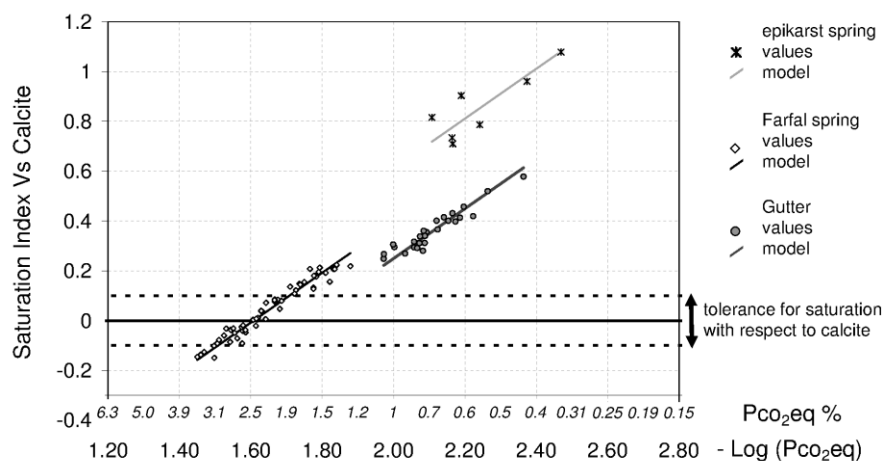


Fig.4 Projection of sample from Subcutaneous spring, Farfal spring and the Gutter in the $(-\log(P_{CO_2eq}) ; SIC)$ reference frame, models are calculated from equation (3) for a temperature of $13^{\circ}C$ corresponding to the average temperature of the samples.

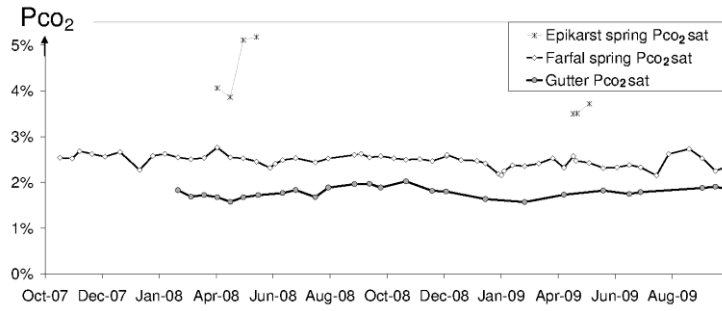


Fig.5 Time series of Pco₂sat of the Gutter (1.8±0.1% representing air Pco₂ baseline of the unsaturated zone at the limit with the saturated zone; Pco₂sat of the Farfal spring (2.5±0.1% representing the unsaturated zone air Pco₂ baseline; Pco₂sat of the Subcutaneous spring (4.0±0.7%) cannot be considered as a base line but gives indications on air Pco₂ in this part of the unsaturated zone

	Temp.	EC	pH	HCO ₃ ⁻	Ca ²⁺	Na ²⁺	K ⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
	°C	µS/cm		mg/L							
Subcutaneous spring	17.4	615	7.8	391	139.2	6.6	0.1	1.2	10.0	0.3	5.2
Farfal spring	12.6	582	7.1	337	115.4	7.2	2.1	2.6	11.3	12.9	6.3
Gutter	12.9	497	7.5	297	99.2	5.4	0.7	2.0	9.4	2.8	4.1

Table.1 Mean values of temperature, electrical conductivity (EC), pH and major ions concentrations.