COBISS: 1.02

LETTER:

CAVEAT: PITFALLS IN THE MEASUREMENT OF PH OF DRIP WATERS IN CAVES

CAVEAT: PROBLEMATIKA MERITEV PH V PRENIKLIH VODAH KRAŠKIH JAM

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UDK: 551.444:66-915

INTRODUCTION

Instrumental cave monitoring has become an important concept to understand climate proxy archives stored in speleothems. Many studies to measure hydrochemical data of drip waters, the isotopic composition of drip water carbonates, and cave climatic parameters, such as temperature, humidity and P_{CO_2} have been performed during the last decade (PAGES News, 2008). Many new projects are in progress in various caves worldwide, e. g. Bunker cave in Germany and Grotta di Ernesto, NE Italy (Riechelmann *et al.,* 2011, Miorandi *et al.,* 2010). An important parameter in the hydrochemistry of drip waters is pH, because it is a master variable determining supersaturation SI_C, which controls calcite precipitation rates on speleothems.

To measure pH drip water samples are collected in glass flasks until a sufficient amount of water is available to measure pH with suitable electrodes. Depending on drip rate the time to collect the sample ranges between few minutes (e. g. 10 drops/min) to hours for drip rates less than 1 drop/min. During this time the sample in the sample container stays as a layer with increasing depth δ. CO_2 contained in the solution degasses from this layer with an exponential time constant $T=4\cdot\delta^2/\pi^2\cdot D_m$, where D_m is molecular diffusivity of the CO_2 - molecules in the solution. D_m depends on temperature by the relation $D_m=5.6\cdot10^{-6}+5.8\cdot10^{-7}\,T_c$ (cm^2s^{-1}), where T_c is in °C (Dreybrodt and Scholz, 2011, Dreybrodt, 2011). After the time, $T_{out} = 3T$, 95% of the aqueous CO_2 has degassed from the water. For a water layer of depth $\delta = 0.2$ cm the time T_{out} of outgassing is 40 min.

Equilibration of the carbonate ions and pH with the reduced concentration of aqueous CO_2 needs several minutes (Dreybrodt and Scholz, 2011, Dreybrodt, 2011). Therefore pH in the solution increases with time.

In this letter we demonstrate this in a simple experiment. From a column of solution CO_2 degasses in time scales much longer than equilibration time with respect to pH. In this case the pH change is controlled by CO_2 outgassing and proceeds with the time constant T.

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Received/Prejeto: 19.4.2012

THE EXPERIMENT

Fig. 1 shows the simple experimental set up consisting of small plastic beakers. They are filled with mineral water from the Harzquelle, Bad Harzburg, which contains 93.9 mg/L of Ca, 18.7 mg/L of Mg, and 254 mg/L of hydrogen carbonate, sulfate 75,2 mg/L, and also minor amounts of Na (11.7 mg/L), Cl (25.9mg/L), and K (1.23 mg/L). The water has been shaken rigidly in its bottle to remove most of the CO_2 from the water until no further bubbles occurred. This warrants that P_{CO2} in the water is below 1 atm and bubbles cannot form any more. The pH of the water was then about 5. 1 cm^3 of this water was added to the first beaker, 2 cm^3 to the second and 3 cm^3 to the third. This corresponds to a depth of the water layer of 0.22 cm, 0.44 cm, and 0.66 cm, respectively. Temperature is 20°C. Outgassing proceeds into the open atmosphere.To monitor the evolution of pH the fluid pH-indicator solution Merck pH-1 was mixed to the water, such that its concentration was equal in all three beakers. The color of the solution changes from red at pH = 5 to green-blue at pH = 9.

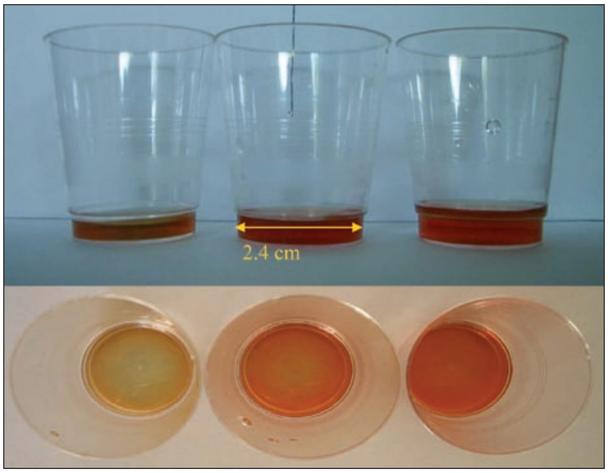

Fig. 1. Three plastic beakers with plain bottom contain an initially identical $CaCO_3$-CO_2-H_2O solution. But the depth of the water layers is 0.22cm, 044cm, and 0.66cm respectively.

Photos from this set up were taken during a time course of 7 hours. Fig. 2 shows how the colors in the three beakers change in time. The color code at the left relates pH to color of the indicator solution Merck pH-1.

The first row with the beaker with a depth of 0.22 cm shows a rapid change in color from orange to green after 40 min, indicating a change of pH from about 5.8 to about 8, as can be seen by comparison to the color code of the pH-indicator at the left hand side. For the beaker in the second row with a depth of 0.44 cm pH of about 8 is reached after 153 min, whereas the water in the third row with depth of 0.66 cm needs about 420 min. This is only a crude estimation by comparison of colors, but it shows clearly that after a sample has been collected pH changes considerably.

Theoretically the times needed for a given shift of pH depend on δ^2. That means the ratio from the thin layer of 0.22 cm, to that of 0.44 and 0.66 cm should be $T_{0.22} : T_{0.44} : T_{0.66}=1 : 4 : 9$. The ratio estimated from the color changes is 1 : 3.8 : 10.5. Regarding the crudeness of the experimental estimation this can be regarded as satisfactory.

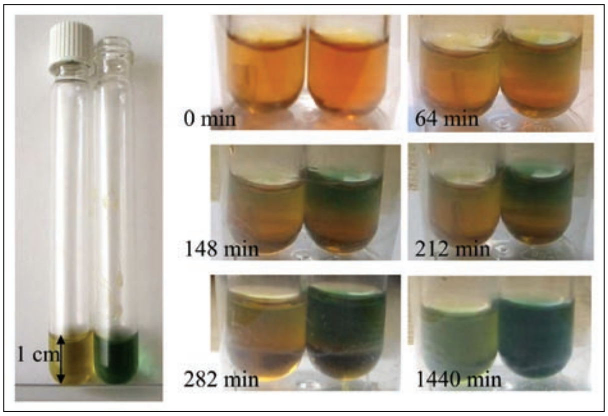

Fig. 3. Evolution of pH when complete outgassing is prevented by limited headspace in the bottle covered by a lid.

In summary the experiment visualizes convincingly that after sample collection the pH-values of drip waters change in time. Only when pH is measured immediately after collection the value is reliable.

To take reliable data from slowly dripping sites one has to measure from small volumes corresponding to only 1 drop of about 0.1ml. This is possible with the Micro pH Probe of Lazarlab, PHR-146 Micro Combination pH electrode (www.lazarlab.com/microph.htm).

To give further evidence that outgassing of CO_2 controls pH in our experiment, we have compared the evolution of pH in two bottles, one with open space to the atmosphere and the other with restricted headspace by covering the bottle with a lid. In the beginning both bottles are filled by 1cm^3 of identical solution of the mineral water with pH at about 6. This is shown in Fig. 3a. Fig. 3b shows the change of color in time. Final pH of about 8.5 (dark blue in the right bottle) is reached after about 1440 min. This corresponds to a time of 4T. The left bottle covered by a lid attains a lower pH, which remains stable for several days. Photo 3a has been taken 2 days later. The reason is that the CO_2, which has degassed from the fluid is trapped in the headspace and P_{CO2} in the open bottle is lower than in the one covered.

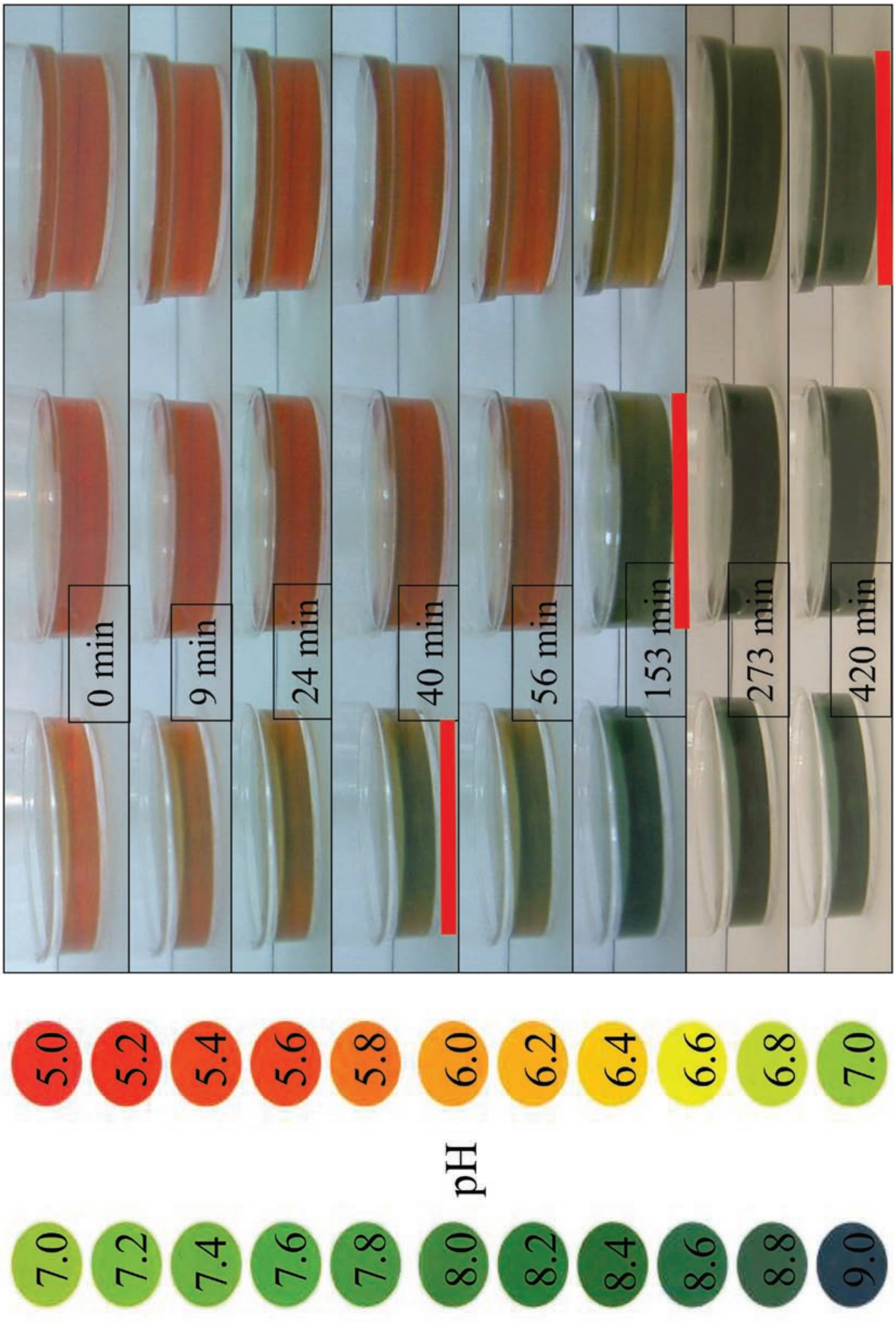

Fig. 2. Change of color in beakers with different layer depth, from left to right, 0.22cm, 0.44cm, 0.66cm. The beakers underlined in red show similar colors and consequently exhibit similar pH-values of the water. Circles on the left show the pH-color relation of the indicator solution.

CONCLUSION

Measurements of pH of drip waters in caves must be performed immediately after collection.. Collecting samples, especially at low drip rates, and performing measurements hours or even days later will give higher pH-values than those in the initial drip water. This is true for drip waters that have a PCO_2 larger than that in the cave atmosphere. If the drip is formed by water flowing in thin ($\delta<0.03$ cm) films slowly towards the drip point there is sufficient time for outgassing, and PCO_2 and pH are close to equilibrium with the cave atmosphere when the drop falls. In this case pH will change only slightly even hours after sampling.

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