

VARIANCES OF KARST CORROSION ON THE BASIS OF DIFFERENCES IN THE SOLUTION OF Ca- AND Mg-CARBONATES

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Summary

In this paper, we present results from the analysis of water samples collected by the karst corrosion measuring system installed at the Aggteleki Karst (NE-Hungary). The measurement sites are located to allow a good observation of vertical changes in solution. The water samples come from a rock surface covered by soil, from the uppermost and lowermost (at bedrock) ground level of the soil-fill of a doline, and from water dripping from the ceiling of Béke Cave which is located at the karstwater-table below the doline above mentioned. We collected the water samples monthly and analysed them in terms of CaCO_3 and MgCO_3 contents. We tried to explain the seasonal variations in the solution of the examined carbonates, and the solution differences between the measurement sites. The total carbonate-content of the water samples shows great fluctuations during the year, but is not dependent on the annual course of temperature. We measured the highest values in early autumn. The dissolved carbonate-content of the water samples of the cave is, naturally, much higher (210-220 mg/l) than that of the water samples collected near the surface (30-80 mg/l). This fact indicates that the water infiltrating through the soil has significant aggressive CO_2 -content when it arrives at the soil-bedrock boundary. The dissolved CaCO_3 content is, on average, 2.5-5 times greater than the dissolved MgCO_3 content and the ratio of the above carbonates increases from the surface towards the cave as a consequence of the fact that the dissolved MgCO_3 content of infiltrating water comes from the soil. Two periods of the year (early summer, autumn) are characterised by lower MgCO_3 solution and abundant precipitation. Since this decrease during these periods is not significant from the point of view of CaCO_3 solution, the qualitative changes in solution can be well characterised by the ratio of the amounts of dissolved CaCO_3 and dissolved MgCO_3 . Summing up, it seems that precipitation is an important factor of karst corrosion not only quantitatively but also qualitatively, changing the ratio of dissolved carbonates.

I. Introduction

The main goal of our investigations was to get a better understanding of vertical changes in karst corrosion processes (such as dissolution and precipitation of carbonates). For this reason, a measuring system was installed at the Aggteleki-Karst, NE-Hungary (Zámbó, 1986., 1997.). For the present examinations, water samples have been collected for 4 years (since 1996) from several characteristic points along a vertical profile from the karstified surface to the ceiling of Béke Cave. The measurement points are shown in *Fig. 1.*

We collected the water samples monthly, and analysed them in terms of dissolved CaCO_3 and MgCO_3 contents. The precipitation during the investigated period (average of the year 1996-97) is presented in *Fig. 2.* Its tendency and the total amount correspond well to the averages of longer periods. The climate is temperate-cool, Dfx according to the Köppen-system.

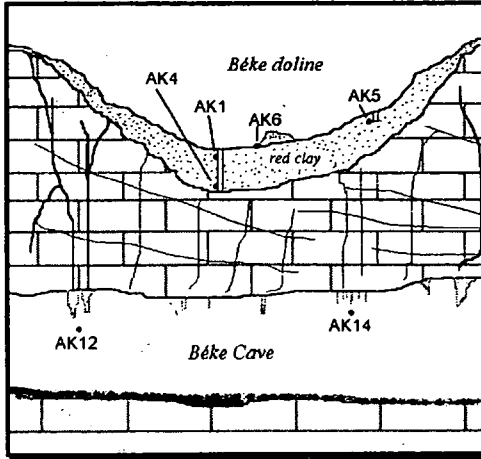


Fig. 1 Sketch of the measurement points

(AK6: Limestone rock surface partially covered by moss [Bryophyte]; AK1: below 0.5 m thick red-clay soil; AK5: below 0.5 m thick red-brown earth; AK4: below 9.5 m thick red-clay soil-fill of a doline [at soil-bedrock boundary]; AK12: 2 medium stalactites in the Béke Cave [at karstwater table]; AK14: a group of small stalactites in the Béke Cave [at karstwater table])

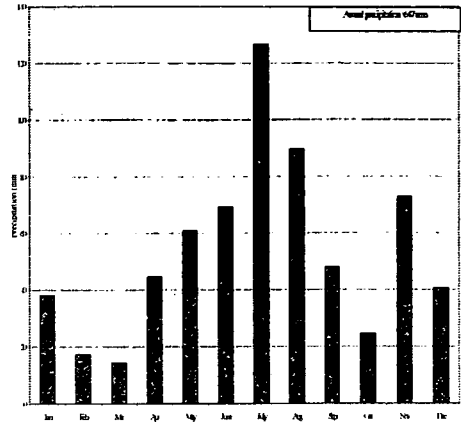


Fig. 2 Precipitation at Aggtelek (averages of the years 1996-97)

II. Results

The monthly averages of the different parameters over the 4-year long investigation period are shown on Fig. 3, 4a, 4b and 4c.

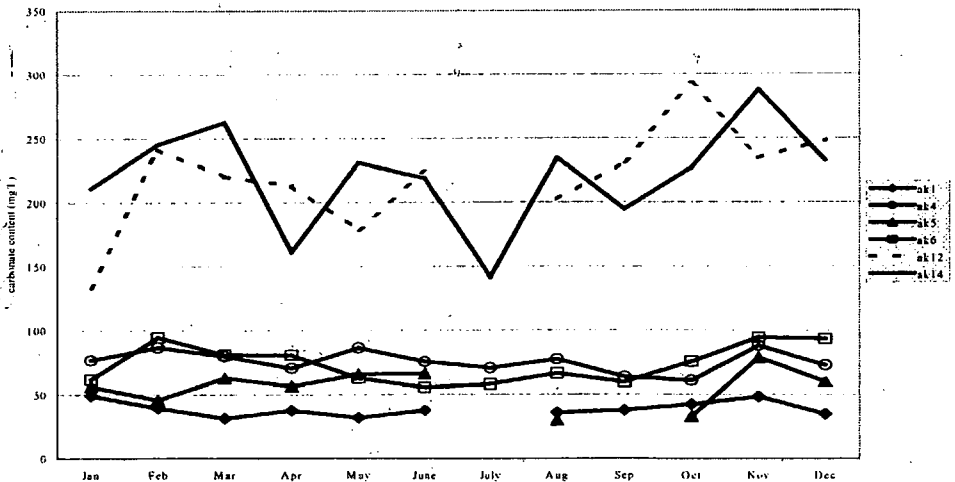


Fig. 3 Total dissolved carbonate-content of water samples

In the water samples (Fig. 3) from near the surface the total dissolved carbonate-content shows only slight fluctuations during the year, but vertical changes are recognisable. The lowest carbonate concentrations are at the uppermost ground level of the soil (AK1 - below red-clay: 30-50 mg/l; AK5- below red-brown earth: 30-80 mg/l. These differences according to soil types correspond to our earlier experimental results on small soil samples in laboratory conditions (Zámbó, 1998). Below the 9.5-m thick red-clay soil the carbonate concentrations are greater (AK4: 60-95 mg/l). The total dissolved carbonate-contents of the dripping waters in Béke Cave are much higher (AK12, AK14: 140-300 mg/l) than of the other measurement points, and their changes are in inverse ratio to the amount of precipitation. The highest concentrations are in accordance with the driest months at AK12, where the medium speleothems have wider feeding fissures. At AK14, where infiltrating water arrives through narrower fissures the highest carbonate-concentrations are a month late compared with the most arid month.

The annual course of $MgCO_3$ -dissolution (Fig. 4b) is less uniform than that of $CaCO_3$ -dissolution (Fig. 4a), and the differences between the samples near the surface and from the cave are also less significant looking at the $MgCO_3$ -dissolution. The correlation coefficients between precipitation and dissolved carbonate-contents are low, but some trends seem likely:

- the dissolved $CaCO_3$ content slightly decreases with increasing precipitation;
- the dissolved $MgCO_3$ content better decreases with increasing precipitation;
- as a result, the ratio of dissolved $CaCO_3$ to dissolved $MgCO_3$ (Fig. 4c) increases with increasing precipitation (in the cases of AK4 and AK14, the correlation coefficients between this ratio and the precipitation are equal to 0.66, in the other cases the value of r is lower.) Similar phenomenon was measured in karstwater-sources, where peak discharges were characterized by high $CaCO_3/MgCO_3$ ratio in the karstwater (Maucha, 1989b, Ovstedal-Lauritzen, 1989). In laboratory conditions Mándy (1954) suggested that an increase in the temperature of the solvent cause an increase in the $CaCO_3/MgCO_3$ ratio, but in natural conditions, the differences in temperature are not high enough to explain this phenomena.

These facts can be explained by the followings:

- the dissolved $MgCO_3$ content of infiltrating water comes mainly from the weathering in the soil and at the surface;
- during intense rainfall (or snowmelt) the infiltration is very rapid and the dissolved CO_2 -content (which comes principally from the soil-air) can't follow this rapid change immediately which results that the concentration of aggressive CO_2 decreases, thus the concentration of dissolved carbonates also decreases. It seems that the Ca^{2+} -ions get to the solution more quickly than Mg^{2+} -ions, which can explain why the ratio of dissolved $CaCO_3$ and $MgCO_3$ increases with precipitation. Since the infiltrating water has no more CO_2 -source after penetrating in the bedrock, the dissolution from there prefers the $CaCO_3$ to the $MgCO_3$, thus

in the dripping water samples of the cave the dissolved CaCO_3 -content is much greater (3-14 times) than the dissolved MgCO_3 -content. This demonstrates that the "time" factor has a very important role in karst corrosion (Jakucs, 1977).

Figure 4a: Total dissolved Ca-carbonate contents of the water samples

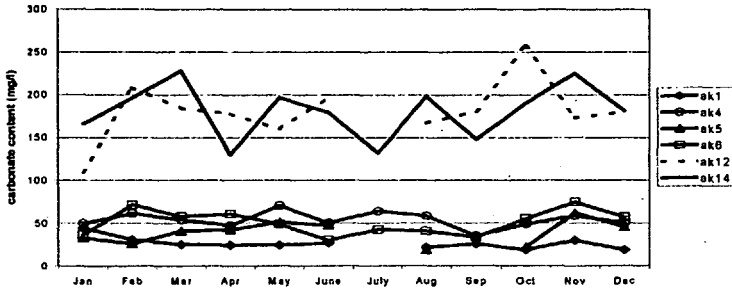


Figure 4b: Total dissolved Mg-carbonate contents of the water samples

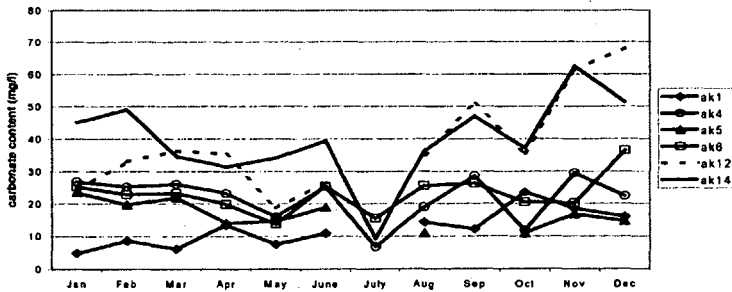


Figure 4c: Ratio of dissolved CaCO_3 and MgCO_3 in the water samples

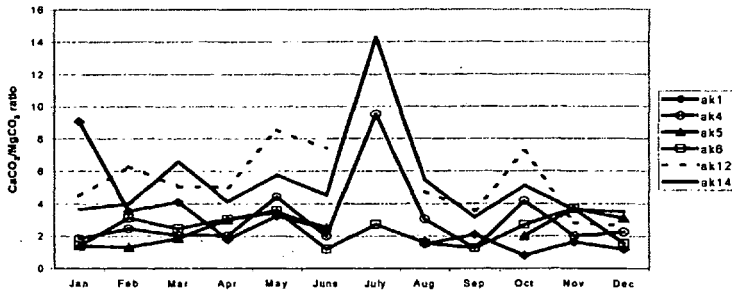


Fig. 4a,b,c Changes of the CaCO_3 and MgCO_3 -content and their ratio in the water samples

Figure 5a: Temporal changes of carbonate-contents at AK1 measurement site

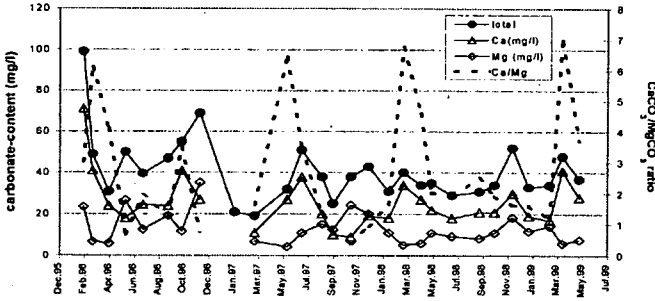


Figure 5b: Temporal changes of carbonate-contents at AK6 measurement site

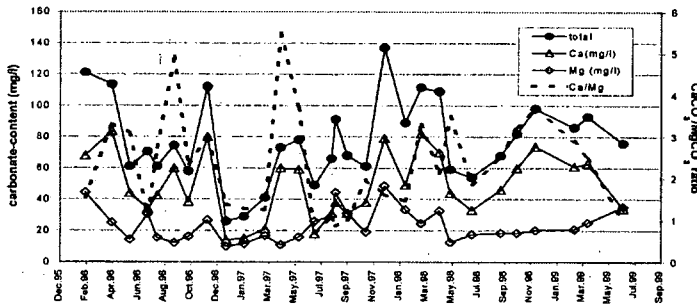


Figure 5c: Temporal changes of carbonate-contents at AK14 measurement site

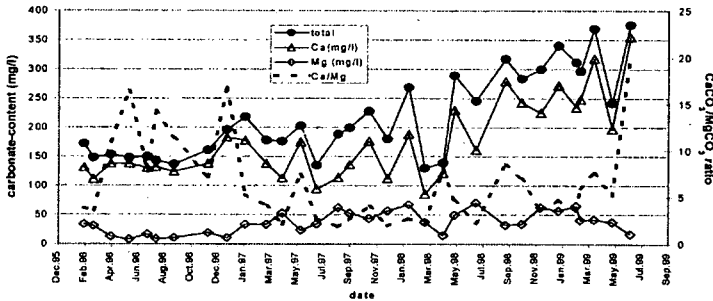


Fig. 5a,b,c Temporal changes of carbonate-contents at different measurement sites

In *Fig. 5a* the significant fluctuations in the ratio of dissolved CaCO_3 and MgCO_3 are well manifested: during the rapid and cold infiltration after snowmelt this proportion increases as explained above. Thus, a relative growth of MgCO_3 content in the soil is realised. A maximum in the total dissolved carbonate-content is also observable in late autumn. This is likely to be a consequence of constant high soil moisture (long but quiet rainfalls in November) and abundant rotting organic material.

In the case presented in *Fig. 5b* the corrosion attacks the rock surface so the runoff water dissolves directly the rock material, i.e. the ratio of dissolved CaCO_3 and MgCO_3 is rather a function of the rock composition and the temporal variations are less significant. It means also, that the dissolved CaCO_3 and MgCO_3 contents change in a parallel way.

In the dripping water from the group of small stalactites (*Fig. 5c*) the seasonal variations in the dissolved carbonate-contents are in a month late referring to the water samples collected from the soil, i.e. a local maximum in the ratio of dissolved CaCO_3 and MgCO_3 is in late spring (as a result of the decrease in the dissolved MgCO_3 content).

In *Fig. 6* a direct factor of corrosion process, the amount of water (runoff at the rock surface and infiltration in the cave) is presented. It is demonstrated here, that after rainfall the runoff water percolates through the soil and can fast arrive at the karstwater table if the infiltration passes in large fissures (AK12). But a great volume of water is transported through narrow fissures (AK14), which delays the beginning of the intense dripping in the cave with 1-1.5 month and makes the duration of abundant infiltration longer (2-3 months). The highest infiltration periods are in early spring in accordance with the measurements of *Maucha (1989a)*.

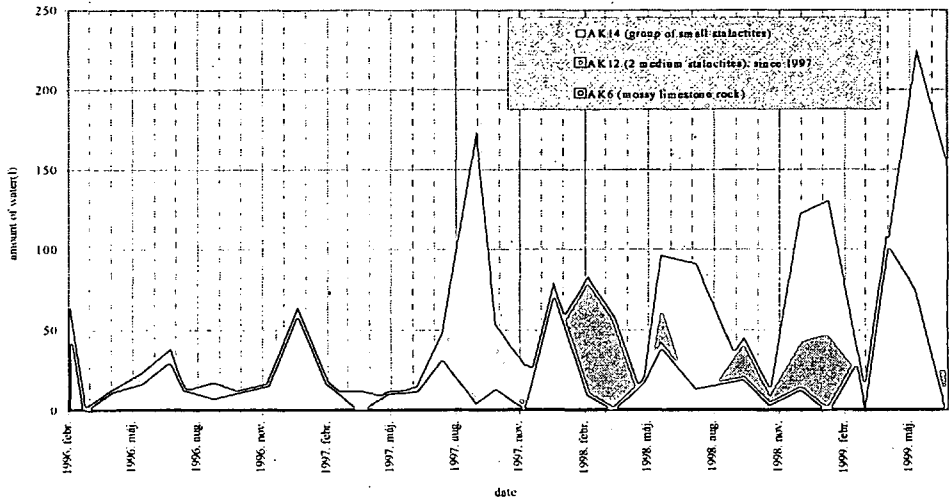


Fig. 6 Amount of water at different measurement sites (AK12 has been working only since 1997)

To get the amount of total dissolved material, the concentration values must be multiplied with the amount of water. Taking these calculations into account, the denudation dynamics can be studied (*Fig. 7*). Since the fluctuations in the carbonate-concentrations are less than in the amount of water, the main dynamics of the sum of dissolved carbonates is determined by the temporal variations of precipitation. The consequence of this dynamics is that the precipitation of carbonates in the speleothems is also dependent on the amount of infiltration. In our data this relationship is demonstrated for a time-resolution of 1 month, but this relationship is valuable for annual data, too, and this fact is responsible for the varied ring structure of speleothems which makes the reconstruction of paleoclimate possible.

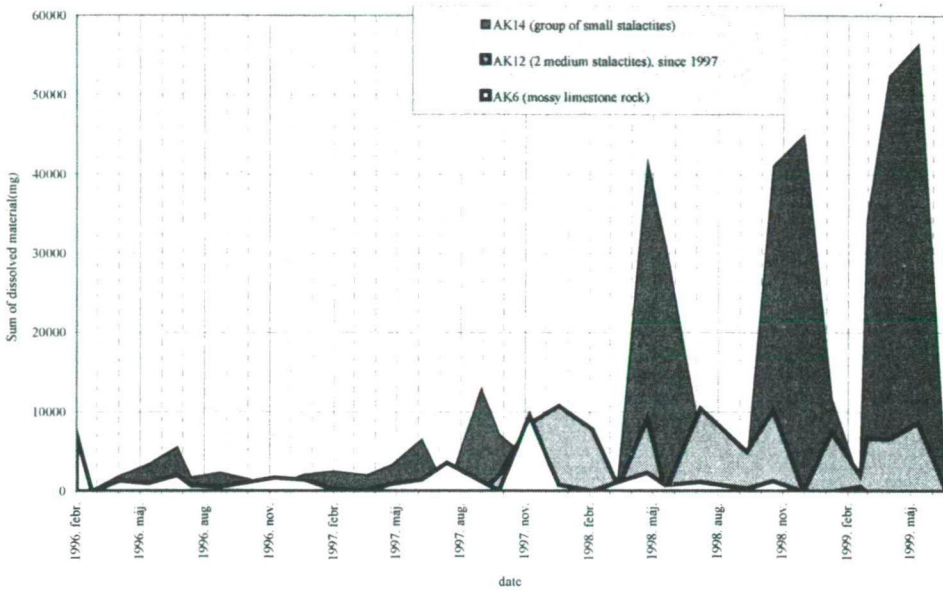


Fig. 7 Sum of total dissolved material at different measurement sites (AK12 has been working only since 1997)

III. Conclusions

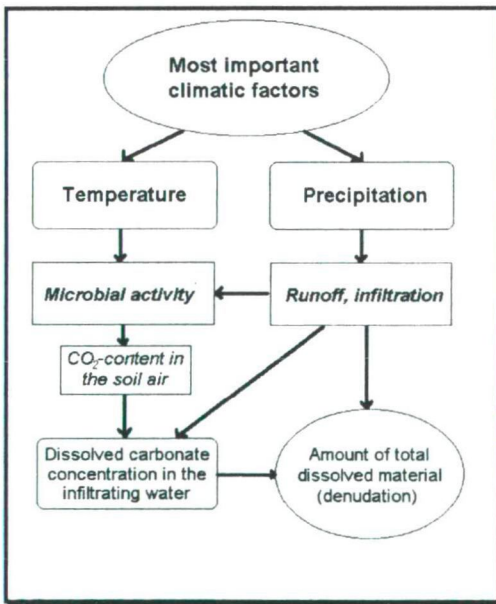


Fig. 8 Sketch diagram of karst corrosion processes

The most important climatic factors and their (in)direct regulative effects for the karst corrosion processes are presented in a simplified arrow-box diagram (Fig. 8).

- The total dissolved carbonate-content increases with depth, but soil type and vegetation can vary this trend.
- The highest total dissolved carbonate-concentrations are in the driest months.
- The narrow fissures cause a 1-1.5 month delay in the concentration and infiltration values.
- The ratio of dissolved CaCO_3 and MgCO_3 increases with increasing precipitation. (These qualitative changes would be also examined in the ring structure of speleothems.)
- In the denudation dynamics precipitation is the most important

climatic factor because the carbonate-concentration changes are less than the variations in the infiltration. (Looking at the temperate climate characteristic to Aggtelek.)

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