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THE KARSTIC CORROSION OF NATURALLY OCCURRING

LIMESTONES IN THE GEOMORPHOLOGY OF OUR AGE

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During recent years the theory of karst corrosion has been considerably modernised, partly due to the new interpretations of the processes resulting from the rapid development of chemistry, partly, however, as a consequence of the ever-increasing mass of karst research data. Thus, the zonal and extrazonal richness of form of the karsts genetically can today be explained only on the basis of the accurate knowledge of the nature and extents of the processes involved. Contributions have been made to the develppment of certain aspects of the theories of dissolution by the results of Hungarian research, including those of the present author. Hence, the review of this subject was considered justified.

The concept of karst corrosion is taken to understand primarily the particular dissolution denudation processes of limestones /and also, in a wider meaning, those of other limestones which dissolve well in water without a residue/.

In connection with the dissolution of limestone in water, three quite different processes must be considered. First, a distinction must be made between <u>carbonate dissolution</u> in pure /distilled/ water, and <u>hydrocarbonate dissolution</u>, that is the dissolution of limestone in water containing carbon dioxide. There are specific qualitative and quantitative differences between the two, but both processes are reversible. The third type of dissolution involves the participation of other chemical agents, mainly organic and inorganic soil acids, etc. In this latter case the new calcium compound formed in solution is generally no longer able to reform $CaCO_3$.

I. <u>The carbonate dissolution of limestone</u>

When limestone /$CaCO_3$/ dissolves in distilled water, its dissociated ions remain unchanged /apart from solvation/, and the act of dissolution can be expressed by the following reversible reaction:

$$CaCO_3 \rightleftarrows Ca^{2+} + CO_3^{2-} \qquad /1/$$
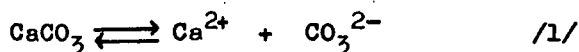
An equilibrium is established between the solid phase /$CaCO_3$/, the solvent /H_2O/ and the dissolved ions, and this can be defined by the solubility product K_1 /TILLMANS 1942, MILLER 1952/. K_1 is a variable index, the absolute value of which generally changes linearly with the temperature of the solution, but it also depends on certain crystal-structural properties of the solid phase. The K_1 for the rhombic dipyramidal modification of $CaCO_3$ /aragonite/ is higher than that for the trigonal calcite /SCHOELLER 1956/.

Table 1 is a collection of the literature data which give the absolute and variable orders of magnitude for K_1.

Table 1

Author /year/	t /°C/	dissolved $CaCO_3$ in mg/l		
		calcite	aragonite	amorphous $CaCO_3$
SCHLOESING[x] /1872/	8,7	10,0	-	-
SCHLOESING /1872/	16,0	13,1	-	-
SCHLOESING /1872/	25,0	14,3	-	-
CHARLOT-ENSCHWILLER /1939/	-	12,4	-	-
TROMBE /1952/	16,0	16,0	-	-
HODMAN /1955/	cold	14,25	-	-
HODGMAN /1955/	warm	18,75	-	-
SCHOELLER /1956/	25,0	14,33	15,28	14,45
SCHOELLER /1956/	50,0	15,04	16,16	15,15
SCHOELLER /1956/	100,0	17,79	19,02	18,16

[x] The pedological wark of SCHLOESING, which appeared in 1872, is not known in the original in Hungary; nevertheless its data are frequently cited by Western authors, e.g. O. LEHMANN /1932/, TROMBE /1952/, etc. The data of SCHLOESING in the Table are therefore given only on the basis of secondary sources.

The views to be found in the literature regarding the
time-requirements for the dissolution of limestone in pure
water are fairly contradictory. According to HARRASOWITZ
1954, BÖGLI 1956, 1960, H. LEHMANN 1956, 1960, BAUER 1964,
FRANKE 1967, etc., the reaction concerned must be extre-
mely fast. This conclusion was based on the fact that when
the above authors analyzed samples of water collected from
limestone surfaces during field-studies they were unable
to detect dissolved $CaCO_3$ in concertrations lower than tho-
se given in the Table. BAUER /1964/, for example, collected
for analysis the moisture trickling down "in statu nascendi"
in a karr-channel; this had been in contact with the surfa-
ce of the limestone for only a few seconds. Accordingly,
BÖGLI /1960, 1963/ denotes the time-requirement for non-
carbonate primary dissolution as about 1 second. /See also
later in connection with the hydrocarbonate dissolution./

In the view of MARKÓ /1963/, however, these experi-
mental results confirm not the high rate of dissolution,
but the fact that the ion-diffusion under the special expe-
rimental conditions was particularly rapid; nevertheless,
the rate of this process, like the dissolution of all solid
substances, is controlled primarily by the rate of diffusi-
on of the dissolved molecules or ions from the saturated
solution layer in the vicinity of the surface of the solid
phase to the more distant solution layers. It is natural,
therefore, that the diffusion conditions will be optimal
in a thin liquid film flowing over the surface; in accor-
dance with the MARKÓ interpretation, this can explain the
greater intensity of the dissolution dynamics.

At the same time, however, GERSTENHAUER and PFEFFER /1966/ go still further and, on the basis of their own extensive investigations, directly cast doubt on the reliability of BÖGLI's analytical data. They had collected limestone samples from various places throughout the world, and checked their time-curves under sterile laboratory conditions; they did not observe such a rapid achievement of saturation, but instead /as shown in Figure 1/ times which were longer by several orders of magnitude. In some samples for example, the time during which the sample was in contact with the water, and which was necessary to attain a solubility of 13 mg/l, was a whole day; this is even more surprising, because the water used contained a little carbon dioxide, which normally accelerates the dissolution.

The cause of these sharp, apparently irreconcilable differences here lies almost certainly in the different chemical investigation methods used by the various authors. Without going into details /these are given by MERCK, MÜLLER and GERSTENHAUER/, it must be pointed out that BÖGLI and FRANKE titrated their water samples by the WARTHA-LUNGE method with methyl orange as indicator, whereas GERSTENHAUER and PFEFFER used titriplex III /chalconecarboxylic acid/. The viewpoint of GERSTENHAUER is in all probability closer to the truth, because the indicator used is definitely calcium-specific; it reacts only with Ca^{2+} ions and gives a reliably clear colour change at the end-point even with quite weak solutions.
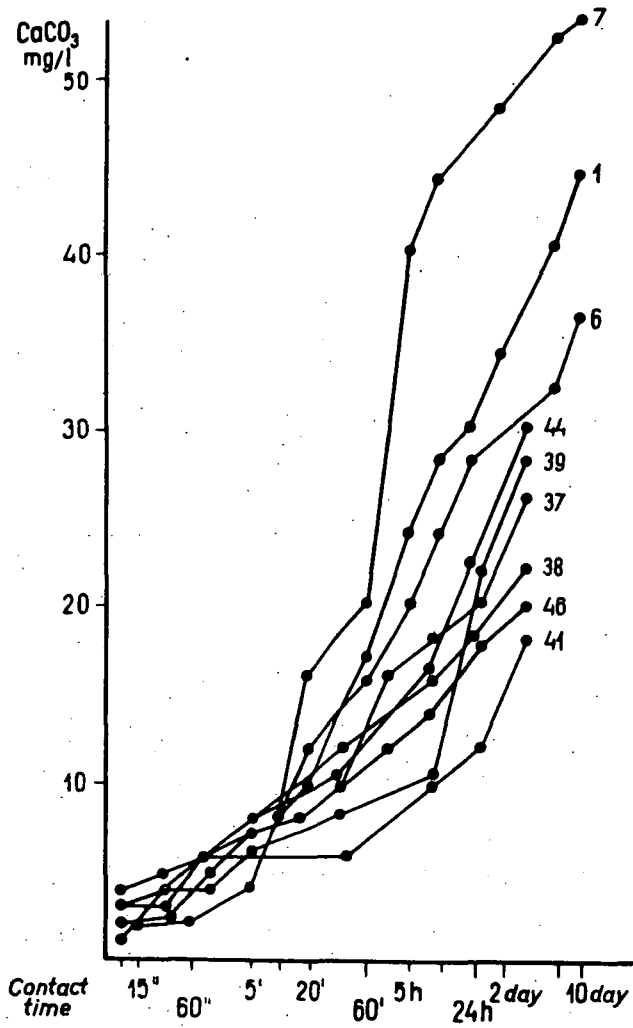
Figure 1. Time courses of the dissolution of various types of limestone in water saturated with atmospheric CO_2 /according to GERSTENHAUER and PFEFFER/.

This carbonate dissolution process is of fairly subordinate practical importance in nature of course, at least directly. Completely pure /quasi-distilled/ water does not exist under the geographical conditions leading to karstification. The freatic waters which must be considered from the point of view of actual karstic corrosion /but rain-water too/ always contain certain amounts of dissolved chemical substances, and the variable amounts and compositions of these change the capacity to dissolve carbonate in a decisive way.

Of these factors, the role of <u>the carbon dioxide saturation of the water</u> is stressed in the literature, since water containing only a little carbon dioxide will dissolve many times the amount of limestone dissolved by the same volume of pure water.

## II. The hydrocarbonate dissolution of limestone

The dissolution of limestone by carbonic acid is termed hydrocarbonate dissolution, because the carbonic acid ions present in the solution react with the limestone to yield the well-soluble calcium hydrocarbonate, $Ca/HCO_3/_2$ /KYRLE 1923, TILLMANS 1932, etc./.

<u>The factor controlling the dissolution of limestone as hydrocarbonate, and the opposite of the dissolution process, the redeposition of the limestone from the solution, is in all cases the carbon dioxide /carbonic acid/ concentration of the water /or solution/ concerned</u>. To a first approximation it can be said that the water in contact with the limestone is capable of dissolving more $CaCO_3$, the greater the concentration of the CO_2 previously dissolved in it.

If the CO_2 content of the water in contact with the limesto-
ne is increased, therefore, the amount of limestone dissolved
will increase, while if the carbon dioxide leaves the solu-
tion /e.g. by evaporation/, the dissolved limestone content
of the solution will decrease by means of its precipitation
from the solution and its accumulation /lime-muds of chemi-
cal origin, stalactites, stalagmites, travertine, etc. are
formed in this way/.

The total dissolved CO_2 content of some natural water
may vary considerably, and since there is a direct connection
between the CO_2 content of the water and its ability to dis-
solve carbonate in order to interpret the corrosion dynamism
of the given water it is of the greatest importance to study
all those factors which affect the amount of CO_2 dissolved
by the water in contact with the limestone.

The following equilibrium is involved:

$$CO_2 \text{ /in the gas-space/} \rightleftarrows CO_2 \text{ /absorbed in the water/} \qquad /2/$$
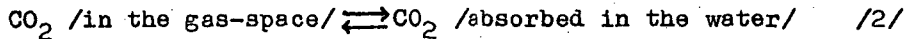
The amount of carbon dioxide absorbed is affected by
the following factors:

1. The carbon dioxide concentration of the gas phase
in contact with the water. This is expressed by the partial
pressure of the carbon dioxide /p CO_2/.

2. The mutual temperature of the water and of the gas,
at which the process of dissolution occurs.

3. The hydrostatic pressure acting jointly on the water
and the gas phase in contact with it.

4. The amount of time available for the dissolution process.

Thus, it can readily be seen that the dissolution of gaseous CO_2 and the decomposition of the solution /reformation/ depend in an extremely complex way on the combination of the above factors, for the change of any one of them can displace the equilibrium in either direction.

Although the conditions controlling the dissolution of CO_2 in nature are so complex, it is nevertheless worthwhile, for the sake of clarity, to consider the above four points separately.

It should first be pointed out that in accordance with the HENRY-DALTON law /1803/ the amount of the gaseous component dissolving in the liquid phase in contact with the gas is directly proportional to p, the partial pressure of that component, and is inversely proportional to the change of temperature. Thus, the amount of CO_2 dissolved in the water can be determined with the help of the following formula:

$$\text{dissolved } CO_2 \text{ in g/l } = \text{ L } . \text{ p } . 1.9634 \qquad /3/$$

where the value 1.9634 is the reciprocal density of CO_2 in l/g, p is the partial pressure of the CO_2, and L is the solubility or absorption coefficient for the CO_2 gas, which varies with the temperature. Table 2 contains the values of L for the more important temperatures involved in the karstification.

Table 2

	dissolution temperature, ^{o}C							
	0	5	10	15	17	20	25	30
L =	1,713	1,424	1,194	1,019	0,958	0,878	0,765	0,665

Equation /3/ was used as long ago as 1872 by SCHLOESING, who calculated and tabulated the amounts of carbon dioxide to dissolve in water at given temperatures and p CO_2 values. The most relevant of his values are given in Table 3.

It can be seen from Table 3 that at 5 ^{o}C, for example, with a typical p CO_2 value for the atmosphere of 0.0003 /0.03 % carbon dioxide content/, the moisture in contact with the air is capable of absorbing about 0.84 mg/l carbon dioxide. At higher temperatures, for instance at 30 ^{o}C, which occurs in Hungary too during the summer, but which is general in the tropics, the amount of CO_2 absorbed is less /0.39 mg/l/.

Table 3

The change of the CO_2-dissolving capacity of water with the temperature and p CO_2 values occurring in practice

p CO_2 in the atmosphere	Total CO_2 dissolved in the water /in mg/l/, at the following temperatures							
	0 °C	5 °C	10 °C	15°C	17°C	20 °C	25° C	30 °C
0,0001	0,34	0,28	0,23	0,20	0,19	0,17	0,15	0,13
0,0003	1,01	0,84	0,70	0,60	0,56	0,52	0,45	0,39
0,0005	1,68	1,40	1,17	1,00	0,94	0,86	0,74	0,65
0,00075	2,52	2,09	1,76	1,50	1,41	1,28	1,12	0,98
0,001	3,36	2,80	2,34	2,00	1,88	1,72	1,49	1,31
0,0015	5,04	4,19	3,51	3,00	2,82	2,58	2,24	1,96
0,002	6,73	5,59	4,69	4,00	3,76	3,45	3,01	2,61
0,0025	8,40	6,99	5,85	5,00	4,70	4,28	3,72	3,28
0,005	16,8	13,98	11,7	10,0	9,4	8,57	7,46	6,56
0,0075	25,2	20,9	17,6	15,0	14,1	12,8	11,2	9,79
0,01	33,6	28,0	23,5	20,0	18,8	17,2	14,9	13,1
0,02	67,3	55,9	46,9	40,0	37,6	34,5	30,0	26,1
0,03	101,	83,9	70,4	60,0	56,6	51,7	45,1	39,2
0,04	135,	112,	93,8	80,1	75,6	69,0	60,0	52,5
0,05	168,	140,	117,	100,	94,1	86,2	74,6	65,3
0,06	202,	168,	141,	120,	113,	103,	90,0	78,4
0,07	236,	196,	164,	140,	132,	121,	105,	91,4
0,08	269,	224,	188,	160,	151,	138,	120,	104,
0,09	303,	252,	211,	180,	169,	155,	135,	118,
0,1	336,	280,	235,	200,	188,	172,	149,	131,
0,2	673,	559,	469,	400,	376,	342,	300,	261,

At the same time, however, it is true that in the tropics, where an intense CO_2 production takes place during the entire year as a result of the decomposition of the rich organic matter and also because of other soil and biogenetic processes, the carbon dioxide content of the air in the vicinity of the soil can attain values somewhat higher than the average. For example, LEHMANN /1955/ determined a value of 2.5 mg/l for the CO_2 content /thought to be of atmospheric origin/ of rain-water collected from air at temperature of 22 $^{\circ}$C. This would correspond to a partial pressure of CO_2 in the atmosphere of about 0.0016 according to the SCHLOESING tabulation /Table 3/ /H. LEHMANN 1956/.

The surprisingly large atmospheric carbon dioxide content calculated from this /0.15 %/, however, was not controlled directly by means of a simultaneous air-analysis, and so the relatively really high dissolved CO_2 value can not be sufficiently convincingly documented as being exclusively of an atmospheric diffusive origin. It is not excluded, for example, that the CO_2 content of the water may have been increased by the mixing with it of fine particles of <u>spray arising from the high-energy collision of the rain-drops with the soil</u>, since it is known that the water component of the aerosols so formed contains ions from the soil in relatively high concentrations /CAUER 1954, JAKUCS 1953, 1959/. A further contributory factor may be that the p CO_2 values of the rain are determined not by the observed temperature of the precipitation zone, but by the much lower temperatures prevailing at the cold vapour-condensation cloud level at a height of several thousand metres.

The fact that the factors mentioned almost certainly do modify the chemical composition of the rain-water collected fairly close to the soil surface, and to a considerable extent /an order of magnitude due mainly to the aerosol factor/, in supported by similar water-analysis

results from the temperate zone, and even from high moun-
tains. Such studies were carried out in the Alps by BÖGLI
/1960/ and BAUER /1964/, and in Hungary by CZÁJLIK /1961/.
Practically agreeing amounts of carbon dioxide were found
volumetrically in rain-water samples collected above the
soil /in the range 1.32-3.63 mg/l CO_2/.

Of course, one can hardly talk of a very significant
hydrocarbonate dissolution of the limestone even in the
presence of 2-3 mg/l dissolved CO_2, for /as can be seen
from Table 4/ in order for the water in contact with the
limestone to dissolve sufficient of it as hydrocarbonate
so as to accord with the simple dissociation given in
equation /1/, i.e. about 13 mg/l $CaCO_3$, a dissolved CO_2
content of about 6 mg/l would be necessary at 17 $^{\circ}C$; this
is equivalent to approximately ten times the p CO_2 to be
found in the atmosphere.

In contrast with this, the actual dissolved CO_2 con-
tent of the soil waters and karst waters occurring in na-
ture, and which are responsible for the karstic corrosion,
is in fact always many times higher /it is very often more
than 100 mg/l even!/. There is no doubt that the rain-water
which falls onto the soil obtains this high carbon dioxide
concentration not from the air, but from the soil itself.

The fact that soils, and thus the soil species cover-
ing limestones too, possess a soil atmosphere with a high
p CO_2 value, was demonstrated long ago by pedological re-
search workers /SCHLOESING 1872, FODOR 1875, WOLLNY 1880,
BOUSSINGAULT and LÉVY 1853, etc./.

The study of the soil atmosphere, that is the gas mix-
ture occupying the pore volume in soils with looser structu-
res, is dealt with in detail later. At this point, however,
it should be mentioned that the pedological investigations
have indicated a CO_2 content of more than 1 % in the atmosphe-
res of humous soils rich in organic matter, while it may fre-
quently even be more than 10 %. This must be regarded as the
most decisive factor governing the dynamism of the karst cor-
rosion, for the rain_water falling onto the soil surface and
absorbed there will be affected immediately by the soil air
which comes into contact there on a very large surface with
the water adhering to the soil particles, and thus even in
the uppermost soil layer the water will become saturated
with carbon dioxide in accordance with the p CO_2 value of
the gas mixture there.

The very important role of the soil atmosphere in re-
gulating the dissolution of the limestone was also observed
relatively early by geographers investigating the genesis of
karsts. KNEBEL analyzed the interaction quite comprehensively
as long ago as 1906, but the relations between the dissolving
power of the water and the soil had been considered long be-
fore him. For example, in 1831 the Hungarian VASS had given
an already detailed account of the stalactite and stalagmi-
te formation theory of PARROT, IANG and SOMMER, which is a
reasonably good approximation to the presently accepted
scientific view. According to VASS, these researchers ex-
plain the stalactite formation by the dissolving work of
the rain-waters seeping through "the layer of decayed plants
and vegetable mould which is saturated with carbonic acid".

CHOLNOKY /1940/ also stressed the role of the carbon
dioxide of the soil in the aggressiveness of the water:
"It is known that a constant decay and a slow oxidation
take place in the soil, with the formation of carbon dioxi-
de. This is then concentrated on the soil particles, since
these always have gas-concentrating natures. If it begins
to rain after dry weather, the "smell of rain" can be de-
tected. This is the characteristic smell of those gases
which are expelled from the surface of the particles of
soil. It can be demonstrated that at such time there is
very much gaseous carbon dioxide in the lower layers of
the air of the wetted area. Here, therefore, much gaseous
carbon dioxide gets into the fallen rain-water, especially
as a result of the dynamic pressure of the colliding rain-
-drops. This considerable amount of gas is carried by the
water into the cracks in the rock." /op. cit. p. 1006./

The measurements of TROMBE and of JACKLY in France
and Switzerland /TROMBE 1951, 1952, 1956/ indicated that
the localization of CO_2 gas in the soil layers covering
the karst formations can reach proportions /10-25 %!/
which are never observed otherwise in the atmosphere.

Very extensive and thorough studies were carried
out in Hungary by FEHÉR /1954/ in order to discover the
variations of the CO_2 content of the soil atmosphere and
the regularities involved, while the present author also
made measurements on Hungarian and Yugoslav karst soils
in 1967-8. The results of all these investigations show
that the composition of the soil atmosphere reacts with
very rapid and sensitive changes to both the macro- and
microclimatic factors, and characteristic simultaneous

differences are shown even within a given study site /e.g. a
single sink-hole/, depending on the type of vegetation li-
ving in the soil, and even on the individual species in the
rhizosphere /between the roots of the plants/ JAKUCS 1970,
1971.

It clearly emerges from what has been said that the
permeating waters originating from the rainfall, which direct
the entire karst development by means of their dissolution of
the limestone, acquire their carbonic acid content /which de-
termines the dynamics of the corrosion/ essentially always
and everywhere in the uppermost layer levels of the soil.
This means therefore that in a certain region the rate of
the corrosion karst-denudation is controlled most impor-
tantly by /in addition to the amount of rain-water seeping
through/ the biological and other soil-development proces-
ses in the thicker or thinner layer of soil covering the
surface.

It should be mentioned that in the interior of the
lithoclase network the water seeping into the network of
cracks in the limestone from the surface humous soil layers
no longer has the possibility to come into contact with ga-
ses whose compositions are significantly different quali-
tatively or quantitatively from that of the soil atmosphe-
re. Thus, the carbonic acid values obtained in the soil
are retained by the water almost unchanged as it seeps
through right to the well ventilated cavern, or again emer-
ges at the surface, where the new environment causes the
evaporation of the dissolved carbon dioxide brought by the
water to give a new equilibrium corresponding of course to
lower p CO_2 values.

The temperature of the water seeping down under the
action of gravitation in the lithoclase system in the in-
terior of the maturing karstic limestone mass is practi-
cally unchanged during its passage as a rule. It is known
that the vertical systems of crevices in which the water
trickles down are at the same time the means for thermal
exchange by convection; these can ensure the uniform tem-
perature corresponding to the yearly average for the re-
gion almost perfectly in the entire system above the karst
water level. In this way, the thermal factor can have an
effect on the CO_2 content of the water more or less only
in the upper soil zone of the infiltration, where its ac-
tion is exerted in accordance with the values given in Ta-
ble 3.

It must be noted, however, that compared to the ef-
fect of the partial pressure differences the role of the
soil temperature differences which occur in nature in
practice and which quantitatively effect the CO_2 dissolu-
tion is much smaller, even in extreme cases; at any p CO_2
level whatever, water at 0 ^{o}C is able to dissolve only
about twice as much as that dissolved by water at 20 ^{o}C.
Thus, in the karst dynamic evaluation of the role of the
thermal factor, in agreement with the majority of the pre-
sent climatic karstmorphogenetic authors /H. LEHMANN, TROM-
BE, BÖGLI, WISSMANN, GVOZDETZKII, etc./, the correct pro-
cedure is probably to conceive the effect of the tempera-
ture levels characterizing the individual climate zones
of the earth not in the direct SCHLOESING sense, but as
an indirect effect composed of the increase of the mate-
rial transport per unit time /intensity of dissolution/,
soil atmospheres containing more CO_2, and more intense
soil processes assisted by the higher thermal level.

For example, the warm rain in the tropics /because of its
higher temperature/ is able to absorb less CO_2 gas than
the cold water from melted snow in the polar regions for
instance. This greatly overrides and subordinates the fact
that at the same time the dissolution process is faster in
the tropics because of the higher temperature, while the
production of carbon dioxide is much more vigorous as a
result of the intense inorganic and biogenetic soil pro-
cesses. As the final complex resultant here, therefore,
the possibilities of the high-level saturation of the wa-
ter with CO_2 will nevertheless be much more favourable.

We have now arrived at the possibility of taking up
a well-founded clear stand in the international controversy
which arose following the ominous attitude of CORBEL /1959/:
it is not CORBEL, but H. LEHMANN and the climatic geomorpho-
logists following in his footsteps who are right. These lat-
ter not only recognise temperature and precipitation-order
differences in the climate factor, but with a real DOKU-
CHAYEV-ian attitude can take into account each of the geo-
morphological, pedological, biological, hydrological, che-
mical, etc. factors resulting in the climatic zonality, and
also their simultaneous complexity even /JAKUCS 1970/.

We have so far studied the roles of the partial gas
pressure and the temperature from among the factors deter-
mining the capacity of the water to absorb carbon dioxide
from the atmosphere or the soil-air. It still remains,
therefore, to analyse the pressure and time factors.

It is not necessary to provide a special proof that
the ability of water to absorb CO_2 increases with increas-
ing pressure. It is sufficient to point to the clear exam-
ple of soda-water, which provides a striking experimental

confirmation. It is less well known, however, that among
the natural actualities of karsts the possibility of the
development of the pressure factor is _ensured by the peri-
odicity of the rainfall_, water or soil atmosphere penetra-
ting from the karst soils into the lithoclases of the li-
mestone, depending on whether there is an ample surface
water supply or a lack of it.

When there is a very rainy period the cracks in the
limestone fill with water. However, if these filaments of
water running down under the action of gravity can no lon-
ger obtain a continuous replacement during a drier period,
then their continuity is interrupted; a weak vacuum forms
and air from the soil is sucked into the network of cracks.

When it again rains, of course, the "entrances" above
the lithoclase network soil again become covered with water,
and this now forces the gas mixture already in the cracks to
greater depths.

The cracks are frequently so thin that the laws rela-
ting to adhesion and capillary attraction overcome the for-
ces striving to arrange the system according to density.
Thus, alternating gas and liquid phases migrate downwards,
somewhat similarly to what can be seen in a thermometer
with a broken mercury thread.

Even in this stage certain hydrostatic pressure modi-
fications will affect the equilibrium of the water - gas
system, since if there would be no pressure distortions
arising from the gravitational and adhesive forces in the
system of cracks, then the water there would not move down-
wards. These pressure changes, however, are still not so

significant that they would substantially modify the water –
carbon dioxide phase-equilibrium formed in the soil. Nevert-
heless, the water sooner or later reaches a level where there
is no longer a free, empty route towards the depths. This is
either because the sub-layer is impermeable and so there is
no network of cracks, or because the existing network is al-
ready filled with water. The arriving water therefore finds
its path blocked, begins to build up, and together with the
accompanying air bubbles is forced to seek an outflow possi-
bility in the lateral directions.

This is not easy, because the cracks, which now should
lead away the water in the three-dimensional network to the
karst level in the horizontal directions, that is superfi-
cially or linearly, are themselves no more developed or wi-
de at the beginning of the karst maturation than the verti-
cal lithoclase system. The water units /and also the gas
bubbles between them/ are therefore compelled to enter zo-
nes where the hydrostatic pressure increases strongly. The
pressure here will be higher, the greater the water supply
from the surface and the lower the possibility for lateral
movement. Thus, a karst water zone flowing at high pressure
develops in the interior of the karsts /JAKUCS 1960, 1968a,
1968b/, in which the water will become enriched by further
amounts of dissolved carbon dioxide, since the pressure is
also exerted on the gas mixture, and this is now practically
compressed into the solution.

In this zone, where the spaces and cracks in the rock
which ensure the passage of water are now filled with water,
a pressure of several atmospheres may result /mining obser-
vations!/. The pressure is particularly considerable <u>in the</u>

lower level of the karst water zone where the movement is
horizontal. Experience has shown that it is not rare, es-
pecially in the case of young karsts, for the pressure to
exceed 10 atmospheres even.

   We shall return to this question later, but in connec-
tion with the magnitude and effectiveness of the role of the
pressure it must be noted here that this comes about essen-
tially via a certain modification of equation /3/. According
to the classical gas law of BOYLE-MARIOTTE, the volume of a
given mass of gas measured at various pressures is inversely
proportional to the pressure. The factor 1.9634 given in
equation /3/ is therefore not a constant value, but is valid
only for the case of a pressure of one atmosphere. For a
pressure of 2 atmospheres this factor must be doubled, for
a pressure of 10 atmospheres it must be multiplied by 10,
and so on, since the weight of the gas too has increased in
these proportions as a result of the compression.

   Let us now assume a case where the value of $p\ CO_2$ does
not change, that is the composition of the gas mixture re-
mains constant. Then, in the gas mixture – water system at
10 ^{o}C and a pressure of 5 atmospheres with $p\ CO_2 = 0.002$,
the total amount of CO_2 gas absorbed by the water will incre-
ase from the value 4.69 mg/l given in Table 3 to a value of
1.194 . 0.002 . 5 . 1.9634 = 23.45 mg/l. Since this number
is exactly five times the amount of CO_2 dissolved from the
air at a pressure of 1 atmosphere, it might be said that up
to a certain limit the capacity of water to dissolve CO_2
varies with the pressure in accordance with the product of
the capacity at 1 atmosphere and the number of atmospheres
/HENRY's law/.

At the same time, it is essential to bear in mind a very important factor, which can modify the validity of the above hypothesis considerably under karstic conditions. This is the fact that <u>as a result of the effect of pressure the composition of the original gas space changes in the closed two-component system in the interior of the karst</u>, in so far as <u>the greater the pressure, the less the partial pressure of CO_2 in the gas space</u>. This is related with the fact that the absorption coefficients /L/ of different gases are not the same. Those of the gases playing the most impartant parts in the gas space are substantially smaller than that of CO_2 /for oxygen at 20 ^{o}C L = 0.031; for nitrogen at 20 ^{o}C L = 0.015; and for carbon dioxide at 20 ^{o}C L= 0.0878/.

This has the result that with the increase of pressure the carbon dioxide is relatively quickly exhausted from the heterogeneously composed gas system, and the higher pressure values are practically powerless to increase still further the total CO_2 content of the solution. Because of this it is our opinion that <u>as regards the increase of the karst water it is the earlier pressure increases /e.g. from 1 to 10 atmospheres/ which play the essential role</u>, the unit pressure increases for hydrostatic pressures of up to even 100 atmospheres on the deep karst waters having much lower effects on the direct increase of the dissolution.

As a result of the differences in the absorption coefficients for the three gases, it is understandable that <u>the composition of the original gas mixture is finally very changed</u>, and at extremely high pressures it consists almost exclusively of the most difficultly soluble nitrogen. /This is why nitrogen always predominates in the gas bubbles coming to the surface with the waters of karst springs rising form great depths, for example at Miskolc-Tapolca, in the warm springs in Buda, etc./

It may explicitly be stated, therefore, that the fact
of the extensive increase of the dissolved CO_2 as a result
of the increase of the hydrostatic pressure is very impor-
tant from the point of view of the development of the karsts,
because the state of the karst corrosion level /the embryonic
cavern formation level/ in the depths is indicated by the
practically secondary aggressivity of the water.

It is plausible that with the later release of the press-
ure, when the water reaches a wider cavity or surface where
its directions of movement are determined by the slope, the
gases compressed into it in the pressure zone will come out
of solution; this is also accompanied by the cessation of
the secondary hydrocarbonate dissolving capacity.

In such places, however, the water is as a rule not on-
ly released from the hydrostatic load, but at the same time
also comes into an environment where the p CO_2 is much lower
than in the infiltration soil zone. Thus, further CO_2 will
leave the solution in accordance with the differnce in p CO_2
values for the two air spaces, until a new equilibrium has
been established corresponding to the p CO_2 /and temperature/
of the new air space as governed by equation /3/.

In the literature one can find the evaluation of the
role of pressure from a different viewpoint. Thus, of the
Hungarian authors particularly DUDICH /1932/, CHOLNOKY /1940/
and KESSLER /1938/ long ago stressed the importance of the
changes in the surface tension of the water. It is a matter
here of the tensile force occurring as a result of the sur-
face tension on the outer surface of the water drop moving
from the crevice in the rock to the ceiling of the cavern,

and also of the surface pressure decreases affecting the karst waters flowing on the convex slope and reduced to spray in the waterfalls. These factors simplifly and <u>accelerate</u> the diffusion of the excess CO_2 into the gas-space.

With this we have already come into contact with the fourth determinant of the CO_2 absorption, <u>the time factor.</u> This is similarly a very important factor in the establishment of equilibrium between the dissolved CO_2 and that in the gas-space. That is, <u>equilibrium is established in accordance with equation /3/ in a time process.</u>

The time requirement for the establishment of equilibrium in a given case could be expressed by an artificial formula, but even today it cannot be correctly calculated in practice. The time requirement for the establishment of the equilibrium could be caldetermined only as the complex resultant of many factors which themselves are also variable, but in several cases the precise mathematical formulation of even these partial factors is not possible.

In the following only some of the determinants which have the most important effects on the time factor will be mentioned, simply to illustrate what has already been said.

The greater the contact surface between the solution and the gas-space, the faster the process. But the reaction is also accelerated by the increase of the temperature. The reaction time is likewise shortened if the gas-space is in turbulent motion. If there is also such a turbulen mixing motion in the solution space, this further increases the reaction rate. The qualitatively and quantitatively different absorption surfaces in the reaction space /e.g. mineral and organic soil particles/ either promote or hinder the absorption, depending on their specific properties.

The rate of the dissolution process will be different if the water is not in contact with limestone, than when there is such a contact and hence the formation of hydrocarbonate can begin simultaneously with the gas absorption. Many more such modifying factors could be listed.

It is undoubtedly true that this is one of the most complicated problems in the interpretation of the corrosion. Nevertheless, in spite of its complexity, at the same time it is one of the key questions in climatic karst morphogenetic analysis, and one of the fundamental modifying factors of the dynamism of limestone dissolution.

So far, the dissolution of the gaseous CO_2 has been studied only as regards the properties of the liquid and the gas phases, and the solid phase /in this case the limestone/ has not yet been considered. In the following we again return to the analysis of the combined steps of the dissolution process when all three phases are present simultaneously.

It is understandable that with the introduction of this new factor the equilibrium relations and interactions become even more extensive than when the binary system of only the water and the CO_2 gas was examined. The question is even more complex, because here it is no longer a matter only of simple dissolution or dissociation, but of the chemical transformations which are closely connected with the dissociation and other physical dissolution equilibria.

According to literature data /HOLLUTA 1927, PIA 1953/, at 4 °C 0.7 % of the absorbed carbon dioxide content of the solution is converted to carbonic acid, in agreement with the well-known classical equation:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad /4/$$
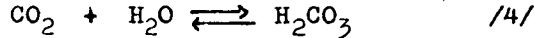
If it comes into contact with $CaCO_3$, the carbonic acid reacts with it, with the formation of calcium hydrocarbonate, and hence the limestone dissolves:

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca/HCO_3/_2 \quad /5/$$

Naturally, the carbonic acid bound to the calcium and thus practically used up is replaced from the physically absorbed CO_2 of the solution /until this is exhausted/, so that in practice almost the entire amount of dissolved CO_2 takes part in the process of dissolving the limestone.

According to the calculations of TILLMANS and HEUBLEIN /TILLMANS 1932, 1940/, the lower the concentration of carbonic acid, the more effective is equation /5/ in the direction of the upper arrow. Thus, in weak solutions /e.g. a total dissolved CO_2 concentration of 10-15 mg/l the reaction proceeds almost completely according to the upper arrow, while in more concentrated solutions it does so only up to a certain fraction of the total absorbed CO_2. The reason for this is that in the case of higher ionic concentrations accessory or equilibrium free carbonic acid must be present in amounts

gradually increasing with the concentration, so as to main-
tain the dissolved hydrocarbonate in equilibrium.

Figure 2 shows the most importantant bonding and equilib-
rium interactions governing the dissolution of $Ca/HCO_3/_2$.

For every mg of CO_2 dissolved in the water, the solu-
tion can dissolve 2.2723 mg $CaCO_3$, independently of the tem-
perature of the system. Accordingly, therefore, at low con-
centrations, where it is still not practical to consider the
equilibrium free carbonic acid requirements, from a know-
ledge of the amount of dissolved CO_2 the limestone dissol-
ving capacity of the solution can be calculated at once.
For example, the concentration of dissolved CO_2 in water
saturated at 10 $^\circ$C with air of normal composition /p CO_2 =
= 0.0003/ is 0.70 mg/l. Without the entry of further ga-
seous CO_2 into the solution, this is capable of dissolving
2,2723 . 0.7 = 1.59 mg of limestone as hydrocarbonate.

Naturally, even under laboratory conditions such a
limestone-containing solution can not occur in the presen-
ce of the solid phase, since the solid phase, since the so-
lution is also bound to contain about 13 mg/l calcium car-
bonate as a result of the primary carbonate dissolution in
accordance with equation /1/. It must also be pointed out
that in addition to carbon dioxide oxygen too is absorbed
in natural soil waters. This is used in bacterial and inor-
ganic oxidation processes in the soil, and hence in the ma-
jority of cases gives rise to an increased CO_2 content
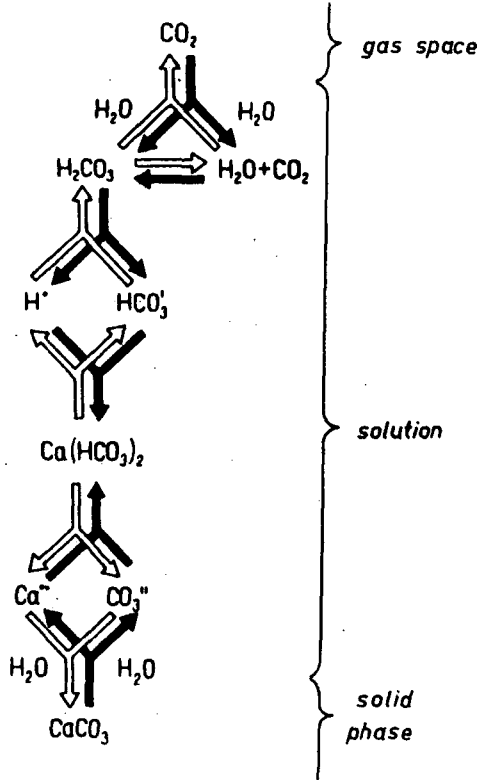/TUCAN 1933, CHRAMUSEV 1941, VENKOVITS 1949, STEFANOVITS ·
1956/.

Figure 2. The most important chemical conditional components of the hydrocarbonate dissolution of limestone. The equilibrium shifts according to the black arrows and to the white arrows result in dissolution and precipitation of limestone, respectively. At the same time the equilibrium shift for the system can occur either only according to the black arrows, or only according to the white ones.

At higher concentrations the question of the dissolu-
tion is more involved only in so far as the total amount of
carbon dioxide in the water can not be taken into account
in the hydrocarbonate reaction, because the equilibrium free
carbonic acid requirement must also be considered. It should
be noted, however, that the amount of this accessory free
carbonic acid now depends not only on the quantity of dis-
solved limestone, but also on the temperature of the envi-
ronment.

In the presence of $CaCO_3$, therefore, the absorbed car-
bon dioxide is to be found simultaneously in the following
forms in the aqueous solution:

1. In the form of hydrocarbonate bound to the the
   calcium.

2. In the form of accessory, or equilibrium free
   carbonic acid necessary to maintain the hydro-
   carbonate in solution.

3. In the form of aggressive carbonic acid, in
   amounts possibly exceeding the equilibrium
   requirements of the hydrocarbonate. This la-
   tter free carbonic acid obtained its name from
   its corrosion capacity, since not being in-
   volved in the existing solution equilibria,
   it can facilitate the dissolution of further
   limestone.

If the relative amounts of these three functional
types of carbonic acid in a solution are known, it can be
decided whether the given solution is capable of further
corrosion, whether the limestone and the carbonic acid
are in equilibrium, or whether the solution is supersa-

turated and hence its tendency is to deposit calcium carbona-
te.

In the international chemical and hydrological litera-
ture, it was earlier possible to find the equilibrium free
carbonic acid indexes only for waters at 17 $^{\circ}$C /TILIMANS
1932, LAPTYEV 1939, TROMBE 1951, 1952, BÖGLI 1960, etc./.
For this reason PAPP /1954, 1956/ calculated the accessory
free carbonic acid contents of waters in limestone — carbo-
nic acid equilibrium for all the more importantan concent-
rations and temperatures. The values most likely to be re-
quired in karst research work are given in Table 4.

It is also possible to decide from the Table the ex-
tents of the function of the temperature changes controll-
ing the solubility, in so far as water possessing an unchan-
ged total CO_2 content is capable of retaining less calcium
carbonate in solution at higher temperatures, because at
higher temperatures the amount of equilibrium free CO_2 ne-
cessary to keep the calcium hydrocarbonate in solution
increases. If, for example, the total CO_2 content of a wa-
ter in limestone — carbonic acid equilibrium at 5 $^{\circ}$C is
957 mg/l /330 mg/l of this is bound CO_2, and 627 mg/l
accessory carbonic acid/, this will keep in solution
$Ca/HCO_3/_2$ corresponding to 749.7 mg/l solid $CaCO_3$. If the
temperature of the water is now raised to 14 $^{\circ}$C, however,
with an unchanged total amount of carbonic acid, the li-
mestone-dissolving capacity decreases, and thus the solu-
tion becomes supersaturated. In this case the 957 mg/l
total CO_2 content now assumes a different distribution:
the bound CO_2 will be 306.2 mg/l, and the equilibrium
CO_2 650.8 mg/l, and accordingly the quantity of $CaCO_3$
which can be kept in solution by the water cannot be more
than 969.1 mg/l. This means that 749.7 - 696.1 = 53.6 mg
$CaCO_3$ must separate out from each litre.

Table 4

The bound and accessory CO_2-requirements of
the hydrocarbonate dissolution of the limestone

$CaCO_3$ mg/l	bound CO_2	accessory CO_2 /mg/l/ at the following temperatures							
		5 °C	7 °C	9 °C	10 °C	11 °C	12 °C	15 °C	20 °C
8,92	3,85	-	-	-	-	-	-	-	-
17,85	7,70	-	-	-	-	-	0,01	0,01	0,01
26,77	11,5	0,03	0,03	0,04	0,04	0,04	0,04	0,04	0,05
35,70	15,6	0,07	0,07	0,07	0,08	0,08	0,08	0,09	0,00
44,52	19,4	0,14	0,15	0,16	0,17	0,17	0,18	0,19	0,23
53,55	23,5	0,23	0,24	0,26	0,26	0,27	0,28	0,30	0,35
62,47	27,3	0,38	0,41	0,44	0,45	0,46	0,48	0,51	0,59
71,40	31,5	0,54	0,58	0,61	0,63	0,65	0,67	0,73	0,84
80,32	35,3	0,79	0,84	0,89	0,92	0,95	0,97	1,06	1,23
89,25	39,2	1,06	1,11	1,18	1,21	1,25	1,28	1,40	1,62
98,17	43,0	1,39	1,52	1,61	1,65	1,71	1,75	1,91	2,21
107,1	47,1	1,82	1,93	2,04	2,10	2,17	2,23	2,43	2,81
116,0	50,9	2,27	2,50	2,65	2,79	2,81	2,89	3,15	3,64
124,8	55,0	2,90	3,08	3,26	3,36	3,45	3,56	3,88	4,48
133,8	58,8	3,60	3,82	4,04	4,16	4,28	4,41	4,81	5,56
142,8	62,7	4,30	4,56	4,83	4,97	5,12	5,27	5,57	6,64
151,7	66,5	5,22	5,53	5,86	6,03	6,21	6,40	7,48	8,06
160,6	70,6	6,14	6,51	6,90	7,10	7,31	7,53	8,21	9,49
169,6	74,4	7,29	7,73	8,19	8,43	8,70	8,96	9,75	11,2
178,5	78,5	8,45	8,96	9,49	9,77	10,1	10,4	11,3	13,1
187,4	82,5	9,92	10,4	11,0	11,3	11,7	12,1	13,2	15,2
196,3	86,5	11,4	11,9	12,7	13,0	13,4	13,8	15,1	17,4
205,3	90,4	13,0	13,6	14,5	14,9	15,3	15,8	17,3	19,9
214,2	94,2	14,6	15,4	16,4	16,8	17,3	17,8	19,5	22,5
223,1	98,1	16,6	17,5	18,6	19,1	19,7	20,2	22,1	25,6

$CaCO_3$ mg/1	bound CO_2	accessory CO_2 /mg/l/ at the following temperatures							
		5 °C	7 °C	9 °C	10 °C	11 °C	12 °C	15 °C	20 °C
232,0	102,1	18,6	19,7	20,8	21,5	22,1	22,7	24,6	28,7
241,0	106,0	20,9	22,1	23,4	24,1	24,8	25,5	27,9	32,3
249,9	110,0	23,2	24,6	26,1	26,8	27,6	28,4	31,0	35,9
258,8	113,9	25,9	27,4	29,1	29,9	30,3	31,7	34,6	40,0
267,7	117,9	28,6	30,3	32,1	33,0	34,0	35,0	38,2	44,2
276,7	121,8	31,6	33,4	35,4	36,5	37,5	38,6	42,2	48,8
285,6	125,6	34,6	36,6	38,8	40,0	41,1	42,3	46,2	53,4
294,5	129,5	38,0	40,3	42,7	44,0	45,2	46,5	50,3	58,7
303,3	133,5	41,5	44,0	46,6	48,0	49,4	50,8	55,5	64,1
312,3	137,4	45,4	48,1	51,0	52,5	54,0	55,6	60,7	70,1
321,3	141,4	49,3	52,3	55,4	57,0	58,7	60,4	65,9	76,2
330,2	145,3	53,5	56,8	60,1	61,9	63,7	65,6	71,6	82,8
339,1	149,2	57,8	61,3	64,9	66,8	68,8	70,8	77,3	89,4
348,0	153,1	62,6	66,4	70,3	72,4	74,5	76,7	83,7	96,9
357,0	157,1	67,5	71,5	75,8	78,0	80,3	82,7	90,2	104,3
365,9	161,0	72,9	77,2	81,9	84,3	86,7	89,3	97,5	112,7
374,8	165,0	78,4	83,0	88,0	90,6	92,3	96,0	104,8	121,1
383,8	168,9	84,3	89,2	94,6	97,4	100,2	103,2	112,6	130,2
392,7	173,5	90,2	95,5	101,3	104,3	107,3	110,5	120,5	139,3
401,6	176,9	96,5	102,2	108,3	112,5	114,8	118,2	128,9	149,0
410,5	180,7	102,8	108,9	115,4	118,8	122,3	125,9	137,4	158,8
419,5	184,6	109,8	116,3	123,3	126,9	130,7	134,5	146,8	169,7
428,4	188,5	116,8	123,8	131,2	135,1	139,1	143,2	156,2	180,6
437,3	192,4	124,5	131,9	139,8	143,9	148,2	152,5	166,8	192,4
446,2	196,4	132,2	140,1	148,4	152,8	157,3	161,9	176,6	204,2
455,2	200,3	140,3	148,7	157,6	162,2	167,0	171,9	187,5	216,8
464,1	204,2	188,5	157,4	166,8	171,7	176,8	182,0	198,5	229,5
473,0	208,1	159,0	166,9	166,8	182,0	187,4	192,9	210,5	243,3

$CaCO_3$ mg/l	bound CO_2	accessory CO_2 /mg/l/ at the following temperatures							
		5 °C	7 °C	9 °C	10 °C	11 °C	12 °C	15 °C	20 °C
481,9	122,1	166,5	176,4	186,9	192,4	198,1	203,9	222,5	257,2
490,8	216,0	176,1	186,6	197,7	203,6	209,6	215,7	235,4	272,1
499,8	220,0	185,7	196,8	208,6	214,8	221,1	227,6	248,3	287,0
508,7	223,9	196,1	207,8	220,2	226,7	233,4	240,3	262,1	303,0
517,6	227,9	206,5	218,8	231,9	238,7	245,8	253,0	276,0	319,1
526,5	231,8	217,3	229,8	244,0	251,2	258,6	266,2	290,4	335,8
535,5	235,7	228,1	241,8	256,2	263,8	271,5	279,5	304,9	352,5
553,4	243,5	251,9	266,9	282,9	291,2	299,8	307,9	336,6	389,2
571,2	251,2	276,5	293,0	310,5	319,6	329,1	338,0	369,5	427,2
589,0	259,2	303,3	321,5	340,7	350,7	361,0	370,8	405,4	468,7
606,9	267,1	331,9	351,8	372,8	383,8	395,1	405,8	443,6	512,9
624,7	275,0	362,8	384,5	407,5	419,5	431,5	443,5	484,9	560,6
642,6	282,7	394,1	417,6	442,5	455,6	469,0	481,7	526,6	608,8
660,3	290,6	428,1	453,6	480,7	494,9	509,5	523,3	572,1	661,4
678,3	298,5	464,0	491,7	521,1	536,5	552,3	567,2	620,1	716,9
696,1	306,2	500,8	530,7	562,5	579,0	596,1	602,2	669,3	773,8
714,0	314,1	540,6	572,9	607,1	625,0	643,4	660,9	722,5	835,3
731,8	322,0	582,5	617,3	654,1	673,4	693,3	712,0	778,5	900,0
749,7	330,0	627,0	664,4	704,1	724,8	746,2	766,4	837,9	968,7
767,5	337,7	671,8	711,9	754,5	776,7	799,6	821,2	897,8	1038
785,4	345,6	720,1	763,1	808,7	832,9	857,1	880,3	962,4	1112
803,2	353,6	770,5	816,6	865,3	890,8	917,1	941,9	1029	1190
821,1	361,2	822,0	871,1	923,2	950,3	978,4	1004	1098	1271
838,8	369,1	877,1	929,5	985,1	1014	1044	1072	1172	1355
856,8	377,0	934,7	990,5	1049	1080	1012	1142	1249	1444
874,6	385,0	995,6	1055	1118	1151	1185	1217	1330	1538
892,5	392,7	1056	1119	1186	1221	1257	1291	1411	1632

The above relations can be illustrated in the form
of a complex graph /Fig. 3/ derived from the values given
in Table 4. The abscissa of this diagram shows the total
amount of CO_2 in the solution, and the ordinate the amount
of $CaCO_3$ dissolved, both in mg/l. If the previously deter-
mined total CO_2 content or dissolved $CaCO_3$ content is pro-
jected into the system, the chemical nature of the water
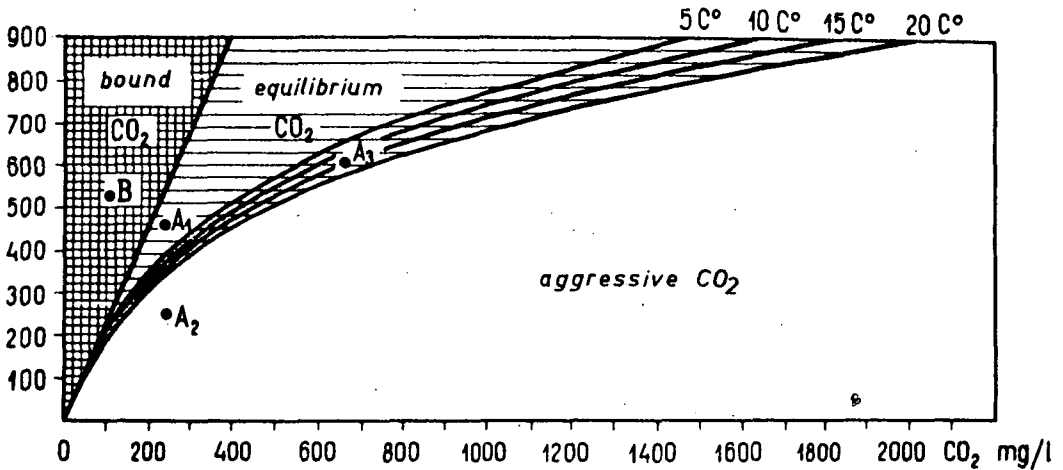studied can readily be read off.

Figure 3. Amounts of bound carbonic acid and
equilibrium free carbonic acid in
waters in limestone – carbonic acid
equilibrium at 5, 10, 15 and 20 $^{\circ}$C.

If, for instance, the total amount of CO_2 is 250 mg/l, and the amount of dissolved $CaCO_3$ is 450 mg/l /in this case the point A_1 denotes the state of the water on the diagram/, it can be seen at once that the water is strongly supersaturated, and thus $CaCO_3$ will precipitate from it. If, on the other hand, the amount of dissolved $CaCO_3$ in only 250 mg/l, then the water is strongly aggressive, because this state /position A_2 on the diagram/ is in a region of unsaturation. At the same time, another water, defined on the basis of analysis by point A_3, and obviously at equilibrium at 12 ^oC, becomes aggressive if cooled to a temperature lower than this, and supersaturated at higher temperatures.

Of course, it is not possible to find a water sample which can be denoted by a point inside the region of bound CO_2 /e.g. B/.

It must be mentioned here that the aggressivity of a water does not lead to the immediate unfailing dissolution of limestone in all cases, for if it is possible for the carbon dioxide to evaporate out of the solution, then this in an alternative method for equilibrium corresponding to the new conditions to be established.

The route by which the system strives to attain equilibrium in a given case depends on many involved factors. In a closed system where there is no possibility for the evaporation of CO_2 into the gas-space, the equilibrium can only be restored by the increase of the corrosion. /This is why waters circulating in a closed network of tubes are so corrosion-dangerous, even if they are only slightly aggressive./

The aggressivity of water can readily be calculated numerically from a knowledge of the total CO_2 content and the carbonate hardness[x] from Table 4.

By the combined use of Table 3 and 4, still further very significant considerations are possible as regards karst research. Thus, from a knowledge of the p CO_2 values of the soil atmosphere determining the chemical nature of the water in the infiltration zone, the extent of limestone transportation can be calculated.

Let us now consider a concrete example of the use of these Tables for such calculations:

The water has been acted on in the soil by air with a partial pressure of 8/100, and the water – carbonic acid equilibrium has been established by contact with a gas-space of this concentration. The temperature of the soil during the infiltration period was 5 °C. In this case the water has a total carbonic acid content of 224 mg/l /see Table 3/. The aggressive water dissolves up limestone in its network of crevices, and during the seepage downwards a limestone

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[x] The carbonate hardness of the water id determined by the sum of the calcium and magnesium hydrocarbonates dissolved in it. One German hardness degree means 10 mg/l CaO, or 17.85 mg/l $CaCO_3$. Thus, for example, water with a German hardness degree of 22, if the hardness is caused only by calcium salts, contains 17.85 . 22 = 392.7 mg/l of $CaCO_3$ dissolved as hydrocarbonate.

— carbonic acid equilibrium is established. The amount of
dissolved limestone is found from Table 4; this is done
by seeing how the total CO_2 content of 224 mg/l is divided
at 5 ^oC between bound and equilibrium free carbonic acid.
Values of these are sought such that their sum corresponds
as closely as possible to 224 mg/l. In this case the sum of
157.1 mg/l bound carbonic acid and the related 67.5 mg/l
accessory CO_2 approximates well to the desired number, the
difference being negligible. It only remains to read off
the value of $CaCO_3$ in mg/l from the first column of Table
4, giving in the present case a figure of 357.0 mg/l.

From this, however, we have so far found only the
amount of limestone which may be dissolved by the karst
water under favourable conditions. As to how much may be
reprecipitated from the solution under given conditions,
such as those in a cavern, this can be learnt only from
further calculations.

If, for instance, the karst water in question finds
its way into a cavity in a cavern at 10 ^oC where the par-
tial pressure of CO_2 in the air is 2/100, then if a suitab-
le amount of time is available a new equilibrium state will
develop corresponding to the CO_2 content of the new atmosphe-
re; this means, according to Table 3, that the total CO_2
content of the solution will be 46.9 mg/l /the rest evapo-
rates/. Next, by the already known method, the $CaCO_3$ value
must be found from Table 4 corresponding to

/bound CO_2/ + /equilibrium CO_2 at 10 ^oC/ =   46.9 mg/l

Concretely, it is seen that under the new equilibrium con-
ditions the solution contains only about 100 mg/l $CaCO_3$.
The difference in the two values /357 - 100 = 257 mg/l/ is
thus the desired amount which is transported by the water
from one point of the karst to another.

It must be noted here, however, that although a good
approximation may often be obtained, nevertheless these
calculations can not always be regarded as entirely realis-
tic. The problem is that in nature there are several factors
which cannot always be calculated at present, e.g. the time
factor, the other gases dissolved in the water /mainly oxy-
gen/, the modifying actions of the humus and root acids in
the zone of decomposition of the organic matter, etc. These
vary from case to case, and at times may make such a signi-
ficant contribution that they can change the quantity of
limestone dissolved considerably.

From another aspect, it also emerges from Table 4 that
while the amounts of CO_2 bound as hydrocarbonate increase
linearly with the amount of dissolved $CaCO_3$, the increase of
the equilibrium free carbonic acid is of a progressive na-
ture; that is, the successively increased amount of dissol-
ved $CaCO_3$ can be kept in an equilibrium state only by the
ensurance of continually more rapidly increasing amounts
of accessory free carbonic acid. The relation is expressed
by the following formula, due to TILLMAS:

$$\text{equilibrium } CO_2 = \frac{/\text{bound } CO_2/^3}{K_t} \qquad /6/$$

where the factor K_t is a constant for a given temperature.

It follows clearly from all this that during the mixing
of equilibrium hydrocarbonate solutions of different concent-
rations /e.g. natural soil and karst waters/ carbon dioxide
will become surplus in the solution, that is the solution
will become aggressive. Depending on the conditions, this
carbonic acid excess will evaporate from the solution, or may
lead to the dissolution of more $CaCO_3$. In such a way, a se-
condary dissolution process can come about; this is known
as mixing corrosion. LAPTYEV /1939/ was the first to draw
attention to its existence, but its role in karstification
has been suitably stressed only by BÖGLI /1963/, and in
Hungary by ERNST /1964/ and BALÁZS /1966/.

The extent of the reaggressivity appearing on mixing
the solutions is the greater, the larger the difference
in the initial hydrocarbonate concentrations of the mixed
equilibrium solution components. Only a minor role is pla-
yed in this question by the temperature factor.

Let us now confirm the above findings by the ex-
amination of some concrete data from Table 4.

Before mixing, the equilibrium solutions A and B had
the following compositions:

solution A /9 °C/	$CaCO_3$ content dissolved as hydrocarbonate	151.7 mg/l
	bound CO_2 content	66.5 mg/l
	equilibrium free CO_2 content	5.8 mg/l

solu- tion B /9 ^{o}C/	CaCO$_3$ content dissolved as hydrocarbonate	508.7 mg/l
	bound CO$_2$ content	223.9 mg/l
	equilibrium free CO$_2$ content	220.2 mg/l

If it is assumed that /for the sake of simplicity/
equal volumes of A and B are mixed, then the product, so-
lution C, will have the following composition:

solu- tion C /9 ^{o}C/	CaCO$_3$ content dissolved as hydrocarbonate	$= \dfrac{151.7 + 508.7}{2} = 330.2$ mg/l
	bound CO$_2$ content	$= \dfrac{66.5 + 223.9}{2} = 145.2$ mg/l
	free CO$_2$ content	$= \dfrac{5.8 + 220.2}{2} = 113.0$ mg/l

If the adequate carbonic acid values related to the
dissolved CaCO$_3$ content of solution C, 330.2 mg/l, are looked
for in Table 4, it is seen that the value for the bound car-
bonic acid is in agreement, whereas at 9 ^{o}C the requirement
of solution C for accessory free carbonic acid is equivalent
to only 60.1 mg/l CO$_2$. Thus, as a result of the mixing there
will be a 113.0 - 60.1 = 62.9 mg/l excess of in statu nasc-
endi CO$_2$ in solution C, which means that the solution now
contains aggressive carbonic acid.

Using the same method as in the above example, we have calculated the concentrations of the aggressive carbonic acid adequate CO_2 released on mixing equal quantities of waters with carbonate hardnesses of 0-50, at 10 ^{o}C. The results are shown in Table 5.

Table 5

Hardness German degrees	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0°	0										
5°	0,5	0									
10°	3,7	1,3	0								
15°	12,4	7,3	2,4	0							
20°	29,2	20,6	10,8	3,1	0						
25°	57,4	43,9	28,8	14,9	2,7	0					
30°	98,8	80,0	58,8	35,8	18,1	4,7	0				
35°	157	132	102	73,5	45,2	22,3	6,0	0			
40°	234	200	164	126	87,6	64,1	24,8	5,8	0		
45°	333	293	247	198	149	102	61,4	30,3	7,7	0	
50°	448	407	351	292	230	169	117	70,1	32,4	7,8	0

Amounts of aggressive carbonic acid CO_2 /mg/l/ formed on the 1:1 mixing of equilibrium waters at 10 ^{o}C with German hardness factors of 0-50

The same data are also plotted graphically in Figure 4. Hence, by means of the continuity of the lines on the diagram the amounts of in statu nascendi CO_2 relating to the intermediate values can be read off directly.

It has been mentioned that temperature changes act in a subordinate way, and only as a modifying factor, in the quantitative control of the aggressive carbonic acid formed on mixing. To illustrate this, let the temperature of solution A in the above example now be 9 $^{\circ}$C still, but that of solution B 15 $^{\circ}$C. After mixing, the temperature of solution C will then be 12 $^{\circ}$C.

In accordance with the new temperature, the equilibrium amount of CO_2 in solution B is now 262.1 mg/l compared with the previous 220.2 mg/l. The other characteristics of solutions A and B do not change. Thus, the total quantity of free CO_2 in solution C can be calculated as:

$$\frac{5.86 + 262.1}{2} = 133.9 \text{ mg/l}$$

Since the equilibrium carbonic acid requirement of solution C at 12 $^{\circ}$C is 65.6 mg/l, then as a result of the mixing there will be a free CO_2 excess of 133.9 - 65.6 = = 68.3 mg/l. This is only 5.4 mg/l more than the amount released on mixing the solutions which were both at 9 $^{\circ}$C.
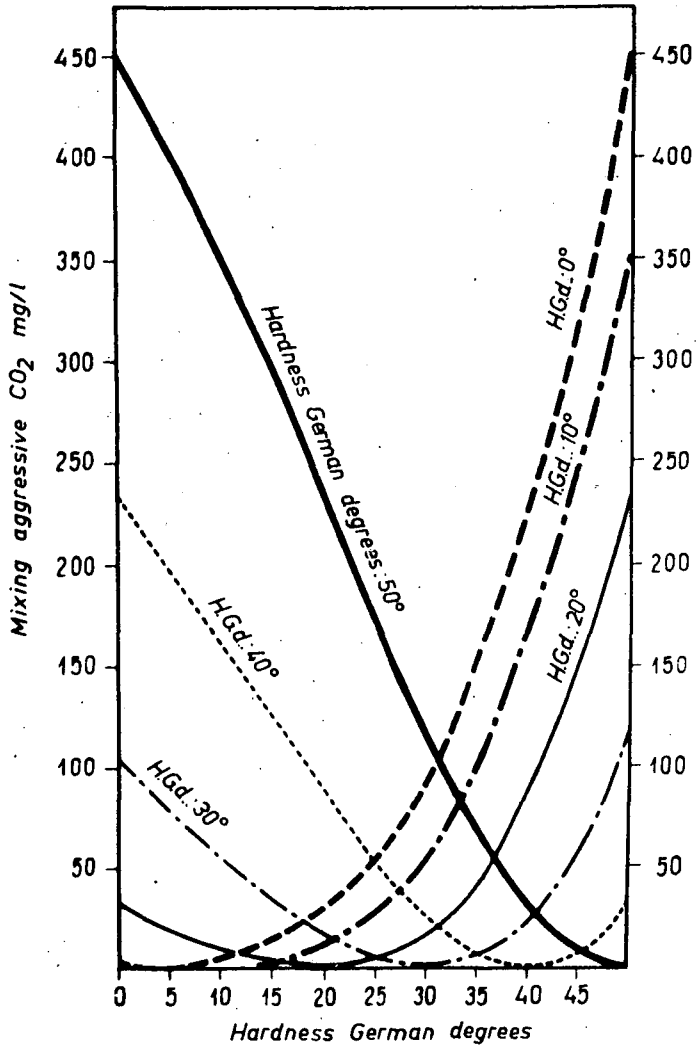
Figure 4. Amounts of aggressive carbonic acid /CO_2 mg/l/ formed in the 1:1 mixing of karst waters of various hardnesses at 10 $^\circ$C.

It can be stated that <u>the larger the temperature di-</u>
<u>fference between the two solutions to be mixed, the greater</u>
<u>the amount of aggressive CO_2 formed</u>. For example, if the
temperature of solution A is only 5 ^{o}C, while that of solu-
tion B is 15 ^{o}C, it can readily be calculated that 60.7
mg/l aggressive CO_2 will be produced in the solution C for-
med with a temperature of 10 ^{o}C. This is 7.8 mg/l more than
the amount formed on mixing solutions A and B, both at 9 ^{o}C.

The diagrams of Figure 5 were plotted from the results
of calculations in this connection. They show the amounts
of in statu nascendi CO_2 released on the mixing of equal
volumes of soft water not containing dissolved chemicals
/pure rain-water/ and equilibrium karst waters of various
carbonate hardnesses. The calculations were performed for
systems at 5, 10 and 20 ^{o}C.

Of course, only part of the unbound carbonic acid re-
leased during the mixing processes in able to dissolve
further $CaCO_3$, for the remainder is required to keep the
newly dissolved amount in equilibrium.

The very important question from the point of view of
the karst researcher, as to how much limestone can be dis-
solved by secondary dissolution as a result of the aggres-
sive CO_2 released when solutions mix, can be answered most
simply in the following way with the use of Table 4:

The concentrations of all the bound and accessory
CO_2 in the equilibrium solutions A and B are added toget-
her, and the result divided by two. The value so obtained
is the total amount of CO_2 in one litre of solution C.
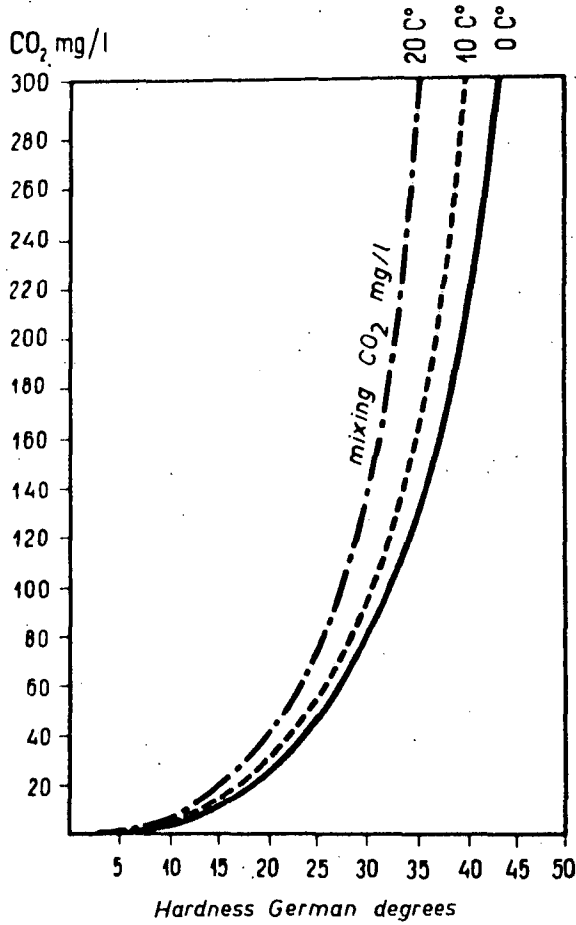The bound CO_2 values and the accessory CO_2 values at the

Figure 5. Amounts of in statu nascendi CO_2 /mg/l/ released on the 1:1 mixing of soft water not containing dissolved chemicals and equilibrium waters of various carbonate hardnesses in systems at 5, 10 and 20 ^oC.

appropriate temperature are taken from the columns of the Table and added together. This is done until the sum is the same as the already calculated total CO_2 concentration. The sought-for amount of secondarily dissolved limestone is given by the difference between the $CaCO_3$ value relating to the row giving the coincidence, and the average $CaCO_3$ value for solution C.

Let us now illustrate the above on the example of solutions A and B at 9 °C.

The total CO_2 supply of solution C, obtained by summing the concentrations in solutions A and B, and averaging, is:

$$\frac{66.5 + 5.8 + 223.9 + 220.2}{2} = 258.2 \text{ mg/l.}$$

The average $CaCO_3$ supply in this same solution C has already been calculated: 330.2 mg/l.

If the sums of the bound CO_2 value and the accessory CO_2 value at 9 °C, as obtained from the relevant columns of the Table, are compared with the total CO_2 content of 258.2 mg/l, with a little interpolation it can readily be found that, in an equilibrium state, this corresponds to 166.7 mg/l bound CO_2 and 91.5 mg/l accessory CO_2.

Next, the amount of $CaCO_3$ actually dissolved by solution C can easily be calculated from the formula N.V, where N = the concentration of bound CO_2 in the solution /mg/l/, and V = 2.2723, a constant.

.In this case, therefore, in its new equilibrium state
solution C will be capable of retaining in solution an amount
of hydrocarbonate equivalent to 166.8 . 2.2723 = 378.8 mg/l
$CaCO_3$. Thus, by means of the mixing corrosion the solution
is capable of the secondary dissolution of 378.8 - 330.2 =
= 48.0 mg/l limestone.

Contradictory views can be found in the literature as
regards the role of the mixing corrosion in karstification.
According to BÖGLI, one of the leading authorities in this
question, /BÖGLI 1963a, 1963b/, it is important only in
those zones deep in the karst where the passages are comple-
tely filled with water and there are no well-ventilated air-
-spaces into which the released aggressive carbonic acid
might evaporate. In contrast with this, it has been pointed
out by Hungarian research workers among others /GÁNTI 1957,
MAUCHA 1960, CZÁJLIK 1962, ERNST 1964/, and supported by
numerous observations and analyses, that the recent corro-
sion of cave waters appearing to be strongly supersaturated
may frequently be **observed** even in wide passages.

It is clear that the debate can be settled by the
study of the rates of the dissolution and gas-diffusion
processes, and in this respect we consider that the opinions
of FRANKE /1965/, ERNST /1964/ and BALÁZS /1966/ most closely
reflect the truth. They hold the view that mixing karst wa-
ters of different hardnesses may become capable of dissolu-
tion even when in contact with a free air-space. The eva-
poration of carbon dioxide from the solution takes place
only at the surface of contact of the two media, and is
therefore a slow process, whereas the rate of mixing of
the water components is much higher since they are in tur-
bulent motion, and so the water molecules in contact with
the rock surfaces are continually being replaced by fresh
ones.

It is correctly stressed by BALÁZS /op. cit. p. 184/ that: "The greatest concentration differences in the waters of our karst caves may appear when the very hard karst waters originating from infiltration and stagnating in the depths, are mixed with the alluvial waters from melting snow or sudden summer storms." In his view, on each such occasion the inrushing waters may permit the secondary dissolution of several hundred kilograms of limestone in the larger Hungarian caves, quite apart from their possible inherent aggressive effects.

As regards the many details of the question and the extent of the dissolution under natural conditions, of course, a final answer can be expected only after the collection and evaluation of many more careful observations. Nevertheless, it can already be stated with certainty that the mixing corrosion, as one of the important components of the hydrocarbonate dissolution process, plays a really factorial role in the development of the karsts.

We have so far made a multilateral analysis of the multicomponent regularities of the interactions governing the amount of carbon dioxide in the atmosphere, the carbonic acid content of the water, and the amount of limestone dissolved by the solution. It still remains to introduce a very important equilibrium relation which must be assumed between the partial pressure of CO_2 in the atmosphere /or soil atmosphere/ and the solution in limestone – carbonic acid equilibrium. This is at the same time the

most refined and the most time-requiring equilibrium of the
hydrocarbonate dissolution. This is why in many cases under
natural conditions the karst water does not attain equilib-
rium.

Here, therefore, the amount of dissolved carbonic
acid consumed during the hydrocarbonate formation process
will show up as a loss in the equilibrium balance for the
first-degree binary system atmophere – water, and this re-
sults in a renewed tendency for the dissolution of atmos-
pheric carbon dioxide. Thus, in other words it could be
said that since the amounts of carbonic acid bound to cal-
cium /or magnesium/ as hydrocarbonate are no longer invol-
ved in the absorption equilibrium, and only the accessory
CO_2 is in an equilibrium relation with it /according to
equation /6//, then the accessory carbonic acid in the so-
lution must come into a new adequate equilibrium relation
with the partial pressure of CO_2 in the air /according to
equation /3//. That is, as shown by Figure 2 the progress
of the limestone-dissolving process produces effects all
the way back to the atmosphere in contact with the solu-
tion, and leads to the absorption of further carbon
dioxide from this.

In this way, the water in contact with a limestone
will continue to absorb carbon dioxide from the atmos-
phere until equilibrium according to equation /3/ has
been established between the atmospheric CO_2 and the
accessory /equilibrium/ free carbonic acid of the solu-
tion. This does not mean, therefore, that the SCHLOESING
Table /Table 3/ is unusable, but simply leads to the

limitation that <u>in the case of a dissolved limestone con-</u>
<u>tent the values of the Table must be referred to the equ-</u>
<u>ilibrium CO_2 values of Table 4 at the appropriate tempera-</u>
<u>ture.</u>

Let us now consider the above in the case of an
earlier used example.

In an equilibrium state at 5 ^{O}C, the partial pressure
of CO_2 in ordinary atmospheric air, 0.0003, corresponds to
0.84 mg/l dissolved CO_2. We have already seen that if this
carbonic acid value is regarded as stationary, then the
hydrocarbonate-dissolving capacity of saturaturated water
in air is very slight. If, however, in accordance with the
extent of its exhaustion in the hydrocarbonate dissolution,
<u>the means and the time</u> are available for further absorption
from the atmosphere, by the time this dissolved CO_2 value
of 0.84 mg/l is again established as the accessory carbonic
acid in equilibrium with the hydrocarbonate, the water has
already dissolved up about 81.97 mg/l $CaCO_3$ /calculated by
interpolation from Table 4/.

Thus, it becomes quite understandable that even the
softest karst waters, which are typical of completely bare
karsts and alpine, snow-zone karsts, may contain as much
as 80-100 mg dissolved limestone per litre. /BALÁZS /1963
reports a value of only 104 mg/l for the limestone content
of the <u>Cadisha spring</u> which emerges from the bare karstic
mass of the 3000 m high <u>Kornet es Saouda</u> in the Lebanon.
The <u>Lodowe Zródlo</u> karst spring which surfaces in the Polish
West Tátra contains 75-85 mg/l $CaCO_3$. KESSLER determined

80–100 mg/l $CaCO_3$ in karst waters originating from the depths
of bare Albanian karsts at a plateau height of 2000 m . BAUER
/1964/ and TELL /1961/ mention karst waters of similarly low
concentrations in the Austrian Alps and in Sweden, respecti-
vely./

As regards order, the above values agree quite well
with the results of theoretical calculations obtained by
other means /MILLER 1952, MÁNDY 1954, GÁNTI 1957, ERNST
1961, MARKÓ 1961, FRANKE 1967/.

The question of <u>the time requirements of the series
of hydrocarbonate limestone dissolving reactions/</u> has been
dealt with recently by BÖGLI /1960, 1963/. He found that
as regards the time requirements of the hydrocarbonate
dissolution of limestone it is convenient ot divide the
dissolution into four stages as follows.

In the first stage, which is very rapid, the simple
physical dissolution of the $CaCO_3$ occurs as in equation
/1/. The partial conversion of the CO_2 absorbed by the
water to give carbonic acid, and the dissociation of
this to H^+ and HCO_3^- ions has already occurred earlier.
The time needed for the first stage is about 1 sec.

The second stage, during which the carbonate ions
/CO_3^{2-}/ of the limestone become bonded to the H^+ ions of
the carbonic acid, can not be distinguished in time from
the first. Because of the loss of CO_3^{2-} ions, however,
the equilibrium which develops in the first stage is
disrupted in this one, and this means that further physi-
cal /carbonate/ dissolution of the limestone must of ne-
cessity follow.

In the second stage, however, the equilibrium of
the physically and chemically dissolved CO_2 in the water
is also disturbed. Because of this the third stage soon
begins. This is the transformation of the physically
dissolved carbon dioxide to carbonic acid.

BÖGLI found the time requirements of this third
stage to be about 1 minute. During this time the origi-
nal CO_2 supply of the water is used for the hydrocarbona-
te dissolution of the limestone. According to him the
fourth stage then begins: further amounts of carbon
dioxide are absorbed from the atmosphere. By this means
the series of dissolution reactions continues until the
final equilibrium state has developed. This is defined
by an equilibrium of the highest order via the repeated
transfer of the amounts of limestone dissolved as hydro-
carbonate and the carbon dioxide content of the atmos-
phere in contact with the water.

In this way, the dynamics of the dissolution of the
limestone in the fourth stage are determined by the rate
of absorption of gaseous carbon dioxide, and this is very
low. According to BÖGLI, 24-60 hours is required for the
establishment of the final equilibrium. FREAR and JOHNSTON,
on the other hand, mention several days.

A very important factor involved in the determina-
tion of the absorption and diffusion rates is the tempe-
rature. When this is low it substantially slows down the
gas absorption, but when it is high the absorption can be
accelerated many times /because of the more rapid motion
of the molecules colliding on the surface between the

media, and hence because of their higher number/. Accor-
ding to the generally accepted view of FEITKNECHT, for
every temperature increase in the solution of 10 ^{o}C the
rate of reaction is approximately doubled. The duration
of the absorption and /for the motion of the process in
the opposite sense/ diffusion is also significantly affec-
ted by the size of the surface per unit amount of water.
Accordingly, the greater the exchange surface /water drops,
aerosol, waterfall, etc./, the greater the material trans-
port in a given unit time. The extent of the material
transport in unit time, however, is also influenced con-
siderably by the hydrostatic pressure, as was shown above.

The modern analytical results of GERSTENHAUER and
PFEFFER /1966/ are in contradiction with the theory of
BÖGLI regarding the duration of the dissolution; in
particular they cast strong doubt /and rightly so in our
view/ on the reaction rates of BÖGLI's stages 1, 2 and 3.
Thus, if we accept BÖGLI's breakdown of the series of
reactions into four stages, because of the didactic
viewpoints of its descriptiveness, we must know that in
practice the individual stages never follow one after
the other. They always come about simultaneously and
mutually, that is they are not separated into discrete
stages. The reversibility chain of the series of disso-
lution reactions, with the narrowest permeable capacity
during unit time, in fact takes place according to the
uppermost arrow shown in Figure 2, that is between the
water and the atmosphere. But in our view for just this
reason it is more correct to formulate the problem so
that the rate of hydrocarbonate dissolution in the three-
- component system is determined fundamentally from the

beginning on by this absorption or diffusion material tran-
sport capacity. The factorial components and comprehensive
regulating conditions of this, however, have already been
studied in detail earlier.

III. Non-karstic corrosion of limestone

While the simple physical /carbonate/ and carbonic
acid /hydrocarbonate/ processes of dissolution of limes-
tone are collectively termed karstic corrosion, the cor-
rosive denudative processes connected with the other
chemical effects form the non-karstic group of the che-
mical weathering of limestone.

In this respect very many, mainly double decomposi-
tion chemical reactions may be given, primarily consisting
of the mutual reactions of the limestone and the chemically
active constituents of the soils of various compositions.
These are in part predominantly the effects of the chemi-
cal products formed by means of inorganic mineralization
weathering processes in the soil; in part the organic and
inorganic chemical products /mainly various acids/ of plant
and animal refuse decomposing under aerobic or anaerobic
conditions in the humus levels of the soils, and selected
by soil microorganisms and the roots of plants living in
the soils. On the action of all such soil processes which
from our point of view can be generally regarded as non-
-karstic corrosive factors, calcium from the limestone
gives up its carbonate bonding and a completely new cal-
cium compound is formed. This is either transported away

in the form of its solution, or it remains for a longer or
shorter time in an autochthonous state as a solid reaction
product.

The up-to-date pedological, agrochemical and soil-
-biological handbooks /FEKETE 1952, 1958, STEFANOVITS 1959,
1963, FEHÉR 1954, PEJVE 1961, DI GLÉRIA 1962, BALLENEGGER
and DI GLÉRIA 1963, FEKETE, HARGITAI and ZSOLDOS 1964,
BECK 1968/ give a detailed analysis of humification pro-
cesses whose dynamics are greatly affected by the clima-
tic conditions, and which are characteristic of soil-le-
vels and of soils of various compositions. Of the dissi-
milation compounds formed during the aerobic decomposi-
tion of organic substances in the soil, or as a result
of the life-functions of the microorganisms in the soil,
those which are the most important form the point of
view of the corrosion of the limestone are formic acid,
oxalic acid, acetic acid, propionic acid, lactic acid,
the various root secretions, and of course the already
discussed carbonic acid. These all form the correspon-
ding calcium salt with the limestone.

It would still be difficult today to decide the
extents of the separate individual dynamics of these
compounds in the dissolution of limestone, all the more
so because their effects in the soil are complex and
simultaneous, and because the proportion of their re-
gional contribution in the soil solution is not con-
stant either. Their overall effect, however, is more
easy to establish. It is sufficient for the demonst-
ration of this for us to point to one of the most cla-
ssical experiments of biochemistry. In this a seed was

caused to germinate on a marble surface; during even a short time the minute root of the seed left a clearly visible trace on the smooth surface of the $CaCO_3$ /SACHS 1865/.

The most important of the corrosive organic acids formed during the aerobic decomposition processes /under anaerobic conditions too, but much more slowly/ are the fulvic and crenic acids. In an acidic soil medium /under aerobic conditions/ these exert particularly active dissolving effects, and their resulting salts remain in solution.

Limestone is also actively corroded by the humous and humic acids of the soil, but in acidic medium the calcium salts of these are precipitated.

The effects of inorganic acids and salts formed in the course of biogenetic or mineral weathering processes in the soil are also of great importance from the point of view of the corrosion denudation of the limestone. Of these, sulphuric and nitric acids among others, as very strong acids, even in very low concentrations give rise to the fact that their double decompositions with limestone are unidirectional /irreversible/:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2 \qquad /7/$$

$$CaCO_3 + 2\ HNO_3 \longrightarrow Ca/NO_3/_2 + H_2O + CO_2 \quad /8/$$
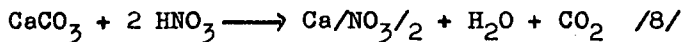
It should be noted that the formation of the above
acids in the soil may be connected with various processes.
Thus, the sulphuric acid most frequently originates from
the inorganic or biogenic /activity of sulphur bacteria/
oxidation of sulphides /e.g. pyrite/ and hydrogen sulphide
/H_2S/. The starting compounds are formed from the chemical
weathering of inorganic constituents of the soil, and more
frequently from the mainly anaerobic process of decomposi-
tion of the organic refuse derived from living organisms.
FEHÉR /1954/ reports that, for example, it is typical of
the functioning of <u>Achromatium</u>, <u>Beggiatoa</u>, <u>Thiotrix</u>, <u>Thio-</u>
<u>ploca</u>, and other genera belonging to the <u>colourless sulphur</u>
<u>bacteria</u>, that they first split off sulphur from the H_2S
released in the decomposition of proteins. This is stored
in the form of drops in their plasma, and gradually con-
sumed so that energy is obtained for their C-assimulation.

In outline, the process is as follows:

$$2 \ H_2S + O_2 \longrightarrow 2 \ H_2O + 2 \ S$$
$$2 \ S + 3 \ O_2 + 2 \ H_2O \longrightarrow 2 \ H_2SO_4 \quad /+244 \ Cal/ \qquad /9/$$
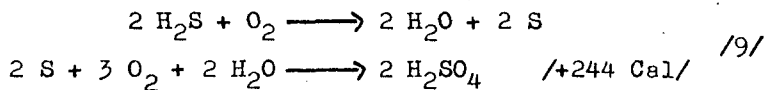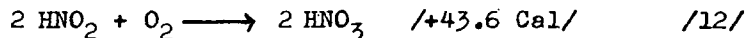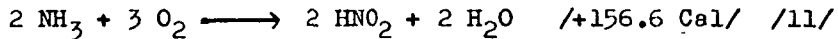
According to FEHÉR /op. cit. p. 115/, the life-func-
tion of the hydrogen sulphide-oxidizing <u>purple bacteria</u>
proceeds via a process which is somewhat more complex than
the previous one. These are also aerobic organisms, and
thus they oxidize hydrogen sulphide and assimilate che-
mosynthetically. With the intervention of bacteriochlo-
rophyll and bacterioerythrin in their plasma, they are
also able to use the photoenergy of the sun, and so they
carry out photosynthetic assimilation at the same time

too. With the help of the hydrogen sulphide, and with the use of photoenergy, the CO_2 is deoxygenated and hydrogenated to give formaldehyde:

$$H_2S + 2\ H_2O + 2\ CO_2 \longrightarrow 2\ HCHO + H_2SO_4 \qquad /10/$$
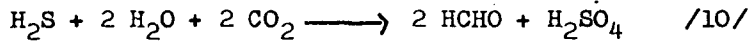
Of the sulphur bacteria living in the soil, _Thiocystis_, _Thiospirillum_, _Rhabdomonas_, _Rhodothece_, and other genera can be classified in this group.

Ammonia, resulting likewise mainly from organic decomposition, must be regarded as the most probable starting substance for the formation of nitric acid in the soil. With the intervention of bacteria, the ammonia is oxidized in the soil to acids which have a corrosive action on limestone. It was already demonstrated in the last century by VINOGRADSKII /1892/ that the process of nitrification in the soil is carried out by two metabiotically cooperating groups of bacteria: the nitrite-forming and the nitrate-forming bacteria. The nitrite bacteria oxidize the ammonia to nitrous acid, and the nitrate-forming bacteria oxidize the nitrous acid so formed to nitric acid:

$$2\ NH_3 + 3\ O_2 \longrightarrow 2\ HNO_2 + 2\ H_2O \quad /+156.6\ Cal/ \quad /11/$$

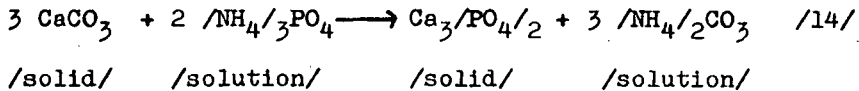$$2\ HNO_2 + O_2 \longrightarrow 2\ HNO_3 \quad /+43.6\ Cal/ \qquad /12/$$

Of course, neither the nitrous acid nor the nitric acid can remain in the soil in an unbound state, and immediately on their formation react with the cations of the soil and the limestone to form their nitrites or nitrates /equation /8//.

It should be noted that a certain amount of nitric acid can enter the soil from the atmosphere. As stressed by FINDEISEN /1939/, HARRASOWITZ /1954/, KILINSKI /1958/ and REITER /1960/, the summer rain almost always contains nitric acid. This is formed in the atmosphere by the electric discharges accompanying the storms. Although it is not yet possible to determine the extent of the participation in the corrosion by the acid of such an origin because of the unsolved difficulties of the experimental methods, nevertheless it must be assumed that this amount of acid constitutes a considerable denudative factor, especially in the tropics, where the atmospheric electric discharges are of consistent frequency.

Because of its importance among the possibilities of non-karstic corrosive processes on the limestone by the soil solutions, the action of phosphate solutions must definitely be stressed. For example, that of calcium dihydrogen phosphate, which reacts with limestone to form calcium monohydrogen phosphate:

$$CaCO_3 + Ca/H_2PO_4/_2 \longrightarrow 2\ CaHPO_4 + H_2O + CO_2 \qquad /13/$$
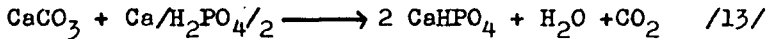
Ammonium phosphate, which occurs in the rendzina soils of limestone mainly as a product of the decomposition of animal bodies, acts on the limestone as follows:

$$3\ CaCO_3 + 2\ /NH_4/_3PO_4 \longrightarrow Ca_3/PO_4/_2 + 3\ /NH_4/_2CO_3 \qquad /14/$$

/solid/   /solution/   /solid/   /solution/

If the volume of the solid tricalcium phosphat formed /calculated from the molecular volume/ is taken as 100, then the unit volume of the mass of the starting $CaCO_3$ solid is 110.7. That is, the double decomposition reaction is accompanied by a volume decrease, and so it can occur even deep in the structure of the limestone. If the new solid mass formed, which replaces the original solid mass in the stone, does not occupy the same volume as the starting mineral, then unfilled spaces remain around the new formation in the structure of the stone /its pore volume increases/. Thus, the aggressive solution can penetrate deep into the interior of the layers, where the total transformation of the original material can be brought about in a very large thickness.
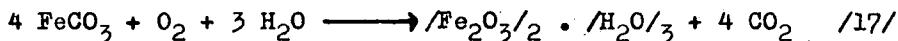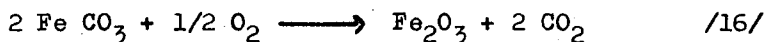
This refers too to all such double decompositions which result in solid reaction products and in which the product formed has a higher mineral density than that of the initial solid phase. This is also the case for the reactions of iron salts with limestone, e.g.:

$$CaCO_3 + FeSO_4 = CaSO_4 + FeCO_3 \qquad /15/$$
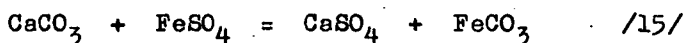
Naturally, not only the sulphates, but also the salts of iron formed with other strong acid radicals can easily bring about the double decomposition, all the more so because the molecular volume of iron carbonate /siderite/ is smaller /30.6/ than that of calcium carbonate /36.9/, and the exchange takes place in a 1:1 molecular ratio.
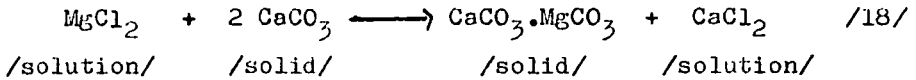
In the above example, a classic case was introduced of the epigenization of limestone by iron salts.

It is worth mentioning that the solid siderite crust forming on the boundary surface between the limestone and the soil can not impede the effect of the iron sulphate in the direction of deeper limestone levels, because it is soon dissolved by the carbonic acid-containing soil solutions. In the presence of water and oxygen /the karstic rendzina soil reaction medium corresponding to this/, the ferrous carbonate is sooner or later oxidized to ferric oxide. This can accumulate in the soil as either the dark-red haematite /Fe_2O_3/, or the brown limonite /$2Fe_2O_3 \cdot 3H_2O$/:

$$2 \ Fe \ CO_3 + 1/2 \ O_2 \longrightarrow Fe_2O_3 + 2 \ CO_2 \qquad /16/$$

$$4 \ FeCO_3 + O_2 + 3 \ H_2O \longrightarrow /Fe_2O_3/_2 \cdot /H_2O/_3 + 4 \ CO_2 \quad /17/$$

It is probable that, similarly to the process of siderite formation, many other exchanges occur for the limestone. Thus, the formation of glauconite and flintstone, and the substitution of sulphides of the heavy metals /e.g. pyrite/ in place of the calcite crystals /pseudomorphs/, may be the results of equivalent processes. ELIE DE BEAUMONT /referred to in CAYEAUX /1935// is surely right when be assumes that the explanation of the subsequent dolomitization of limestone in contact with sea-water is also to be sought in this phenomenon. In this case the magnesium chloride of the sea-water reacts with the calcium carbonate and the well-known double salt dolomite is obtained. The reaction is possible even in the interior of the limestone, because the density of the double carbonate, which is more poorly

soluble than the calcium and magnesium carbonates, is much higher than that of calcite.

$$MgCl_2 \quad + \quad 2\ CaCO_3 \longrightarrow CaCO_3 \cdot MgCO_3 \quad + \quad CaCl_2 \qquad /18/$$

/solution/   /solid/   /solid/   /solution/

$$2\ V_1 = 73.8 \quad > \quad V_2 = 63.6$$

A role is also played in the non-karstic corrosion of limestone by the often appreciable amounts of ammonium sulphate in the soil:

$$CaCO_3 \quad + \quad /NH_4/_2\ SO_4 \rightleftarrows CaSO_4 + /NH_4/_2CO_3 \qquad /19/$$
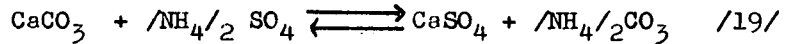
It should be taken into account, however, that this reaction takes place in the directionof the upper arrow only when the compounds on the right side of the equation are more dilute than those on the left side. That is, the continuity of transportation away of the calcium sulphate and ammonium carbonate formed must be provided by some effect such as the motion of the soil water, or a biogenic force. If, however, for some reason the concentrations are higher on the right side /e. g. in sea-water/, the double decomposition proceeds in accordance with the lower arrow /BECK 1968/.

The corrosive action of aluminium sulphate, if present in the soil, proceeds in an intersting way:

$$6\ CaCO_3 + Al_2/SO_4/_3 + 6\ H_2O$$
$$= 3\ CaSO_4 + 3\ Ca/HCO_3/_2 + 2\ Al/OH/_3 \qquad /20/$$
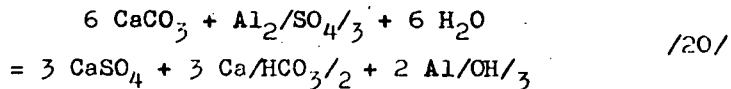
It should be noted that the above reaction takes place
only in neutral or acidic soils. In aqueous medium the aci-
dically hydrolyzing aluminium sulphate is first consumed in
decreasing the alkalinity of the soil, according to the fol-
lowing equation:

$$Al_2/SO_4/_3 \; + \; 3 \; Na_2CO_3 \; + \; 3 \; H_2O$$
$$= 3 \; Na_2SO_4 \; + \; 2 \; Al/OH/_3 \; + \; CO_2 \qquad\qquad /21/$$
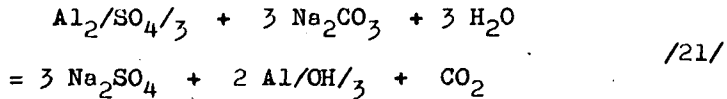
In order for us to form as complete a picture as pos-
sible of the effective forms of non-karstic corrosion, which
has received fairly scant attention in the karst literature,
it must still be mentioned that the dynamism of the dissolu-
tion may be significantly affected not only by the possible
formation of chemical bonds with the various ions occurring
in the soil solutions, but also by their simple mass ac-
tions, and in such a way that the effectiveness of the hyd-
rocarbonate dissolution is indirectly regulated merely by
their presence.

It is known that the solubility of a salt decreases
in the presence of a salt of the same ion, whereas it is
increased by the presence of a salt of different ions
/GRÓH 1939, PAPP 1954, etc./. Thus, for example, the so-
lubility of sodium chloride can be decreased by magnesium
chloride, but at the same time the alkali chloride content
/NaCl, KCl/ of the water increases the solubilities of cal-
cium carbonate, calcium sulphate, calcium phosphate, etc.
The solubility of $CaCO_3$ is similarly increased if the soil
solution contains magnesium chloride, for example.

The modern view is that the hydrocarbonate dissolution of limestone is decreased by the other dissolved carbonates by changing the value of the denominator, K_t, of equation /6/ to a minimum. This has the result of increasing the accessory carbonic acid necessary to keep the calcium in solution. Because of this, natural karst waters, which always contain greater or lower amounts of carbonates of other ions too, generally require more free carbonic acid than that calculated on the basis of the calcium hardness.

According to PAPP /op. cit. p. 39/, the practical extent of this increased requirement is for the most part not appreciable, because especially in hard waters, which usually contain other carbonates too, compared to the otherwise considerable amounts of equilibrium carbonic acid the extra CO_2 requirement is insignificant. At the same time, it should also be taken into account that the decrease in the solubility of $CaCO_3$ produced by salts of the same ion may easily be counterbalanced by those salts of other ions which are always present in various amounts in karst waters, and which generally tend to increase the solubility of the $CaCO_3$. This means, therefore, that in the majority of cases the data of Table 4 calculated from equation /6/ do in fact correspond to the accuracy requirements of a good approximation.

In this short section we have by no means exhausted all the factorial possibilities of non-karstic corrosion of limestone in nature. We have attempted to stress only the most important of the components, as reflected in their observable, objective effects.

It must be pointed out, however, that the extremely fact-
-requiring and labour-consuming study of the many details
and the evaluation of the extents of the effects involved
in the question forms one of the perspective tasks of
karst science. The future answers to these questions may
provide very much to the entire karst science; it may well
be that a certain fundamental reevaluation of the present
axioms of karst theory will be necessary. But primarily
perhaps we can still expect an impetus from the growth
of the information available, in the settling of diver-
gent problems of the denudation-dynamism of the climate
zonal karst regions.

REFERENCES

BALÁZS, D. /1963/: Karst genetic problems - Földr. Értesitő, 1963, 4.

BALÁZS, D. /1966/: The role of the mixing corrosion in karstification - Hidr. Közl. 1966, 4.

BALLENEGGER - DI GLÉRIA /1962/: Methods of study of soil and manure - Budapest, 1962.

BAUER, F. /1964/: Measurement of limestone ablation in the Austrian Limestone High Alps - Erdkunde 1964, 18.

BECK, T. /1968/: Microbiology of soils - Munich-Basle-Vienna, 1968.

BÖGLI, A. /1956/: The chemism of the dissolution process and the influence of the rock state on the development of karsts - Report of the Commission on Karst Phenomena IGU, New York, 1956.

BÖGLI, A. /1960/: Limestone dissolution and karr formation - Zeitschrift f. Geomorph., Supplem. 2. Berlin-Nikolassee, 1960.

BÖGLI, A. /1961/: Cave-clay - Mem. V della Rassegna Spel. Ital., Como, 1961.

BÖGLI, A. /1963a/: The origin of karst caves - Die Höhle, 1963, 3. Vienna.

BÖGLI, A. /1963b/: Cave-karrs - Akten III. Intern. Kongr. f. Speläologie, Bd. 2. Vienna, 1963.

CAUER, H. /1954/: Chemical-physical studies of the climatic conditions in the Klutert cave - Archiv für Physikalische Therapie, Berlin, 1954, 1.

CAYEAUX, L. /1935/: Rocks, Carbonates, Limestones and Dolo-
        mites - Paris, 1935.

CHOLNOKY, J. /1940/: The formation of tufaceous limestone or
        travertine - Matem. és Term.-tud. Ért. 1940, 3.

CORBEL, J. /1959/: Erosion in a limestone region. Rate of
        ersion and morphology - Ann. de Géogr., 1959. Paris.

CZÁJLIK, I. /1961/: New results of a detailed hydrological
        study of the Imre Vass cave - Karszt- és Barlang-
        kutatás, III. 1961.

DI GLÉRIA, J. /1962/: Agricultural chemistry - Budapest, 1962.

DUDICH, E. /1932/: The Aggtelek drip-stone cave and its en-
        vironment - Budapest, 1923.

ERNST, L. /1961/: The saturation of karst waters - Karszt- és
        Barlangkutatás, 1961, 1.

ERNST, L. /1964/: The question of mixing corrosion - Die Höhle,
        1964, 3. Vienna.

FEHÉR, D. /1954/: Soil biology - Budapest, 1954.

FEKETE, Z. /1952/: Soil science - Budapest, 1952.

FEKETE, Z. /1958/: The science of soils and fertilization -
        Budapest, 1958.

FEKETE - HARGITAI - ZSOLDOS /1964/: Soil science and agroche-
        mistry - Budapest, 1964.

FINDEISEN, W. /1939/: Condensation nuclei, their origin,
        chemical nature, size and amount - Beitr. Phys.
        fr. Atmosph. 1939, 25.

FRANKE, H. /1965/: Mixing corrosion on hairline cracks - Die
        Höhle, 16, 1965, 3. Vienna.

FRANKE, H. /1967/: Dynamics of dissolution of limestone - Mitt. des Verbandes Deutscher Höhlen u. Karstforscher, Jahrg. 13. Munich, 1967.

GÁNTI, T. /1957/: Chemical aspects of the formation of caves - Hidr. Közl. 1957.

GERSTENHAUER-PFEFFER /1966/: The dissolution ability of limestones - Abhangl. zur Karst u. Höhlenkunde, Heft 2, 1966. Munich.

GRÓH, Gy. /1939/: General chemistry - Fourth edition. Budapest, 1939.

HARRASSOWITZ, H. /1954/: Chemical effect of precipitation on karst - Proceedings of the Intern. Karst Comm. in Frankfurt/Main, 27-30 Dec. 1953. Erdkunde 8, Bonn, 1954.

HOLLUTA, J. /1927/: The chemistry and chemical technology of waters - Stuttgart, 1927.

JAKUCS, L. /1953/: The discovery of the Béke cave - Budapest, 1953.

JAKUCS, L. /1959/: The first results of the study of the curative effect of the Béke cave - Természettud. Közl. 1959, 1.

JAKUCS, L. /1960/: Study of general karst genetic, morphological and hydrographic problems on the Aggtelek karst - Candidate's dissertation, Budapest, 1960.

JAKUCS, L. /1968a/: Some aspects of the interpretation of the denudation processes and morphogenetics of karstic regions - Földr. Ért. XVII. 1968, 1.

JAKUCS, L. /1968b/: Open questions in the morphogenetic explanation of the karst form wealth of the North Borsod karst according to plateau leven - Acta Geogr. Szegediensis, Tom. VIII. 1968.

JAKUCS, L. /1970/: The role of climate in the quantitative and qualitative control of karstic corrosion - Acta Geogr. Szegediensis, Tom. X. 1970, 3-19.

JAKUCS, L. /1971/: Dynamic differences of the karstification processes in microspaces - Internat. Geogr. Union, European Regional Conference, Action Committee on Karst-Morphogenesis, pp. 1-58. Hungary, 1971.

KESSLER, H. /1938/: Hydrography of the Aggtelek cave-system - Földr. Közl. 1938.

KILINSKI, E. /1958/: Textbook of atmospheric electricity - Leipzig, 1958.

KNEBEL, W. /1906/: Cave-science with regard to karst phenomena - Braunschweig, 1906.

KYRLE, G. /1923/: Fundamentals of theoretical speleology - Vienna, 1923.

LAPTYEV, F.F. /1939/: Aggressive action of water on carbonate rocks, plasters and concretes - Leningrad--Moscow, 1939.

LEHMANN, H. /1955/: The tropical "Kegelkarst" in the West Indies - Proceedings of the German Geogr. Meeting in Essen, Wiesbaden, 1955.

LEHMANN, H. /1956/: The influence of climate on the morphological development of karsts - Rep. of the Comm. on Karst Phenomena. Intern. Geographical, 1956. New York.

LEHMANN, H. /1960/: The classical terminology of the karst
        from the critical aspect of climatic modern
        morphology - Revue de Géogr. de Lyon, Vol.
        XXXV. N°. 1. 1960.

LEHMANN, O. /1932/: The hydrography of karsts - Enzykl. d.
        Erdkunde, Vienna-Leipzig, 1932.

MARKÓ, L. /1961/: The solubility of mixtures of calcium car-
        bonate and magnesium carbonate in water in the
        presence of carbon dioxide - Karszt- és Barlang-
        kutatás, 1961, 1.

MARKÓ, L. /1962/: The role of the cave air circulation in the
        formation of karst caves - Karszt- és Barlang,
        1962, I.

MARKÓ, L. /1963/: Karszt- és Barlang. 1963, I. p. 37.

MAUCHA, L. /1960/: Account of a cave system - Karszt- és
        Barlangkutatás, 1960. I.

MÁNDY, T. /1954/: Dissolution study of limestones and dolo-
        mites - Hidr. Közl. 1954, 11-12.

MILLER, I.P. /1952/: A portion of the system $CaCO_3 - CO_2 - H_2O$
        with geological implications - Amer. Journ. of
        Sci. 250, 1952, 16.

PAPP, Sz. /1956/: The chemistry of water - Budapest, 1956.

PEJVE Ya. /1961/: The biochemistry of soil - Moscow, 1961.

PAPP, Sz. /1954/: Chemical aspects of hydrological research
        - Publ. of the Mérnöki Továbbképző Int., Budapest,
        1954.

PIA, J. /1953/: Theories of the capacity of carbonic acid to
        dissolved limestone - Mitt. Geol. Ges., Vienna,
        1953.

REITER, R. /1960/: Meteorobiology and Electircity of the
        atmosphere - Leipzig, 1960.

SACHS, J. /1865/: Handbook of experimental physiology -
        Leipzig, 1865.

SCHOELLER, H. /1956/: Geochemistry of subterranean waters -
        Soc. des Edit. Technik, Paris, 1956.

STEFANOVITS, P. /1959a/: Genetic soil-geographical classi-
        fication of Hungarian forest soils - Agrokémia
        és Talajtan, 1959.

STEFANOVITS, P. /1959b/: Results and tasks of soil-geography
        in Hungary - Földr. Közl. 1959.

STEFANOVITS, P. /1963/: The soils of Hungary - Budapest, First
        edn. 1956, Second edn. 1963.

TELL, L. /1961/: The rate of erosion with special reference
        to the caves of Lumelunda - Arch. of Svedisch
        Speleology, Norrköping, 1966.

TILLMANNS, J. /1932/: The chemical research of water and outler
        water - Halle, 1932.

TILLMANS - BÖMER - JUCKENAK /1940/: Handbook of food chemistry
        /Vol XIII.: Water and air/ - Berlin, 1940.

TROMBE, F. /1951/: Some aspects of subterranean chemical
        phenomena - Annal. de Spéléologie, 1951.

TROMBE, F. /1952/: Speleology - Paris, 1952.

TROMBE, F. /1956/: Speleology - Paris, 1956.

TUCAN, F. /1933/: Data on the geochemistry of Dinar karsts
        - Zagreb, 1933.

VENKOVITS, I. /1949/: Changes in the chemical composition of
            infiltration rain-waters - Földt. Int. Évi Jel.
            1949. Budapest,

VINOGRADSKII, S. /1892/: Research into the nitrification or-
            ganisms. - Arch. Sci. Biol. St. Petersburg, 1.
            1892.