# POSSIBILITIES OF CARBONATE CONTENT DETERMINATION OF SEDIMENTARY ROCKS

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## INTRODUCTION

The determination of the carbonate content, or in narrower sense that of the quantity of the single carbonates of sedimentary rocks is of double aim. On the one hand this is necessary for the determination of the mineral composition of sedimentary rocks and for the characterization of a profile from the geochemical point of view, and it makes possible the determination of the quantities of Ca and Mg being in non-carbonate bond in the sedimentary rocks on the other. This latter is of special interest in the investigation of the evolution of the sediment.

Investigating the shales of the Russian platform VINOGRADOV and RONOV [1956, cited by VAN MOORT, 1973] observed the increase of Ca/Mg ratio from the Proterozoic towards the Tertiary. The same trend has been indicated by the shales of the North American platform [RONOV and MIGDISHOV, 1971, cited by VAN MOORT, 1973]. The older the rock, the higher Mg-content can be observed. The conclusions drawn from the data of chemical analyses were supported also by the results of investigations concerning the mineral composition, *i. e.* the carbonates of the older samples are dolomites while in the younger ones first of all calcite predominates. Having investigated the composition of the silicate fraction of carbonates of the sediments VAN MOORT [1973] observed the same trend of the Ca/Mg ratio though in the silicate fraction the absolute quantity of calcium and magnesium proved to be very low and the MgO-content shows an apparent decrease since the Paleozoic.

Out of the carbonate determination methods the simplest one resulting only informatory values is that used in the geological practice, in the course of which $CO_2$ is released from the sample by means of treatment with hydrochloric acid, whereas the cations form soluble chlorides. The $CO_2$ content can be determined from the weight loss following the release of $CO_2$ taking into account the reacting weights.

Numerous methods of carbonate determination are known, i. e. gasometric $CO_2$ determination, gravimetric $CO_2$ determination and the complexometric determination of Ca and Mg after acidic treatment, respectively. Any method, however, based on exact measurements is unable to produce the real quantities of calcite and dolomite when starting from the $CO_2$ content, at most informations can be obtained. The determination of the quantities of different carbonates may be problematic also in case of carbonate rocks. In case of sedimentary rocks where the carbonate content can vary within broad limits and the presence of numerous other minerals should also be taken into account, the determination of the $CO_2$-content is insufficient to that of the total carbonate quantity either. On the other hand, when the CaO and MgO content bound in silicate bond ought to be determined, this cannot be performed on the basis of the consideration that the carbonates will be dissolved by acidic treatment and in the acidic solution the CaO and MgO quantities being really in carbonate bonds are determined (and in this way the quantities being in silicate bond, too). This is unfeasible since in case of acidic treatment not only the carbonates are dissolved and not only the Ca, Mg and Fe contents of carbonates will be in the solution, but more or less other silicate minerals will also be dissolved, e. g. chlorite, first of all when dolomite of considerable quantity should be taken into account. In this case the major part of the carbonate phase does not dissolve in diluted acid without heating. Consequently, the solution will contain not only the carbonate minerals .

Thus, in case of more particular investigations other determination methods are needed.

To determine the quantitative relations of calcite and dolomite the X-ray diffractometric method is available. This is based upon the fact that using the records of standard mixtures and applying the calibration curves the ratio of the two carbonates mentioned above can be determined [TENNANT, BERGER, 1957].

In the cases when only the quantities of calcite and dolomite are to be determined, an other value should be taken into account for the determination of the absolute quantities of the two carbonates instead of their ratio. It seems to be practicable to connect the $CO_2$ determination to the X-ray diffractometric method.

In the paper of VAN MOORT quoted above the method initiated by GULDBRANDSEN [1960] is described and has been applied. We apply the method of TENNANT and BERGER [1957] for several years.

In the following a short review will be given that how reliable informations can be obtained regarding the calcite and dolomite content of the sedimentary rocks applying the X-ray diffractometric method together with the determination of the $CO_2$ content and with the investigation of the derivatograms concerning the carbonate content.

## QUANTITATIVE DETERMINATION OF CALCITE AND DOLOMITE

### *Determination with X-ray diffractometer*

The determination of the calcite/dolomite ratio can be performed by the method of internal standards [KLUG, ALEXANDER, 1954] which should be taken, however, with care since due to the mineralogical error only the calibration curve recorded from the samples of the area in question is suitable to the rapid and exact analysis of the minerals of the area. In case of samples deriving from other localities the analysis is less correct as a result of the mineralogical error.

When using the method of NÁRAY-SZABÓ and PÉTER [1964] the quantity of not only the carbonates but all the phases present in the sample can be determined on the basis of one record. It is disadvantageous, however, that in case of natural mineral mixtures which may contain considerable quantity of weakly crystallized minerals, moreover amorphous component, the application of this method may become problematic.

The absolute intensity of the strongest lines of calcite and dolomite is nearly 1:1 when their quantity is nearly the same in the sample. To determine this ratio the curve determined experimentally by TENNANT and BERGER [1957] can be applied. On the basis of the calibration curve the accuracy can be ±5 per cent in case of 10 to 90 per cent dolomite content. The lower limit of identification is 2 to 3 per cent. DIEBOLD, LEMISCH and HILTROP [1963] obtained similar calibration curves.

*Calibration series and preparation of the samples*

To prepare the calibration series calcite from Parádsasvár and dolomite from Ratkószuha were used. Samples were powdered in agate grinding mill during a short time. The fractions of required grain size were separated by sedimentation. To make the calibration curves the fractions below 10 microns resp. between 10 and 30 microns were used. A calibration series of nine members were prepared from both fractions, the mixtures were mechanically homogenized so that no further change in grain size could follow. X-ray records were made with an X-ray diffractometer DRON—I, with Cu-radiation (30 kV, 20 mA). Detection was made by means of scintillation counter in front of which radiation has been monochromatized to $CuK_{\alpha 1}$. The rotation speed of the goniometer was 1/4° per minute.

To determine the percentual quantity of dolomite in the mixtures the intensity quotients of the strongest lines of 3.035 Å of calcite and of 2.886 Å of dolomite were counted and these were plotted as a function of the dolomite content of the mixtures of known composition.

The positions of the 104 reflexions as well as the ratios of peak-heights of the mixtures are summarized in Table 1. When plotting the values obtained in this way according to TENNANT and BERGER, the following calibration curves were obtained:

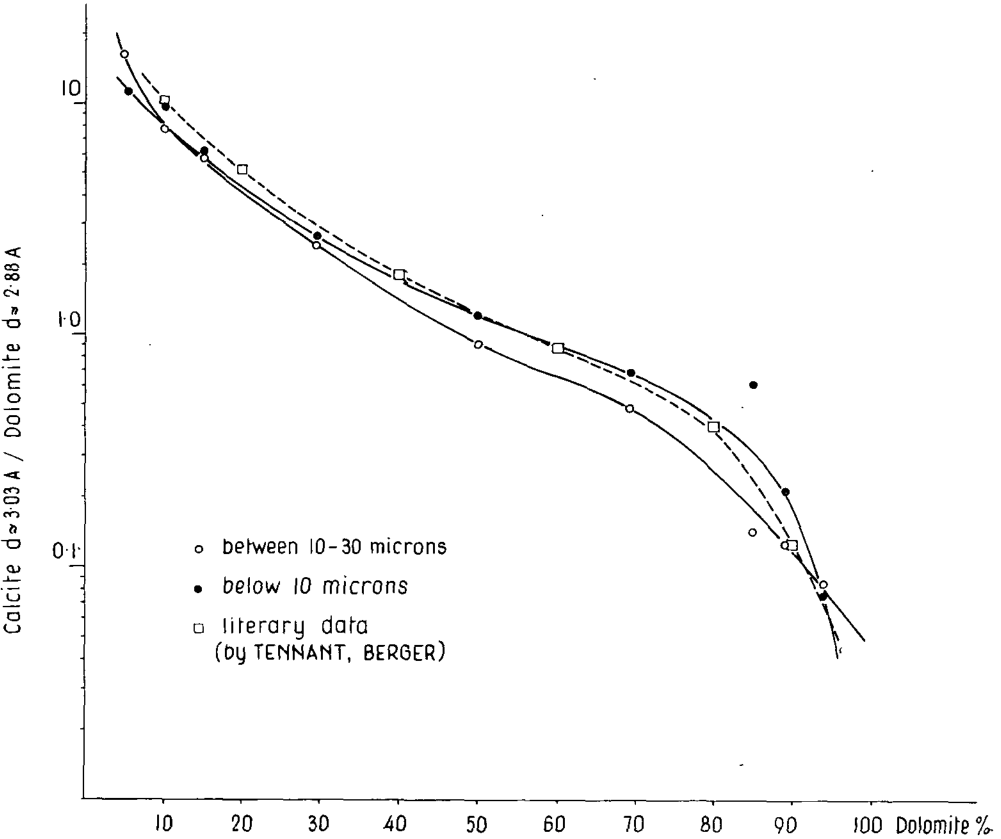

*Fig. 1.* Determination of calcite/dolomite ratio by means of intensity measurement of the strongest peaks of calcite and dolomite

The curves obtained are of the same shape than the calibration curve published by TENNANT and BERGER. In case of this demonstration, however, considerable subjective error can be introduced when plotting the curve, especially in case of the extreme values though these cases are most frequent in the investigated sedimentary rock samples. Thus we tried to introduce the plot of GULDBRANDSEN where

$$x = \log 100 \frac{\text{calcite } \%}{\text{dolomite } \%}; \quad y = \log 100 \frac{\text{peak-height of calcite}}{\text{peak-height of dolomite}}$$

The data obtained in this way can be connected by a straight line. The plot can be made more precise when calculating the equation of the straight line from the measurements approximating most exactly them using the least square method. The following equations were obtained: to the fraction less than 10 microns $y = 0.4724 + 0.8253x$, to the fraction between 10 and 30 microns $y = 0.1154 + 0.9453x$. We tried to plot the data of the calibration curve published by TENNANT and BERGER also by this method and the calculated equation of the straight obtained in this way: $y = 0.1540 + 0.9713x$.

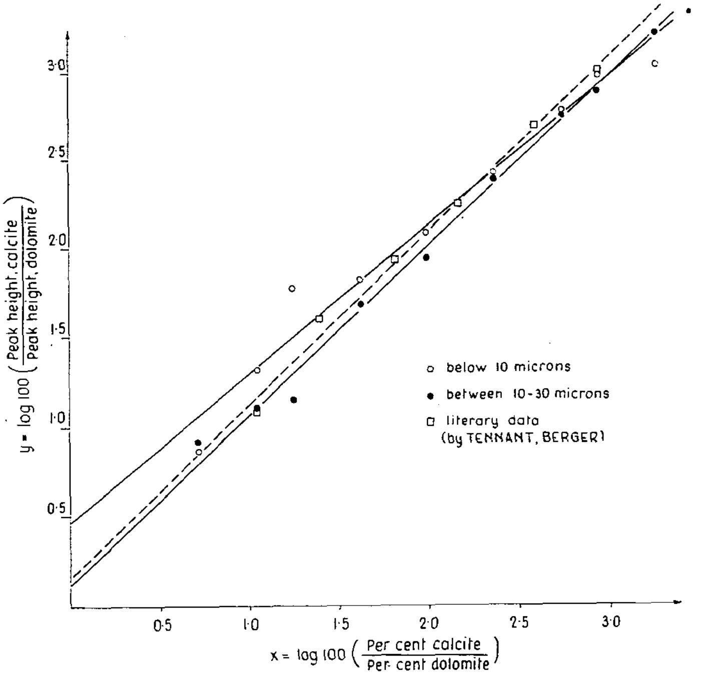

*Fig. 2.* Peak-height ratios of calcite to dolomite plotted against percentage ratios

The rise of the straight concerning the fraction between 10 and 30 microns approaches well that of the straight calculated from the data of TENNANT and BERGER, while that of the fraction below 10 microns is similar to the straight published by GULDBRANDSEN to the rocks of phosphate shales ($y = 0.3921 + 0.7885x$). The differences can be explained by those in localities and grain size.

Parallel with the X-ray diffractometric investigations the CaO, MgO and $CO_2$ contents of the mixtures were determined. The determination of the CaO and MgO content was done by means of Komplexon III using Erichrom-Blue SE resp. Erichrom-black indicators. $CO_2$ was determined by means of gasometry. The prepared mixtures were of the following composition: calcite 55.92 per cent CaO and 43.84 per cent $CO_2$; dolomite 30.49 per cent CaO, 21.65 per cent MgO and 47,59 per cent $CO_2$. The calculated and measured compositions of the mixtures are shown in Table 2.

In the dolomite used for the mixtures the $CaCO_3/MgCO_3$ ratio proved to be 1.012 which hardly deviates from the stoichiometric composition.

The X-ray diffractometric method is favourable since by means of it really the calcite/dolomite ratio can be obtained. Knowing the calcite/dolomite ratio determined in this way and the $CO_2$ content the $CaCO_3$ and $CaMg(CO_3)_2$ contents of the samples can be determined. Subtracting these values from the total CaO and MgO contents the quantities of CaO and MgO bound in the silicates are obtained. This calculation, however, introduces another uncertainty because it supposes the presence of only calcium and magnesium in the carbonates though Fe(II) may also be present in carbonates. Further, when calculating the quantities of calcite and dolomite only calcite and Ca—Mg-dolomite of 1:1 ratio were taken into consideration though magnesium may be present in the calcite lattice without the presence of dolomite-phase and dolomite is not Ca—Mg-dolomite of 1:1 ratio, either, respectively. When the position of the 104 reflexion of calcite shows deviation from the literature data this fact relates to the built-in of $MgCO_3$ into the calcite lattice. Such Mg-calcite occurrences play predominant role mainly in recent marine sediments. The relation between the $MgCO_3$ content built-in in the calcite lattice and the position of the strongest calcite line ($d = 3.036$ Å) was investigated by GOLDSCHMIDT, GRAF and JOENSUU [1955] in case of Mg-containing calcites and by GOLDSCHMIDT and GRAF [1958] in case of Mg-containing synthetic calcite. When the position of the 104 reflexion of dolomite deviates from the literature value this always relates to the deviation from the stoichiometric composition of dolomite. When the $CaCO_3$ builts in into the lattice of dolomite the peak occurring at $d = 2.886$ Å follows at ever higher d-values [FÜCHTBAUER, GOLDSCHMIDT, 1965].

### *Thermal analyses*

To control the mixtures the derivatograms of the grain size fraction of 10 to 30 microns were also recorded. In the course of our investigations the question should be answered that the decrease of weight being determinable by means of DTG and TG curves how accurately give the $CO_2$ content deriving from the thermal decomposition of carbonates. The losses of weight read off in the TG-curve and the $CO_2$ content determined gasometrically are summarized in Table 3. In the samples the average $CO_2$ content calculated on the basis of the TG-steps is 45.88 percent while the average value of the gasometrically determined $CO_2$ content proved to be 45.82 per cent. In case of investigation of 31 sedimentary rock samples the results showed similar agreement (10.59 per cent — by means of derivatograph, resp. 10.52 per cent by means of gasometry).

This really good agreement of the $CO_2$ contents determined by the two kinds of methods does not mean that in case of single samples considerable differences do occur; these, however, become equalized in case of averaging. The greater deviations can be explained by the fact that the beginning of the step indicating the thermal decomposition of carbonates is very difficult to be determined since in addition to the carbonates of the sedimentary rocks different phyllosilicates should also be taken into account the main endothermal effect of which just precedes the decomposition of the carbonates. Besides the mineral composition the grain size of carbonates is

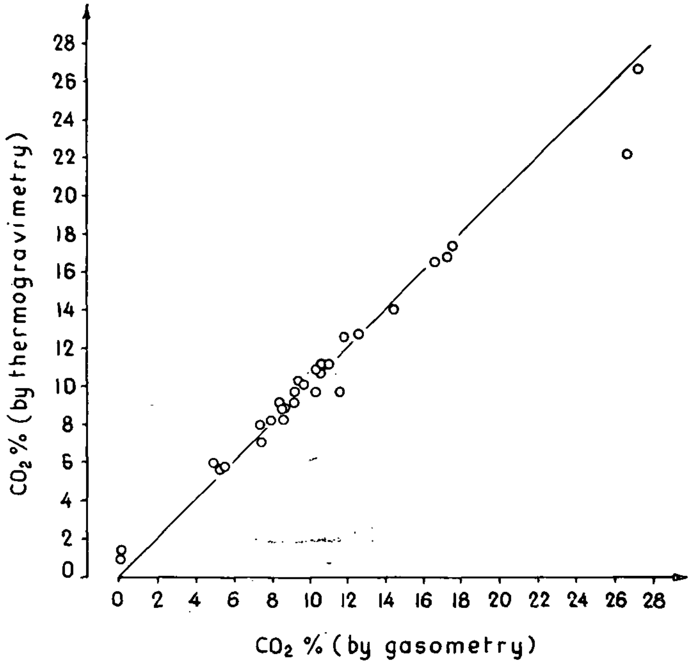

*Fig. 3.* Relation obtained by gasometric and derivatographic methods in the natural sedimentary rock samples

also influencing factor. When exact data are not required, the change of carbonate content *e. g.* as a function of depth can be characterized by the $CO_2$ content determined by derivatograph, in general.

The change of the endothermal peaks and of the temperatures of the inflexion point of the TG-curve are shown in Table 4.

The first endothermic peak about 780 °C showed only a fluctuation of about 2 to 3 °C when having changed the ratios of carbonates. The change of the second

TABLE 1

| Grain size / Composition of the mixture | between 10 and 30 microns | | | below 10 microns | | |
|---|---|---|---|---|---|---|
| | Calcite $d_{104}$ Å | Dolomite $d_{104}$ Å | $\frac{d_{3,035}\ \text{Å}}{d_{2,886}\ \text{Å}}$ | Calcite $d_{104}$ Å | Dolomite $d_{104}$ Å | $\frac{d_{3,035}\ \text{Å}}{d_{2,886}\ \text{Å}}$ |
| 5% C+95% D | 3,026 | 2,883 | 0,084 | 3,016 | 2,874 | 0,075 |
| 10% C+90% D | 3,026 | 2,883 | 0,125 | 3,026 | 2,883 | 0,210 |
| 15% C+85% D | 3,026 | 2,883 | 0,140 | 3,026 | 2,883 | 0,600 |
| 30% C+70% D | 3,026 | 2,883 | 0,480 | 3,026 | 2,883 | 0,680 |
| 50% C+50% D | 3,026 | 2,883 | 0,890 | 3,026 | 2,883 | 1,220 |
| 70% C+30% D | 3,026 | 2,883 | 2,450 | 3,026 | 2,883 | 2,600 |
| 85% C+15% D | 3,026 | 2,874 | 5,750 | 3,021 | 2,874 | 6,030 |
| 90% C+10% D | 3,026 | 2,874 | 7,700 | 3,026 | 2,883 | 9,720 |
| 95% C+5% D | 3,021 | 2,870 | 16,410 | 3,,021 | 2,874 | 11,050 |

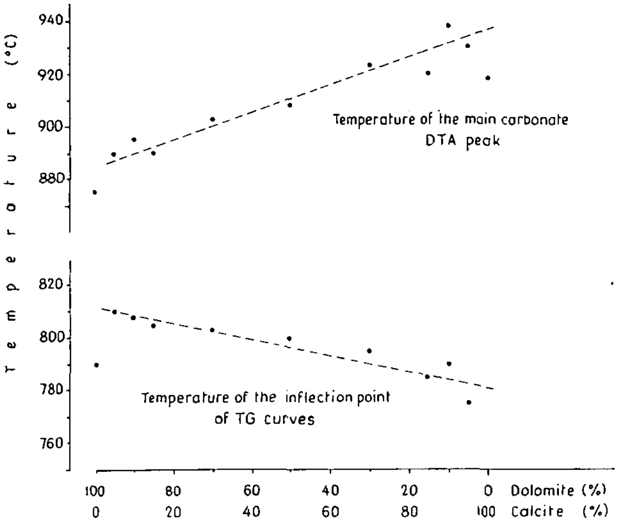

*Fig. 4.* Change of the second endothermal peak and of the temperature of inflexion of the TG-curve as a function of the composition of the mixture

endothermic peak, however, is more conspicuous, i. e. the more calcite contains the sample, it is displaced towards the higher value. On the TG-curve the temperature of the inflexion point shows a definite decrease with increasing calcite content though to a smaller extent.

The peak-temperature value of the endothermic main effect of carbonates are influenced by the grain size, the quantity as well as by the calcite to dolomite ratio. The lower is the grain size resp. the smaller is the total quantity of carbonates, the lower is the temperature of the endothermic main effect of the DTA curve. Similar

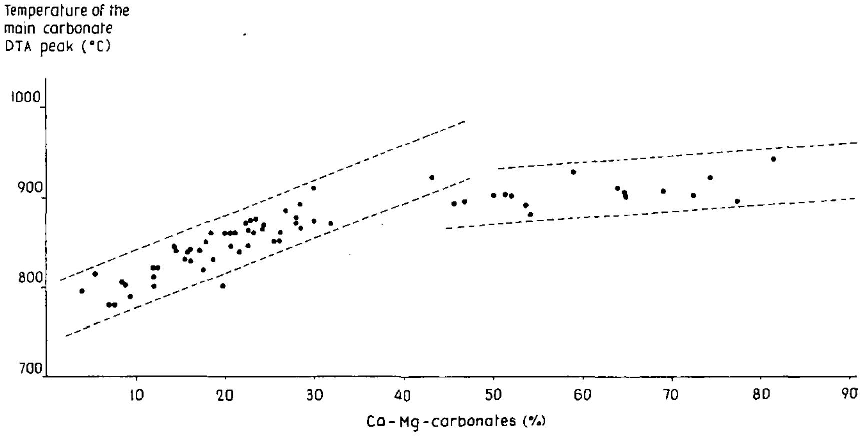

*Fig. 5.* Relation of the peak temperature of the carbonate endothermic main effect to the quantity of carbonates

TABLE 2

| Mixture | Calculated composition | | | Measured composition | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | < 10 µm | | Grain size | | 10—30 µm | |
| | CaO % | MgO % | $CO_2$ % | CaO % | MgO % | $CO_2$ % | CaO % | MgO % | $CO_2$ % |
| 5% C+95% D | 31,75 | 20,57 | 47,40 | 32,42 | 19,50 | 47,50 | 32,08 | 19,27 | 47,28 |
| 10% C+90% D | 33,03 | 19,48 | 47,21 | 32,92 | 19,11 | 47,20 | 32,89 | 19,52 | 47,32 |
| 15% C+85% D | 34,31 | 18,40 | 47,03 | 34,71 | 18,11 | 47,10 | 34,15 | 18,46 | 47,31 |
| 30% C+70% D | 38,12 | 15,16 | 46,46 | 37,84 | 14,88 | 46,60 | 37,83 | 14,84 | 47,12 |
| 50% C+50% D | 43,21 | 10,83 | 45,71 | 42,85 | 10,67 | 45,70 | 43,12 | 11,17 | 45,65 |
| 70% C+30% D | 48,29 | 6,49 | 44,97 | 47,82 | 6,35 | 45,07 | 48,18 | 6,35 | 45,14 |
| 85% C+15% D | 52,10 | 3,25 | 44,40 | 52,06 | 3,47 | 44,38 | 51,98 | 3,48 | 44,41 |
| 90% C+10% D | 53,38 | 2,17 | 44,22 | 52,83 | 2,78 | 44 30 | 52,66 | 2,69 | 44,29 |
| 95% C+ 5% D | 54,64 | 1,08 | 44,03 | 54,06 | 1,82 | 44,10 | 53,81 | 1,82 | 44,18 |

TABLE 3

| Mixture | Loss of weight in the lst step (%) | Loss of weight in the 2nd step (%) | Total loss of weight (%) | $CO_2$ per cent, determined gasometrically |
|---|---|---|---|---|
| 100% D | 22,50 | 25,60 | 48,10 | 47,59 |
| 5% C+95% D | 21,25 | 25,60 | 46,85 | 47,28 |
| 10% C+90% D | 20,48 | 26,83 | 47,31 | 47,32 |
| 15% C+95% D | 19,25 | 28,00 | 47,25 | 47,31 |
| 30% C+70% D | 16,00 | 30,75 | 46,75 | 47,12 |
| 50% C+50% D | 10,00 | 35,50 | 45,50 | 45,65 |
| 70% C+30% D | 7,48 | 38,00 | 45,48 | 45,14 |
| 85% C+15% D | 5,00 | 39,75 | 44,75 | 44,41 |
| 90% C+10% D | 5,00 | 39,25 | 44,25 | 44,29 |
| 95% C+ 5% D | 3,50 | 40,50 | 44,00 | 44,18 |
| 100% C | — | 44,50 | 44,50 | 43,84 |

TABLE 4

| Mixture | Temperature of the lst endothermic peak (°C) | Temperature of the 2nd endothermic peak (°C) | Temperature xf the inflexion point on the TG curve (°C) |
|---|---|---|---|
| 100% D | 772 | 875 | 790 |
| 5% C+95% D | 782 | 890 | 810 |
| 10% C+90% D | 780 | 895 | 808 |
| 15% C+85% D | 780 | 890 | 805 |
| 30% C+70% D | 780 | 903 | 803 |
| 50% C+50% D | 780 | 908 | 800 |
| 70% C+30% D | 783 | 923 | 795 |
| 85% C+15% D | 780 | 921 | 785 |
| 90% C+10% D | 780 | 938 | 790 |
| 95% C+ 5% D | 778 | 930 | 775 |
| 100% C | — | 918 | — |

relations were obtained in the course of thermal investigation of 69 carbonaceous rock samples deriving from a sequence of the South Great Plain.

Similarly to the mixture series in case of the demonstrated samples the peak temperature of the first endothermic effect showed much smaller fluctuation than the second (main) one (between 780 and 800 °C). When investigating the temperature of the main endothermic peak it can be stated that the points indicating the samples are divided into two groups. In the samples belonging to the first group the dependence of the temperature of the endothermal effect on the carbonate quantity is more apparent and in spite of all deviations the peak temperature increases. In the second group the peak temperature increases to less considerable extent. In the samples belonging to the first group the maximal carbonate content is 33 per cent, while in the secodn group the minimal quantity of carbonates is 43 per cent. In the samples of the second group the calcite/dolomite ratio determined by means of X-ray diffractometer varies between 100:0 and 90:10 and it rarely decreased to the value of 80:20. The samples of the first group, however, are predominantly dolomitic or the ratio of the two carbonate minerals is nearly the same.

The grain size, however, causes a change which is opposite to that of the quantity. In the DTA-curve of the samples belonging to the second group such secondary effect was observed on the main endothermal effect which relates to the presence of a carbontae phase of finer grain size than the average. This is the explanation that the increase of the temperature of the endothermic main effect is of more moderate rate than in case of the samples of the first group within which the increase of the carbonates' total quantity is the primary determining factor of growth.

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