COMPARISON BETWEEN THE X-RAY DIFFRACTOMETRIC QUANTITATIVE DETERMINATION METHODS OF CALCITE AND DOLOMITE ON THE BASIS OF THE INVESTIGATION OF NEOGENE SEDIMENTS OF THE GREAT PLAIN

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INTRODUCTION

In the course of the investigation of the clastic sedimentary rocks the qualitative and quantitative determination of the carbonate ingredients being in most of the cases calcite and/or dolomite, is necessary.

The procedure is well-known from literature that in the X-ray diffractograms the quantitative ratio of calcite/dolomite can be determined on the basis of the ratio of most intense peaks of calcite and dolomite. This is advantageous mainly in the cases when the rock does not contain other main components. In case of 10 to 90 per cent dolomite content the determination is of ± 5 per cent accuracy by means of the calibration curve constructed by C. B. TENNANT and R. W. BERGER [1957].

Applying this method the absolute quantity of the clastic calcite/dolomite can also be determined when the CO_2-content has been previously determined. In this case taking into account the CO_2 quantity the quantities of calcite and dolomite can be computed by means of the calibration curve [J. C. VAN MOORT, 1973].

In case of deep-bore samples there is an ever increasing demand for the qualitative and quantitative determination of clay minerals, chlorites, carbonates, feldspars and quartz. In case of the X-ray diffractometric investigations the possibility of serial analyse is given and within smaller limits of error the quantities of these minerals can be determined from one diffractogram; thus without the CO_2 determination the quantities of calcite and dolomite are obtainable from one diffractogram. In this case when multiplying the intensity of the most characteristic peaks of the single crystalline phases with the corresponding constants, the intensity ratios will give quantitative ratios. In the present paper the calcite and dolomite quantities computed by this method from the diffractograms will be compared with the calcite and dolomite quantities obtained from the intensity ratio of the diffractograms and from the gasometrically determined CO_2 content.

DETERMINATION TECHNIQUES

The part of the core sample to be investigated, cleaned from drilling mud and of small faciological differences was crumbled down to pea-size than it was pulverized in ball and tube mill for 5 to 15 minutes depending on the quality of the material (clay, sandstone, etc.). Unfortunately, the required homogeneity could not be reached in all cases after grinding and this fact is responsible for the deviations between the methods. Inhomogeneity occurred mainly at those samples the marly part of which contained aleurite and sand strips often of mm-size. Both the X-ray record and the CO_2 determination were carried out from the average sample obtained in this way.

The latter one resulted in the CO_2 content of all the carbonates, since in these formations siderite and magnesite occurred only in negligible quantities, their determination was neglected and only the quantities of calcite and dolomite were determined.

It is well-known that in the diffractograms the size of the most intense reflexions of the single crystalline phases are to a certain extent proportional to their quantities in the mixtures (e.g. in clastic sedimentary rocks). The number of factors determining the intensity itself is highly depending on the structure's stability. Within the carbonate series the stability of the single phases is relatively high, consequently the coefficients used in the computations is rather similar in the literature. In case of these investigations the constants of 0.81 and 0.85 were used for the peaks of 3.03 Å of calcite resp. 2.88 Å of dolomite. It is obvious that not only the calcite and dolomite were identified in the diffractograms but all the phases amounting to more than 4 to 5 per cent were determined, while the amorphous phase was neglected since its quantity proved to be less than 5 per cent in most of the cases.

EVALUATION OF THE RESULTS

In the majority of the cases the calcite and dolomite quantity determined from the X-ray diffractograms was higher by 1 to 5 per cent than the directly computed calcite-dolomite values. In the samples of the bore Makó-2 the quantitative changes of calcite and dolomite determined by both methods are shown in Fig. 1. It is apparent that the values concerning dolomite show good agreement, these are within the limit of error. The quantity computed from the X-ray diffractograms shows greater deviations in case of sandstones and aleurites which may be attributed to the late diagenetic dolomitization.

In case of calcite more considerable deviation was obtained in the clayey rocks. This is probably because of the slightly ordered illite and illite/montmorillonite structures of small reflexion and micron-size resulting in only shifts in proportions, further for the insufficient homogeneity of the samples from which the CO_2 determinations and X-ray diffractograms were recorded.

Similar phenomena were observed in the samples of Ferencszállás where mainly sandstones and aleurites were investigated, the marls and lime-marls were subordinate (Fig. 2.). In these samples the sandstones showed positive deviation of 4 to 5 per cent in case of both calcite and dolomite while the lime-mud has given identical results. This latter fact was probably engendered by the accumulation of the sandy, resp., fine-sandy fraction at the expense of the clayey fraction.

The results obtained in the investigation of the Upper and Lower Pannonian formations of Endrőd show also good agreement, in general. In case of calcite deviation occurred when the carbonate phase was accompanied by considerable amount of clayey fraction, in the other samples the difference of data of the two methods did not exceed 4 to 6 per cent.

In case of dolomite slight deviation was observed in sandstones and aleurites, the other values show identical results.

H. FÜCHTBAUER and H. GOLDSCHMIDT determined the features which are characteristic of the early and late diagenesis. One of them is an important factor, i.e. the change of grain size. The grain size of the early diagenetic dolomites falls for the most part below 10 microns, while in case of late diagenesis when dolomitization followed only after the solidification of the sediment the grains are usually greater than 10 microns. Consequently, when treating the rock sample with H_2O_2 and having obtained the original grain size and separating the grain size fraction of less than
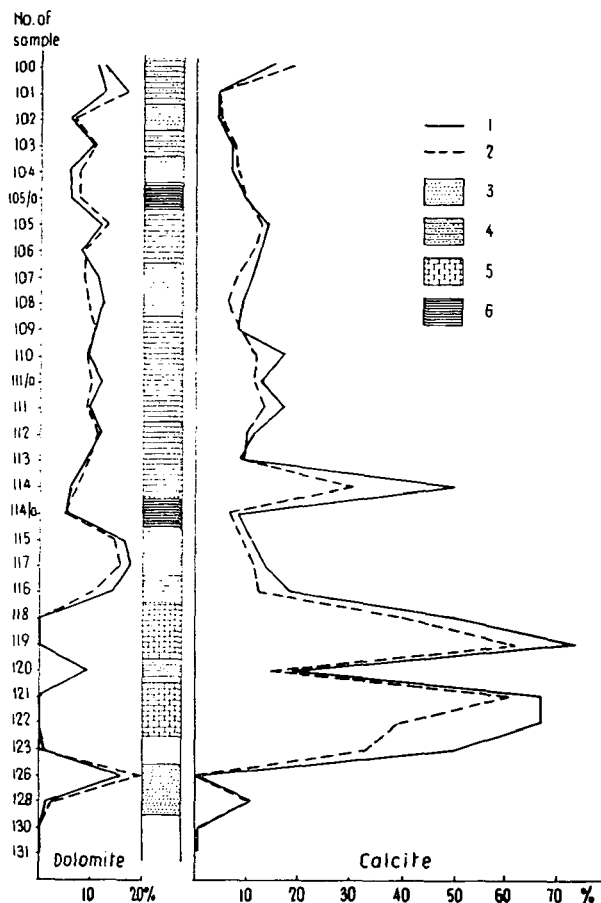
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Fig. 1. Calcite and dolomite content in the samples from the bore Makó-2
Legend: 1) The amount of calcite and dolomite, respectively, in per cent determined by x-ray diffractometry; 2) Amount of calcite and dolomite, respectively, calculated on the basis of CO_2 content determined gasometrically; 3) Sandstone; 4) Aleurite; 5) Lime-marl — limestone; 6) Clay, clay marl.

10 microns, then in case of late diagenetic dolomite the quantity should decrease in this fraction. Results are summarized in Fig. 4. It can be seen that in the fraction of less than 10 microns the dolomite quantity decreased as compared to the original average sample, and in certain cases this decrease amounted to 10 per cent, as well. This relates to the fact that dolomite is a late diagenetic mineral, in part at least, in these Neogene clastic formations.

The late diagenesis is characterized by the total absence of $CaSO_4$, and this typical also in these samples since neither anhydrite nor gypsum were found in these strata.

The formation of syngenetic dolomite should be taken into account to a certain extent which is proved by the fact that the lime-mud strata do not contain dolomite but show transition into dolomite-bearing strata within small distances. This pheno-

menon can be followed in the samples of Makó, Ferencszállás and Endrőd, as well. It can be said in general that where the quantity of calcite exceeds 50 per cent the dolomite is absent, and in such cases only minimal MgO was determined by the chemical analyses. This was probably resulted by the modification of the paleogeographic situation, or salinity has perhaps changed, to prove the latter statement, however, no exact data are available.
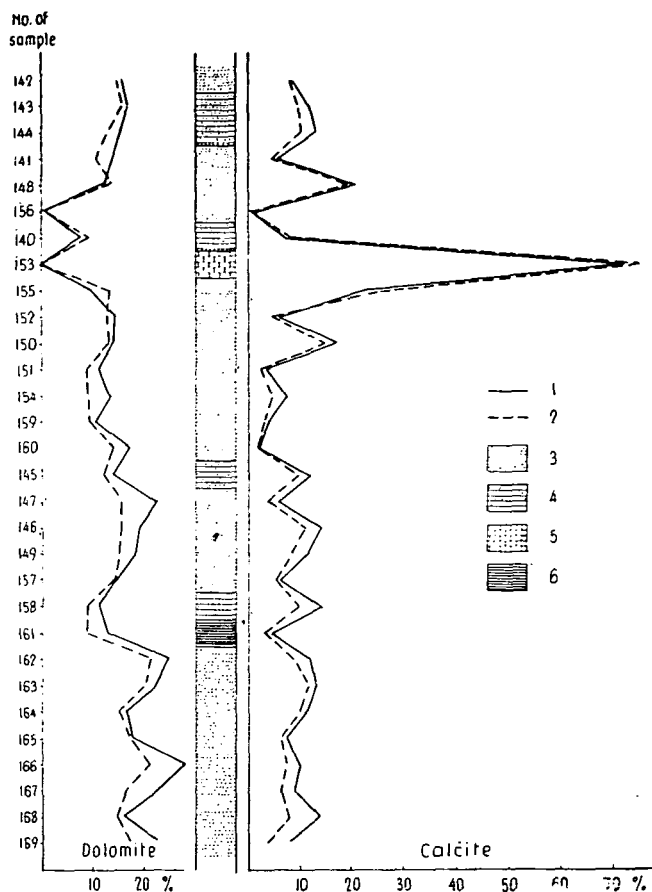

Fig. 2. Calcite and dolomite content of samples from the bore Ferencszállás (legend see *Fig. 1.*)

Dolomite is not always of stoichiometric composition and the experiences proved this in these samples. In case of increasing calcium surplus the orderedness of dolomite lattice decreases and the value of the d_{104} index is displaced towards the lower 2θ values. The built in of iron results in similar changes. Taking into consideration the changes of the d_{104} value of dolomite in the samples of Makó, Ferencszállás and Endrőd it can be stated that these values lye for the most part between 2.880 and 2.890 Å (*Fig. 5.*). In the bore of Makó the d_{104} value of dolomite of the clay-marl exceeds the 2.890 Å which corresponds to a composition of $Ca_{55}Mg_{45}$ (according to
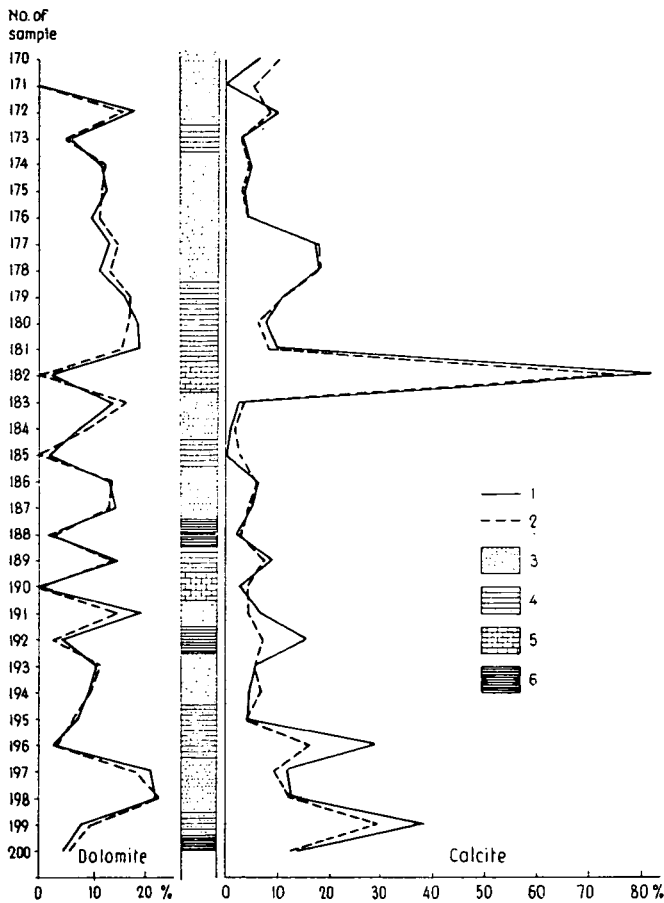
Fig. 3. Calcite and dolomite content of samples from the bore Endrőd (legend see *Fig. 1.*)

FÜCHTBAUER and GOLDSMIDT) this, however, equals to 46 mole per cent $MgCO_3$ after GOLDSCHMITH and GRAF. In the samples of Ferencszállás the values above 2.890 Å are absent. The $MgCO_3$ content varies between 47 and 49 per cent and hardly deviates from the stoichiometric composition. Out of the bores of Endrőd only below and above the Lower Pannonian lime-mud levels appears dolomite which was of a *d*-value higher than 2.890 Å and this equals to about 46 mole per cent $MgCO_3$ content. The other samples are nearly of stoichiometric composition. Consequently, in these samples it can be followed that when calcium ions are built in into the structure of dolomite, the d_{104} values are displaced towards that of calcite.

In some samples the d_{104} value of dolomite proved to be less than 2.880 Å. Taking into consideration the structural data and references of literature it should be assumed that the composition of dolomite was displaced towards magnesite. This is in accordance with the investigations of J. FR. SUREAU. As to his measurements the d_{104} value of dolomite etalon is 2.885 Å while that of the mineral of $Ca_{55}Mg_{45}$ com-

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position is 2.897, in case of magnesitic dolomite 2.879 Å. All of these formations contained coalified plant remnants and proved to be sandstones or perhaps aleurites.

In our case protodolomite is out of question since it is a less ordered structure and does not occur in the Neogene clastic formations. The intensity relations of I 2,54/I 2,38 indicating the degree of orderedness of dolomite could not be measured partly because of the coincidence and partly for the smaller quantity of dolomite.
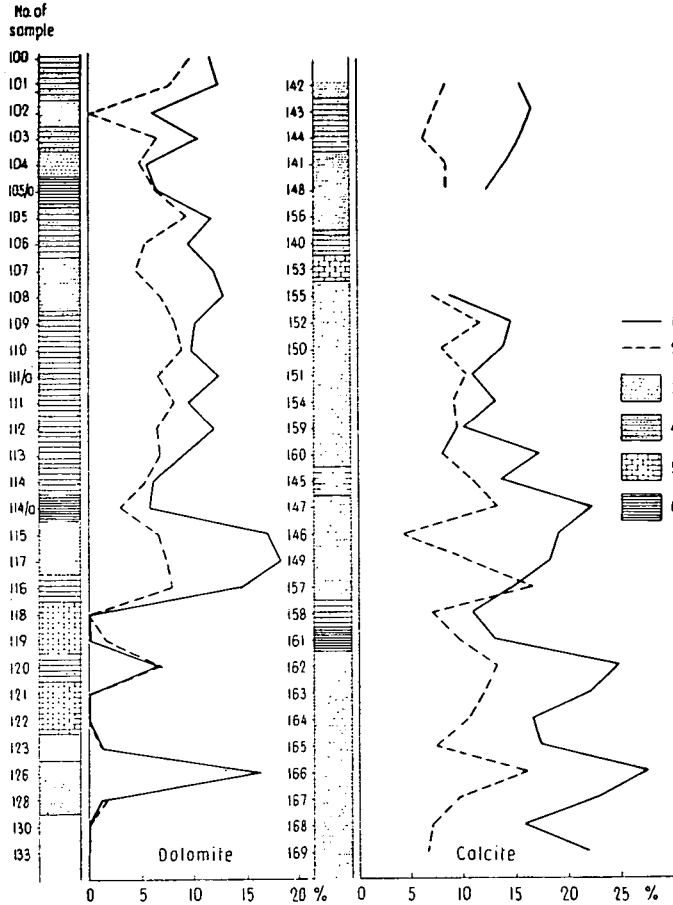

Fig. 4. Calcite and dolomite content of fraction less than 10 microns (legend see *Fig. 1.*)

SUMMARY

Calcite and dolomite quantities of the sandstones, aleurites, marls, lime-muds and clays deriving from the deep-bores of the Great Plain, were investigated. The data determined in the X-ray diffractograms were compared with those calculated from the gasometrically determined CO_2 content and values of peak intensities. Deviation was greater only in case of certain clayey samples, the other values remained within the limits of 'error. In respect of dolomite the results were identical, in general. Thus, in case of using the corresponding constants not only the quantities of clay
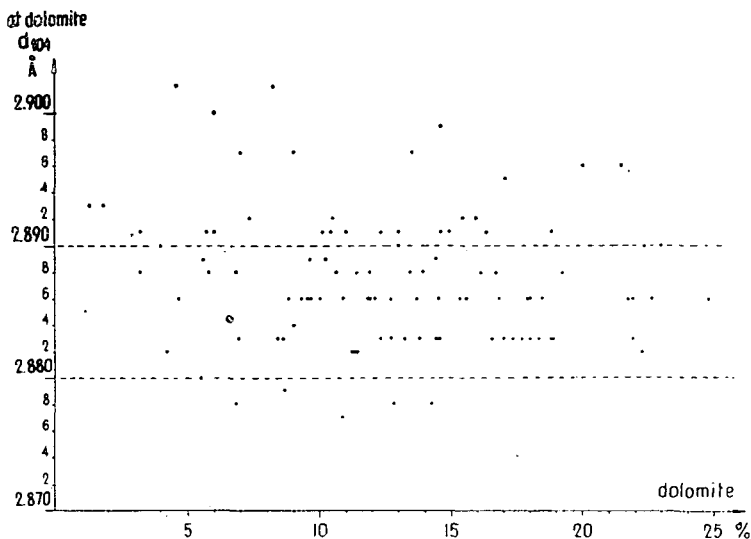
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Fig. 5. Change of the composition of the dolomite in the samples on the basis of the d_{104} value

minerals, chlorite, quartz and feldspars but those of carbonates can also be computed from the *X*-ray diffractograms. This method is relatively rapid and investigations can be carried out in series. In case of preparation, however, specific care should be taken in homogenization.

In the samples investigated the dolomite was absent when the calcite content exceeded 50 per cent. Since the calcite-containing layer is nearly in contact with that of calcite and dolomite content, this can be attributed only to salinity changes.

Part of dolomite is a result of late diagenesis, which is proved partly by the coarser grain size (these separated out of the fraction of 10 microns), partly by the absence of gypsum and anhydrite.

Dolomite is for the most part of stoichiometric composition. On the basis of the d_{104} value of dolomite the calcium surplus can be observed only in a few samples and the displacement towards the magnesite composition was followed only in several samples.

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