PROBLEMS IN X-RAY DIFFRACTION DETERMINATION OF MINERAL COMPOSITION OF SEDIMENTARY ROCKS*

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ABSTRACT

Quantitative determination of the mineral composition of core samples originating from deep-bores of the South Great Plain was performed by means of X-ray diffractometry. The difficulties occurring at the determination of muscovite, illite, illite/montmorillonite and chlorite were investigated. The change in mineral composition in the fraction less than 10 microns as compared to the average sample was investigated separately.

It was stated that there is a correlation between the quantities of FeO and chlorite of the investigated samples. A definite relationship can be determined between the amount of chlorite and that of B, V, Ni and Cr. Positive correlation can be determined between the ppm values of Sr and the carbonate minerals.

In the samples of 10 microns the quantity of calcite increased at the expense of dolomite, while dolomite is mostly absent in the fraction of 10 microns.

In the core samples of the "Makó depression trench" albite and acidic plagioclase were found only in the Lower Pannonian strata, in the Upper Miocene formations only albite occurs in determinable quantity. On the basis of the diffractograms the potash-feldspars are absent, under microscope their quantity is subordinate.

INTRODUCTION

In sedimentary sequences the presence of clay minerals is determined on the one hand by the mineral composition of the erosion area, and by transformation resp. neo-formation, i. e. by the diagenetic and epigenetic mineral formation, on the other. Thus, in the sediments such minerals will be found which had undergone certain weathering in the course of fragmentation, transportation and sedimentation. Further, minerals will occur which show certain features of diagenesis, i. e. regarding the structure of the minerals transported into the sedimentary basin it was not in equilibrium with the new pressure and temperature conditions; during the diagenesis such structures were developed which reflected the new conditions.

In the South Great Plain the basement is covered by consolidated sediments of several hundreds, locally of several thousands metres thickness. The material of this huge sediment mass are aleurite, aleurolite, sandstone, marl, lime-marl, occasionally conglomerate. The mineral substance of these formations is partly the fragmented detritus of the erosion area, partly the product of degradation, resp., aggradation followed during diagenesis. The clay minerals or in a general sense the phyllosilicates are of special importance both from the petroleum-geological and from the geochemical point of view.

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EXPERIMENTAL PART

Preparation of the samples for examination

Two kinds of preparation of the samples were used. In the first case the average sample was investigated from which chemical, geochemical, derivatographic, etc. analyses were produced. In this case the grinding of a greater quantity was taken in a ball mill, consequently the material became relatively homogeneous though certain increase of the amorphous phase should have taken into consideration. In the other case the original, non-powdered rock was treated with H_2O_2. In this way material has fragmented into the natural grain size. This treatment caused only a slight chemical change in the minerals, the original grain size, however, remained and became measurable, further the quantitative and qualitative changes of the single fractions could be performed. The suspension obtained in this way was washed out with ion-free water until it became neutral and without using stabilizator the grains less than 10 microns were separated.

Suspension of same concentration was prepared from each material for X-ray diffractometric investigations. The substance was deposited onto the sample holder from the suspension, the deposition time was the same in case of every samples. In this way a film-like oriented preparation was obtained in which the base reflexions of phyllosilicates proved to be exactly measurable. When having performed the X-ray records every samples were held under an atmosphere of ethylen-glycol, during two hours and at 60 °C. Then a new record was done to investigate the expanding layers.

Possibilities and results of quantitative determination of the minerals in several deep-bores of the Great Plain

In these formations in addition to illite (illite-montmorillonite mixed structure), chlorite, muscovite, biotite, quartz, feldspar, calcite and dolomite other minerals occurred only in subordinate quantity (which rarely surpassed one per cent), thus their quantitative and qualitative determinations were neglected.

The routine-like quantitative determination of clay minerals and of the phyllosilicates in general has not developed yet which is due to the wide range of isomorphic replacement possibilities, to polytypics of these minerals and in many cases the uncertainty of the structure, etc. In the sedimentary rocks, such as the material of the deep-bores of the Great Plain, theoretically all the minerals may occur which appear in the erosion area or which got the basin through manifold redeposition. Only a few of them occurs, however, regionally and in greater quantities. The number of predominating minerals is small in these sediments, as well.

One of the most frequent minerals is muscovite-illite. The term illite-hydromuscovite-hydromica is not used in a uniform sense. MAREL, H. W. [1950] and NEMECZ, E. [1973] gives review on the uncertainty and abundance of the terms.

NEMECZ, E. and VARJU, GY. [1970] demonstrated that the position occupation and charge distribution of the illite component of the illite/montmorillonite minerals is continouus towards muscovite. In the illite/montmorillonite of sedimentary origin the Fe and Mg content is higher than in that of hydrothermal origin, further, in the illite/montmorillonite of sedimentary origin the interbedded swelling layer may reach 60 per cent. As to their statement the formation process is probably influenced by the K^+-concentration, in case of higher pH value illite layers are formed. When the pH value decreases, the Al-quantity replacing the Si in the tetrahedral layers also decreases due to the co-ordination change of Al^{IV}/Al^{VI} and swelling layers will

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be interbedded. Thus the following minerals can be distinguished in the range: muscovite — hydromuscovite — illite — illite/montmorillonite — montmorillonite.

In the X-ray diffractograms it is troublesome to separate illite and muscovite. This is increased also by the fact that the most intense peaks of these minerals coincide or nearly cover each other and the 3.344 Å peak of the quartz. When the records were made using 2°/minute goniometric angular speed the fact can be only observed that in presence of illite of greater quantity the 3.344 Å peak of the quartz becomes assymmetric towards the smaller angle range, in case of muscovite of greater quantity, however, towards the greater angle range; rarely the two peaks are separated *(Fig. 1)*.
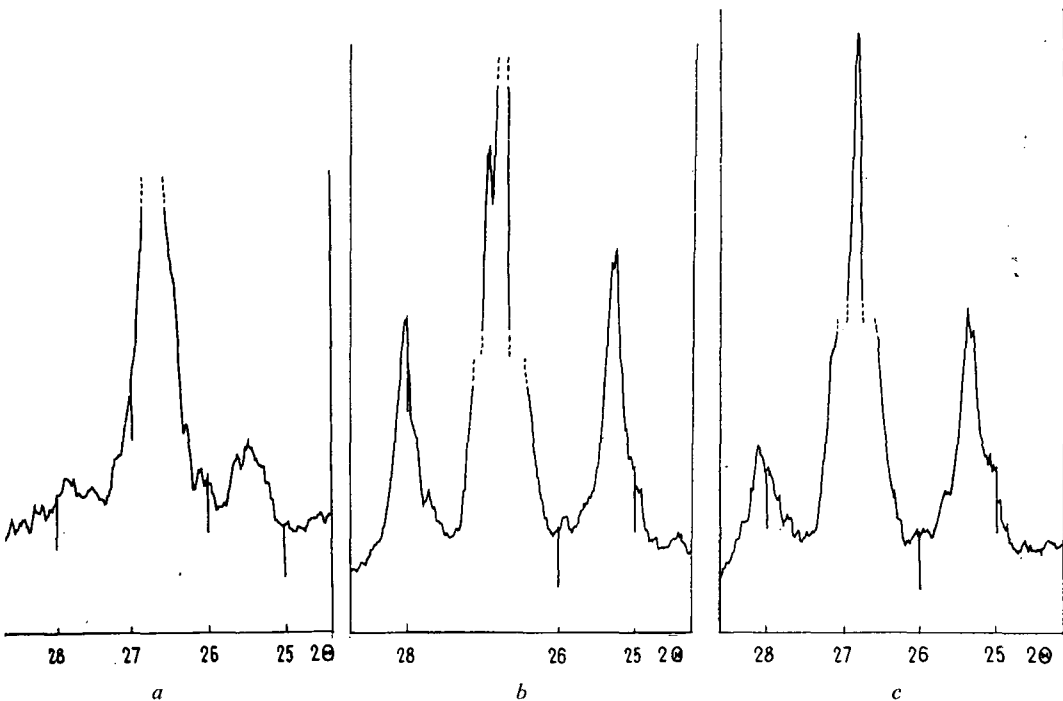
Fig. 1. Asymmetry at the quartz peak of 3.344 Å caused by illite *(a)* and muscovite *(b)*; separated muscovite — quartz peak *(c)*

The polytypics of illite and of the micas in general is well-known. In these formations muscovite is of 2M, illite is of 1M, occasionally 1Md variety. The 001 resp. 002 base reflexion, however, is characteristic of every variety at around 10 Å.

In case of illite and muscovite when investigating the shape and position of the base reflexions 001 (002), the the d-value varied between 9.30 and 9.90 Å in case of predominating muscovite. This resulted in a sharp reflexion of small angle breadth and the intercalations between 11.0 and 12.5 Å were usually absent *(Fig. 2)*. When illite — illite/montmorillonite predominated in the sample, however, the peak of the reflexion of about 10 Å is of greater angle breadth and became asymmetric towards the smaller angle range, the reflexions between about 11.0 and 12.5 Å have appeared (as a result of intercalation, *Fig. 3*). The researches of KUBLER, B. [1966] and LAPHAM, D. M., JARON, M. G. [1964] related also to such a phenomenon.

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The quality of the intercalated layers should also be taken into account in case of illites. Concerning this problem LUCAS, J. *et al.* [1959] have made investigations. They distingushied three types of the intercalated minerals. The most frequently intercalated layers are:

montmorillonite-type	d_{001}	14 Å (possibly 12 Å)
chlorite	d_{001}	14 Å
vermiculite	d_{001}	14 Å

When illite is the base mineral, on the basis of the investigations performed till now the following possibilities can be expected in the sediments of the Great Plain:

In case of illite/montmorillonite$_{14}$ the position of the peak will be at around 12 Å (in case of montmorillonite$_{12}$ at around 11 Å), the peaks of illite remain unchanged. In case of treatment with ethylene glycol or glycerine the layer of about 14 Å will swell, the peak will be displaced to 15 to 16 Å, and the peak of about 8,85 Å of the montmorillonite will occasionally appear.
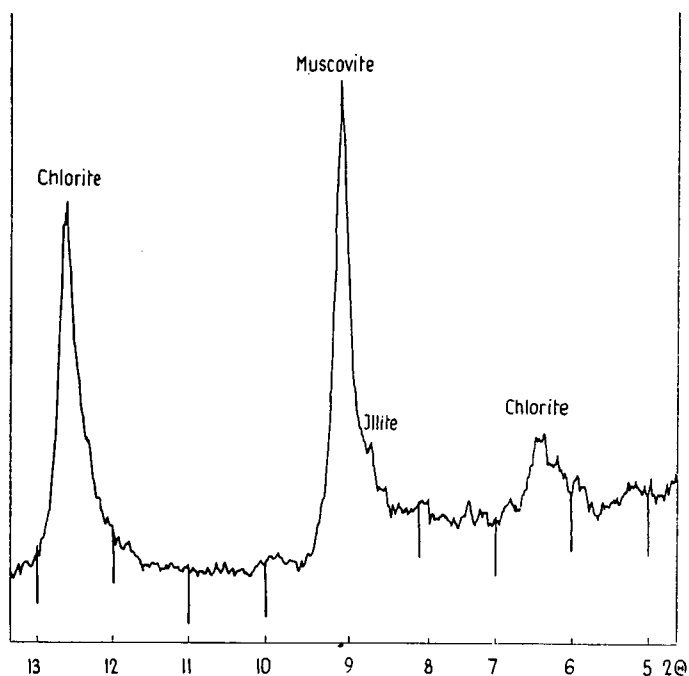

Fig. 2. Diffractogram of muscovite in presence of subordinate illite quantity in the range between 5 and 10°

In case of illite/montmorillonite$_{12}$ the peak at 12 Å will be displaced to 14 Å. When heating the sample at 550 °C, only the peak of about 10 Å of illite remains.

In case of illite/chlorite on the basis of the X-ray diffractograms it cannot be decided whether there is an intercalation or the mixture of these minerals. No change follows even in case of treatment with ethylene glycol. The same can be observed in case of chlorite/montmorillonite, too. No change appears when treating it with ethylene glycol.

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Regarding the peak at around 10 Å another phenomenon should be taken into account. It appears mainly in the colloid fraction (less than 2 microns) that this peak is widely elongated and no specially intense peak develops up to the angle range of $2\vartheta \approx 10°$ (in case of CuK$_\alpha$ radiation, *Fig. 4*). In these cases X-ray amorphous material of greater quantity is also present. When muscovite has been in the sample, this practically delimited the possibilities of occurrence of illite and chlorite by a peak of small angle breadth *(Fig. 5)*.
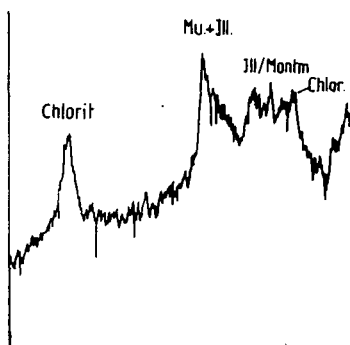

Fig. 3. Appearance of illite and illite/montmorillonite in the lower angle range of the diffractograms

In addition to the differences above several characteristic differences were observed though numerous peaks of muscovite and illite coincide. In this way, when the peak at about 4.45 Å proved to be intensive, illite was present in the sample, when not then rather muscovite could be taken into account. The relative intensity of the peak of about 5.0 Å was greater in every case when muscovite was in the sample
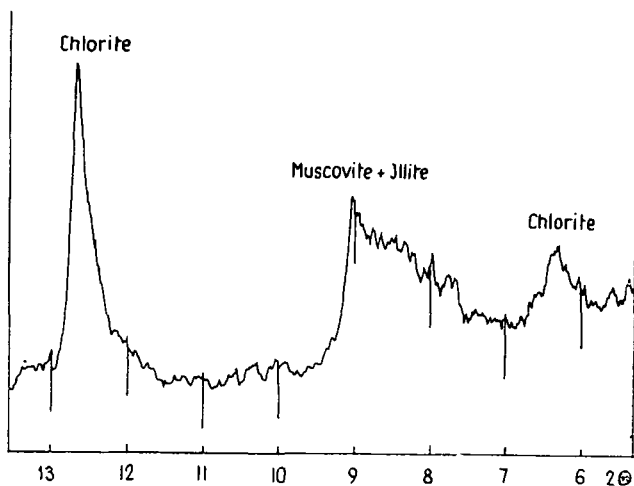

Fig. 4. X-ray diffractogram of illite and X-ray amorphous colloid fraction

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TABLE 1

2M (1M) index	predominantly muscovite	illite	about the same illite-muscovite	
d_{002} (d_{001})	9.821 Å	10.297 Å	9.821—10.216 Å	
I_{rel}	115	42	95	32
angle breadth	3°		3°	12°
d_{004} (d_{002})	4.952	5.008	4.952	4.952
I_{rel}	55	10	35	35
d_{110}	4.448	4.482	4.459	4.459
I_{rel}	16	50	35	35
$d_{11\bar{5}}$ (d_{112})	3.050	3.067		
	4	15		

rather than illite. The peak of about 3.08 Å was of medium relative intensity in case of illite, in that of muscovite this peak was absent.

It is interesting to compare the above-mentioned peaks' relative intensities on the basis of values measured, as well (X-ray diffractograms were recorded under the same conditions; Table 1.):
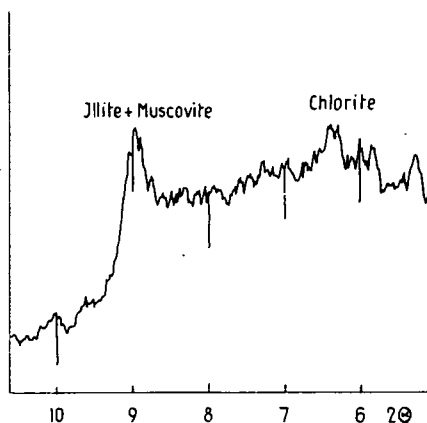

Fig. 5. Joint appearance of muscovite, illite and amorphous phase in the X-ray diffractogram

According to MAREL, H. W. [1950] in case of pure members muscovite and illite can be separated in the range of about 1.64 to 1.66 Å since muscovite gives a sharp peak while illite results in diffuse bands. In mixtures of several phases, however, e. g. in the sediments of the Great Plain no difference can be observed in this way. In this case the intensity relations of the base reflexions should be taken into account (001/002 and 004/005), if the quantity of the phases in question is large enough in the sample. Due to the changing quantity of Fe^{VI}, Mg^{VI} and Al^{VI} the regularity index of MAREL is unable for use owing to its uncertainty.

The X-ray diffractometric determination of chlorites is theoretically possible on the basis of the subsequent 002 base reflexions. The chlorites occurring in the sediments of the Great Plain do not swell, do not show adsorption and in case of

heating their lattice changes only above 500 °C. BROWN, B. E. and BAILEY, S. W. [1962] produced representative d-values for the frequent polytypes, but on this basis their exact determination is impossible. Regarding the intensities of the peaks $20\overline{1}$ and 201 there is significant difference. It is unfavourable, however, that in this range characteristic peaks of numerous minerals can also be found.

The isomorphous replacements influence also the distance between lattice planes. While the replacement of Si and Al decreases the distance d_{001} now the Fe^{+2} $(Mn^{+2}) - Mg^{+2}$ replacement following in the octahedral layer causes changes in the b parameter of the cell, i. e. in case of built in of Fe^{+2} the b_0 value grows linearly. In the octahedral layer of chlorite the number of heavy atoms can be approximately determined (Fe^{+2}, Mn^{+2}, Ni^{+2}, Fe^{+3}, Cr^{+3}, Ti^{+4}) on the basis of the 001 base reflexion intensities. As to PETRUK, W. [1964] on the basis of the I 002 + I 004/I 003 relation this relative number will grow parallel with the increase of the numbers of heavy atoms, when in the octahedral layers Fe^{+2} can be predominantly found. As to RISCHÁK, G. and VICZIÁN, I. [1974] the relation I 002/I 003 can be applied more favourably or in case of unfavourable line coincidence the relation I 004/I 003 is suitable. In this latter case, however, it is unfavourable that I 003 does not give an always exactly measurable peak.

Grain size also influences the base reflexions of chlorites. When this is small, the base reflexions usually widened and the d_{hkl} reflexions often disappear or occur only with very slight intensity. This is valid also of the epigenic chlorite of core samples deriving from the deep-bores of the Great Plain.

The methods elaborated for quantitative mineral determination on the basis of X-ray diffractograms are based on the measurement of base reflexion intensities, in general. Concerning the relative intensities of the single minerals there are numerous data in the literature. Since intensity is influenced by numerous factors discussed above, it is obvious that the value of the constants used in case of quantitative and semi-quantitative determinations of each minerals shows rather great deviations. The number of influencing factors grows in general from the ordered structures towards the less ordered ones. Regarding the phyllosilicates the constants mentioned in the literature were collected by RISCHÁK, G. and VICZIÁN, I. [1974]. In case of the phyllosilicates and of the inosilicates to a certain extent recently only semi-quantitative determinations are available on the basis of X-ray diffractograms owing to the great number of influencing factors.

. In case of quantitative determination when giving the percentual distribution the amorphous phase should have been neglected since its quantity could not be exactly determined. When combining the diffractogrammatic method with that used by VARSÁNYI, I. [1974] the quantitative determination could be probably more exact since the amorphous phase can be easily and rapidly determined by chemical methods.

In case of quantitative determinations based on X-ray diffractograms there are such minerals the constants of which are nearly the same as to different references, thus in these cases no difficulties occurred either (quartz, calcite, dolomite, feldspar) because these are exactly identified and ordered structures. The case of phyllosilicates proved to be more troublesome. In the range of difficulties the first phenomenon was that in the investigated sediments of the Great Plain illite and muscovite occur together, moreover in numerous cases there are illite/montmorillonite mixed structures. When muscovite and illite proved to be separable, their quantitative determination was taken using the adequate constant. If this separation proved to be impossible then the constant of the predominating mineral species was taken into con-

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·sideration. When the intercalation of illite/montmorillonite has been of greater importance, the value of the constant was proportionally decreased.

The influence of Fe^{2+} on the peak intensities of chlorites is well-known. Thus in these cases the determination of the relative number of $I\ 002 + I\ 004/I\ 003$ was ·done in each case. This has mostly lain within the limits given by literature, which made possible the use of uniform constants.
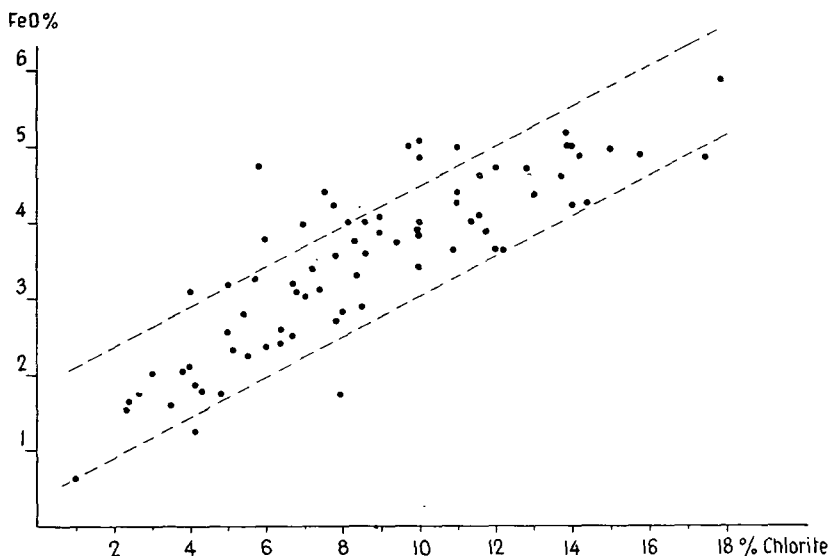

Fig. 6. Quantitative relationship between FeO and chlorite

When evaluating the diffractograms either the height of the peak or the area ·of peak is taken into account. In both cases the right delineation of the base line is very important, especially at the peaks of highest intensity of the phyllosilicates and :feldspars. When having investigated the different grain size fractions of the samples it could be stated that in the range less than 50 microns there was no remarkable de- ·viation between the measurements of peak intensity and area (this proved to be about 3 to 5 per cent), e. g. within the fraction less than 10 microns the two calibration curves were nearly beside each other, the curve of peak area has lain somewhat higher than that of peak height.

When investigating the average sample and the fraction less than 10 microns the quantity of chlorite has doubled in the latter fraction in every case, the quantities of illite-muscovite increased by a smaller extent. The quantities of quartz, feldspar and dolomite decreased in each case, the two latter minerals were absent in several cases.

In the investigated samples major part of Fe^{+2} is connected to chlorites. This is demonstrated by Fig. 6. shown the correlation between the FeO quantity deter- mined analytically and the quantity of chlorite determined by means of X-ray dif- fractometry. On the basis of this it unambiguously stated that the FeO-content grows parallel with the chlorite content, in general. Where deviation occurred, the core sample had contained pyrite being determinable macroscopically as well. Devi- ation appeared in a negative sense in several cases, when greater quantities of fine-

grained epigenic chlorites could be taken into account, in this case the base reflexions were widened and their intensity showed considerable decrease.

Between the change of quantity of the chlorites and certain trace elements definite correlation could be determined. As regarding the illite-muscovite only a loose relationship could be determined concerning B, V, Ni and Cr, these elements show definite correlation whith chlorite. The increase of quantity of these elements given in ppm is proportional to that of the chlorites *(Fig. 7)*.
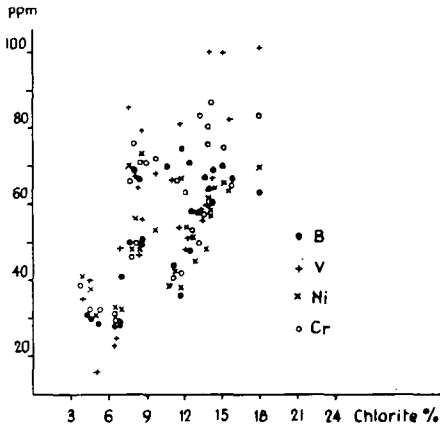
Fig. 7. Relation between the quantities of B, V, Ni and Cr with that of chlorite

A positive correlation could be determined between Sr and carbonate minerals (calcite, dolomite), too. The quantity of Sr given in ppm has proportionally increased with the increasing calcite and dolomite quantity *(Fig. 8)*.
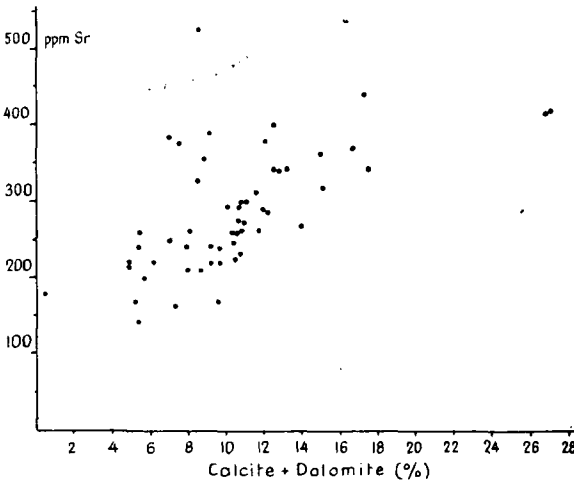
Fig. 8. Relation between the quantitative change of Sr and calcite-dolomite

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In connection with the appearance of the carbonate minerals it can be stated that when investigating the sample of 10 microns the quantity of dolomite proved to be always less than in the average sample. From this phenomenon conclusion could be drawn that dolomitization followed usually during the diagenesis and the dolomite originated in this way is always coarser-grained, this it was separated out of the finer fraction.

In the samples of the „Makó depression trench" most of the feldspars being able for evaluation proved to be albite which is proved in the diffractograms by the only maximum at about 3.19 Å. The reflexion of about 3.22 Å appears locally but it is less intense and indicates the displacement of composition towards the oligoclase-andesine in the range of plagioclases. This peak, however, is always of weaker intensity. The peak at about 4.02 Å always appears in these cases.

When the quantity of feldspars remained below 5 to 6 per cent, only the albite occurred of measurable quantity, above 6 per cent the oligoclase-andesine could be usually determined, too. The increase of feldspar quantity followed mostly at the expense of muscovite-illite-quartz. The change of species and quantity of the feldspars can be attributed by all means to the change of the erosion area and this is also proved by the fact that albite and acidic plagioclase occur only in the Lower Pannonian, while in the Upper Miocene sediments only albite could be determined.

Regarding the potash-feldspars, microcline did not occur in measurable quantity (under microscope only several grains could be determined) and orthoclase could not be identified either, the characteristic peaks of high intensity were absent.

In the region of Ferencszállás the feldspar species show a more variegated assemblage. The diffractometric determinations relate both to albite, acidic plagioclase and orthoclase. Regarding their quantitative changes and distribution conditions no tendency can be demonstrated owing to the small number of data.

In both regions the quantity of feldspars considerably decreased in the fraction of 10 microns, sometimes they were absent and separated out of the original sample which related to the appearance of them in the coarser fraction.

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