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Maciej PAWLIKOWSKI *

CONTINUOUS X-RAY ANALYSIS OF MUD-SANDY ROCKS

UKD 543.73:552.517 4'527(438.31 Wieliczka)

Abstract. Mud-sandy sediments assigned to the Bogucice sands (Miocene) occurring near Wieliczka were taken as an illustrative case to demonstrate the usefulness of continuous X-ray analysis for determining the distribution of minerals in sedimentary rocks. It has been found that the rocks studied are made up of quartz and feldspars which are accompanied by subordinate illite, kaolinite and montmorillonite, as well as carbonate minerals.

INTRODUCTION

The methods of preparing peels have been described extensively in the literature. Peels were obtained mainly from various types of sedimentary rocks (Dollar 1942, Easton 1942, Sternberg *et al.* 1942. Cuklin 1956, Bissell 1957, Hamblin 1962, Mc Crone 1963, Ashley 1973, Price 1975, and others). Moreover, manifold techniques of preparing peels and casts from carbonate rocks have been developed (Apple 1933, Buchler 1948, Lane 1962, Frank 1965, Katz *et al.* 1965, and others).

Bouma (1969) published a comprehensive compilation of the available methods of preparing peels, which have very wide application in sedimentological studies. The preparation of peels requires a specific approach, depending on the type of rock and its lithological and sedimentological features. The wide application of peels, which are a faithful image of the rock, determined the author to use them for studying their mineralogical composition by X-ray method, with the aid of a goniometer attachment of his own design. Ostler *et al.* (1973) indicated the possibility of making X-ray analyses on peels; however, these authors have never carried out such studies themselves. Investigations of similar nature, involving X-raying of thin sections, were performed by Przybora (1966), Stanley *et al.* (1967), and others.

X-ray semi-quantitative and quantitative analyses have been the subject of many publications. Yet, the investigations carried out to-date fo-

* Academy of Mining and Metallurgy, Cracow (Kraków, al. Mickiewicza 30).

cussed mainly on the analyses of point samples (Bouma 1964, Schultz 1964, Tatlock 1966, Hausen 1973, Stokke *et al.* 1973, Kazi 1975). There are several factors making X-ray quantitative analysis of the mineralogical composition of rocks a complex problem. The major one is the absorption of X-rays by the sample (Alexander *et al.* 1948), but the grain size also plays a significant role (Tatlock 1966). A problem of different nature is the method of intensity measurement. Kazi (1975) mentions among other methods the following: measurement of the total height, half-height and the corrected height of peaks (the method of triangle). In general, all those methods involve measurements of the linear height or the area of a peak.

In the continuous X-ray analyses discussed in this paper the linear method of measurement of the total reflection intensities was used.

EXPERIMENTAL

Sampling

The samples were taken using two methods: the point method and the method of peels.

1. Point samples were taken from the upper part of the profile at intervals of 25 cm over a length of 2 m. Each sample weighed 100 g.

2. Sampling by the method of peels was carried out over the same 2 m length of the profile. The wall was smoothed first with a shovel and then with a spatula (Bouma 1969) in such a way as to preserve its verticality. After smoothing, the wall was dried with a blowtorch (the equipment used for making peels is shown on Phot. 1) held at a distance of about 80 cm, so that the temperature of the heated wall was about 50°C. When the surface layer of the wall was dry, it was sprayed with an aqueous solution of glue (diluted white emulsion paint) using a compressed-air spray-gun. The glue was diluted with water in the ratio of 1 : 3. It has been found that after 14 days of drying on the rock face it does not yield any diffraction lines in X-ray powder patterns, nor does it raise the background level in the range of 0—18° CuK_α. The wall was sprayed twice from a distance of 50 cm, the air pressure being 2.5 at. After the wall was partly dried with a blowtorch, a 7 cm wide bandage was placed against it and coated with non-diluted glue using an ordinary paint brush in such a way that the glue spread beyond the bandage. The operation of coating was repeated twice (Phot. 2). The profile thus prepared was dried again with a blowtorch and then the bandage was peeled off gently together with the thin layer of rock stuck to it (Phot. 3). After shaking off the excess material, the strips with peels were rolled up and transported in plastic bags to the laboratory.

Preparation of samples for X-ray analysis

The point samples were loosened in water and non-ground preparations were made, coating a glass plate with a thin layer of the material. Another series of samples was prepared by grinding the same material in an agate mortar. In both cases the same amount of the material (3 g) was used. The samples thus obtained were subjected to conventional X-ray analysis.

The peels were subjected to special treatment prior to the analyses. After mechanical smoothing of the surface, they were thinned in a hydraulic press to about 0.7 mm. Then the peels were cut into 1 m segments and glued together so as to form a closed endless series.

Equipment

The analyses were carried out in a TUR-61 diffractometer, using Fe-filtered CuK_α radiation. A goniometer attachment of special design was used for investigations of peels. It is made from plexiglass and metal and consists of a base (Fig. 1) with two rollers, one of which is driven by an electric motor (220 V, 50 Hz, 375 r.p.m.) through a system of toothed gears. The other roller moves freely and has a spring guy of a force of 5 kG mounted on it to secure a steady tension of the strip with a peel. The attachment is lined with the goniometer (Phot. 4), and the strip with a peel is placed in it. The strip moves at a constant speed on the rollers and over a special head, mounted where the standard sample holder should be, in such a way that the side with the pressed rock material is always in the same plane. The latter condition is extremely important; if it fails to be satisfied, variations in the Θ angle, characteristic of the definite d_{hkl} reflections, will result.

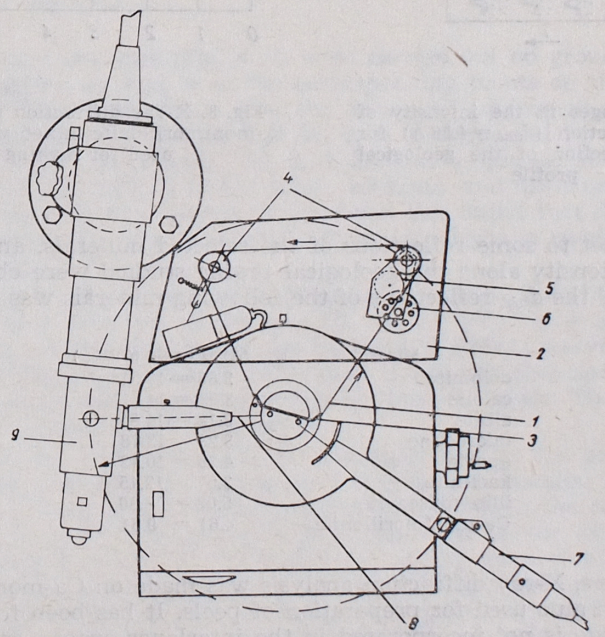

Fig. 1. Diagram of the equipment and goniometer used for analyses
1 — strip with a peel, *2* — attachment for moving the peel, *3* — goniometer head, *4* — rollers for moving the peel, *5* — system of toothed gears, *6* — electric motor, *7* — G—M counter, *8* — X-ray beam, *9* — X-ray tube, Arrows indicate the direction of tape feed

X-ray analysis

X-ray analysis of point samples was carried out in the conventional way. Instrument settings used were: slits 0.7/1.2, sensitivity 1, scanning speed 1°/min., chart speed 600 mm/h.

Two different procedures were adopted to analyse the peels. One involved X-ray analysis with the strip stopped and the goniometer arm with a G-M counter moving. In this way, analyses were made at eight points (I—VIII) of the peel, corresponding to the places of point sampling.

In the other procedure, the tape with a peel was moving while the goniometer was immobilized. The G-M counter, mounted on the goniometer

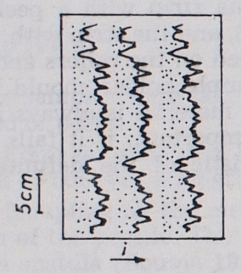

Fig. 2. Changes in the intensity of quartz reflection (d_{hkl} = 4.26 Å) for the same section of the geological profile

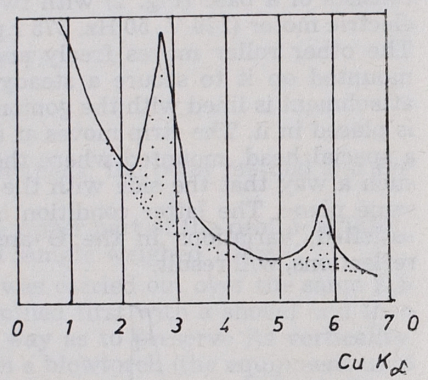

Fig. 3. X-ray diffraction pattern of Ca-montmorillonite mixed with some glue used for making peels

arm, was set to some reflections of the selected minerals, and variations in their intensity along the geological profile studied were observed. The intensity of the d_{hkl} reflections of the following minerals was analysed:

Mineral	d_{hkl} (Å) Θ angle (CuK α)
dolomite	2.88 = 15.51
calcite	3.03 = 14.71
albite	3.18 = 14.01
microcline	3.23 = 13.78
quartz	4.26 = 10.42
kaolinite	3.57 = 12.45
illite/muscovite	5.03 = 8.80
Ca-montmorillonite	4.61 = 9.61

Moreover, X-ray diffraction analysis was made on Ca-montmorillonite mixed with glue used for preparation of peels. It has been found (Fig. 2) that the glue is not incorporated in the interlayer spaces, so it does not produce any changes in the d_{001} values of montmorillonite. It has been also ascertained that the method of continuous intensity measurements yields reproducible results (Fig. 3).

Sediments studied

The mud-sandy sediments studied occur at Psia Górka near Wieliczka, transgressing the rocks of the Opole stage. They are assigned to the Bogucice sands, the latter being a separate facies of the Grabowiec Formation (Skoczylas-Ciszewska, Kolasa 1959). From the bottom upwards, the sediments in question are represented by a sand bed more than 5 m in thickness, with claystone balls and disrupted clay laminae in its top part. The upper part of the profile is made up of laternating mud and sand layers, containing in places thin clay intercalations which are a barrier for ground water. Under the clay intercalations goethite-limonite horizons have been noted in the sands. The concentrations of iron minerals have a character of ortstein. The upper part of the profile is about 2 m thick. It is overlain by a 1.5 m loessial cover, which is presumably a source of iron for the ore inserts. The grain size of the mud-sandy rocks is similar throughout the profile, the bulk of grains being 0.5—0.1 mm in diameter. The sands in question owe their origin to the denudation of the Istebna Beds, the conditions of their deposition being similar to those of flysch sedimentation (Skoczylas-Ciszewska, Kolasa 1959).

RESULTS

Point analyses

X-ray point analyses (Fig. 4 *A*) were carried out on ground and non-ground samples, as well as at the corresponding points on the peel (Fig. 4 *A*, *B*, *C*). They have shown that the dominant component of the rocks studied is quartz (d_{hkl} = 4.26, 3.34 Å). It is accompanied by plagioclases, albite (d_{hkl} = 4.02, 3.85, 3.66, 3.50, 3.18, 3.14 Å), orthoclase and microcline (d_{hkl} = 3.81, 3.46, 3.23, 2.87 Å). Illite, kaolinite and Ca-montmorillonite appear as subordinate minerals. It has been also found that dolomite and calcite are present in the rocks under study, occurring in small and nearly equal amounts.

The analyses of ground preparations have revealed a slightly increased amount of clay minerals in samples *III*, *IV*, *V*, *VI* (Fig. 4 *A*), in which a higher content of feldspars has also been noted. From observations of the intensity of the basal feldspar reflections it appears that samples *V*, *VI* and *VIII* contain the greatest amounts of those minerals. The content of carbonates is similar in all the samples.

The analyses made on non-ground samples and at the corresponding points on the peel (Fig. 4 *B*, *C*) yielded very similar results. Their X-ray diffraction patterns show different proportions between the reflections of respective minerals compared with those observed on the diffractograms of ground samples (Fig. 4 *A*). The reflections of clay minerals (fine-grained) are less pronounced whereas those of coarse-grained minerals (quartz, feldspars) have a higher intensity. It has been noticed at the same time that changes in the reflection intensities of respective minerals recorded for the peel and ground samples are very similar. A decrease in the intensity of clay mineral reflections noted in the case of ground samples and peel material is due in the first place to the grain-size distribution and the une-

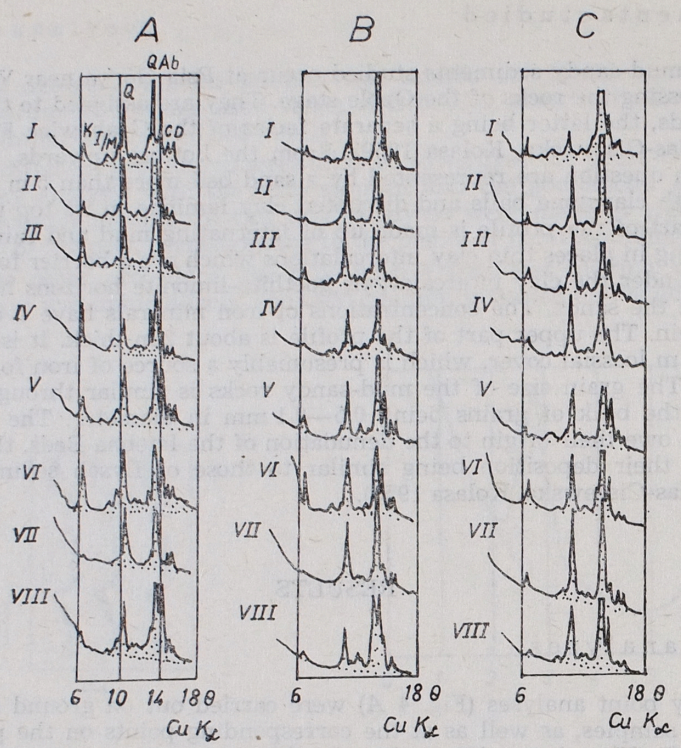

Fig. 4. X-ray diffraction patterns of point samples taken from the profile studied

A — ground samples, *B* — non-ground samples, *C* — samples on the strip with the peel; *I—VIII* — places of point sampling; K — kaolinite, I/M — illite-muscovite, Q — quartz, Ab — albite, C — calcite, D — dolomite

venness of the sample surface. As a result of this, reflections with the d_{hkl} values higher than 8 Å may fail to be recorded in the diffraction patterns or, if recorded, are not proportional to the amount of mineral actually present in the sample. It apears therefore that non-uniform grain-size distribution, as well as the orientation of minerals, affects the intensity of respective reflections in ground and non-ground samples. Considering all this, those reflections were used for continuous intensity measurements which do not coincide with any other reflections and lie in the angle range below 5,8° CuK_α, i.e. which have the d_{hkl} values less than about 7.5 Å.

Continuous analyses

Experiments with the measurements of the reflection intensity of the selected minerals have shown that, the amount of minerals in the samples studied being as it is, different instrumental parameters (slits) must be used. Accordingly, slits 0.7/2.0, 0.9/2.2, 0.9/2.2, 0.9/2.2, 0.9/2.2 were used for

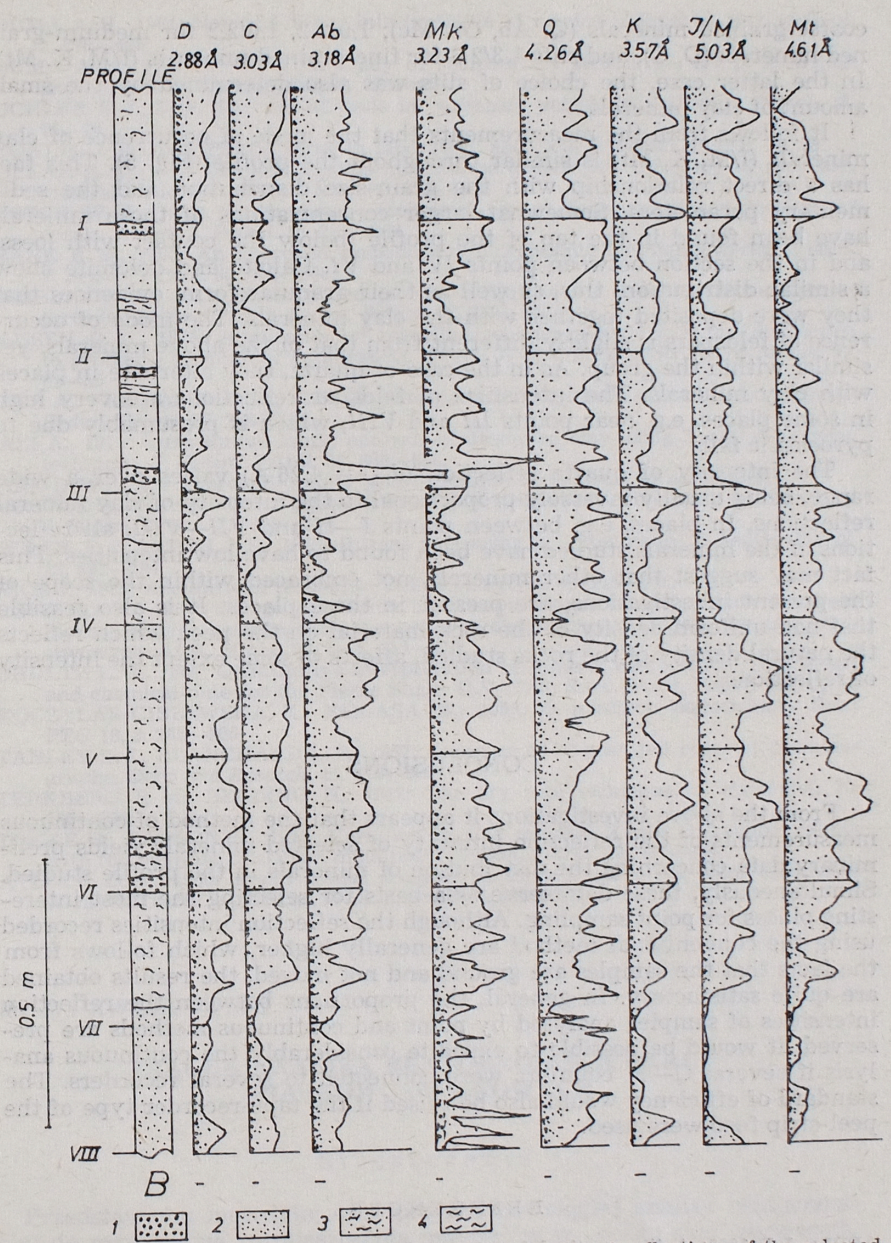

Fig. 5. The geological profile and changes in the intensity of reflections of the selected minerals

D — dolomite, C — calcite, Ab — albite, Mk — microcline, Q — quartz, K — kaolinite, I/M — illite-muscovite, Mt — Ca-montmorillonite, B — background measured near the reflections studied; *I—VIII* — places of point sampling; *1* — coarse-grained sand, *2* — fine-grained sand, *3* — mudstone, *4* — claystone

coarse-grained minerals (Q, Ab, Or, Mc); 1.0/2.2, 1.0/2.2 for medium-grained minerals (D, C), and slits 1.3/2.6 for fine-grained minerals (I/M, K, Mt). In the latter case, the choice of slits was also determined by the small amount of clay minerals.

It follows from the measurements that the mode of occurrence of clay minerals (I/M, K, Mt) is similar throughout the profile (Fig. 5). This fact has a direct relationship with the grain-size distribution and the sedimentary parameters. Somewhat larger concentrations of those minerals have been found in the top of the profile (below the contact with loess) and in the section between points *IV* and *VI*. Calcite and dolomite show a similar distribution; this, as well as their granular form, evidences that they were deposited together with the clay minerals. The mode of occurrence of feldspars is slightly different from that of the above minerals, yet similar within the group. As in the case of quartz, they alternate in places with clay minerals. The intensities of feldspar reflections are very high in some places, e.g. near points *III* and *VIII*, which is presumably due to pyroclastic falls.

The intensity of quartz reflection (d_{hkl} = 4.26 Å) varies over a wide range, being usually inversely proportional to the intensity of clay mineral reflections. In places, e.g. between points *I—II* and *VII—VIII*, all reflections of the minerals studied have been found to have low intensities. This fact may suggest that other minerals, not embraced within the scope of the present investigations, are present in those places. It is also feasible that non-uniform density of the rock material on the peel, which reflects the natural density of the rocks studied, affects to some extent the intensity of reflections.

CONCLUSIONS

From the above investigations it appears that the method of continuous measurements of the reflection intensity of selected minerals yields preliminary data concerning the distribution of minerals in the profile studied. Simultaneously, these data serve as a basis for selecting the most interesting places for point sampling. Although the reflection intensities recorded using the conventional method are generally higher, which follows from the facts that the samples are ground and not moved, the results obtained are quite satisfactory. In general, the proportions between the reflection intensities of samples analysed by point and continuous methods are preserved. It would be possible to expedite considerably the continuous analysis if several G—M counters were connected to several recorders. The standard of efficiency would also be raised if the tape-recorder type of the peel-strip feed were used.

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CIĄGŁA ANALIZA RENTGENOWSKA SKAŁ PIASKOWO-MUŁKOWYCH

Streszczenie

Przedstawiono metodykę oraz przydatność ciągłej analizy rentgenowskiej do rozpoznania rozmieszczenia minerałów w profilu skał osadowych. Badania przeprowadzono na przykładzie skał piaszczysto-mułkowych zaliczanych do piasków bogucickich (miocen) występujących w okolicach Wieliczki. Stwierdzono, że badane skały zbudowane są głównie z kwarcu i skaleni którym towarzyszą obecne w podrzędnych ilościach illit, muskowit, kaolinit, montmorillonit a także minerały węglanowe.

OBJAŚNIENIA FIGUR

Fig. 1. Schemat urządzenia i goniometru wykorzystywanego w badaniach
1 — piasek z profilem odrywanym, *2* — przystawka do przesuwania profilu odrywanego, *3* — głowica goniometru, *4* — rolki do przesuwania profilu, *5* — system przekładni, *6* — silnik elektryczny, *7* — licznik G—M, *8* — wiązka promieniowania rentgenowskiego, *9* — lampa rentgenowska

Fig. 2. Wykres zmian intensywności refleksu kwarcowego ($d_{hkl} = 4{,}26$ Å) dla tego samego odcinka profilu
i — intensywność

Fig. 3. Dyfraktogram rentgenowski montmorillonitu wapniowego wymieszanego z niewielką ilością kleju stosowanego do profili odrywanych

Fig. 4. Dyfraktogramy rentgenowskie próbek punktowych z badanego profilu
A — próbki ucierane, *B* — próbki nieucierane, *C* — próbki na pasku z profilem odrywanym, *I—VIII* — miejsca opróbowania punktowego, *K* — kaolinit, *I/M* — illit/muskowit, *Q* — kwarc, *Ab* — albit, *C* — kalcyt, *D* — dolomit

Fig. 5. Profil geologiczny oraz wykres zmian intensywności refleksów wytypowanych minerałów
D — dolomit, C — kalcyt, Ab — albit, Mk — mikroklin, Q — kwarc, K — kaolinit, I/M — illit/muskowit, Mt — Ca-montmorillonit, B — tło pomierzone w pobliżu badanych refleksów, *I—VIII* — miejsca opróbowania punktowego, *1* — piaski gruboziarniste, *2* — piaski drobnoziarniste, *3* — muły, *4* — iły

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Przedmioty stosowane przy preparowaniu profili odrywanych
Fot. 2. Wykonywanie profilu odrywanego o długości 2 m
Fot. 3. Materiał skalny na fragmencie profilu odrywanego
Fot. 4. Goniometr wraz z lampą rentgenowską, licznikiem G—M oraz przystawką do przesuwania profili odrywanych

Maciej PAWLIKOWSKI

БЕСПРЕРЫВНЫЙ РЕНТГЕНОВСКИЙ АНАЛИЗ ИЛИСТО-ПЕСЧАННЫХ ПОРОД

Резюме

В работе представлены метод и пригодность беспрерывного рентгеновского анализа при исследованиях размещения минералов в профиле осадочных пород. Исследования проводились на примере илисто-песчанных пород, которые причисляются к богуцицким пескам (миоцен), залегающим в районе Велички. Подтверждено, что исследуемые породы сложены главным образом кварцом и полевыми шпатами, которым сопутствуют во второстепенном количестве иллит, мусковит, каолинит, монтмориллонит и карбонатные минералы.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Схема прибора и гониометра, который использовался в исследованиях
1 — лента со срываемым профилем, *2* — приспособление к перемещению срываемого профиля, *3* — головка гониометра, *4* — ролики для перемещения профиля, *5* — система передач, *6* — электрический двигатель, *7* — счётчик Гейгера-Мюллера, *8* — пучок рентгеновских лучей, *9* — рентгеновская лампа

Фиг. 2. График перемен интенсивности кварцового рефлекса ($d_{hkl} = 4{,}26$ Å) для того же участка профиля
i — интенсивность

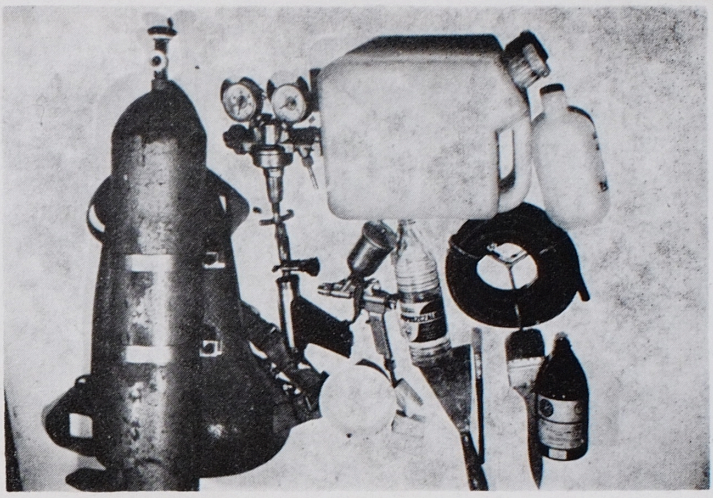
Фиг. 3. Рентгеновская дифрактограмма кальциевого монтмориллонита перемешанного с небольшим количеством клея, который используется в срываемых профилях

Фиг. 4. Рентгеновские дифрактограммы пунктовых образцов изучаемого профиля
A — протёртые образцы, *B* — непротёртые образцы, *C* — образцы на ленте со срываемым профилем, *I—VIII* — места отбора пунктовых образцов, K — каолинит, I/M — иллит/мусковит, Q — кварц, Ab — альбит, C — кальцит, D — доломит

Фиг. 5. Геологических профиль и график изменений интенсивности рефлексов для избранных минералов
D — доломит, C — кальцит, Ab — альбит, Mk — микроклин, Q — кварц, K — каолинит, I/M — иллит/монтмориллонит, Mt — Ca-монтмориллонит, B — фон измеренный вблизи изучаемых рефлексов, *I—VIII* — места отбора пунктовых образцов
1 — крупнозернистые пески, *2* — мелкозернистые пески, *3* — илы, *4* — глины

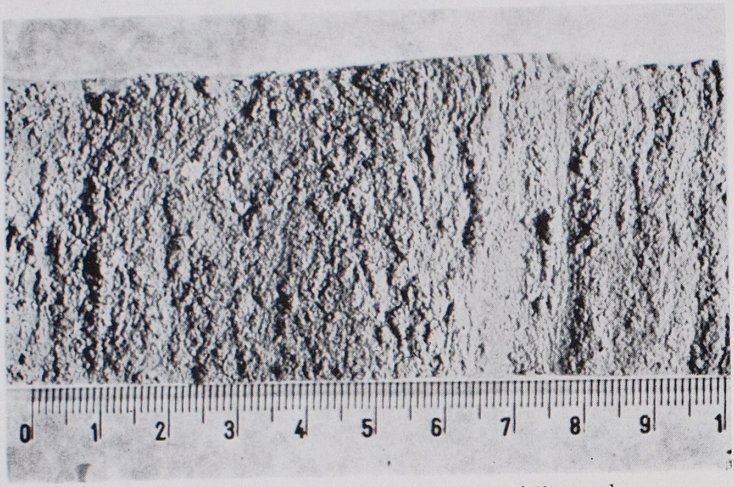
ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фот. 1. Предметы, которыми пользовались при препарировании срываемых профилей
Фот. 2. Изготовление срываемого профиля длиной 2 м
Фот. 3. Фотография скального материала на части срываемого профиля
Фот. 4. Фотография гониометра с рентгеновской лампой, счётчиком Гейгера-Мюллера и приспособлением к перемещению срываемых профилей

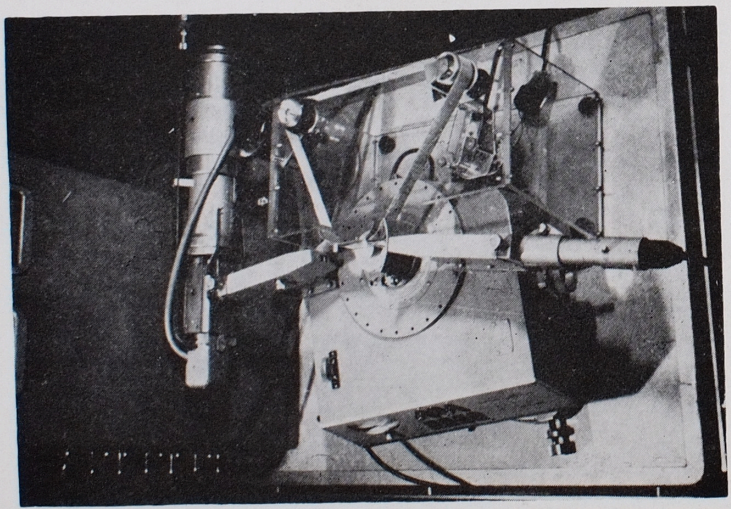


Phot. 1. Equipment used for preparation of peels

Phot. 2. Making of a peel of 2 m length



Phot. 3. Rock material on a fragment of the peel



Phot. 4. Goniometer with an X-ray tube, G—M counter and an attachment for moving the peels