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SYNGENETIC ALTERATION OF ANDESITE VOLCANOCLASTIC ROCKS OF THE NERESNICA FORMATION IN AN AQUATIC ENVIRONMENT (JAVORIE, WESTERN CARPATHIANS)

VLADIMÍR ŠUCHA[1], VLASTIMIL KONEČNÝ[2], JAROSLAV LEXA[2] and HELENA GERTHOFFEROVÁ[3]

[1]Department of Geology of Mineral Deposits, Faculty of Sciences, Comenius University, Mlynská dolina G, 842 15 Bratislava
[2]D.Štúr Institute of Geology, Mlynská dolina 1, 814 73 Bratislava
[3]Geological Institute, Faculty of Sciences, Comenius University, Mlynská dolina G, 842 15 Bratislava, Slovak Republic

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Abstract: Alteration of glassy andesite rocks was studied by detailed lithological and textural analyses in Neresnica Formation near Zvolen. Products of this alteration were investigated by X-ray diffraction, IR-spectroscopy, TEM and chemical analyses. Lithological and textural phenomena indicate syngenetic alteration in aquatic environment producing mixture of halloysite, mixed layer illite/smectite, kaolinite (halloysite)/smectite and amorphous iron.

Key words: Neresnica Formation, syngenetic alteration, clay minerals.

Introduction

Andesites are an essential component of the Neogene volcanics in Central Slovakia. During their geological and petrographic study, specific products of alteration related to aquatic environment, were observed in various places. To study this fenomena we have chosen a locality west of Zvolen, belonging to the Neresnica Formation of the Central Slovakia volcanic field.

Geological structure

The Neresnica Formation, extending west of Zvolen, represents products of extrusive volcanism of pyroxene-hornblende andesites with accessory garnets. The formation includes extrusive domes, protrusions to a lesser extent shallow intrusions of laccolithic type (body at Babiná), and deposits of mostly coarse epiclastic volcanic breccias.

Andesite bodies, with dimensions from several tens of metres to 1.5 km (occasionally up to 3 km), are regularly elliptical to isometric in cross section, or markedly oriented in one direction (Fig. 1). At their margins, andesite extrusions are often bordered by zones of brecciation, with marked angularity of fragments, indicating fragmentation in a highly viscous to almost solid state, in the course of their extrusion. Several petrographic varieties of andesites have been observed with variable contents of garnets, quartz and biotite. Groundmass texture varies from microdioritic or microgranular in internal parts of andesite bodies to pilotaxitic, hyalopilitic or glassy at marginal parts of andesite bodies and volcanoclastic rocks. On the basis of dating by the K/Ar method (Konečný et al. 1969) and fission track method (Repčok 1982) the Neresnica Formation is of the Early Badenian age.

Materials and methods

The locality, which we have chosen for more detailed lithological and mineralogical study, is represented by a rock wall, under a hill with a height of 443.6 m - Veľká Stráž, along the state highway west of the town Zvolen.

Alteration products are found in the form of crack filling, with thicknesses from several millimetres to 25 cm. They are fragile, shiny, homogeneous, of red-brown colour. On contact with water they hydrate violently with sound effects, breaking up into small pieces.

The samples taken for mineralogical study were disintegrated by ultrasonic probe and then were treated with Na-acetate buffer and sodium dithionite (Jackson 1975). After chemical treatment, the various fractions of the sample (<1, <2, 1 - 2, 2 - 5 μm) were separated by sedimentation. Fraction <0.1 μm was separated using a centrifuge.

X-ray diffraction analysis (XRD) was carried out on a Philips PW-1710 diffractometer (CuK_α radiation, Ni filter). Oriented specimens, in the air dried state, saturated with ethyleneglycol and heated at 450 °C, were used for the analysis.

The IR spectrum was obtained using a Perkin-Elmer 983 G spectroscope, by the potassium bromide tablet method.

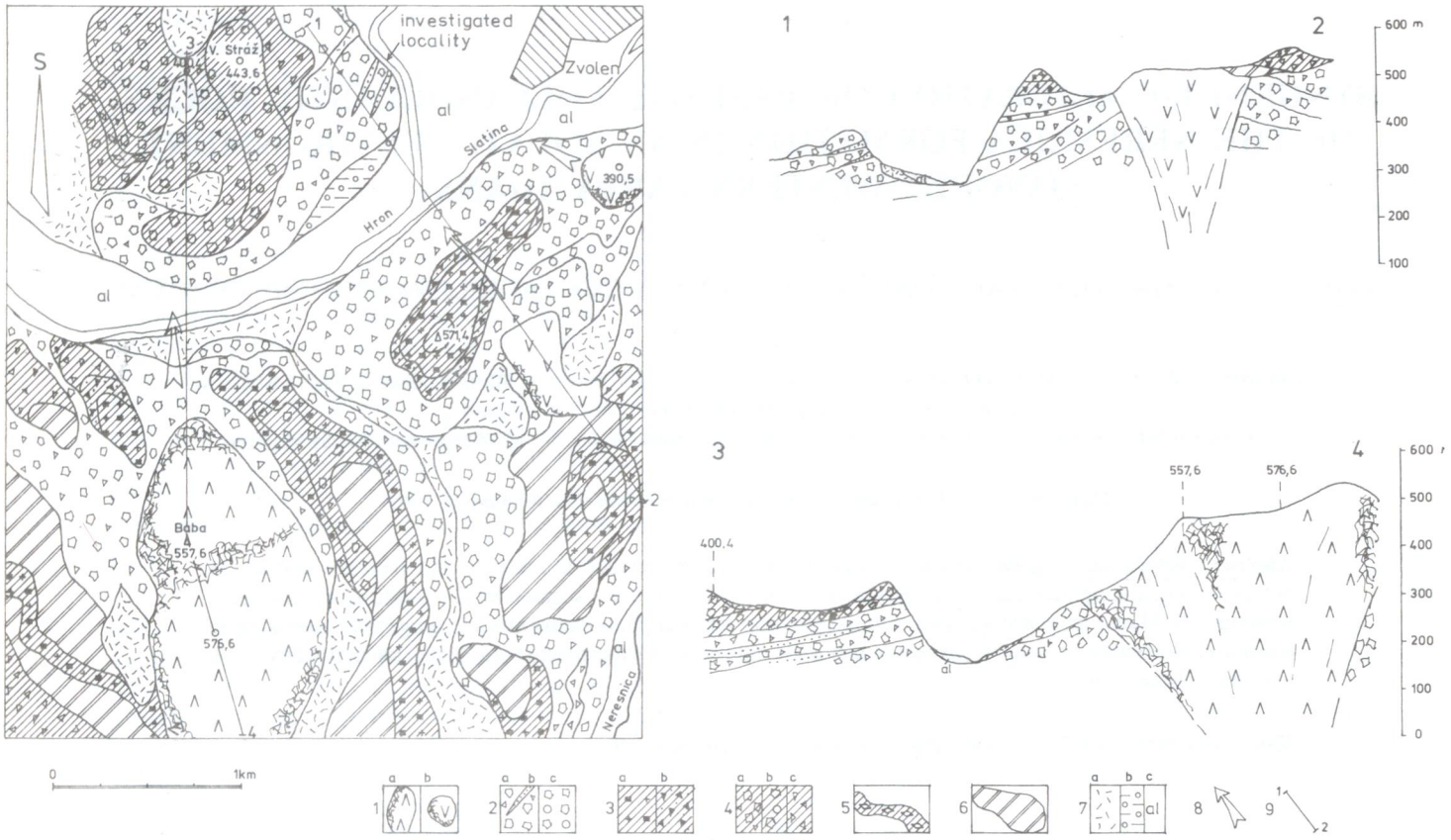

Fig. 1. Geology of the volcanic complex west and south-west of Zvolen.
The Neresnica formation: 1 - extrusive domes of hornblende-pyroxene andesite (a) and hornblende andesite with accessory hyperstene and quartz (b); 2 - fine to coarse subaquatic breccia flow deposits (a), sandstone and siltstone intercalations (b), coarse epiclastic volcanic breccias/songlomerates (c). *The Javorie formation:* 3 - pyroclastic flow breccias (a), reworked pyroclastic rocks (b); 4 - coarse epiclastic volcanic breccias (a), epiclastic volcanic breccias (b), fine epiclastic volcanic breccias; 5 - pumice tuffs; 6 - hornblende-pyroxene andesite lava flows. *Quaternary deposits*: 7 - scree (a), gravel terraces (b), recent fluvial deposits; 8 - mean direction of material transport in the Neresnica formation; 9 - sections.

The chemical composition was analysed by X-ray fluorescence and atomic absorption spectroscopy.

Electron microphotography was done on a Tesla BS 500 transmission electron microscope, by the method of a suspension dried on carbon foil.

Lithology and textures

Deposits of coarse to block breccias represent reworked products of syngenetic disintegration of growing extrusive bodies, situated 1 - 1.5 km to the south to south-east from the locality (Fig. 1). Chaotic deposition in proximity to the extrusive bodies, marked angularity of fragments, and often large dimensions of blocks (up to 80 cm, occasionally up to 3 - 4 m) are the characteristic features. The matrix is granular and detritic with a high content of small fragments often of vesicular and vitreous andesites. In the marginal parts of chaotic breccia deposits, intercalations of fine grained sandstones to conglomerates and siltstones are present. They divide individual bodies of chaotic breccias transported by means of mass movements and subaquatic sliding.

Deformation textures point to gravity instability in the course of deposition in this environment. Pressure textures in underlying siltstone layers indicate sudden deposition of coarse grained material (Fig. 2). Slip type textures in unconsolidated sediment are a frequent result of local inclination of the bottom (Fig. 3). Segmentation of siltstone inserts and movement of the divided parts in a sandy matrix occured. The present inclination of the bedded sediments 15 - 20° also bears witness to the continuing block movements after their deposition. Dislocation of the volcano-sedimentary complexes occurred with subsidence of separated blocks. Layers of siltstone - sandy sediments were amputated by this movements (Fig. 3). Movements of blocks of the gravitation slip type often used the surfaces of the favourable lithological boundaries represented by inserts and layers of fine grained sediments, dividing deposits of chaotic breccias. The beds of sandstones and siltstones were broken, crushed and dragged apart by this movement (Fig. 4). The features described are characteristic for gravitationally unstable accumulations of volcanoclastic rocks in aquatic environment.

Mineralogical composition of the alteration products

X-ray diffraction data

The individual separated size fractions of 5-2, 2-1, <1 and <0.1 μm were analysed first using X-ray diffraction. The best reflections were found with the use of the fraction <1 μm. With other fractions, the reflections were significantly lower and diffuse. Therefore in further study we used, above all, the fraction <1 μm. The X-ray diffraction results show the presence of various clay minerals. The reflections for minerals from the kaolinite group (kaolinite, halloysite) and the reflections for smectite (or mixed-layered illite/smectite with random interstratification) are the most significant. After saturation with EG, the diffraction pattern significantly changed (Fig. 6). The reflections at 15.75 and 31.40 degrees 2Θ show that it is not pure smectite, but mixed-layered illite/smectite (Srodon 1980), with a content of 10 - 15% illite layers in the structure. An unchanged reflection, in both air dried and EG state, at 12.0° 2Θ indicate the presence of halloysite, rather than kaolinite. After EG saturation a reflection between the I/S peak at 10.4° 2Θ and the peak of halloysite at 12.0° 2Θ was observed. This reflection was not visible in the air dried state. After heating all reflections in this area (10 - 17.2° 2Θ) disappeared (Fig. 5).

The X-ray diffraction pattern for oriented and randomly oriented specimens did not confirm the presence of other crystalline phases in the samples.

Transmission electron microscope data

TEM microphotographs (Fig. 7) show that material studied contains extraordinarily small particles not only in the separated samples. The average length of particles is 0.25 μm, and the average width is 0.09 μm (number of measured particles was 174). This fact also explains why we have obtained diffuse X-ray diffraction patterns using coarser fractions. At the same time, TEM shows the presence of particles with a siphonal habit, which confirms the presence of halloysite in the samples. Apart from the siphonal particles, thin particles of an isometric shape, which could belong to the identified mixed layer mineral, have been observed on the micrographs.

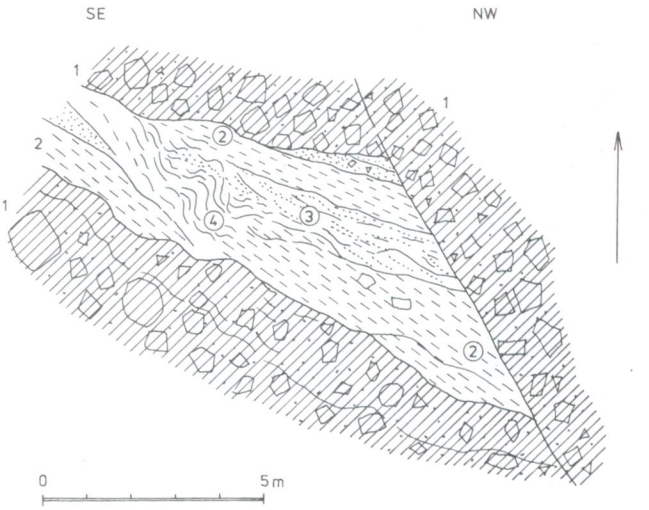

Fig. 3. Deformation of fine grained sediments by syngenetic sliding.
1 - coarse subaquatic breccia flow deposits; 2 - epiclastic volcanic siltstones; 3 - fine to medium grained epiclastic volcanic sandstones; 4 - deformation texture.

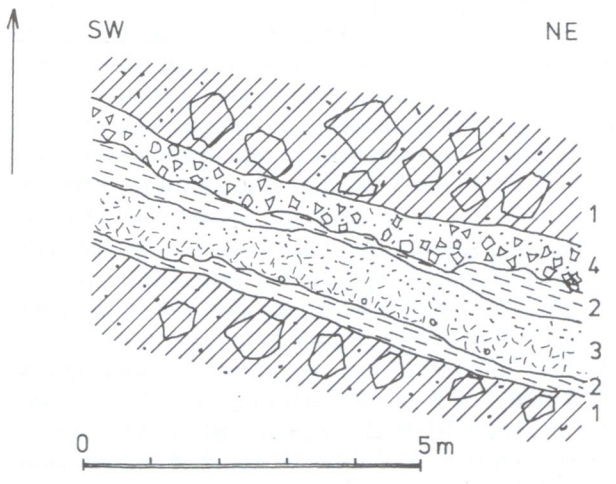

Fig. 2. Deformation of siltstone and sandstone layers by a sudden deposition of breccia flows.
1 - coarse subaquatic breccia flow deposits; 2 - epiclastic volcanic sandstone; 3 - graded coarse grained epiclastic volcanic sandstone; 4 - fine epiclastic volcanic breccia.

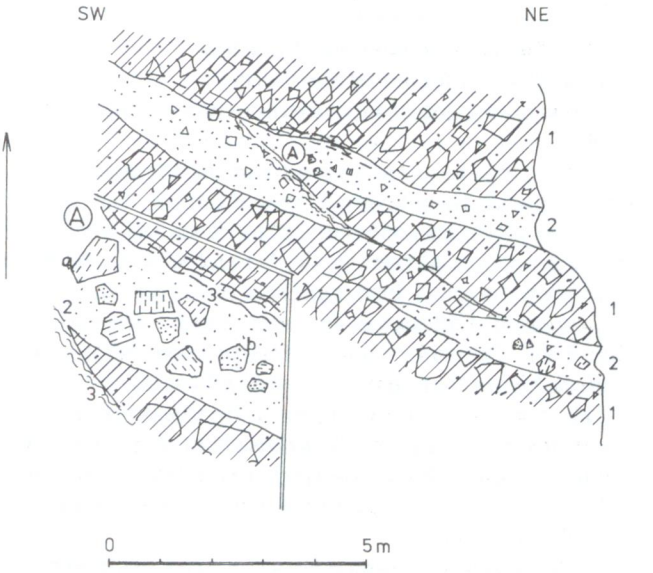

Fig. 4. Dismembering of fine grained layers by slumping.
1 - coarse subaquatic breccia flow deposits; 2 - epiclastic volcanic sandstones containing fragments of deformed siltstones (a) and fine grained sandstones (b); 3 - deformation at the base of sliding blocks.

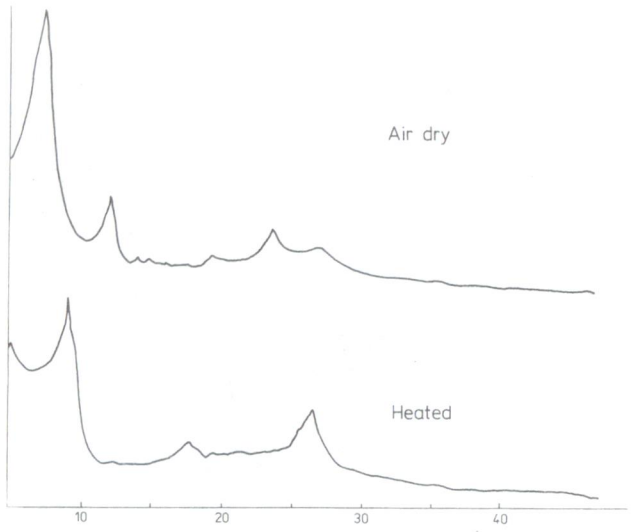

Fig. 5. X-ray diffraction patterns of air dried and heated (400 °C) specimens.

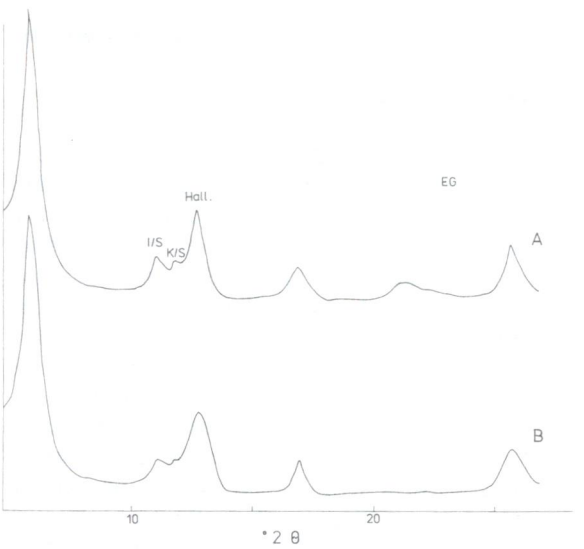

Fig. 6. X-ray diffraction patterns of glycolated specimen (A) and mixture of diffraction patterns calculated by NEWMOD computer program (B). Mixture contains 50 % of mixed-layer illite/smectite, 30 % of halloysite and 20 % of mixed-layer kaolinite/smectite.

IR data

The IR spectrum (Fig. 8) confirmed the presence of minerals of the kaolinite group (3670 cm^{-1}), as well as the presence of an I/S mineral in which the smectite has a montmorillonitic character (Russel 1987), with a relatively low content of iron in the structure. An N-H (ammonia) vibration, at 1420 cm^{-1} was also identified in the IR spectrum (Chourabi & Fripiat 1981).

Chemical composition

Chemical composition of three different whole rock samples was determined (Tab. 1):

1 - andesite unaffected by alteration

2 - andesite affected by alteration

3 - pure alteration product (without relicts of the original rock)

Comparing these analyses we can see the main differences between the individual types of sample. The content of all the elements analysed, except Fe and Al, decreased in the process of alteration. Ca, Na and K show the most significant decrease. Iron content is stable and content of Al increased. Differences in water content are also very significant. The water content of the products of alteration is much higher than that of the original rocks.

The trends mentioned are more significant in the fine fraction separated from the products of alteration. The higher content of Na in fine fraction represents exchangable cation, which was added to the samples during chemical treatment.

To identify forms in which Fe occurs, we submitted powdered samples to partial dissolution in 6M HCl (by the method according to Novák & Čičel 1978). The dissolution was brief - 5 and 10 minutes. By using such a short time, we excluded possible influence on structures of the minerals present in the samples. A minimum change of the Al content also bears witness to this. Analysis of the samples after treatment with HCl showed a significant decrease of the Fe content. It implies that the majority of Fe does not occur in the structure of the clay minerals.

Discussion

Lithology and textures of volcanoclastic rocks at the locality investigated document with the greatest probability an aquatic environment, and a dynamically changing regime of deposition. The changes are connected mainly with the stages of mass accumulation of clastic material, as well as with contemporary movements. Movements might be related to the growth of extrusive bodies, in the near to immediate surroundings, but may not exclude the existence of a body directly underlying the locality studied.

Looking at the mineralogical composition of alteration products, the presence of a reflection between 10.4 and 12.0° 2Θ on the X-ray diffraction pattern, after saturation with EG, is the most interesting. The fact that the reflection appears after the saturation with EG indicates the presence of expandable layers. The position of the reflection indicates with high probability the presence of the mixed layer mineral kaolinite (or halloysite) /smectite. To confirm this, we tested this assumption, with a model of X-ray diffraction pattern by the computer program NEWMOD (Reynolds 1985). On the basis of comparison of the modeled and experimental X-ray diffraction patterns, it was shown that mixed layer kaolinite (halloysite)/smectite with random interstratification and a smectite content of 40 - 50 %, fits best the pattern (Fig. 9). Comparing intensities of individual reflections we assume that mixed layer illite/smectite represents about 50 %, halloysite about 30

Tab. 1: Chemical composition of the samples studied measured by XRF and AAS.

	1	2	3	3A	3B	3C
SiO_2	54.10	50.24	42.31	N	N	N
Al_2O_3	15.81	19.46	21.01	22.25	20.96	20.18
TiO_2	0.94	0.91	.0.35	N	N	N
Fe_2O_3	9.10	9.01	9.08	8.08	4.70	3.86
MgO	3.08	2.78	2.33	N	N	N
MnO	0.19	0.07	0.08	N	N	N
CaO	8.19	6.99	1.80	0.06	N	N
K_2O	2.41	0.82	0.25	0.13	N	N
Na_2O	4.08	2.42	0.17	1.50	N	N
LOI	1.68	7.04	22.26	N	N	N

Explanation: 1-unaltered andesite; 2-altered andesite; 3-pure alteration product; 3A-fraction $<1\ \mu m$ of the alteration product; 3B-sample 3 after 5 minutes in 6M HCl; 3C-sample 3 after 10 minutes in 6M HCl; N-not analysed.

%, and kaolinite (halloysite)/smectite about 20 % of crystalline phases presented in alteration products. We also used these proportions for modelling the X-ray diffraction pattern of the mixture mentioned (Fig. 6).

Infrared spectroscopy shows the presence of a certain quantity of ammonium in the clay fraction. Ammonium occurs relatively frequently in the illite interlayers (Kozáč et al. 1977; Juster et al. 1987; Šucha & Širáňová 1991), so we can assume the presence of ammonium in the interstratified illite/smectite mineral identified in the clay fraction. The presence of potassium in the samples indicates that determined by chemical analysis (Tab. 1) we can assume a combination of K and NH_4 as cations fixed in the illite interlayers. Different properties of potassium and ammonium could underestimation the content of illite layers obtained by the method of Srodon (1980). However, the difference could not exceed 5 - 8 % (Šucha & Širáňová 1991).

Considering the possible origin of alteration products it is necessary to take into account not only the mineralogical composition, but also the properties of the environment, and especially the simultaneous effects of an aquatic environment and the heat of volcanic products. We assume that the presence of hot solutions (mixed-layered illite/smectite with a high content of smectite layers indicates that their temperature could not have been very high), caused significant mineralogical and chemical transformation of the primary rocks. The combination of alterations dependent on solutions of raised temperature with lithological phenomena indicating subaquatic breccia flows implies that breccia flows were not syngenetic with the growth of extrusive bodies in an aquatic environment.

Fig. 7. TEM micrograph of studied sample prepared by suspension method.

Conclusion

The material studied represents a product of syngenetic alteration of glassy andesite material in an aquatic environment. From the mineralogical point of view alteration products are formed exclusively by clay minerals, of very small sizes, and non-crystalline forms of Fe. Clay minerals identified in the samples represent a mixture of halloysite, together with mixed layer illite/smectite and kaolinite(halloysite)/smectite with random interstratification (R=0). The I/S mineral contains perhaps 10 - 20% of illite layers in its structure. The illite interlayer is probably occupied by both potassium and ammonium.

During alteration a significant decrease of the content of Na, Ca and K, occurred. The content of aluminium increased, and the Fe content remained unchanged. The majority of iron occurs outside the structure of the minerals present in the samples.

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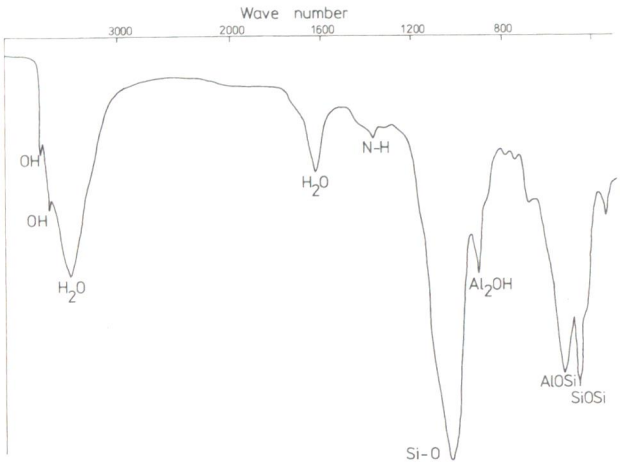

Fig. 8. Infrared spectra of fraction $<1\,\mu$m.

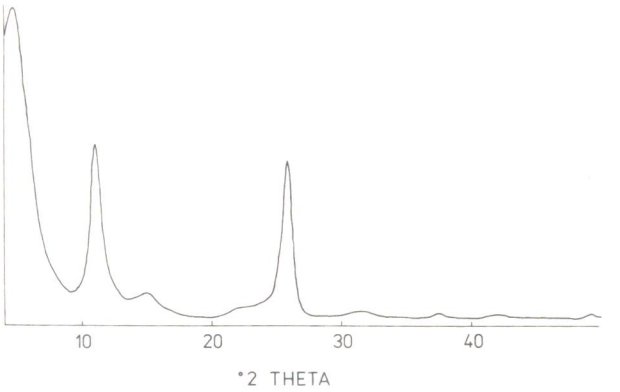

Fig. 9. X-ray diffraction pattern of mixed-layer kaolinite/smectite calculated by NEWMOD program with 60 % of kaolinite and 40 % of smectite (R=0).

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