GEOLOGICA CARPATHICA - SERIES CLAYS, 1, BRATISLAVA, JUNE 1992

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# MIXED - LAYER ILLITE/SMECTITE FROM THE DOLNÁ VES HYDROTHERMAL DEPOSIT, THE WESTERN CARPATHIANS KREMNICA MTS.

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**Abstract:** Mixed-layer illite/smectite minerals from the Dolná Ves hydrothermal deposit were studied. Expandability ranged between 45 to 6 %. Two types of interstratification R1 and R3, were observed, and only 1M polytype was found. The variability in chemical composition of the I/S minerals was small. Layer charge is mainly tetrahedral. Mixed-layer I/S minerals were formed by reaction between K-bearing hydrothermal solutions and smectites. A zonation in expandability was observed in the studied area. It decreases from the south to the north and is related to decrease of the temperature of hydrothermal solution coming from the north. The solutions probably had temperatures that ranged between 120 to 200 °C.

**Key words**: illite/smectite, expandability, illite polytypes, chemical composition, IR spectroscopy, hydrothermal activity.

## Introduction

Mixed-layer illite/smectite is one of the most abundant clay minerals in the Earth crust. It is frequently used as an indicator of burial history (diagenesis or anchimetamorphosis) in clay-rich sediments (Burst 1959; Perry & Hower 1970; Weaver & Beck 1971; Hower et al. 1976; Środoń 1979; Jennings & Thompson 1986; Hunziker et al. 1986; etc.). Studies of illite/smectite minerals also give information about hydrothermal processes, particularly those in active geothermal regions (Eslinger & Savin 1973; McDowell & Elders 1980) and in hydrothermal ore fields (Böhmer et al. 1969; Matsuda et al. 1981; Kraus et al. 1982b; Inoue & Utada 1983; Horton 1985; Eberl et al. 1987).

The first report concerning minerals with mixed-layer clays structure in the Dolná Ves region was published by Kraus (1977). The present paper discusses some of the mineralogical aspects of smectite to illite conversion in a hydrothermal environment.

## Geological setting

The region studied is situated in S-W part of Kremnica Mts. It is a part of the Jastrabá Formation which represents discontinuous sets of volcanic extrusions, flows and volcanoclastics of rhyolitic composition with apparent connection to a North-South fault system. The age of Jastrabá Formation was estimated according paleontological data as Upper Sarmatian - Lower Pannonian ( Konečný et al. 1983).

Most of the rocks of this region are composed of rhyolitic volcanoclastics of explosive origin (Bezák & Lexa 1983). A typical feature of the final volcanic activity was sedimentation of volcanic sediments in lacustrine and fluviolacustrine environments, where they were preferentialy converted to clay minerals.

Four different mineralogical associations (see Fig. 1) were distinguished in these clays (Kraus et al. 1982a):

*1* - smectite kaolinite and cristobalite;

*2* - kaolinite smectite, halloysite and cristobalite;

*3* - mixed-layer illite/smectite kaolinite and quartz;

*4* - mordenite and clinoptilolite kaolinite, smectite and cristobalite.

Two types of mixed-layer I/S minerals were delineated in the Dolná Ves hydrothermal deposit, based on their geotechnical properties (Fig. 2). The first type has a large amount of the fine, less than 0.002 *mm* fraction (> 70 %) and a very small amount of the fraction >0.063 *mm* (< 15 %). The second type has a relatively large percent of the material > 0.063 *mm* (about 45 %). Thickness of the deposit ranges between 2 and 55 *m*.

## Material and methods

All studied samples come from shallow wells (up to 50 *m*) covering the entire areal extent of the hydrothermal deposit. Collected samples were mixed with distiled water and disaggregated using an ultrasonic probe. Then the fraction less than 2 $\mu m$ and less than 1 $\mu m$ were separated. Samples were treated before separation with Na-acetate buffer and Na-dithionite (Jackson 1975). Separated fractions were exchanged with 1N NaCl, 1N $SrCl_2$ or 1N KCl to produce Na, Sr or K form. Excess salts were removed by dialysis.

X-ray diffraction (XRD) analysis was carried out using Philips 1075 and Siemens D 500 diffractometers using CuK $\alpha$–radiation. Oriented specimens were prepared by sedimentation of the fine fraction on glass slides (10 $mg/cm^2$). The X-ray slides were analysed in air dried state, and after saturation by ethyleneglycol (8 hours at the temperature of 60 °*C*). Randomly oriented specimens were prepared by mixing the fraction with colophony.

Chemical compositions were determined in 2 $\mu m$, Na-saturated fraction. Si, Al, Mg, Ca, Fe were analysed by spark emission spectroscopy, and Na and K were analysed by flame spectrometry. Exchange cations were replaced by anilinhydrochloride (Mocik et al. 1973) and analysed by atomic absorption spectroscopy. Fine, 2 $\mu m$ fraction separated without any chemical treatment, was used for this determination.

Infrared spectra were carried out with a Perkin-Elmer 500 spectrophotometer. Analysed pellets were prepared by pressing the fine fraction with KBr (0.7 or 1.5 *mg* of sample with 200 *mg* KBr).

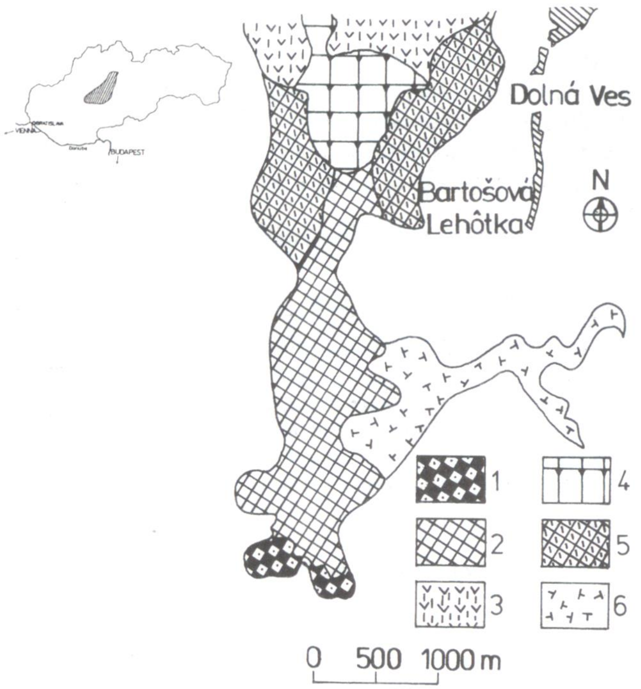


**Fig.1.** Regional distribution of mineralogical associations of SW part of Kremnica Mts.
1 - smectite; 2 - smectite ± kaolinite and cristobalite; 3 - kaolinite ± smectite, halloysite and cristobalite; 4 - mixed layer illite/smectite ± kaolinite and quartz; 5 - kaolinite, smectite and cristobalite; 6 - mordenite and clinoptilolite ± kaolinite smectite and cristobalite (according Kraus et al. 1982a).

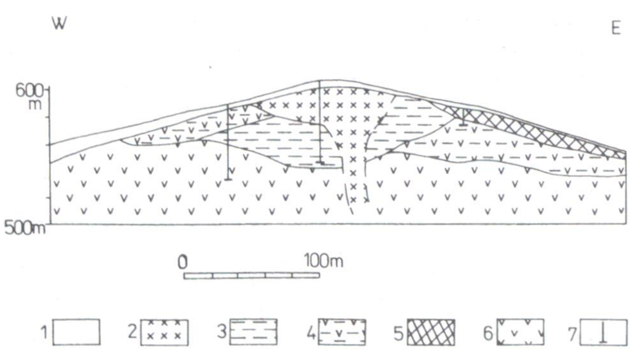


**Fig. 2.** Geological section of Dolná Ves deposit.
1 - overburden; 2 - altered rhyolites; 3 - rhyolitic tuffs with mixed layer I/S minerals of the first technological type; 4 - rhyolitic tuffs with mixed layer I/S minerals of the second technological type; 5 - rhyolitic tuffs with smectites; 6 - non altered rhyolitic tuffs; 7 - wells.

## Results

### *Expandability*

The expandability of mixed-layer illite/smectite minerals was determined from XRD pattrens by using the method published by Środoń (1984). Expandability ranged between 45 and 6 % (Fig. 3a).

The samples with the highest expandability were formed in the south part of the deposit and the most illitic samples came from the north part. No vertical zonation of expandability has been observed in the studied wells. R1 interstratification (Drits & Sakharov1976; Reynolds 1980; Watanabe 1988) was identified for I/S minerals having expandability >15 %. Ordering becomes R3 in samples with expandabilities less than 14 to 15 %. We looked for R2 interstratification, which could exist in the expandability interval between 15 and 35 % (Inoue & Utada 1983), by comparing our XRD patterns with published diagrams (Drits & Sakharov 1976), and by calculating XRD patterns using the NEWMOD computer program (available R.C. Reynolds, Dept. of Earth Sciences, Dartmouth College, Hanover, NH 03755 USA). We did not find any sample with R2 interstratification (Fig. 3b).

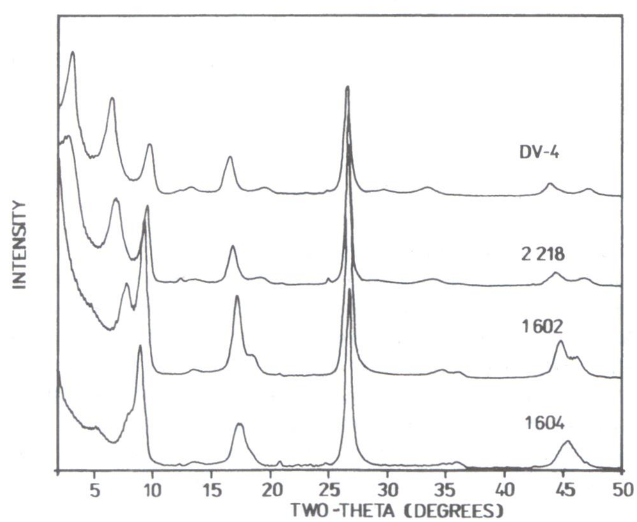


**Fig. 3a.** X-ray diffraction patterns of mixed layer I/S minerals after EG saturation (expandability 45, 29, 14, 6 %).

The samples with the largest amount of expandable layers are K-rectorites with regularly interstratified 1.0 and 1.7 *nm* layers. Such interstratification leads to a first basal reflection having a *d*-value of 2.7 *nm* (Fig. 3). The position of this peak which is found at a very low 2 theta angle, could be affected by several

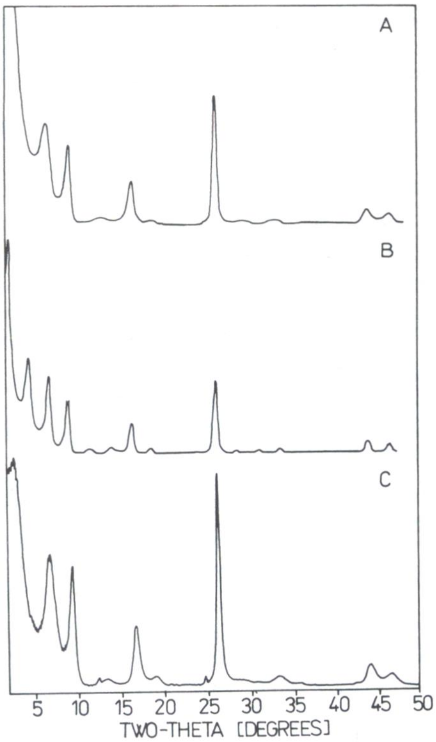


**Fig. 3b.** X-ray diffraction pattern of I/S minerals (expandability 29 %) with interstratification R1 (A) and R2 (B) calculated using computer program NEWMOD. C - real XRD pattern of sample 2218 (29 % of expandability).

XRD factors (Reynolds 1980). Therefore the existence of K-rectorite required independent proof. We tried to verify its occurrence by measuring particle thickness distributions, using transmission electron microscopy of sample 2838 (expandability 36 %). The measured distribution, obtained according to the methods described by Nadeau & Tait (1987), have an unambiguous distribution maximum at a thickness of 2 *nm* (Fig. 4). This result indicates that the fundamental particles are two 2 : 1 layers thick, layers that are presumably joined together by fixed K-ions. According to the theory of interparticle diffraction (Nadeau et al. 1984; Środoń et al. 1990), an expanding layer is situated between two TEM fundamental particles. This gives rise to

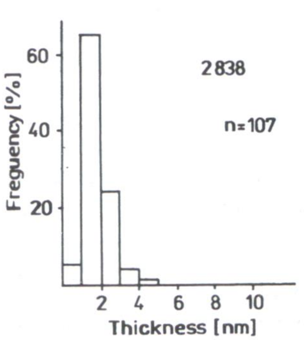


**Fig. 4.** Particle thickness distribution histogram of illite particles measured by TEM on sample 2838.

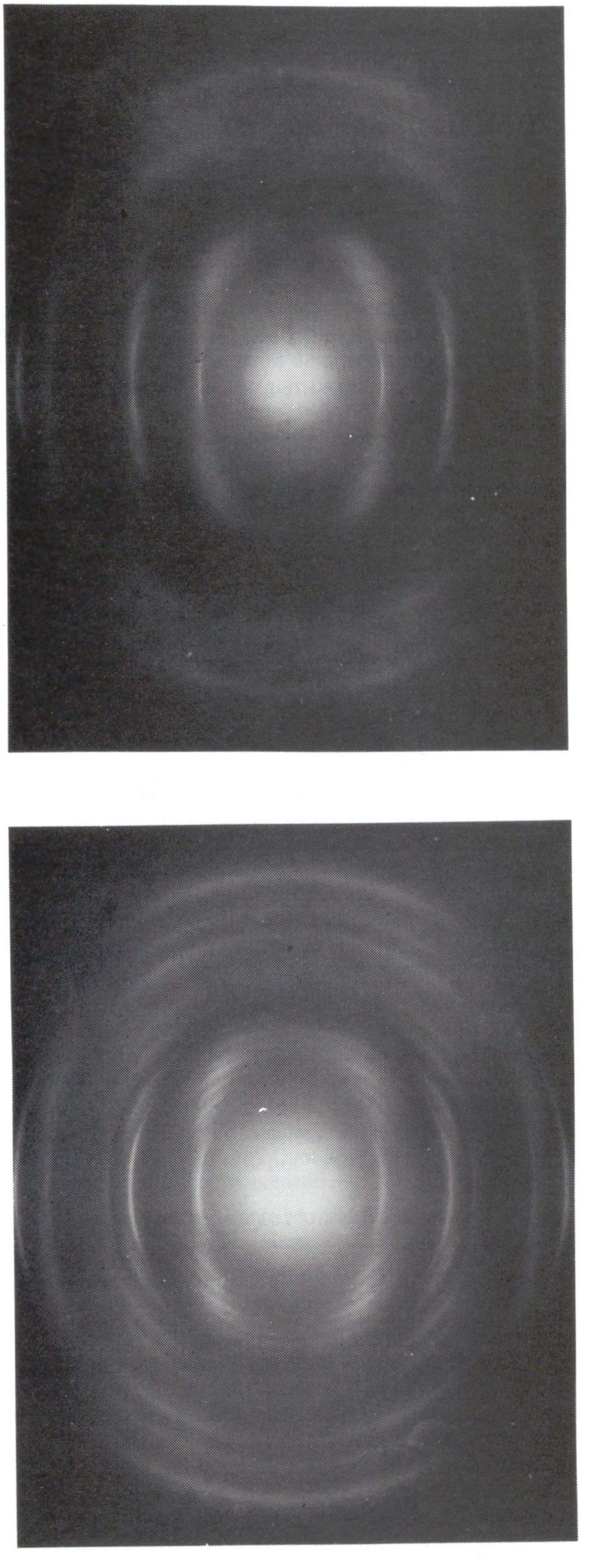

**Fig. 5.** Oblique texture micrographs. A - sample DV-4 disordered type, polytype 1M; B - sample 1603 ordered type, polytype 1M.

regular interstratification of expandable and non-expandable layers in the sample.

### *Polytype analysis*

XRD patterns of randomly oriented specimens were used for the polytype analysis. Polytypes were identified on the basis of modelled XRD patterns (Weiss & Wiewióra 1986). Peaks typical for 1M polytype were observed in all samples. The reflections are more diffuse with increasing expandability. The more illitic samples (expandability 14 %) were clear 1M polytypes. No reflection of the 2M polytype was found.

Similar results were obtained by oblique texture method (measured on samples 1603, 1602, 2218 and DV-4). The 1M polytype was identified in all samples. There were, however, some differences in the ordering of the structure (Fig. 5). The best ordering was observed in sample 1603 (expandability 10 %) and the worst in sample DV-4 (expandability 45 %).

In addition to the polytypes, chracteristics of unit cell also were determined by oblique texture method (Tab. 1). Reflection intensity distribution of the sample 1603 is typical for dioctahedral Al-illites. Parameter -c.cos$\beta$/a is higher than 1/3 indicating that octahedral trans-positions are vacant (Tsipursky & Drits 1984). It is typical feature of dioctahedral illite polytypes with -c.cos$\beta$/a value 0.36 - 0.37 (Soboleva 1987). Sample 1602 has ordering similar to sample 1603, but -c.cos$\beta$/a value is considerably lower, close to 1/3.. Sometimes this phenomenon could be caused by high amount of Li which could fill vacancies in octahedral position (Soboleva 1987).

Chemical analysis of studied samples showed low amounts of Li (Tab. 2). Another possibility to account for the phenomenon would be an equal distribution of octahedral cations (Tsipursky & Drits 1984). Sample 2218 is identical to sample 1602 but it clearly has lower structural ordering. Sample DV4 has the smallest structural ordering.

**Table 1:** Parameters of elementary cells, measured by oblique texture method.

| Sample | a [*nm*] | b [*nm*] | c [*nm*] | *beta* | -c.cos$\beta$/a |
|---|---|---|---|---|---|
| 1603 | 0.5170 | 0.8956 | 1.0112 | 100.58 | 0.359 |
| 1602 | 0.5191 | 0.8993 | 1.0118 | 99.84 | 0.333 |
| 2118 | 0.5189 | 0.8989 | 1.0146 | 99.75 | 0.331 |
| DV-4 | 0.5180 | 0.8970 | 1.0170 | 99.60 | 0.327 |

### *IR spectra*

Samples representing the whole expandability interval (45 - 6 %) of the Dolná Ves hydrothermal deposit were analysed by IR-spectroscopy in interval 4000 - 300 $cm^{-1}$. One sample was pure smectite (100 % expandability), which was not affected by hydrothermal alteration (Fig. 2, part 5).

Wave numbers of identified vibrations are listed in Table 3. Wave numbers of OH vibrations of all observed samples are more-less the same, about 3630 $cm^{-1}$. This position suggests that the composition of expandable layers in I/S minerals is close to that of montmorillonite (Russel 1987). The position of the OH vibration of the pure smectite sample is the same.

Wave numbers of all other vibrations in the measured interval were very similar, without any relation to change of expandable layer content. However, in comparison with pure smectite (not altered by K-hydrothermal solutions), we did observed a decrease in the wave number of the AlMgOH vibration for the I/S minerals. Tetrahedral Al-O-Si vibrations (750 $cm^{-1}$) were not found in pure smectites, but the vibration increased with decreasing expandability. This observation is similar to previous ones published by Flehmig & Gehlken (1988) and Inoue & Watanabe (1989).

**Table 2:** Li content of studied I/S minerals determined by AAS.

| Sample | Li [ppm] |
|---|---|
| 1555 | 5.0 |
| 2199 | 10.6 |
| 2204 | 8.8 |
| 2211 | 11.3 |
| 1602 | 1.4 |
| 1603 | 2.5 |

Analyzed by E. Martíny.

**Table 3:** Wave numbers of identified vibrations of smectite (JP-1) and I/S minerals from Dolná Ves deposit.

| Sample | Infrared absorption bands [$cm^{-1}$] | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| JP-1 | 3630 | N | 912 | 840 | 792 | - | - | 698 | 624 | 530 | 480 |
| DV-4 | 3636 | 1030 | 920 | 825 | - | - | 755 | 698 | 620 | 533 | 480 |
| DV-3 | 3630 | 1030 | 919 | 825 | - | - | 755 | 697 | 621 | 530 | 475 |
| 2218 | 3630 | 1040 | 919 | 825 | 800 | - | 757 | 697 | 620 | 531 | 478 |
| 1555 | 3630 | 1025 | 915 | 829 | 800 | 780 | 758 | 700 | 621 | 529 | 478 |
| 1602 | 3630 | 1038 | 917 | 828 | 801 | 780 | 755 | 700 | 618 | 528 | 480 |
| 1603 | 3632 | 1031 | 920 | 827 | 801 | 780 | 759 | 698 | 621 | 529 | 478 |
| 1604 | 3630 | 1024 | 919 | 829 | 803 | 780 | 754 | 700 | - | 532 | 480 |

### *Chemical composition*

Chemical composition and calculated crystallochemical formulas of studied mixed-layer I/S minerals in Na-form are listed in Tabs. 4 and 5. Sodium was determined separately by analyzing clays in Sr-form. Na was extremely low (in most samples less than 0.01 %) therefore the clays did not contain fixed Na. A very low content of Na also was found during exchange cation determination (Fig. 6). Sodium was probably transported with potassium from original rhyolitic tuffs during alteration, thereby allowing smectite to form. Then potassium was reintroduced into the rocks by hydrothermal solutions to form illite. The whole rocks with I/S contain 3 times more K than do whole rocks that contain pure smectites (Tab. 6), giving evidence for this history.

The chemical composition of the I/S minerals is quite monotonous. Also, the layer charge of these minerals is fairly constant, concenrated mainly in tetrahedral sheets (Fig. 7). Octahedral charge is low.

Expandability correlates with amount of fixed cations in interlayer (Fig. 8). A good relation with correlation coeficient -0.79

**Table 4:** Chemical composition of the fine fraction of mixed layer I/S minerals and smectite (JP-10 from Dolná Ves hydrothermal deposit.

| Sample | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $K_2O$ | $Na_2O$ | L OI |
|---|---|---|---|---|---|---|---|---|
| 1604 | 48.6 | 26.9 | 3.7 | 1.58 | 0.7 | 8.09 | 0.05 | 8.54 |
| 1603 | 53.6 | 26.9 | 2.8 | 1.59 | 0.1 | 7.15 | 0.02 | 7.11 |
| DV-2 | 53.7 | 28.8 | 1.9 | 1.16 | 0.3 | 6.49 | 0.23 | 6.64 |
| 1602 | 54.2 | 30.1 | 1.0 | 1.46 | 0.1 | 6.87 | 0.50 | 6.59 |
| 2227 | 54.2 | 27.4 | 3.5 | 0.93 | 0.1 | 5.79 | 0.72 | 7.56 |
| 2204 | 52.8 | 28.2 | 2.8 | 1.35 | 0.1 | 5.82 | 0.81 | 7.89 |
| 2211 | 52.0 | 28.1 | 3.4 | 1.11 | 0.1 | 5.72 | 0.82 | 8.11 |
| 2217 | 50.8 | 29.4 | 3.3 | 0.97 | 0.1 | 6.00 | 0.48 | 7.77 |
| 1555 | 52.9 | 29.3 | 2.9 | 0.85 | 0.1 | 6.17 | 0.82 | 6.99 |
| DV-1 | 53.6 | 30.1 | 2.3 | 0.62 | 0.1 | 5.97 | 0.55 | 6.34 |
| 2199 | 52.8 | 27.4 | 3.0 | 1.11 | 0.1 | 5.55 | 0.91 | 8.95 |
| 2223 | 53.5 | 28.2 | 2.9 | 1.55 | 0.1 | 5.55 | 0.92 | 7.44 |
| 2218 | 50.8 | 29.7 | 2.9 | 0.67 | 0.3 | 5.18 | 0.79 | 7.51 |
| 1616 | 52.8 | 27.7 | 1.6 | 1.66 | 0.1 | 5.37 | 1.10 | 7.77 |
| 1623 | 53.2 | 28.0 | 1.5 | 2.05 | 0.1 | 5.57 | 0.97 | 7.20 |

**Table 5:** Crystallochemical formula of clays from Dolná Ves.

| Sample | Si | Al(IV) | Al(VI) | Fe | Mg | Ca | Na | K |
|---|---|---|---|---|---|---|---|---|
| 1604 | 3.39 | 0.61 | 1.62 | 0.19 | 0.17 | 0.00 | 0.05 | 0.72 |
| 1603 | 3.57 | 0.43 | 1.69 | 0.14 | 0.16 | 0.00 | 0.00 | 0.61 |
| DV-2 | 3.54 | 0.46 | 1.78 | 0.09 | 0.11 | 0.02 | 0.03 | 0.54 |
| 1602 | 3.51 | 0.49 | 1.80 | 0.05 | 0.14 | 0.00 | 0.06 | 0.56 |
| 2227 | 3.57 | 0.43 | 1.71 | 0.17 | 0.09 | 0.00 | 0.09 | 0.48 |
| 2204 | 3.51 | 0.49 | 1.72 | 0.14 | 0.13 | 0.00 | 0.10 | 0.49 |
| 2211 | 3.49 | 0.51 | 1.72 | 0.17 | 0.11 | 0.00 | 0.10 | 0.49 |
| 2217 | 3.43 | 0.57 | 1.76 | 0.16 | 0.09 | 0.00 | 0.06 | 0.51 |
| 1555 | 3.48 | 0.52 | 1.76 | 0.14 | 0.08 | 0.00 | 0.10 | 0.52 |
| DV-1 | 3.50 | 0.50 | 1.82 | 0.11 | 0.06 | 0.00 | 0.07 | 0.49 |
| 2199 | 3.55 | 0.45 | 1.72 | 0.15 | 0.11 | 0.00 | 0.12 | 0.48 |
| 2223 | 3.52 | 0.48 | 1.71 | 0.14 | 0.15 | 0.00 | 0.12 | 0.46 |
| 2218 | 3.44 | 0.56 | 1.80 | 0.14 | 0.06 | 0.02 | 0.10 | 0.44 |

(significant at a probability level of 99.9 %) between $K_2O$ and expandability was obtain. The content of fixed cations increases with decreasing of expandability.

## Discussion and conclusion

Expandability in the Dolná Ves hydrothermal deposit increases from the north to the south. This increase also probabaly marks the direction of K-hydrothermal solution transport. It also corresponds with geologic data concerning the direction of fluid transport in the Kremnica polymetallic ore field (Böhmer 1966; Böhmer et al. 1969). The border between occurrence of mixed layer I/S and pure smectites is very sharp. We suggest that this border marks the border of K-hydrothermal activity. The problem is to explain the cause of the systematic change of expandability. There are two possibilities:

*1* - decrease of temperature from north to south during penetration of hydrothermal solutions.

*2* - decrease in potassium content of the hydrothermal solutions from north to south.

Test of K - fixation in samples with highest expandability could support first possibility. If the expandability trend is related only to a trend in the potassium content of the solutions, then smectite layers should irreversibly collapse after KCl treatment in laboratory (Whitney & Northrop 1987). Several samples were subjected to 10 wetting and drying cycles in KCl solution (method according Eberl et al. 1986) but no potassium was fixed in smectites.

The expandability of mixed-layer illite/smectite often correlates with the temperature of active geothermal environments and is used as a paleothermometer. We also attempted to esti-

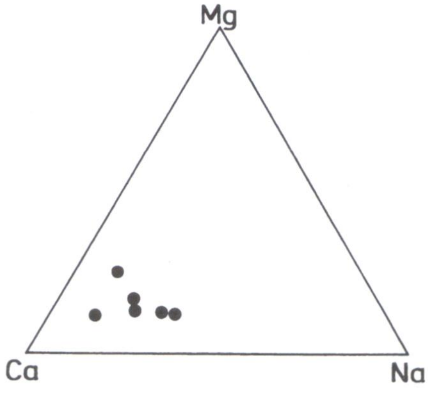


**Fig. 6.** Distribution of exchange cations in mixed layer I/S minerals.

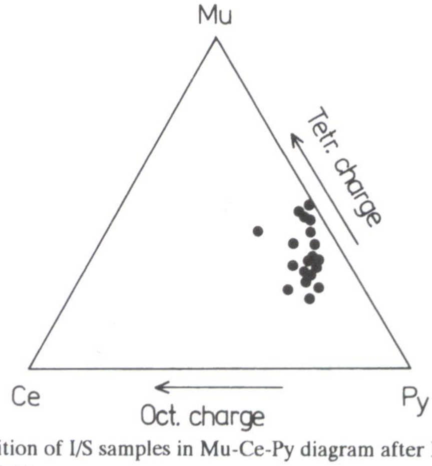


**Fig. 7.** Position of I/S samples in Mu-Ce-Py diagram after Hower & Mowatt (1966).

**Table 6:** Whole-rock chemical analyses of samples from the Dolná Ves hydrothermal region.

| | 1 | 2 | 3 |
|---|---|---|---|
| $SiO_2$ | 73.84 | 66.49 | 76.20 |
| $Al_2O_3$ | 11.60 | 19.72 | 13.70 |
| $Fe_2O_3$ | 2.90 | 2.46 | 1.48 |
| $TiO_2$ | 0.14 | 0.32 | 0.09 |
| CaO | 1.26 | 0.64 | 0.17 |
| MgO | 0.63 | 0.51 | 0.61 |
| $K_2O$ | 4.00 | 1.15 | 3.90 |
| $Na_2O$ | 2.12 | 0.06 | 0.04 |
| LOI | 2.96 | 5.69 | 3.66 |

1 - unaltered rhyolite; 2 - altered rhyolitic volcanites; mean value, n = 3; 3 - rocks containing I/S minerals; mean value, n = 8.

mate the temperature of I/S formation in the studied area by correlation with data from the East Slovak Basin (Šucha 1991; Šucha et al. in press). Bentonites in this region, having similar origin as in the Dolná Ves region, were converted to illite/smectite minerals by burial diagenesis. The temperature of this conversion was measured directly in wells (Král et al. 1985). Using the data from the East Slovak Basin we estimated lower temperature limit (100 - 130 °C) in the Dolná Ves region. The upper temperature limit could not be estimated using this extrapolation because the highest illitic material in the East Slovak Basin still has an expandability of 18 %. An upper limit (about 200 °C) was estimated by analogy to other papers dealing with the same type of clays (McDowell & Elders 1980; Horton 1985; Eberl et al. 1987). This temperature correlates well to the temperatures given by quartz inclusions from ore veins (240 - 260 °C, Böhmer 1966).

The polytype distribution of the I/S minerals showed no relation to expandability. The 1M polytype was identified in all samples by two independent methods. Inoue et al. (1988) studying similar hydrothermal set of minerals observed both 1M and 2M polytypes in the expandability interval between 20 and 12 %, and dominantly a 2M polytype in samples with expandabilities less than 12 %.

The existence of minerals with different distributions of cations in octahedral positions situated very close one to another is a new observation which deserves separate study on bigger number of samples

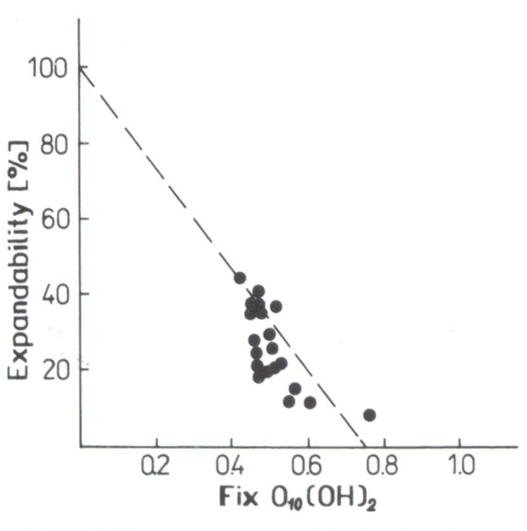


**Fig. 8.** Expandability versus amount of fixed cations from the interlayer.

**Acknowledgement**: The study was completed within the Grant 120 at the Slovak Academy of Sciences. The authors thank J. Środoń and D. D. Eberl for helpfull comments and fixing English, B. Čížel for providing us 4 of the samples and E. Martíny for AAS analyses.

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