

HYDROTHERMAL ALTERATION OF A SERPENTINITE NEAR TAKOVO, YUGOSLAVIA, TO CHROMIUM-BEARING ILLITE/SMECTITE, KAOLINITE, TOSUDITE, AND HALLOYSITE

ZORAN MAKSIMOVIC

Faculty of Mining and Geology, University of Belgrade, Yugoslavia

G. W. BRINDLEY

Mineral Sciences Building, the Pennsylvania State University
University Park, Pennsylvania 16802

Abstract—Hydrothermal alteration products of serpentinite near Takovo, Yugoslavia, were studied by X-ray powder diffraction and chemical analysis. A zone of mainly blue clays adjacent to the hydrothermal vein contains intimately associated chromium kaolinite and tosudite at higher hypsometric levels and chromium halloysite(10Å) form at lower levels. A second zone of green clays contains principally illite/smectites, with predominantly illite layers nearer the first zone and smectite layers at greater distances. The potassium content diminishes as the proportion of illite layers diminishes. The composition of the smectite layers in the illite/smectite with the least proportion of illite is shown to be beidellitic. The mineralogical and chemical changes across the zone of alteration are interpreted in terms of two stages of alteration in which the second is more acidic than the first and is responsible for the inner zone of chromium-bearing kaolinite and tosudite and chromium halloysite.

Key Words—Cr-halloysite, Cr-illite/smectite, Cr-kaolinite, Cr-tosudite, Hydrothermal, Serpentinite.

INTRODUCTION

The hydrothermal alteration of serpentinite in the region of Takovo, Yugoslavia, was studied by Maksimovic (1952) as part of a detailed geologic mapping of the area. The hydrothermally altered zone, approximately $3.5 \times 0.2 \text{ km}^2$ in area, contains silicified serpentinite with pyrite, cinnabar, and rarely stibnite. The argillic zones, in some places up to 10 m thick, contain chromium-bearing kaolinite or halloysite in the inner part and smectites in the outer part. Some of these alteration products were described previously by Maksimovic and Crnkovic (1968), Maksimovic (1972), and Maksimovic and White (1973).

The incentive to reexamine the argillic zones in more detail was the discovery of tosudite in association with the kaolinite, and of variously interstratified illite/smectites. The mineral tosudite was named by Frank-Kamenetsky *et al.* (1965) in recognition of the work of Toshio Sudo who identified this mineral as a regularly interstratified dioctahedral chlorite/dioctahedral smectite (see Sudo and Shimoda, 1978, particularly Ch. 2 and 8). With additional chemical and mineralogical data, it is now possible to present a more detailed and integrated account of the alteration processes which have occurred in the original serpentinite.

EXPERIMENTAL

Selection of material for detailed study was undertaken entirely by one of us (Z.M.). Material was obtained mainly from preliminary mining operations in

1951. Two adits at levels 12 m apart provided materials that suggested certain differences in the alteration processes with depth. When exploration work ceased at the end of 1951, the two adits collapsed. Additional samples were collected more recently from surface exposures.

Laboratory studies included X-ray powder diffraction (XRD) analysis with Ni-filtered $\text{CuK}\alpha$ radiation and $1^\circ 2\theta/\text{min}$ recording rate. Oriented samples on glass slides and random powder mounts were used. Materials were examined in relative humidities from near 100% RH to near 0% RH at room temperature, at elevated temperatures mainly 20–200°C, and after ethylene glycol saturation at about 40°C for several days.

Chemical analyses were carried out on a few samples by wet chemical methods and on a wide range of samples by using a Kevex attachment for EDX analyses with a scanning electron microscope (I.S.I.-Super IIIA model) and also by electron microprobe analysis using an ARL instrument.

RESULTS

Zonal alteration of the serpentinite

The mineralogical and chemical data will be discussed in relation to five major zones as follows: I, the hydrothermal vein; II, an argillic zone ranging in color from pale to dark blue; III, an argillic zone of green coloration; IV, a zone of partial alteration; and V, the unaltered serpentinite.

The bulk chemical variations across these zones

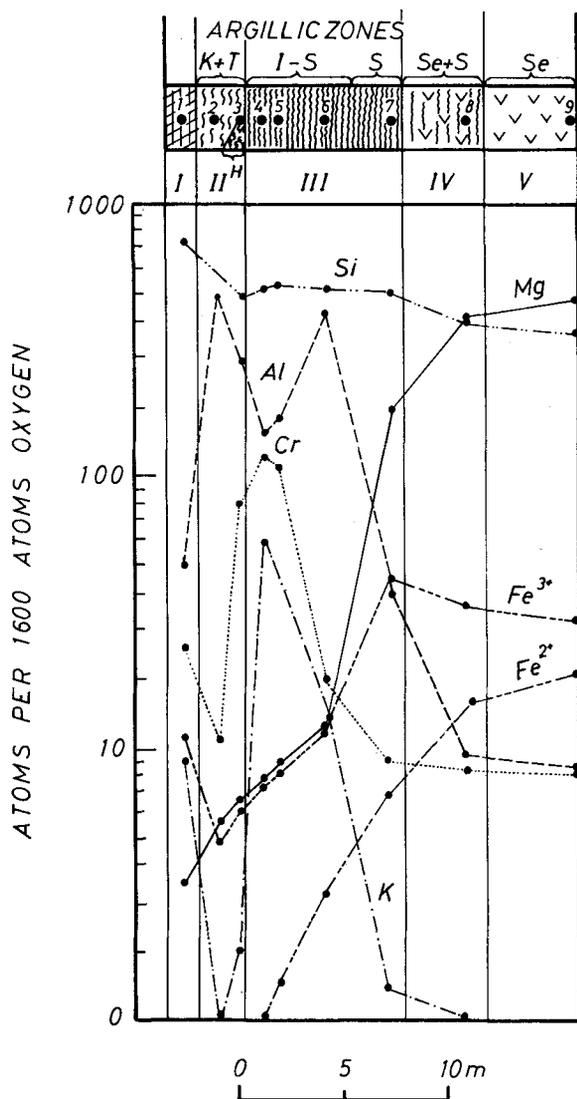


Figure 1. Variation of atomic proportions across the zones of alteration in serpentinite at Takovo, Yugoslavia. K = kaolinite, T = tosudite, H = halloysite, I = illite, S = smectite, Se = serpentinite containing mainly lizardite. (●) points of sampling.

were broadly established by Maksimovic and Crnkovic (1968). They can now be given in more detail, as shown in Figure 1, where atomic proportions with respect to 1600 oxygen atoms are plotted on a logarithmic scale against distance from the hydrothermal vein. This representation follows essentially that introduced by Barth (1948; 1952, p. 82 *et seq.*). The data are based on eleven chemical analyses and nine Kevex EDX analyses.

Prior to the hydrothermal alteration, the serpentinite was fractured and under tectonic pressure became more or less schistose. The remains of this schistosity are seen throughout the alteration zone and indicate a

Table 1. X-ray basal reflections (00 ℓ) from tosudite, Takovo, Yugoslavia.

ℓ	d (Å)	I	d (Å)
1	29.7	~80	29.7
2	14.7	100	29.4
3	9.71	7	29.1
4	nr	—	—
5	—	—	—
6	4.957	25	29.74
7	—	—	—
8	nr	—	—
9	3.306	6	29.75
10	2.951	6	29.51
11	2.671	5	29.38
15	1.983	2	29.74
18	1.656	4	29.80
20	1.489	3	29.78

nr = not resolved.

metasomatic process without appreciable volume changes.

The minerals of zone II

The principal minerals are pale blue Cr-bearing kaolinite and tosudite, and deep blue halloysite (10-Å form). The latter appears to be predominant at the lowest accessible levels where, in the samples examined, tosudite has not been found. At locations about 12 m higher, tosudite and kaolinite occur in intimate association and in highly variable proportions.

XRD data. Fourteen samples of tosudite and kaolinite were examined. Under normal laboratory conditions, the tosudite shows a basal spacing of 29.5 Å with many higher orders (Table 1). The (004) and (008) tosudite reflections nearly coincide with the (001) and (002) kaolinite reflections; since the latter are always present and are more-or-less strong reflections, the spacings and intensities of the tosudite reflections cannot be recorded. The basal spacings of the tosudite after various treatments are summarized in Table 2 which also indicates their interpretation. The results agree generally with other recorded data for tosudite (see, for example, Ichikawa and Shimoda, 1976). From these

Table 2. d(001) of tosudite under various conditions.

Conditions	d(001) (Å)	Range of ℓ	Interpretation (Å)
Ethylene glycol, 2 days	31.1 ± 0.1	1-16	14.2 + 16.9
H ₂ O vapor, 20 hr	33.05 ± 0.05	1-12	14.2 + 18.8
20°C, 60% RH	29.5 ± 0.2	1-18	14.2 + 15.3
110°C, 20 hr	29.6 ± 0.2	1-20	14.2 + 15.4
300°C, 2 days	29.6 ± 0.2	1-10	14.2 + 15.4
400°C, 20 hr	~24	1-5	14.2 + 9.8
500°C, 7 hr	23.3 ± 0.1	1-7	13.9 + 9.4

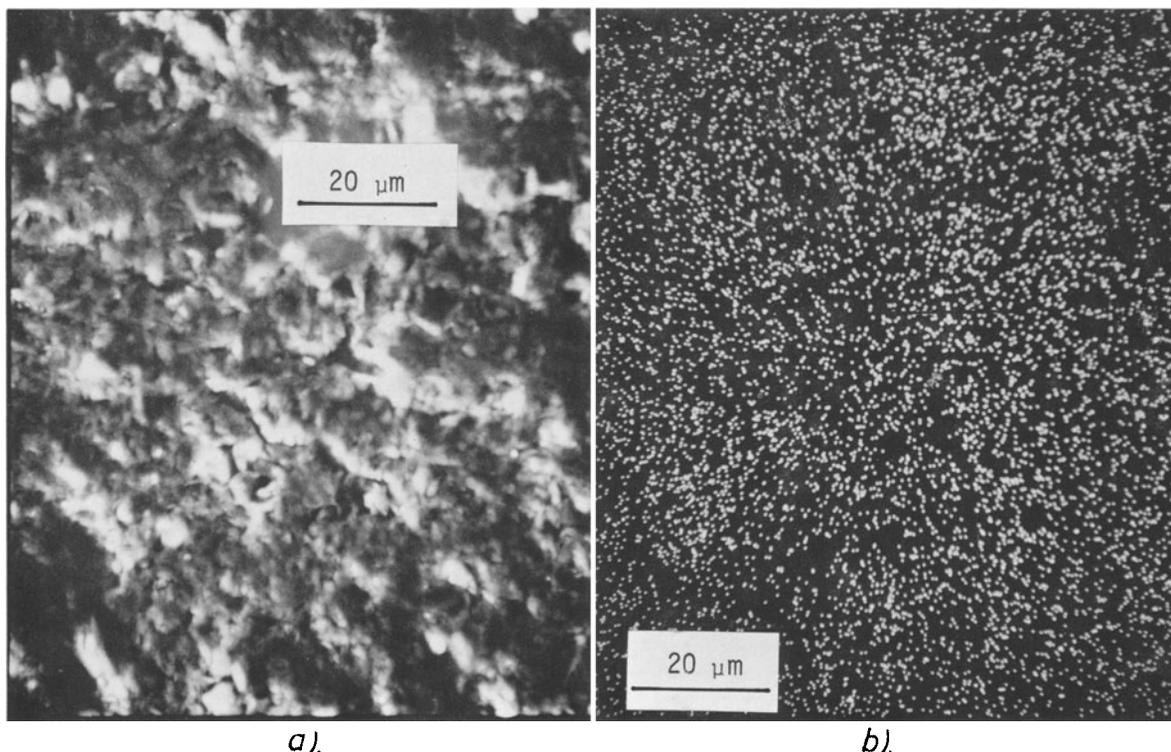


Figure 2. (a) Scanning electron micrograph of kaolinite + tosudite from zone II; (b) Electron microprobe picture of the same area at the same magnification, taken with CrK α radiation.

results, tosudite appears to be a regular alternation of non-expanding chlorite layers and variable smectite layers.

A medium-strong sharp reflection at $d = 1.489 \text{ \AA}$ is presumably a combined (060) reflection from kaolinite and tosudite. The b -parameters of both minerals therefore are near 8.93 \AA , and the tosudite appears to be a dioctahedral mineral.

The proportions of tosudite and kaolinite are variable. Exact determinations of their proportions were not attempted, but from the ratio R of XRD peak intensities, $R = I(002, \text{tosudite})/I(001, \text{kaolinite})$, the variation could be followed. For the fourteen samples examined, R varied from 0.05 to 0.73. When kaolinite is the dominant component, it shows most of the reflections to be expected from a well-ordered structure. When the maximum amount of tosudite is present, the kaolinite, still present in an appreciable proportion, appears to be less well ordered. One can only guess that when conditions favor tosudite formation, they are less favorable for the formation of a well-ordered kaolinite.

Halloysite (10- \AA form) without tosudite has been found at lower levels than the kaolinite and tosudite. Fresh material examined in the present study gives an excellent XRD pattern showing only the 10- \AA form of halloysite. Exposure to a dry atmosphere in a desiccator for 24 hr collapses the basal spacing to about 7.4

\AA which does not rehydrate appreciably in 100% RH atmosphere for 1 week. The basal spacing diminishes to about 7.25 \AA at 150°C and persists to about 450°C . The two-dimensional order shown by the hk diffraction bands persists to about 550°C . Maksimovic and White (1973) recorded Cr $_2$ O $_3$ contents up to 11.7%.

Chemical data. Chemical analyses indicate that the kaolinite and tosudite clays contain on the order of 1–3% Cr $_2$ O $_3$. There is no significant correlation of Cr $_2$ O $_3$ with the ratio R which suggests that the chromium is distributed over both the kaolinite and the tosudite, i.e., there is no selective concentration in either mineral. Figure 2 shows an electron microprobe examination of a kaolinite + tosudite sample. The chromium appears uniformly distributed, so that *either* the Cr is distributed in both mineral components, *or* the fine-grained components are thoroughly mixed.

In Table 3, columns 1–4 present typical electron microprobe analyses of kaolinite + tosudite mixtures, and column 5, a wet chemical analysis. It is seen that with increase of Cr $_2$ O $_3$ + Fe $_2$ O $_3$, there is a corresponding decrease of Al $_2$ O $_3$. For comparison, Table 3 also gives in column 6 the ideal composition of kaolinite, and in columns 7–9, the analyses of three Japanese tosudites. The present results and those of the Japanese investigators are in broad agreement, except that the

Table 3. Analyses of Cr-(kaolinite + tosudite), Takovo, Yugoslavia, compared with analyses of kaolinite and of tosudites from Japan.¹

	Samples from Takovo					Kaolinite 6	Tosudites from Japan		
	1	2	3	4	5		7	8	9
SiO ₂	41.19	42.71	42.58	44.31	44.78	46.54	44.20	42.14	41.60
Al ₂ O ₃	40.48	39.84	38.68	38.48	35.29	39.50	36.65	37.38	36.40
Fe ₂ O ₃	0.22	0.26	0.34	0.40	0.44	—	1.24	0.30	1.82
Cr ₂ O ₃	0.79	0.96	0.90	1.19	2.69	—	—	—	—
MgO	0.13	0.28	0.36	0.48	0.39	—	0.54	0.08	0.29
CaO	0.20	0.52	0.54	0.49	0.27	—	2.56	1.65	0.38
Li ₂ O	—	—	—	—	—	—	0.60	—	1.04
Na ₂ O	tr	tr	tr	tr	0.45	—	0.12	0.15	0.14
K ₂ O	tr	tr	tr	tr	0.57	—	0.58	1.40	0.38
H ₂ O(+)					13.28	13.96	11.54	11.22	11.12
H ₂ O(-)					2.10	—	1.97	6.16	6.87
Total	83.01	84.57	83.40	85.35	100.26	100.00	100.00	100.48	100.04

¹ 1–4, Analyses by electron microprobe. 5, Chemical analysis (Maksimovic and Crnkovic, 1968). 6, Ideal kaolinite. 7, Ichikawa and Shimoda (1976). 8, Shimoda (1969). 9, Nishiyama *et al.* (1975).

present results include appreciable Cr₂O₃. In all cases, SiO₂ > ΣR₂O₃, which also is valid for kaolinite. Since the main oxide components of tosudite are similar to those of kaolinite, the compositions of the mixtures in columns 1–4 are not dependent to any appreciable extent on the kaolinite:tosudite ratio.

In relation to the overall problem of the present study, the nature of the alteration processes, it is important to emphasize that MgO is almost absent from the samples in zone II. It may also be remarked that there is an enrichment of some trace elements in the kaolinite + tosudite samples, with boron up to 1350 ppm, arsenic up to 360 ppm, strontium up to 650 ppm, and scandium up to 230 ppm. Their presence as well as that of pyrite in some samples indicates a hydrothermal origin of these clays and not a supergene formation.

The minerals of zone III

This zone contains green-colored clays which are mainly mixed-layered illite/smectites with variable proportions of the component layers and variable chemical compositions which correlate with the variable mineralogy.

XRD data. In those parts of zone III immediately adjacent to zone II, pale green clays are mixtures of kaolinite, tosudite, and a predominantly illitic mineral. In other words, although there is a color change from the material of zone II, the mineralogy does not change abruptly, i.e., insofar as material can be selected by hand-picking. Figure 3 shows XRD patterns for such a material, sample 6913, using an oriented sample on a glass slide, (a) under normal atmosphere conditions, (b) after ethylene glycol treatment. The sharp (001) and (002) kaolinite reflections are clearly seen. The strong (002) tosudite reflection, $d \approx 14.5 \text{ \AA}$, is poorly resolved from the reflection of the illite/smectite mixed-layer

phase, with $d \approx 11.8 \text{ \AA}$. The reflections of the illite/smectite mixed-layer phase at 11.8, 4.95, and 3.27 Å are not integral orders even when allowance is made for the uncertain 11.8 Å value. Ethylene glycol expands the tosudite (002) spacing to 15.5 Å, and an illite/smectite reflection near 13.0 Å is more clearly seen. Comparison of the available data with the mixing function curves of Ruiz Amil *et al.* (1967) suggests the following conclusions: if the air-dry sample is a mixture of A layers with 10-Å spacing and B layers with 15-Å spacing, $P_A \approx 0.8$, $P_B \approx 0.2$, and $P_{AA} \approx 0.8$. If the glycolated sample contains A layers with 10-Å spacing and B layers with 17-Å spacings, then $P_A \approx 0.7$, $P_B \approx 0.3$, and $P_{AA} \approx 0.6$. Comparison of the data for the glycolated sample with the theoretically calculated diffraction patterns given by Reynolds and Hower (1970) gives the best fit with their Figure 5b for $P(10\text{\AA}) = 0.8$, $P(16.9) = 0.2$, and $P(16.9, 16.9) = 0$. The conclusion from these comparisons is that the proportions of illite and smectite layers are respectively about 0.7–0.8 and 0.3–0.2. Evidently the phase is an illite/smectite mixed-layer clay with predominantly illite layers and with little tendency for consecutive smectite layers; otherwise stated, there is a tendency towards . . . ABAB . . . ordering within the limitations imposed by the predominance of one type of layer.

Dark green clays from locations which are further from zone II give patterns similar to those in Figure 4, for sample 6914. Kaolinite and tosudite are absent. The strong diffraction peak at 13.7 Å expands to 15.1 Å with glycolation. Evidently a higher proportion of swelling smectite layers is present than in the previous sample. If the illite layers are again denoted as A layers and the smectite layers as B layers, then the mixing function curves of Ruiz Amil *et al.* (1967) indicate $P_A \approx 0.4$ –0.5, $P_B \approx 0.6$ –0.5, and $P_{AA} \approx 0.4$. Comparison with the

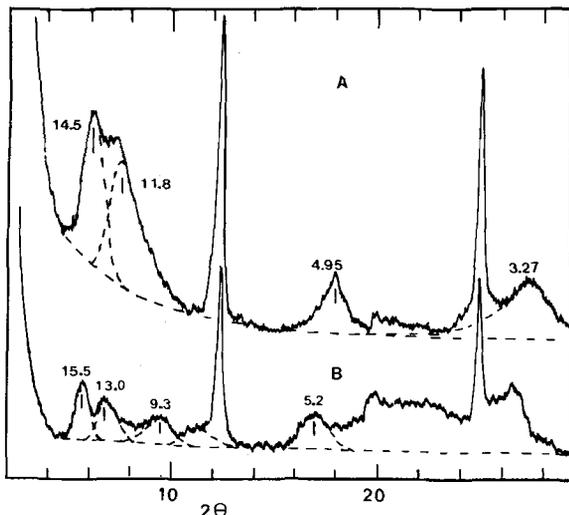


Figure 3. X-ray diffractometer patterns of pale-green sample 6913, (A) under normal conditions, (B) after ethylene glycol saturation, taken with Ni-filtered $\text{CuK}\alpha$ radiation, $1^\circ 2\theta/\text{min}$ recording rate.

curves of Reynolds and Hower (1970) gives the best fit with their Figure 5a for $P_A = 0.4$, $P_B = 0.6$, and $P_{AA} = 0$. Evidently the illite and smectite layers are in more nearly equal proportions, and again there is a tendency towards alternation of the two kinds of layers.

The diffraction patterns shown in Figure 4 may be suggestive of a heterogeneous mixture of random and ordered illite/smectites, and that the observed sequence from smectite through illite/smectite to a kaolinite + tosudite association may be similar to that discussed by Eberl (1978) for the synthesis of kaolinite + tosudite + illite/smectite starting with Li-saturated smectite. Unfortunately, the much poorer quality of the patterns in Figures 3–5 as compared with those shown by Eberl (1978) renders any more specific evaluation very questionable. A conservative interpretation, indicating the broad trends of the changes apparently taking place, is therefore preferred.

Dark green clays from locations further away from zone II are more closely related to smectite than to illite, and Figure 5 shows one example, sample 2742. Glycolation expands the spacing to a value near 17.5 \AA , but successive orders do not give an exactly integral series. The precise value of the "17- \AA spacing" is rendered uncertain because of the displacement of the diffraction maximum towards smaller 2θ by the steeply rising background and by the operation of the $L_p|F|^2$ function in the low-angle range. With the same notation as before, $P_A \approx 0.4$, $P_B \approx 0.6$, and $P_{AA} \approx 0.3$ from the curves of Ruiz Amil *et al.* (1967), and general agreement with Figure 4a of Reynolds and Hower (1970) gives $P_A = 0.4$, $P_B = 0.6$, and $P_{AA} = 0.4$. The smectite layers now predominate, but the illite layers are present

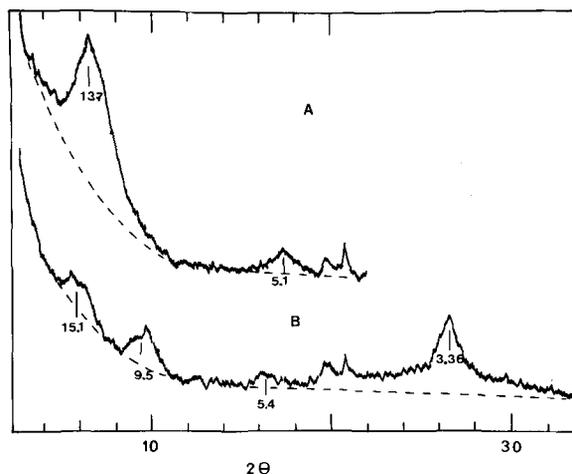


Figure 4. X-ray diffractometer patterns of dark-green sample 6914, (A) and (B) as for Figure 3.

to a larger extent than one would initially estimate simply from the expansion of D(001).

The results indicate that as one moves across zone III, away from zone II, the illite/smectite mixed-layer clays become poorer in illite and richer in smectite layers. There are tendencies toward regular alternations of the two kinds of layers, but no examples have been found of a regular alternating sequence.

Chemical data. Chemical compositions of the pale green clay, sample 6913, from the marginal part of zones II and III, and of three dark green clays, samples 6910, 6914, and 2742, from positions labelled 4, 5, and 6 in Figure 1, are recorded in Tables 4 and 5. Table 4 gives analyses based on Kevex data and which assume a total water content of 11.0%. The interlayer water of

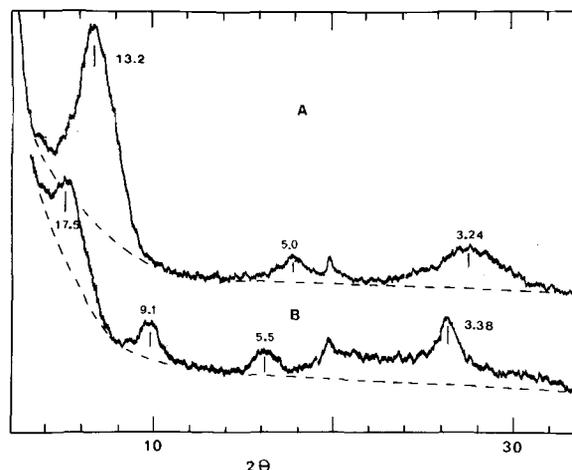


Figure 5. X-ray diffractometer patterns of dark-green sample 2742, (A) and (B) as for Figure 3.

Table 4. Analyses of illite/smectites from Takovo, a Cr-illite, and average illites.

	Samples from Takovo ¹			Cr-illite ³ 5821	Average illites ⁴	
	6913	6910	6914		1	2
SiO ₂	44.9	48.0	49.8	51.68	51.74	49.78
Al ₂ O ₃	28.9	13.3	14.7	19.11	23.98	26.35
Cr ₂ O ₃	8.7	15.2	14.2	7.78	—	—
Fe ₂ O ₃	1.7 ²	5.0 ²	4.7 ²	—	4.57	4.30
FeO	—	—	—	1.68	1.09	0.61
MgO	—	tr	tr	2.02	1.99	2.75
CaO	—	2.4	1.1	tr	0.97	0.32
Na ₂ O	—	tr	tr	tr	0.36	0.25
K ₂ O	5.7	4.2	3.5	6.61	5.59	7.02
NiO	—	0.9	1.0	0.29	—	—
TiO ₂	—	—	—	—	0.68	0.42
Total without water	89.0	89.0	89.0	89.17	90.95	91.80

¹ 6913, 6910, 6914. Kevex-EDX analysis normalized to 89.0% total.

² Fe expressed as Fe₂O₃.

³ 5821. Electron microprobe analysis of sample from Avala Mountain, near Belgrade.

⁴ 1 = Average analysis of seven Fithian illites—see text. 2 = Average analysis of 24 illites—see text.

the smectite layers will be largely removed under the vacuum conditions and electron beam heating in the electron microscope. Table 5 gives a more complete chemical analysis with a separation of FeO and Fe₂O₃ and with the exchangeable cations separately determined.

Table 4 also shows various illite analyses; sample 5821 is a Cr-illite from Avala Mountain near Belgrade (so-called "avalite") analyzed by electron microprobe; an average analysis of seven Fithian illites and an average analysis of 24 illites are taken from tables given by Weaver and Pollard (1973, p. 6, 8, and 9).

The progressive decrease in K₂O content in passing from sample 6913 (Figure 3), to samples 6910 and 6914 (Figure 4), to sample 2743 (Figure 5) corresponds to the decrease of illite layers found from the XRD data. The K₂O content of sample 2742 is seen in Table 5 to be mainly nonexchangeable, i.e., it is in the illite layers.

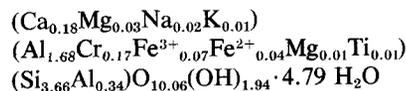
The Cr₂O₃ content has its highest values 14–15% towards the boundary with zone II but the amount diminishes in sample 6913, a pale green sample which has features characteristic of zone II (i.e., considerable kaolinite + tosudite). It is known that some illites and smectites can contain up to 14.59% and 13.74% Cr₂O₃, respectively (Lozanitsch, 1884; Stangatchilovich, 1956); Ross (1960) discussed data for volchonskoite with 15.02% Cr₂O₃. This enrichment of chromium is encountered particularly in clays of hydrothermal origin.

The chemical analysis of the dark green clay, sample 2742, Table 5, Figure 5, merits special consideration.

Table 5. Chemical analysis of illite/smectite, sample 2742.

	Wt. %	Exchangeable
SiO ₂	47.59	
TiO ₂	0.18	
Al ₂ O ₃	22.72	
Cr ₂ O ₃	2.30	
Fe ₂ O ₃	1.76	
FeO	0.30	
NiO	0.55	
MgO	0.51	0.25
CaO	0.16	1.80
Na ₂ O	0.00	0.19
K ₂ O	1.13	0.11
H ₂ O(+)	6.95	
H ₂ O(-)	13.10	
Total	97.25	2.35
Exchangeable Total	2.35	
	99.60	

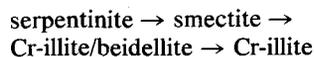
If the illite component is assumed to have a composition similar to the average illite composition (2) in Table 4, then 16% of the total composition is attributable to illite. This proportion of illite composition is less than the result estimated from the XRD data. Both estimates are uncertain. However, if one proceeds on the basis of 16% illite composition and subtract this from the total composition of sample 2742, an estimate of the smectite composition can be obtained, with the following formula:



This result is entirely consistent with other smectite compositions. The interlayer charge is +0.45, the net tetrahedral charge is -0.34, and the octahedral charge is -0.10. The octahedral cations add to 1.98. Since the layer charge is largely tetrahedral, the smectite is beidellitic. The exchangeable cations (Table 5) amount to 84.9 meq/100 g clay and if these originate from 84% of smectite component, the exchange capacity of the smectite is 101 meq/100 g smectite. These conclusions are not strongly dependent on the assumed proportion of illite layers nor on the precise composition assumed for the illite.

DISCUSSION

The field evidence and the analytical data indicate that the first stage of mineral transformation around the epithermal vein was as follows:



The first step in this sequence is not studied in the present paper because samples of the smectite from zones III and IV are no longer available. However, XRD and chemical data were obtained earlier and were used in a previous report in discussing the mineralogical changes (Maksimovic and Crnkovic, 1968). The final stage involving pure Cr-illite is not included but we have observed the progressive enrichment of the illite component in the mixed-layer illite/beidellite and the increase of potassium as the vein is approached.

The formation of mixed-layer illite/smectites is frequently found as a transitional stage in the alteration of smectites to illite. According to Frank-Kamenetski *et al.* (1979), this transformation occurs more readily with increasing content of tetrahedral aluminum in the smectite phase, i.e., with beidellite rather than montmorillonite as the smectite. The present results also point to a beidellitic composition.

Leaching of Mg^{2+} and Fe^{2+} ions by the hydrothermal solutions was the dominating process in the first alteration process with consequent increase *in situ* of Si, Al, and Cr. The highest observed content of chromium is 15.2% Cr_2O_3 . Evidently Cr^{3+} ions play the same role as Al^{3+} ions in octahedral coordination sites because of their similar size and equal charge and this is apparent in the reciprocal contents of Cr and Al in zones III and II, as shown in Figure 1.

A second stage of hydrothermal alteration resulted in the formation of chromium-bearing tosudite and kaolinite in zone II. Tosudite is closely associated with illite/montmorillonite in hydrothermally altered rocks around some ore deposits in Japan (Sudo and Shimoda, 1977; Ishikawa and Shimoda, 1976). The latter authors have shown that tosudite can be synthesized in the laboratory starting from an illite/montmorillonite. A similar distribution pattern of tosudite and illite/smectite (beidellite) is seen in the Takovo area. The field evidence and the mineralogical changes indicate that the mixture of Cr-tosudite and Cr-kaolinite was formed by the transformation of Cr-illite/beidellite by a leaching of most of the components other than SiO_2 and Al_2O_3 under conditions of decreasing pH as the vein is approached. In this process, chromium was mostly removed with enrichment of aluminum, probably due to the different dissolution pH values of their hydroxides, with $Cr(OH)_3$ dissolving at pH 5.3 and $Al(OH)_3$ at pH 4.1 (Britton, 1925).

The spatial relation of Cr-halloysite and Cr-(kaolinite + tosudite) is still uncertain, but from the mapping of the exploration adits, it seems that the latter occurs nearer to the vein. Cr-halloysite in this locality can be very rich in chromium (up to 11.7% Cr_2O_3 , Maksimovic and White, 1973), and therefore may have been formed under less acidic conditions than the kaolinite and tosudite.

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Резюме—С помощью порошкового метода рентгено-структурного и химического анализов изучались продукты гидротермального изменения серпентинита вблизи Таково, Югославия. Зона преимущественно синих глин, прилегающая к гидротермальной жиле содержит близко ассоциирующиеся хромовый каолинит и тосудит на высоких гипсометрических уровнях и хромовую галлузитовую (10Å) форму на низких уровнях. Вторая зона зеленых глин содержит в основном иллиты/смектиты, с преимущественно иллитовыми слоями ближе к первой зоне и смектитовыми слоями при удалении от нее. Содержание калия уменьшается по мере уменьшения пропорции иллитовых слоев. Показано, что состав смектитовых слоев в иллите/смектите с наименьшей пропорцией иллита является бейделлитовым. Минералогические и химические закономерности в зоне изменения интерпретируются в предположении двух стадий изменения, причем вторая является более кислотной, чем первая и ответственна за внутреннюю зону хромоносного каолинита и тосудита и хромового галлузита. [N.R.]

Resümee—Die hydrothermalen Umwandlungsprodukte des Serpentinits in der Nähe von Takovo, Jugoslawien, wurden mittels Röntgenpulverdiffraktometrie und chemischen Analysen untersucht. Eine Zone von hauptsächlich blauen Tonen, die unmittelbar an die hydrothermale Ader angrenzt, enthält eng miteinander verwachsenen Chrom-Kaolinit und Tosudit in den oberen Bereichen, Während sich in den unteren Bereichen Chrom-Halloysit (10Å) bildet. Eine zweite Zone von grünen Tonen enthält hauptsächlich Illit/Smektit, wobei die Illit-Lagen näher an der ersten Zone und die Smektit-Lagen in größerer Entfernung sind. Der Kaliumgehalt nimmt ab, wenn der Illitanteil abnimmt. Die Zusammensetzung der Smektit-Lagen ist im Illit/Smektit mit dem geringsten Illitanteil beidellitisch. Die mineralogischen und chemischen Veränderungen über die Umwandlungszone werden als zwei Umwandlungsstadien interpretiert, wobei das zweite Stadium saurer als das erste ist und für die innere Zone aus chromhaltigem Kaolinit und Tosudit sowie chromhaltigem Halloysit verantwortlich ist. [U.W.]

Résumé—Les produits d'altération hydrothermale de serpentine près de Takovo, Yougoslavie, ont été étudiés par diffraction poudrée aux rayons-X et par analyse chimique. Une zone contenant surtout des argiles bleues, adjacente à la veine hydrothermale, contient de la kaolinite intimement associée et de la tosudite à des niveaux hypsométriques plus élevés; et de l'halloysite (10Å) de chromium est formée à des niveaux plus bas. Une deuxième zone d'argiles verts contient principalement des smectites/illites, avec surtout des couches d'illite près de la première zone et des couches de smectite à de plus grandes distances. Le contenu en potassium diminue à mesure que la proportion de couches d'illite diminue. La composition des couches de smectite dans la smectite/illite avec la moindre proportion d'illite peut être montrée être bédellitique. Les changements minéralogiques et chimiques en travers de la zone d'altération sont interprétés en fonction de 2 stages d'altération dans lesquels le second est plus acide que le premier et est responsable pour la zone intérieure de kaolinite et tosudite contenant du chromium et d'halloysite de chromium. [D.J.]