

# CHROMIUM-BEARING DICKITE AND CHROMIUM-BEARING KAOLINITE FROM TESLIĆ, YUGOSLAVIA<sup>1</sup>

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**Abstract**—Three samples of bluish chromium-bearing dickite and chromium-bearing kaolinite were examined by X-ray powder diffraction, chemical analysis, electron microprobe, optical, and infrared techniques to determine whether chromium is part of the mineral structure or present in an impurity phase. Two of the samples studied contain a single dominant chromium-bearing phase (either dickite or kaolinite); the third contains equal proportions of both minerals. The optical absorption and infrared spectra are consistent with the presence of octahedrally coordinated chromium. The range of Cr<sup>3+</sup>–Al<sup>3+</sup> substitution is rather limited: up to 0.06 atoms per unit cell. The electron microprobe study revealed the presence of very rare, minute grains of chromite, as well as a uniform distribution of chromium in dickite and kaolinite, indicating that chromium occupies octahedral sites in the structure of these minerals.

**Key Words**—Chromium, Dickite, Infrared, Kaolinite, Optical absorption.

## INTRODUCTION

Enrichment of chromium is encountered in clays formed by hydrothermal alteration of ultramafic rocks. Some illites and smectites contain as much as 14.59% and 13.74% Cr<sub>2</sub>O<sub>3</sub>, respectively (Maksimović and White, 1973). Due to a lack of alumina in ultramafic rocks Cr<sup>3+</sup> may substitute for Al<sup>3+</sup> in octahedral position.

Cr-kaolinite and Cr-dickite are exceptionally rare in nature. Chromium-rich kaolin materials were discovered in the argillic zone outward from an epithermal sulfide vein in ultramafic rocks near Teslić in Bosnia, Yugoslavia. The argillic alteration zone was described by Maksimović and Crnković (1968). The chromium-rich kaolin subzone is located closer to the sulfide vein than is the smectite subzone, but chromium attains the greatest concentration in the latter subzone. Aluminum, on the other hand, is most abundant closer to the vein in the kaolin subzone, due probably to the different dissolution pHs of Al- and Cr-hydroxides. With increasing acidity from the neutral point, Cr(OH)<sub>3</sub> begins to dissolve at pH 5.3, whereas Al(OH)<sub>3</sub> does not enter solution until pH 4.1 (Britton, 1925). If the acidity of

hydrothermal solutions were between these two pHs for a long period of time, chromium would be selectively dissolved from the solid phase. It seems, therefore, that conditions associated with formation of kaolinite and dickite enhance the geochemical separation of chromium from aluminum.

## RESULTS AND DISCUSSION

### Materials

Three samples of bluish chromium-containing kaolin materials were collected from the 12-m thick kaolin subzone, which becomes more silicified close to the sulfide vein itself. The samples are various shades of blue or blue-green: Sample 2378 is grayish blue-green (5 BG 5/2; Rock Color Chart, 1975) and contains 0.69% Cr<sub>2</sub>O<sub>3</sub>. Sample 664 is pale blue-green (5 BG 7/2) and contains 0.57% Cr<sub>2</sub>O<sub>3</sub>. Sample 665 is very pale blue (5 B 8/2) and contains 0.26% Cr<sub>2</sub>O<sub>3</sub>. The intensity of the color increases with the chromium content. Due to variations in quartz content and to inhomogeneity of the samples, the relation between mean index of refraction and the chromium content could not be determined.

### X-ray powder diffraction measurements

X-ray powder diffraction (XRD) patterns were obtained with a Philips PW 1051 diffractometer using Ni-

<sup>1</sup> Journal Paper No. 8328, Purdue University Agricultural Experiment Station, West Lafayette, Indiana 47907.

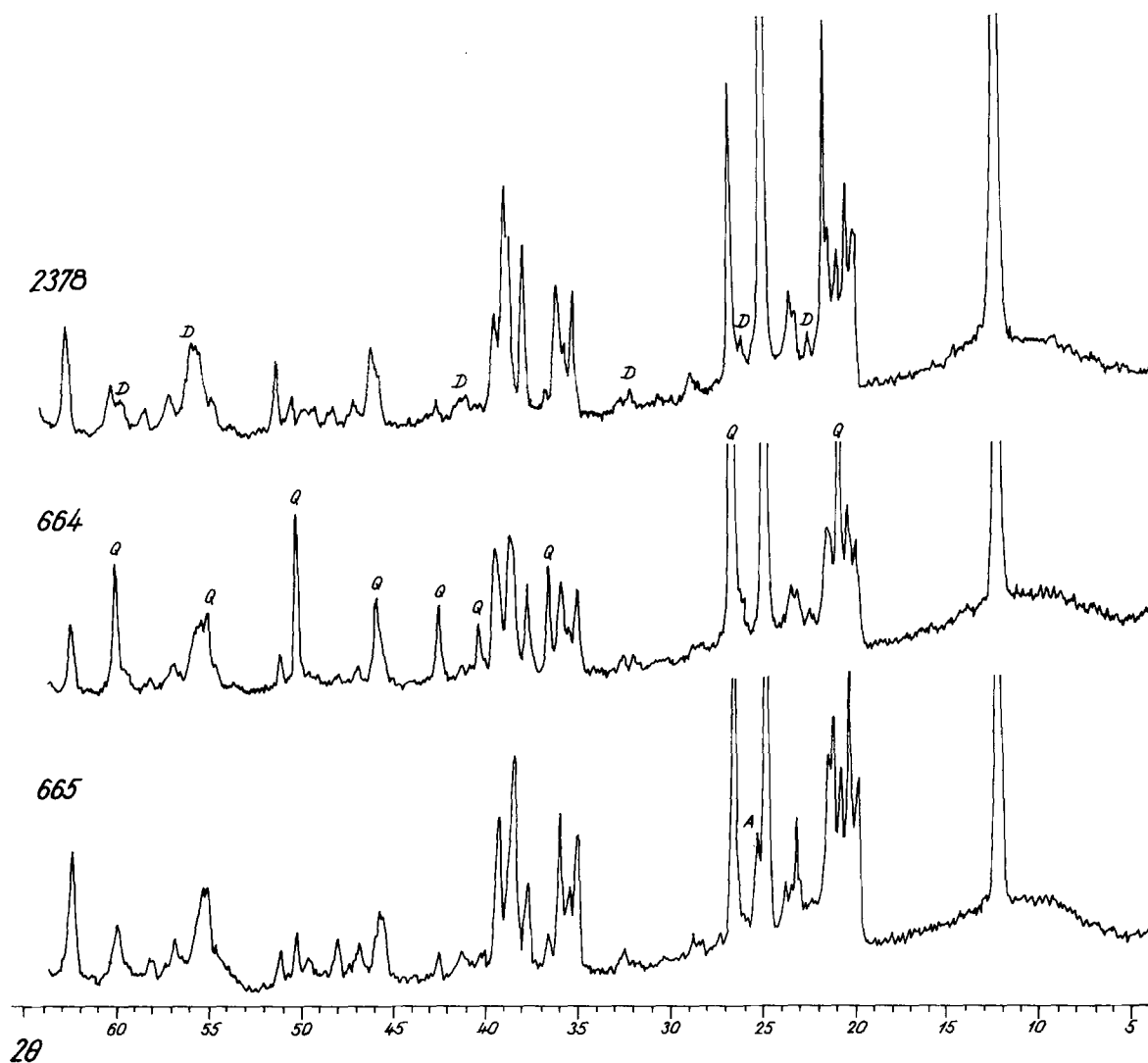


Figure 1. X-ray powder diffraction patterns of Cr-dickite and Cr-kaolinite from Teslić, Yugoslavia.  $\text{CuK}\alpha$  radiation. D = dickite; A = anatase; Q = quartz.

filtered  $\text{CuK}\alpha$  radiation and a scanning speed of  $1^\circ/2\theta$  min. As seen from Figure 1 the XRD data show well-crystallized kaolinite and dickite to be present in various proportions in all samples. According to line intensity data, sample 2378 contains dickite as a major component; sample 664 consists of kaolinite and dickite in about equal proportions and a large amount of quartz; and sample 665 contains kaolinite as a dominant phase, with only a trace of dickite (anatase was identified only in this sample).

The substitution of  $\text{Cr}^{3+}$  for  $\text{Al}^{3+}$  in octahedral sites in Cr-halloysites caused an increase in the b-dimension, as measured by the 060 spacings (Maksimović and White, 1973). Although the 060 peak in samples of Cr-dickite and Cr-kaolinite was recorded at high sensitivity, a similar shift of the 060 spacings of the three samples listed above was not established with certainty,

probably due to the relatively small amount of chromium present.

#### Chemical analysis

The chemical compositions of the kaolinite and dickite are similar. Small amounts of various ions may substitute in the structure, but because of the fine-grained nature of the clays it is difficult to be certain that all impurities have been eliminated. The chemical analyses of the three samples of dickite and kaolinite are presented in Table 1. Assuming that  $\text{TiO}_2$  occurs as anatase (detected by XRD in sample 665), chromium is the only possible substitute for aluminum. This substitution is facilitated by the similarity in ionic size ( $\text{Cr}_{\text{VI}}^{3+} = 0.70 \text{ \AA}$ ;  $\text{Al}_{\text{VI}}^{3+} = 0.61 \text{ \AA}$ ; Whittaker and Muntus, 1970).  $\text{Cr}^{3+}$ - $\text{Al}^{3+}$  substitution has been shown to exist in Cr-halloysites and gives rise to a blue color of the samples

Table 1. Chemical analyses of Cr-dickite and Cr-kaolinite from Teslić, Yugoslavia.

	Sample 2378 dickite <sup>1</sup>	Sample 664 kaolinite + dickite <sup>2</sup>	Sample 665 kaolinite + quartz <sup>3</sup>
SiO <sub>2</sub>	48.98	62.19	49.80
TiO <sub>2</sub>	0.33	0.10	1.60
Al <sub>2</sub> O <sub>3</sub>	36.83	27.83	35.89
Cr <sub>2</sub> O <sub>3</sub>	0.69	0.57	0.26
Fe <sub>2</sub> O <sub>3</sub>	0.09	tr	tr
MgO			
CaO			tr
Na <sub>2</sub> O	0.03	0.06	
K <sub>2</sub> O	0.02	0.02	tr
H <sub>2</sub> O+	13.06	9.14	12.25
H <sub>2</sub> O-	0.33	0.25	0.35
	100.36	100.16	100.15
Number of ions based on 9(O,OH) after subtraction of impurities.			
Si	2.00	2.03	2.03
Al	1.98	1.99	1.99
Cr	0.03	0.03	0.01
OH	3.98	3.73	3.85
	2.01	2.02	2.00

<sup>1</sup> Sample 2378 = dickite with a small amount of kaolinite and ~5% quartz.

<sup>2</sup> Sample 664 = kaolinite and dickite with ~28% quartz.

<sup>3</sup> Sample 665 = kaolinite with ~6.5% quartz and ~1.6% anatase.

(Maksimović and White, 1973). Therefore, this substitution might be expected to some degree in kaolinite and dickite as well.

If all of the chromium is present as structural cations, the range of Cr<sup>3+</sup>-Al<sup>3+</sup> substitution in kaolinite and dickite is rather limited—less than 0.06 atom per unit cell. Halloysite containing the upper limit of approximately 1.00 Cr atom per unit cell was dark blue in color in contrast to the pale blue-green color of dickite and kaolinite containing approximately 0.06 Cr atom per unit cell.

Trace elements determined by an emission spectrographic technique are listed in Table 2. Except for 190–310 ppm vanadium, most of the other elements occur in very small quantities.

Table 2. Trace elements in samples of Cr-dickite and Cr-kaolinite (in ppm).

Element	Sample 2378	Sample 664	Sample 665
Ga	7	6.5	10
V	190	230	310
Cu	<sup>1</sup>	26	1.5
Ni	60	92	25
Co	3.5	4.5	<sup>1</sup>
Zr	23	<sup>1</sup>	100
Sc	9	<sup>1</sup>	11
Mn	60	22	6

<sup>1</sup> Below detection limit.

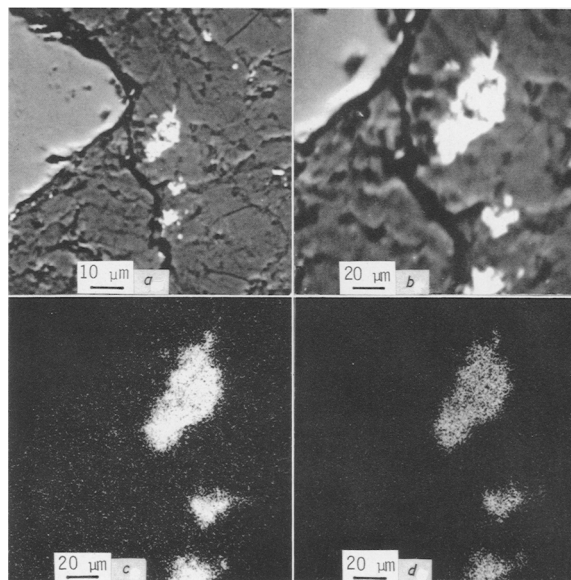


Figure 2. Electron micrographs and X-ray maps of sample 2378: a. Electron micrograph showing Cr-dickite (gray), minute grains of chromite (white), and quartz (light gray). The length of the bar indicates 20  $\mu\text{m}$ . b. Higher magnification of part of Figure 2a. The length of the bar indicates 10  $\mu\text{m}$ . c. CrK $\alpha$  X-ray map of area shown in Figure 2b. d. FeK $\alpha$  X-ray map of area shown in Figure 2b.

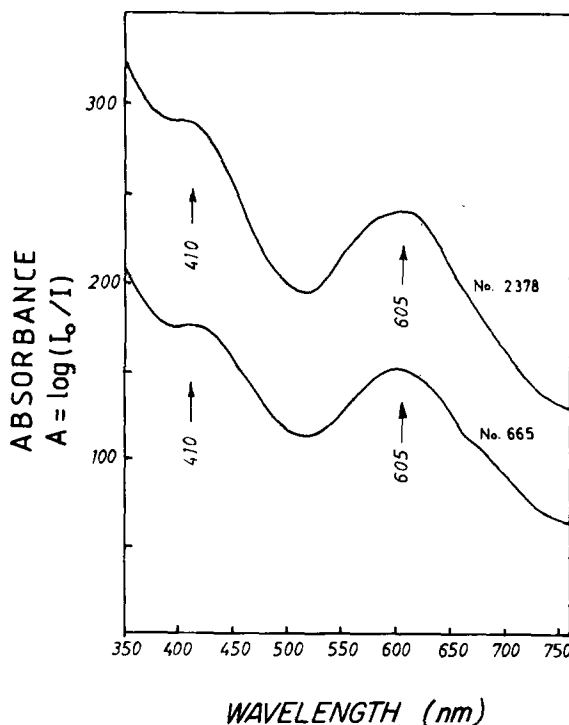


Figure 3. Optical absorption spectra of Cr-dickite (2378) and Cr-kaolinite (665).

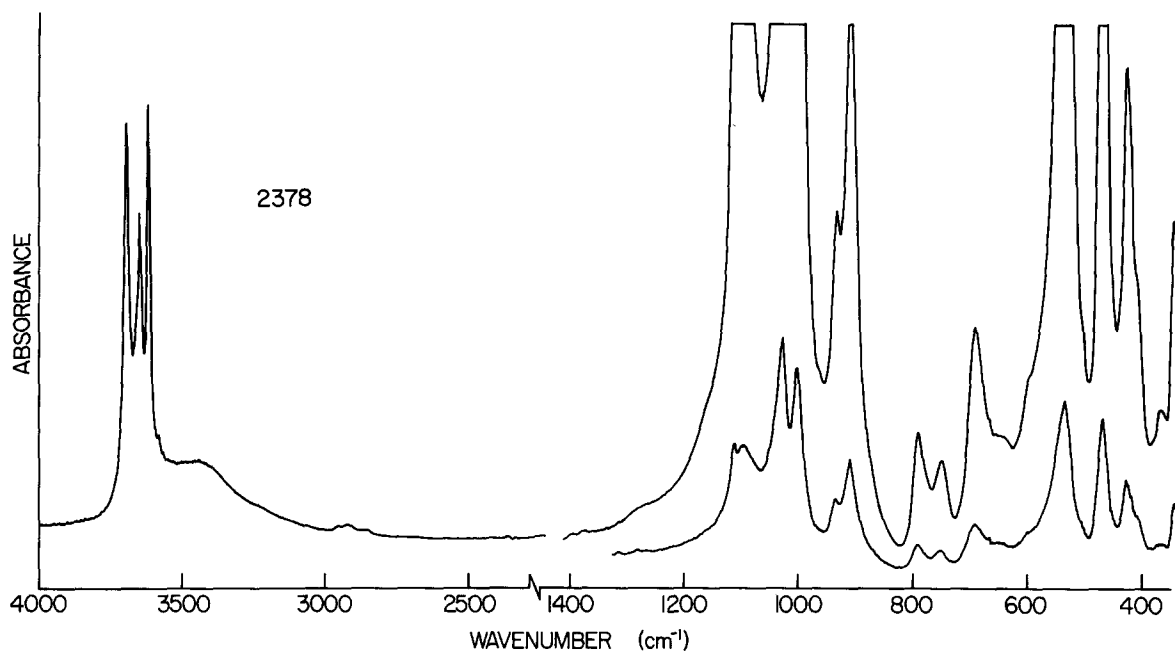


Figure 4. Infrared spectra of sample 2378, Cr-dickite, Teslić, Yugoslavia.

#### Electron microprobe study

Electron microprobe analyses were carried out by means of a JEOL JXA-5 electron microprobe at an accelerating voltage of 25 kV. A combination of back-scattered electron images and searching by the characteristic wavelength of chromium detected very rare, minute chromite grains in sample 2378 (Figure 2). Apart from the chromite grains themselves the X-ray map of CrK $\alpha$  (Figure 3c) shows a uniform distribution of about 1.0% Cr throughout the dickite portion of the sample and no traces of this element in quartz. The same results were obtained for samples rich in kaolinite (664 and 665). Thus, the chromium in dickite and kaolinite is not present as a chromium-rich impurity, such as chromite, but as a substitution in the mineral structure.

#### Optical absorption spectra

Optical absorption spectra between 350 and 750 nm (28,570 and 13,330  $\text{cm}^{-1}$ ) of powdered samples were obtained using a diffuse reflectance attachment and Hilger Uvispek spectrophotometer with a quartz monochromator. The absorption spectra of two samples examined are essentially identical (Figure 3). Absorption peaks at 410 nm (24,390  $\text{cm}^{-1}$ ) and 605 nm (16,529  $\text{cm}^{-1}$ ) are similar to those found in several related chromium-containing samples and are fully consistent with octahedral Cr $^{3+}$  electronic transitions. There is no indication of tetrahedral Cr $^{3+}$ , which would probably lead to noticeable absorption at about 685 nm, as indicated by Bish (1977).

The absorption spectra show that Cr $^{3+}$  in Cr-dickite (sample 2378) and Cr-kaolinite (sample 665) occupies

only octahedral sites where it substitutes for Al $^{3+}$ . The absorption bands are responsible for the blue-green color of these minerals, similar to that of Cr-halloysites in which Cr $^{3+}$  substitutes for Al $^{3+}$  in octahedral coordination.

#### Infrared measurements

The infrared (IR) spectrum for sample 2378 (KBr pellet, 1 mg sample/300 mg KBr and 0.2 mg sample/300 mg KBr) is shown in Figure 4. The predominant OH-stretching frequencies at 3696, 3654, and 3622  $\text{cm}^{-1}$  are typical of the three strong bands of dickite (van der Marel and Beutelspacher, 1976, pp. 70–71; Farmer 1974, p. 335). In addition, a spectral feature uncharacteristic for kaolin minerals occurs at 3586  $\text{cm}^{-1}$  and may be due to perturbation of the OH-stretching frequency by the Cr $^{3+}$  in octahedral sites (see below). The presence of dickite is further confirmed by the presence and relative intensities of the bands at 1100 and 1120  $\text{cm}^{-1}$  (van der Marel and Beutelspacher, 1976). The spectra of samples 664 and 665 show similar features, but to a lesser degree.

Figure 5 shows the OH-stretching region for the three Cr-containing samples. The OH-stretching frequencies at 3696, 3654, and 3622  $\text{cm}^{-1}$  are dominant for sample 2378 (0.69% Cr $_2$ O $_3$ ) with a very slight shoulder at 3670 and a small but distinct band at about 3586  $\text{cm}^{-1}$ . As indicated above, these bands are characteristic of dickite; the band at 3586  $\text{cm}^{-1}$  is well resolved upon 10  $\times$  scale expansion and it may be associated with the octahedral grouping Al $^{3+}$ Cr $^{3+}$ OH in which Cr $^{3+}$  has an effect similar to that of Fe $^{3+}$  (Farmer, 1974, p. 337). The

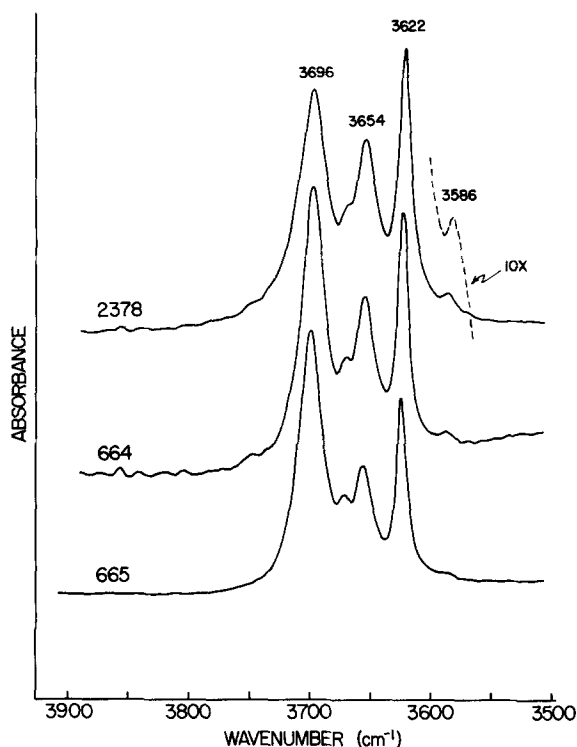


Figure 5. Infrared spectra of OH-stretching region for samples 2378, 664, and 665.

substitution of  $\text{Cr}^{3+}$  for  $\text{Al}^{3+}$  in these samples is somewhat analogous to that in Cr-halloysite (Maksimović and White, 1973), but the extent of substitution is much lower for the Cr-dickite and Cr-kaolinite (0.69%  $\text{Cr}_2\text{O}_3$ ) compared to 11.7%  $\text{Cr}_2\text{O}_3$  for the Cr-halloysite. The intensities of the 3654 and 3586  $\text{cm}^{-1}$  bands of samples 664 and 665 decrease with decreasing Cr-content, whereas the band at 3670 becomes better resolved. The proportion of kaolinite increases as the Cr-content decreases as indicated by variation of the relative intensity of the band at 3696  $\text{cm}^{-1}$  vs. the band at 3622  $\text{cm}^{-1}$ .

Commenting on the structural differences between kaolinite and dickite, Bailey (1980) stated

“Kaolinite and dickite both are based on the 1M stacking sequence of layers, and would be identical if trioctahedral. In kaolinite the vacant octahedral site is in the same place in each layer, and can be located at site B or site C in Fig. 1.3. In dickite the vacant octahedral site alternates between

B and C in successive layers to create a 2-layer structure. The alternation of vacant sites creates monoclinic glide planes parallel to (010) and balances the stress distribution in the two layers so that the cell shape remains monoclinic also. Thus, dickite can be considered as a regular alternation of right- and left-handed kaolinite layers, in one sense, or as a superstructure of the ideal 1M polytype due to a particular ordering pattern of octahedral cations and vacancies.”

The presence of the slightly larger  $\text{Cr}^{3+}$  ions in the kaolinite structure likely increases the probability that there will be alternation of vacant sites which favors the formation of the dickite structure. Thus, an increase in the proportion of dickite with increasing Cr-content was observed.

#### ACKNOWLEDGMENTS

The authors thank Dr. Gy Panto of the Hungarian Academy of Sciences for the electron probe pictures of the investigated samples. Assistance given by C. B. Roth and R. L. Hutchinson in obtaining IR spectra is greatly appreciated.

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- (Received 14 July 1980; accepted 26 November 1980)

**Резюме**—Три образца синеватого дикита и каолинита, содержащих хром, были исследованы путем рентгеновской порошковой дифракции, химического анализа, рентгеновского микроанализатора, оптических, и инфракрасных техник, чтобы определить, присутствует ли хром в структуре минералов или как примесная фаза. Два из исследованных образцов содержали единичную преобладающую фазу, включающую хром (дикит или каолинит); третий содержал равные пропорции обоих минералов. Оптическая абсорбция и инфракрасные спектры соответствовали присутствию октаэдрически координированного хрома. Диапазон замещения ионов  $\text{Cr}^{3+}$  ионами  $\text{Al}^{3+}$ , пожалуй, является ограниченным—до 0,06 атома на элементарную ячейку. Исследование при помощи рентгеновского микроанализатора показало присутствие очень необыкновенных, мелких зерен хромита, а также однородное распределение хрома в диките и каолините. Это указывает на то, что хром занимает октаэдрические места в структуре этих минералов. [E.C.]

**Resümee**—Drei Proben von blau-gefärbtem chromhaltigem Dickit und chromhaltigem Kaolinit wurden mittels Röntgenpulverdiffraktometrie, chemischer Analyse, Elektronenmikroskopie, optischen Methoden, und Infrarotspektroskopie untersucht, um festzustellen, ob das Chrom in der Mineralstruktur vorhanden ist oder als Verunreinigung vorliegt. Zwei der untersuchten Proben enthalten eine einzige überwiegende, chromhaltige Phase (entweder Dickit oder Kaolinit); die dritte Probe enthält beide Minerale zu gleichen Teilen. Die optische Absorption und die Infrarotspektren bestätigen die Anwesenheit von oktaedrisch koordiniertem Chrom. Der Bereich der  $\text{Cr}^{3+}$ - $\text{Al}^{3+}$ -Substitution ist ziemlich begrenzt: bis zu 0,06 Atomen pro Elementarzelle. Die Untersuchung mit der Elektronenmikroskopie zeigte sowohl das Vorhandensein von sehr wenigen, kleinen Chromitkörnern als auch eine einheitliche Verteilung des Chroms im Dickit und Kaolinit, was darauf hindeutet, daß das Chrom Oktaeder-Positionen in der Struktur dieser Minerale besetzt. [U.W.]

**Résumé**—Trois échantillons de dickite bleuâtre contenant du chrome et de kaolinite contenant du chrome ont été examinés par diffraction poudrée aux rayons-X, analyse chimique, et microprobe à électrons et par techniques optiques et à l'infrarouge pour déterminer si le chrome fait partie de la structure minérale ou est présent comme phase impure. Deux des échantillons étudiés contiennent une seule phase dominante contenant du chrome (soit la dickite ou la kaolinite); le troisième contient des proportions égales des deux minéraux. L'absorption optique et les spectres infrarouges sont compatibles avec la présence du chrome coordonné octaédralement. L'étendue de substitution de  $\text{Cr}^{3+}$ - $\text{Al}^{3+}$  est plutôt limitée: jusqu'à 0,06 atomes par maille. L'étude au microprobe à électrons a révélé la présence de très petits, rares, grains de chromite, ainsi qu'une distribution uniforme de chrome dans la dickite et la kaolinite, indiquant que le chrome occupe des sites octaédraux dans la structure de ces minéraux. [D.J.]