# **CHROME CHLORITE (KOTSCHUBEITE) FROM THE NUGGIHALLI SCHIST BELT\***

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#### *(Received* 19 *Au~lust* 1975)

Abstract Chrome chlorite associated with the chromite deposits of the Nuggihalli schist belt has been investigated by detailed mineralogical, chemical, X-ray diffraction, differential thermal and i.r. spectral analyses. Following the nomenclature of Lapham (1958) it is inferred that the chromium of the chrome chlorite is in the tetrahedral position and therefore the mineral is kotschubeite and not kaemmererite as suggested by earlier workers.

#### *Nomenclature of chrome chlorite*

The term "chrome chlorite" is used for the violet colored chlorite containing chromium to differentiate it from the green Fe-Mg chlorite. Orcel (1927) limits the percentage of  $Cr_2O_3$  to 2.0 for chrome chlorite, whereas Hey (1954) suggests the term "chrome chlorite" for chlorites with less than  $4\%$  of Cr<sub>2</sub>O<sub>3</sub>. Lapham (1958) has given a brief historical account of the nomenclature of the chromium chlorites and proposed a classification for them on the basis of crystallochemical studies. He concluded that the presence of  $Cr_2O_3$  up to 2.0% will not affect the crystal structure of chlorite and for all such chlorites he used the prefix "Cr". For chlorites containing more than 2.0% of  $Cr_2O_3$ , he proposed a nomenclature on the basis of the position of chromium in the chlorite structure. Chromium substitutes for A1 in the octahedral as well as in the tetrahedral position due to positional diadochy or comorphism (Lapham, 1958). Lapham restricts the term kaemmererite to the former variety and kotschubeite to the latter. Lapham's nomenclature is followed in the present investigation.

## INTRODUCTION

The term "Nuggihalli schist belt" is used for a narrow band of ultrabasics, green schists and amphibolites with workable deposits of chromite, found in the vicinity of Nuggihalli (Long. 76° 28' 37"E; Lat.  $13^{\circ}$  31"N). The schist belt extends over a length of 40 km and has an average width of 1.5 km. In the course of detailed geological mapping of the chromite deposits and the associated ultramafics, the attention of the authors was drawn to the brilliant pink chrome

chlorite occurring as veins and lenses. These veins contain calcite, serpentine, chromite and chrome chlorite. The object of this paper is to record the various properties of the chrome chlorite and to assign a name (from Lapham's classification) to this mineral as there is no unanimity amongst the researchers on its nomenclature. Varadarajan (1957) considered the flaky and the fibrous varieties as kaemmererite and kotschubeite, respectively, on the basis of the tetrahedral A1 content and  $Fe:Fe + Mg$ ratio. Viswanathaiah *et al.* (1974) concluded that both the flaky and fibrous varieties are kaemmererite following the nomenclature of Lapham *(op. cit.)* on the basis of differential thermal analyses, X-ray powder diffraction and chemical composition. As a part of the detailed investigation of the chromite deposits and the associated minerals of this schist belt, the authors studied the flaky variety of chrome chlorite by using various analytical techniques like DTA, X-ray powder diffraction, chemical and i.r.-absorption studies.

#### *Thin section study of the chrome chlorite*

The thin section study of the chrome chlorite lenses and veins reveals the presence of chromite, chrome chlorite, serpentine and calcite. Euhedral grains of chromite show numerous inclusions of chrome chlorite and calcite giving the appearance of a sieve texture. Chromite grains are highly fractured and a few have been reduced to a fine powder while a few occur as skeletal crystals, which indicates the intense corrosion undergone by the chromite grains. These grains of chromite appear to have been cemented together by chrome chlorite.

The chrome chlorite is present as scales and flakes and shows effects of deformation. Chrome chlorite is colorless and shows marine blue interference colors. Most of the grains are uniaxial negative, but a few

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biaxial negative grains are also discernible with  $-2E$ varying from  $15^\circ$  to  $17^\circ$ .

# *Methods of study of chrome chlorite (kotschuheite)*

The chrome chlorite is separated from the remaining minerals by grinding to  $-200$  mesh (B.S.S.), using heavy liquids, a Frantz's Isodynamic Separator and by hand picking. The purified mineral is subjected to X-ray powder diffraction using a Shimadzu diffractometer with  $CuK\alpha$  radiation. Chemical analysis of the chrome chlorite was carried out on a spektromorn 202 after the methods of Shapiro and Brannock (1956). Chromium content was determined volumetrically after the method of Mall (1967). The differential thermal analysis was carried out on a recording type of Shimadzu unit at the heating rate of  $12^{\circ}$ C/min. The i.r. spectrum of the sample was taken on Carl Zeiss equipment in a Nujol Mull.

## *X-ray study*

The purified fraction of the chrome chlorite was subjected to X-ray powder diffraction. The  $d$  spacings together with their intensities are given in Table 1. Lapham (1958) has established a relationship between the intensities of the interplanar spacings and the percentage of chromium oxide after a detailed study of the chrome chlorites. Viswanathaiah *et al.* (1974) have given X-ray powder diffraction data for the two forms of chrome chlorites of the Nuggihalli schist belt. The intensity of (001) for the flaky and fibrous varieties reported by Viswanathaiah *et al.* (1974) are 25 and 29, respectively. When these are plotted on the diagram of Lapham (Fig. 1) against the percentage of  $Cr_2O_3$  they indicate that 7.75 and 6.70% of  $Cr_2O_3$ are present if the intensities of (001) are correctly determined. On the contrary, Viswanathaiah *et al.*  (1974) have determined only 3.9 and 4.0% of  $Cr_2O_3$ by analysis, an amount very much less than the quantity inferred from Fig. 1. The intensity of (215) and the difference in the intensities of  $(003)$  and  $(001)$ recorded by Viswanathaiah *et al.* (1974) are very high and when plotted on the appropriate diagrams of Lapham (Figs. 2 and 3) they do not fall even within



Fig. 1. Variation in chrome oxide content with (001) intensity (after Lapham, 1958). A and B-Samples of Viswanathaiah et al. K-Sample under study.



Fig. 2. Variation in chromic oxide content with (215) intensity (after Lapham, 1958). K-sample under study.



Fig. 3. Variation in chromic oxide content with (003) intensity minus (001) intensity (after Lapham, 1958). A and B-Samples of Viswanathaiah et al. K-Sample under study.

reasonable limits on the curves. Similarly the intensities of (007) and (002) of the samples of Viswanathaiah et al. (op. cit.) show considerable dispersion when plotted on Figs. 4 and 5. From the plotting of the intensities of the various d spacings and  $Cr_2O_3$ percentages given by Viswanathaiah et *al.* (1974), the authors think that there is some discrepancy between the intensity of the d spacings and the percentage of  $Cr_2O_3$ .

When the intensities of the various interplanar spacings of the chrome chlorite (kotschubeite) under



Fig. 4. Variation of chromic oxide content with (007) spacing (after Lapham, 1958). A and B-Samples of Viswanathaiah et al. K-Sample under study.



Fig. 5. Variation in chromic oxide content (002) intensity (after Lapham, 1958). A and B-Samples of Viswanathaiah *et al.* K-Sample under study.

investigation are plotted on the various diagrams of Lapham (1958) it is observed that not only the percentage of  $Cr<sub>2</sub>O<sub>3</sub>$  corresponds with the intensities of the various d spacings, but also the plottings indicate that Cr is in the tetrahedral position and that the mineral is kotschubeite. The  $d$  spacings and the intensities of chrome chlorite (kotschubeite) readily correspond with the  $d$  spacings and the intensities of kotschubeite reported by Lapham (I958), and are given in Table 1 for purposes of comparison.

# *Differential thermal analysis of chrome chlorite (kotschubeitel*

The DTA curve of the chrome chlorite is given in Fig. 6. The curve has two endothermic peaks, one at  $720^{\circ}$ C and the other at  $850^{\circ}$ C, and one exothermic peak at  $825^{\circ}$ C. Lapham (1958) after thermal analysis of nine chrome chlorites states that most of the samples are characterized by the presence of one exothermic peak and two endothermic peaks and in most of the samples an additional exothermic peak at  $350^{\circ}$ C is recorded. Out of the nine chrome chlor-

Table 1. X-ray powder diffraction data of chrome chlorite



Fig. 6. Thermogram of chrome chlorite.

ites, two do not show the presence of an exothermic peak at 350°C.

Lapham *(op. cir.)* opines that the broad peak at 350°C indicates weak oxidation. It is interesting to note that the chrome chlorite of Byrapur, the chemistry and the X-ray powder diffraction of which closely agree with the chrome chlorite (kotschubeite) of Siskiyou Country, does not show an exothermic peak at 350°C suggesting the absence of oxidation during heating. In order to confirm this chrome chlorite was heated in a muffle furnace up to a temperature of 350°C and later was analysed chemically. The chemical analyses showed hardly any difference in the chemistry from the pre-heated sample except for the loss of water. The first and second endothermic peaks of the chrome chlorite of Byrapur area are at 720 and 850°C as in the chrome chlorite (kotschubeite) of Siskiyou County, (Lapham. 1958: Sabatier, 1950) reported that the increase in the substitution of iron for magnesium in the octahedral sites decreases the decomposition temperature from a maximum of 700 to below 600°C. Comparatively, a higher percentage of Mg in the chrome chlorite of Byrapur. as revealed by the chemical analysis, points out a lesser amount of substitution and hence the resultant endothermic peak is at a higher temperature. Lapham (op. cit.) has correlated the percentage of  $Cr_2O_3$  with the temperature of the first endothermic peak and obtained



1. Chrome chlorite (kotschubeitel. Byrapur. India.

2. Kotschubeite. Siskiyou County, California



Fig. 7. Variation in chromite oxide content with temperature of decomposition of the brucite layer (after Lapham, 1958). A and B--Samples of Viswanathaiah et al. K--Samples under study.

Table 2. Chemical analyses of the chrome chlorites (kotschubeites)

Constituents.		$\mathbf{1}$		$\cdot$ 2	×.	$-3$	
$\sin \theta$		32.68		32.08		32.53	
$A1_20_3$		12.85	÷,	13.98	i.	13.28	
$Fe_{2}0_{3}$			$\therefore$ 0.87 $\therefore$ Total iron	$-0.42$		$-1.84$	
FeO		0.38					
$Cr_2O_3$		$3 - 60$		3.40		3.61	
Mn0		0.34		0.02			
Ti0 <sub>2</sub>		Traces		Traces		Traces	
Mg <sub>0</sub>		37.39		34.66		37.04	
Ca0		1.18		0.72			
N i 0		n.d		0.09		0.16	
$H_20$		0.45		0.32			
$H20+$		10.97		12.93		10.18	
$K_{2}0$		n.d		Traces			
Na <sub>2</sub> 0		n.d		Traces			
	Total:	99.91		99.98		99.47	

1. Chrome chlorite (kotschubeite), Byrapur, India; Analyst: K. T. Damodaran.

2. Kotschubeite, Siskiyou County, California; Analyst: W. H. Herdsman.

3. Kotschubeite, East Siberia; Analyst: V. V. Lyakhovich.

Calculated structural formula from chrome chlorite (kotschubeite).

 $Ca_{0.12}$  (Si<sub>3.15</sub> Al<sub>0.58</sub> Cr<sub>0.27</sub>)<sub>4</sub>.<br>(Al<sub>0.88</sub> Fe<sub>0.035</sub> Fe<sub>0.03</sub> Mn <sub>0.03</sub> Mg<sub>5.4</sub>)<sub>6.34</sub> O<sub>18</sub> H<sub>7.0</sub>.

two curves, each one of them representing Cr in tetrahedral and in octahedral positions. The temperature of the first endothermic peak and the  $Cr_2O_3$  content of the chromium chlorite under study when plotted on Fig. 7 fall on the curve which represents chromium in tetrahedra! position and thereby suggest that the mineral is kotschubeite. From the first set of endothermic peaks obtained by Viswanathaiah *et al.* (1974) it stands to reason that an increase in  $0.1\%$  of  $Cr_2O_3$ has increased the decomposition temperature by  $9^{\circ}$ C. But it should be noted that the temperature of the first set of endothermic peaks of both the minerals (A)  $(710^{\circ}$ C) and (B)  $(702^{\circ}$ C) (Viswanathaiah *et al.* (1974) when plotted on Fig. 7 indicate the presence of only 2.9 and 3.1% of  $Cr_2O_3$ , whereas 3.9 and 4.0% of  $Cr_2O_3$  are determined by chemical analyses (Viswanathaiah *et al.,* 1974). According to the conclusions drawn by Viswanathaiah *et al.* (1974) the temperature of the first set of the endothermic peaks logically should fall between 90 and  $81^{\circ}$ C. Such a lowering of the temperature of the first set of endothermic peaks has not been recorded by Viswanathaiah *et al.*  (1974) and therefore it appears that there is a considerable disagreement between the temperatures of the endothermic peaks and the percentage of  $Cr_2O_3$ .

#### *Chemistry of the chrome chlorite (kotschubeite)*

A glance at the chemical analysis of the chrome chlorite (kotschubeite) given in Table 2, shows that the mineral contains  $3.6\%$  Cr<sub>2</sub>O<sub>3</sub>. The chemical com-

Table 3. I.r. spectral bands showing absorption at different wavelengths

ı. 2.73W 2.79 M 2.90 M	6.12 W	10.04 S	12.16 W	
	9.25W 9.60 M	10.40 S 11.50 W	15.26 W	
$\overline{2}$ . 2.71 W 2.77 M 2.90 M	6.10W 9.17 W 9.62S	10.10 S $10.48$ M 11.50 W	12.18 W 15.29W	

1. Kotschubeite, Siskiyou County, California (Tuddenham and Lyon 1959).

2. Chrome chlorite (kotschubeite), Byrapur, India.

position of this chrome chlorite of the Nuggihalli schist belt on comparison readily agrees with the chemical composition of the kotschubeites reported by Lapham (1958) and Lyakhovich (1961) and are given in Table 2. The structural formula of the mineral is calculated on the basis of 18 oxygen atoms.

# *l.r. spectroscopic study of chrome chlorite (kotschubeite)*

Tuddenham and Lyon (1959), after a detailed study of the "relation of i.r. spectra and chemical analyses of some chlorites and related minerals", arrived at some important conclusions. According to these authors "an unknown chlorite mineral sample can be classified from an i.r. study alone". Phillips (1954) proposed the name kotschubeite for the chrome chlorite from Siskiyou County, CA, on the basis of optical, X-ray powder diffraction and Lapham *(op. cit.)* also named the chrome chlorite of Siskiyou County as kotschubeite on the basis of crystallochemical studies. Tuddenham and Lyon (1959) analysed 21 different chlorites including kotschubeite. The absorption bands obtained by Tuddenham and Lyon *(op. cit.)*  at various wavelengths are given in Table 3, together with the absorption bands for the chrome chlorite (kotschubeite) of Byrapur. The bands of the i.r. spectrum of the chrome chlorite under study, on comparison, correspond with those of kotschubeite given by Tuddenham and Lyon (1959). Chemical, X-ray powder diffraction and DTA studies establish that the chrome chlorite is kotschubeite. It is interesting to note that the i.r. spectroscopic study also indicates that the chrome chlorite of Nuggihalli schist belt is *kotschubeite* and not kaemmererite as suggested by earlier researchers.

*Acknowledgements--The* authors wish to thank Dr. M. S. Sadashivaiah, Professor and Head of the Department of Geology, Karnatak University, Dharwar for his careful reading of the manuscript and valuable suggestions. The authors wish to express their gratitude to Prof. S. W. Bailey, University of Wisconsin and Prof. J. Zussman, the University of Manchester for their criticism and suggestions. Thanks are due to the authorities of the Indian Institute of Science, Bangalore for the i.r. spectrum of chrome chlorite. One of the authors (K.T.D.) is thankful to CSIR for financial assistance.

#### **REFERENCES**

- Hey, M. H. (1954) A new review of the chlorites: *Min. Mag.* 30, 227-292.
- Lapham, D. M. (1958) Structural and chemical variation in chromium chlorite: *Am. Miner.* 43, 921-956.
- Lyakhovich, V. V. (1961) Chrome chlorite-kotschubeite from East Siberia: *Geol. i. Geofiziki*. **11,** 144 146 (Original not referred) Min. Ahst. 17.
- Mall, A. P. (1967) A Scheme for the rapid analysis of chromite and chrome ore: *J. Geo. Chem. Soc. Ind. 2,*  111-121.
- Orcel, M. J. (1927) Recherches sur la composition chimique des chlorites: *Bull. Soc. France. Min.* 50, 75-456.
- Phillips, W. R. (1954) Crystal chemical classification of the chlorite minerals: Ph.D. thesis, University of Utah (Original not referred).
- Sabatier, G. (1950) Sur l'influence de la dimension des cristaux de chlorites sur leurs courbes d'analyse thermique differentieUe: *Soc. Franc. Min. Crist. Bull* 73, 43-48.
- Shapiro, L. and Brannock, W. W. (1956) A rapid analysis of silicate rocks: A contribution to geochemistry: *U.S. Geol. Surv. Bull.* 1036 C.
- Tuddenham, W. M. and Lyon, R. U. P. (1959) Relation of i.r. spectra and chemical analysis for some chlorites and related minerals: *Anal. Chem.* 31, 377-380.
- Varadarajan, S. (1957) Chrome chlorites from the ultrabasic rocks near Byrapur, Hassan District: *J. Mysore Univ.* 16, 239-252.
- Viswanathaiah, M. N., Tareen, J. A. K. and Satish, P. N. (1974) Kaemmererites from chromite deposits of Byrapur, Hassan District, Karnatak State: *Curr. Sci.* 43, 202-205.