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A spectroscopic and X-ray study of the coordination of Cr^{3+} ions in chlorites

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Abstract

Ten chromian chlorites were examined by X-ray power diffraction and optical spectroscopic methods to determine the coordination of the chromium ion. The absorption spectra of all ten chlorites are essentially identical and are fully consistent with the presence of octahedrally coordinated chromium. There is no evidence for the presence of tetrahedrally coordinated chromium. These results are consistent with the high octahedral site preference energy of the Cr^{3+} ion. Application of determinative curves to the X-ray data yields total octahedral heavy atom contents that agree approximately with published chemical analyses if all heavy atoms are placed in octahedral sites rather than partitioned between octahedral and tetrahedral sites. The experimental data indicate appreciable segregation of heavy atoms into the interlayer octahedral sites.

Because of the small amounts of chromium involved and the absence of tetrahedral chromium, the author supports the view of Bayliss (1975) that the names kotschubeite and kämmererite should be dropped. A "Cr" or "chromian" prefix used with the currently accepted chlorite name appears adequate.

Introduction

The chlorite species kotschubeite and kämmererite were originally designated as chromium-containing penninite and clinochlore. Since that time, the names have been given to chlorites of a variety of compositions and have occasionally been applied interchangeably. Lapham (1958) and Bailey (1975) give historical accounts of Cr–chlorite classification and nomenclature. Lapham (1958), using X-ray, optical, chemical, and DTA data of chromium-containing chlorites, proposed a classification based on whether the chromium occupies octahedral or tetrahedral sites. For chlorites containing less than 2 percent Cr_2O_3, he recommended adding "Cr" as a prefix to the name. For Cr_2O_3 contents greater than 2 percent, he suggested the name kotschubeite when chromium occupies the tetrahedral sites and kämmererite when chromium occupies octahedral sites. In spite of the difficulties in unambiguously determining the structural position of the chromium, this classification appears to be gaining acceptance. McCormick (1975) reported a Cr–chlorite from North Carolina which he called kotschubeite based on determination of the Cr coordination by acid-leaching studies, and he supported retention of Lapham's classification. Damodaran and Somasekar (1976), using the determinative methods outlined by Lapham (1958), concluded that a Cr-chlorite from India, previously called kämmererite, was actually kotschubeite.

Since the time of Lapham's investigation, the structures of several Cr-containing chlorites have been solved by single-crystal X-ray methods (Steinfink, 1958; Brown and Bailey, 1963; Lister and Bailey, 1967). No examples of tetrahedral Cr^{3+} ions were encountered, and in two of the three chlorites the chromium was found preferentially enriched in the interlayer octahedral sheet.

Crystal field theory has found wide application in mineralogy, especially in rationalizing and predicting observed cation ordering and segregation. Burns (1970) showed that the octahedral site preference energy for Cr^{3+} is the largest of the first-series transition metals (see Burns (1975) for a discussion of the $3d$ orbital splitting and the crystal field stabilization energy acquired by Cr^{3+}). In a survey of Cr-containing minerals, Burns and Burns (1975) stated that "no validated examples exist of tetrahedrally coordinated Cr^{3+} ions in mineral structures" and that both kotschubeite and kämmererite have the same optical absorption spectra. Neuhaus (1960) also concluded from optical absorption spectral data that the chromium in one sample each of fuchsite and kämmererite was octahedrally coordinated.

For these reasons and because of the recent publications describing tetrahedral chromium in chlorites, a spectroscopic and X-ray examination of Cr–chlorites, including those examined by Lapham, seemed in order.

Experimental

A total of ten chromium-containing chlorites was examined. Four samples were from the F. A. Genth collection of the Pennsylvania State University, a sample from Day Book, North Carolina was kindly donated by G. R. McCormick (see McCormick, 1975), and five samples from the same material studied by Lapham (1958), three of which were reported to contain tetrahedral Cr^{3+} ions, were obtained from the Smithsonian Institution. Sample identifications and localities are presented in Table 1.

Optical absorption spectra between 350 and 2500 nm (*i.e.* 28,570 and 4000 cm^{-1}) of powders and solid samples were obtained, using the diffuse reflectance attachment of a Beckman DK-2A spectrophotometer. X-ray intensities of basal reflections were obtained on a Philips high-angle diffractometer with Ni-filtered Cu$K\alpha$ radiation using cavity mounts and a scanning speed of 0.5° 2θ/min. Particular care was taken in assuring that the sample area fully contained the X-ray beam for all reflections; a 1/4° divergence slit was used, and the irradiated area was examined using a fluorescent screen.

Results

The absorption spectra of all ten chlorites are essentially identical, and the spectra of several chlorites are shown in Figure 1. Absorptions at 1400, 1900, and 2300 nm due to overtones and combinations of OH^- and H_2O vibrations are the only features obvious between 900 and 2500 nm and are identical for all chlorites. The absorption bands and crystal field parameters are tabulated for all ten chlorites in Table 2 to facilitate comparison with the data of Poole (1964), White *et al.* (1971), and Burns (1975). Two prominent absorptions are present in all spectra; one about 555 nm (ν_1, 18,000 cm^{-1}) is assigned to the $4_{A_{2g}}$–$4_{T_{2g}}(F)$ transition and one about 390 nm (ν_2, 25,600 cm^{-1}) is assigned to the $4_{A_{2g}}$–$4_{T_{1g}}(F)$ transition,

Table 1. Chromian chlorite identification and description

Sample Number*	Locality, Identification, and Description
1	Kotschubeite, Ufaleisk, S. Urals. F. A. Genth #468.6. Large mass of single crystals.
2	Kotschubeite, Schischimsk, Ural. F. A. Genth #468.7. Thin coating on chromite.
3	Kämmererite, Moro Phillips Mine, Marple, Delaware Cty., Pa. F. A. Genth #468.A.9. Fibrous material aligned across a vein.
4	Kämmererite, Moro Phillips Mine, Marple, Delaware Cty., Pa. F. A. Genth #468.A.10. Massive material on chromite.
5	Kotschubeite, Day Book Body, Yancey Cty., N. Carolina. Given by G. R. McCormick. Small separate flakes.
6	Kämmererite, Texas, Pa. USNM #R4534. Small mass of chlorite plus serpentine.
7	Kämmererite, Webster, N. Carolina. USNM #97548. Small separate flakes.
8	Kämmererite, Siskiyou Cty., Calif. USNM #104723. Large crystals on chromite.
9	Clinochlore (kotschubeite), Bilimbaievsk District, Urals. USNM #16261. Mass of single crystals.
10	Kämmererite, Deer Creek, Wyoming. USNM #93908. Mass of crystals on chromite.

*Samples will be referred to throughout the paper using these numbers.

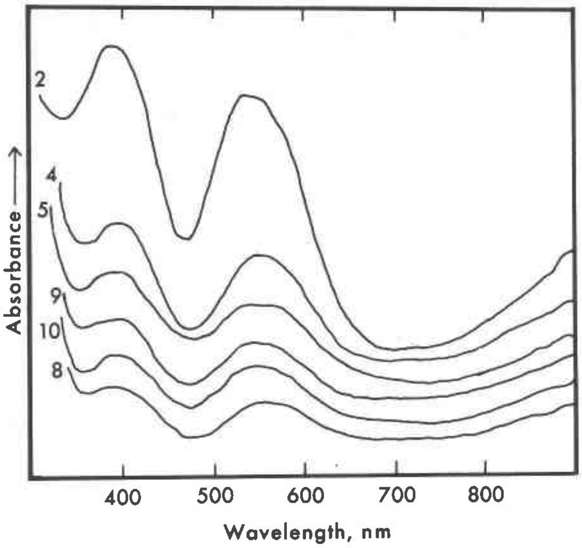

Fig. 1. Optical absorption spectra of various chromian chlorites. Numbers next to the individual spectra refer to sample numbers in Table 1.

both of which are in very close agreement with the data for a kämmererite given by Neuhaus (1960) and various data presented by Burns (1975) and White *et al.* (1971). The $4_{A_{2g}}$–$4_{T_1}(P)$ transition at higher frequencies is obscured by intense oxygen-metal charge-transfer bands (Burns and Vaughan, 1975, p. 47). All absorption bands and crystal field parameters are fully consistent with octahedral Cr^{3+}, and there is no evidence for the presence of tetrahedrally coordinated Cr^{3+} ions. Tetrahedral ion transitions have absolute intensities between 10 and 100 times larger than the corresponding octahedral transitions, and small amounts of tetrahedral Cr^{3+} ions would probably lead to noticeable absorption at about 685 and 1540 nm (calculated from $Dq_{\text{tet}} = \frac{4}{9} Dq_{\text{oct}}$). The crystal field splitting parameter, *Dq*, which is a measure of the strength of interaction between the Cr^{3+} ion and its surroundings, is given by $Dq = 1/10\nu_1$. *Dq* is directly related to the crystal field stabilization energy by a factor 6/5. The Racah B parameter is

$$B = \frac{1}{3} \frac{(2\nu_1 - \nu_2)(\nu_2 - \nu_1)}{9\nu_1 - 5\nu_2}$$

(Poole, 1964) and is related to the "covalency" of the Cr–O bond.

Table 2. Absorption bands and crystal field parameters for various chlorites

Sample Number	ν_1(nm)	ν_2(nm)	Dq (cm^{-1})	B (cm^{-1})
1	548	384	1825	795
2	547	390	1829	735
3	551	nr*	1815	---
4	555	391	1802	765
5	552	391	1811	757
6	557	394	1795	752
7	553	nr.	1808	---
8	561	391	1782	800
9	554	390	1805	773
10	552	393	1812	735

*not resolved

The X-ray powder data reveal that all the chlorites examined are of the IIb polytype, and the patterns are very similar to those presented by Lapham, with the exception of his sample from Turkey, which is a Ia chlorite (Bailey and Brown, 1962). Intensities for the first five basal reflections are presented in Table 3 as peak heights relative to the strongest reflection (002). Peak areas were also measured and yielded similar results. Application of the curves constructed by Lapham (1958) yields no information in this case; intensity differences on his curves are well within experimental error. However, the determinative curves of Petruk (1964) and the graph of Oinuma *et al.* (1973) yield useful results. Both methods are designed to determine total octahedral heavy-atom content (Fe, Cr, Mn, Ni) and the degree of asymmetry in octahedral heavy-atom distribution, defined as the number of heavy atoms in the talc-like octahedral sheet minus the number of heavy atoms in the interlayer octahedral sheet. Results obtained after application of the two methods, assuming a total cation valence of 28, are presented in Table 4. There are appreciable differences between the values obtained by the two methods and those determined in the published chemical analyses; however, total heavy atom contents are reasonably approximated in most cases if all heavy atoms are placed in octahedral sites. In every case, values of asymmetry are negative and indicate appreciable segregation of heavy atoms into the interlayer octahedral sites.

Table 3. Observed peak heights for the first five basal reflections*

Sample Number	I_{001}	I_{002}	I_{003}	I_{004}	I_{005}
1	53	100	81	72	19
3	40	100	75	73	18
4	61	100	76	67	19
5	66	100	75	71	19
7	59	100	79	76	21
8	66	100	78	74	20
9	42	100	83	73	19
10	47	100	82	69	19

*Peak heights relative to I_{002} = 100

Table 4. Degree of asymmetry and total octahedral heavy atom content determined from determinative curves*

Sample No.	Asymmetry (P)	Asymmetry (O,S,S)	Oct.(P)	Oct.(O,S,S)	Oct.(Obs.)	Cr^{3+}(obs.)
1	-0.63	-0.46	0.45	0.51	na**	na
3	-0.57	-0.57	0.53	0.75	na	na
4	-0.50	-0.35	0.38	0.60	na	na
5	-0.45	-0.30	0.39	0.60	0.61	0.47
7	-0.32	-0.40	0.20	0.51	0.63	0.27
8	-0.42	-0.34	0.33	0.50	0.47	0.26
9	-0.68	-0.60	0.39	0.60	na	
10	-0.66	-0.55	0.38	0.55	0.76	0.60

*(P) - determined from the curves of Petruk (1964), (O,S,S) - determined from the plot of Oinuma, Shimoda, and Sudo (1973), (Obs.) - Observed total heavy atom content and Cr^{3+} ions taken from the literature, samples 7,8,10 from Lapham (1958) and sample 5 from McCormick (1975), all data normalized to a total cation valence of 28.

**na - not analyzed.

Discussion and conclusions

The absorption spectra show unambiguously the presence of Cr^{3+} ions in octahedral coordination in all chlorites examined, including those which have been reported previously as containing tetrahedral chromium. There is no evidence for tetrahedral Cr^{3+} ions in any of the spectra. X-ray determinative curves give octahedral heavy-atom contents in approximate agreement with published chemical analyses if all Cr^{3+} ions are octahedrally coordinated. In addition, asymmetry values are all negative, indicating that a large proportion of the octahedral heavy atoms are present in the interlayer octahedral sheet. These results are in agreement with the structure analyses of Cr–chlorites showing preferential enrichment of Cr^{3+} ions in the interlayer octahedra (Brown and Bailey, 1963; Lister and Bailey, 1967). Neuhaus and Richartz (1958) suggested that the chromium in a sample of kämmererite must be contained in the interlayer octahedra in order to explain the large optical absorption-energy differences between fuchsite (Cr–muscovite) and kämmererite (23,580 and 15,820 cm^{-1} for fuchsite versus 25,640 and 18,180 cm^{-1} for kämmererite). The difference in size between the 2:1 octahedra and the interlayer octahedra is probably insufficient to cause such a large shift in the absorption bands; differences in the local environment of the octahedra in the *c* direction must be partly responsible for the observed changes.

Reasons for disagreement with previous determinations may arise from the fact that correct intensities of low-angle reflections are difficult, if not impossible, to obtain without a very narrow divergence slit on the diffractometer. Otherwise, only part of the radiation hits the sample at low angles but all of it hits at higher angles. Thus, low-angle reflections will appear abnormally weak in comparison with high-angle reflections. In addition, Lapham's intensity curves rely on intensity measurements accurate to better than ±5 percent, accuracy usually not obtained without employing special precautions. Damodaran and Somasekar (1976) not only quote intensities supposedly accurate to better than ±1 percent, they tabulate intensities without normalizing the strongest reflection to 100 and then apply Lapham's curves to these intensities. Their results would have been quite different had they normalized the intensities.

The reason for the disagreement with McCormick's (1975) conclusion that tetrahedral chromium is present, which he based on acid-dissolution studies, is not readily apparent. However, Ross (1969) presents arguments that acid-dissolution studies do not readily discriminate between octahedral and tetrahedral cations. His chemical data support a two-dimensional diffusion model, and microscopic examination of chlorite crystals shows that the acid attack begins along cracks and structural defects.

Because of the present evidence arguing against the presence of tetrahedral Cr^{3+} ions, it appears that the classification of Lapham (1958) based on the structural site of the chromium is not well-founded. Due to the very high octahedral site preference energy of Cr^{3+}, it is unlikely that a chlorite containing tetrahedral chromium will be found. Considering the small amounts of chromium involved (<10% Cr_2O_3, yielding less than one out of six octahedral cations) and the apparent absence of tetrahedrally coordinated

Cr^{3+} ions, the author supports the suggestion of Bayliss (1975) that the names kotschubeite and kämmererite should be dropped in favor of using a "Cr" or "chromian" prefix with the currently accepted name.

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