

A Chemical Study of Kämmererite, Day Book Body, Yancey County, North Carolina

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Abstract

Single crystal X-ray photographs of purple kämmererite from the Day Book Body, Yancey County, North Carolina, exhibit cell dimensions of $a_0 = 5.24 \pm 0.01 \text{ \AA}$, $b_0 = 9.17 \pm 0.01 \text{ \AA}$, $c_0 = 14.39 \pm 0.1 \text{ \AA}$, $\beta = 97^\circ 5'$. A chemical analysis yields a structural formula of $[\text{Al}_{1.7}\text{Cr}_{0.4}\text{Mg}_{0.5}\text{Fe}_{0.2}\text{Ni}_{0.7}]^{\text{VI}}_{12.5} [\text{Si}_{8.5}\text{Cr}_{0.5}\text{Al}_{1.0}]^{\text{IV}}_8\text{O}_{20.8}(\text{OH})_{16.7}$. Since the Cr was neither predominantly tetrahedral nor predominantly octahedral it could not be classified by Lapham's classification. The author proposes that traditional meanings of kämmererite and kotschubeite be preserved and extended so that kämmererite contains $\text{Cr}^{\text{VI}} \geq \text{Cr}^{\text{IV}}$ (in number of atoms) and kotschubeite contains $\text{Cr}^{\text{VI}} < \text{Cr}^{\text{IV}}$ (in number of atoms).

Chrome Chlorite Nomenclature

Chlorites may contain up to 15 percent Cr_2O_3 ; amounts over 2 percent impart a distinctive pink color to the chlorites. Five varietal names have been proposed for these pink colored chlorites (Dana, 1892): kämmererite, rhodophilite, chrome-chlorite, rhodochrome, and kotschubeite.

Lapham (1958) has proposed the following classification for Mg, Fe, and Cr-bearing chlorites. Those containing less than 2 percent Cr_2O_3 are called Cr-penninite, Cr-clinocllore, Cr-prochlorite, or Cr-corundophilite depending on the content of Si in the tetrahedral layer; those containing greater than 2 percent Cr_2O_3 are called kotschubeite if the Cr is in the tetrahedral sites and kämmererite if the Cr is in the octahedral sites. The author has several objections to Lapham's classification. The only difference between clinocllore as originally described by Blake (1852) and chlorite as the term was used at the time was that clinocllore contained 1.686 percent Cr_2O_3 ; to exclude Cr_2O_3 -bearing chlorites from the clinocllore classification, in view of the original definition of clinocllore, appears unreasonable. A more serious objection is Lapham's use of the kotschubeite and kämmererite; the use of the terms in the proposed manner is not in accordance with the firmly established traditional usage of Dana. Another strong objection is that basing the name on whether the Cr is in the tetrahedral or octahedral sites, until the present, has required a time consuming structural analysis to identify the

variety. Nevertheless, Lapham's classification is gaining acceptance.

Chrome Chlorite Occurrences

An extensive search of the literature reveals that pink chromium chlorites occur almost invariably in dunites, harzburgites, or lherzolites associated with chromite and magnesiochromite. The chlorite usually occurs in the chromite in small veins or as coating on fractures. The ultrabasic host rock is often altered to a serpentinite; however, serpentinitization is not necessary for the formation of kämmererite since it is found in fresh dunite at the Day Book Body.

Geology of the Day Book Body

The Day Book Body, about a mile long and half a mile wide, is located on North Carolina state highway 197 at Mine Fork Creek about three miles north of Burnsville, Yancey County, North Carolina. The country rock surrounding the body is a mica gneiss interlayered with hornblende gneiss (Kulp and Brobst, 1954). Field relations suggest that the dunite intruded the country rock before emplacement of pegmatites but after the start of regional metamorphism. The contact between the body and the country rock is marked by a zone a few inches to a few feet thick of talc, enstatite, anthophyllite, and serpentine. The core of the body is fresh olivine cut by east-striking chromite veins, north-striking fractures coated with vermiculite, and random pegmatite

dikes. Kulp and Brobst (1954) have shown that the pegmatites reacted with the dunite to form a sheath of talc, anthophyllite ($\beta = 1.638 \pm 0.001$; $\alpha = 1.63$), and phlogopite ($\beta = 1.612 \pm 0.002$; $2V = 2-3^\circ$). The phlogopite has weathered within 40 feet of the surface to vermiculite.

Kämmererite is found intergrown between chromite and olivine grains seemingly at the expense of olivine or chromite and as fracture filling in massive chromite. The olivine in the dunite of the Day Book Body is high in magnesia (48.77 wt percent), contains ninety mole percent forsterite, and has $\beta = 1.670 \pm 0.001$. The chromite in the Day Book Body occurs both in small disseminated grains in the dunite and as massive nodules in thin, discontinuous veins in the dunite; the disseminated and massive chromite are both high in magnesia and alumina ($\text{Cr}_2\text{O}_3 = 44.20$; $\text{MgO} = 14.48$; $\text{Fe}_2\text{O}_3 = 20.05$; and $\text{Al}_2\text{O}_3 = 21.30$).

X-Ray Analysis

The Day Book Body kämmererite cell dimensions obtained from equi-inclinal Weissenberg and precession photographs are: $a_0 = 5.24 \pm 0.01 \text{ \AA}$, $b_0 = 9.17 \pm 0.01 \text{ \AA}$, $c_0 = 14.39 \pm 0.01 \text{ \AA}$, and $\beta = 97^\circ 5'$. This agrees reasonably well with values reported by Brown and Bailey (1960) and Garrido (1959).

The photographs indicate monoclinic symmetry; on the basis of spacing and extinctions the kämmererite was assigned to the space group $C2/m$. Although the Weissenberg photographs show monoclinic symmetry, the intensities of corresponding spots are unequal and some workers believe such unequal intensities indicate a triclinic space lattice. Brown and Bailey (1960) reported a space group of $C\bar{1}$ for a Turkish kämmererite on the basis of statistical tests made on $k \neq 3n$ reflections and theoretical stacking models. However, since there was no conclusive evidence that unequal intensities were caused by different symmetry rather than a mechanical cause inherent in the camera or film, it seemed reasonable to assign the $C2/m$ space group rather than $C\bar{1}$.

Chemical Analysis

Fragments of kämmererite were hand picked under a binocular microscope from fractures in massive chromite. The fragments were then crushed to -200 mesh and run through a magnetic separator to remove any residual chromite. The crushed samples were dried for a week at 186°C to drive off absorbed water. Weighed splits (0.1 gm) were heated to 750°C

for three days, then reweighed to determine hydroxyl content. The splits were then dissolved using the method of Rader *et al* (Belt, 1967) except that excess acid was used for the size of the sample. The solutions were analyzed by the atomic absorption method, and the cation weight percents were recalculated to weight percent oxide (Table 1).

The amounts of Si, Al, Mg, and Cr in the tetrahedral and octahedral sites were determined directly by a method of acid dissolution described by Brindley and Youell (1951) and Gastuche and Fripiat (1962). In order to use the method it was first necessary to determine the rates of solution of Al, Mg, and Cr in acid to see if the rates of dissolution of tetrahedral cations are sufficiently different from the rates of dissolution of octahedral cations to allow for site determination. For this study the rates of dissolution of Mg and Al as determined by Brindley and Youell (1951) were used. They found that after $1\frac{1}{4}$ hours 100 percent of the Mg and 47 percent of the Al was in solution. The rate of solution of Al is greatly reduced after $1\frac{1}{4}$ hours, which is interpreted to mean that tetrahedral Al has a much slower rate of dissolution in acid than does octahedral Al. The rate of solution of Cr in acid was determined (Fig. 1) and was found to become much slower after 4 hours. This change in rate is attributed to the solution of octahedral chrome versus the solution of tetrahedral chrome.

A 0.1 g sample was placed in 1:1 HNO_3 , heated to 70°C for 4 hours, filtered, and the filtrate brought to volume in a 100 ml flask. X-ray diffraction patterns of the residue yield a cristobalite pattern which indicates that the tetrahedral layer is still present whereas the brucite layer and octahedral portion of the talc layer are in solution. The residue was then fused with 0.6 gm $\text{NaB}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ at 1000°C for 15 minutes. The sample was quenched, dissolved with HCl, and brought to volume in a 100 ml flask. Both solutions

TABLE 1. Total Chemical Analysis of Kämmererite from the Day Book Body

	weight percent		weight percent
SiO_2	34.29	CaO	0.02
Al_2O_3	12.22	NiO	0.43
Cr_2O_3	6.39	Na_2O	0.08
FeO	1.33	K_2O	0.01
MgO	33.82	H_2O	12.56
MnO	0.01	Total	101.16

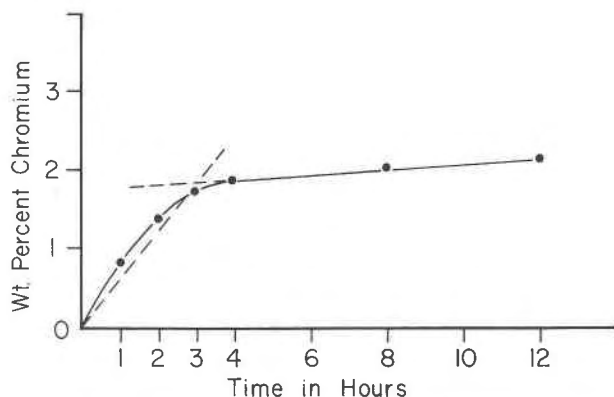
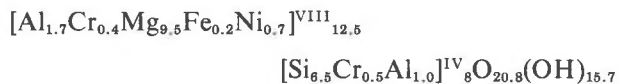


FIG. 1. Rate of solubilities of chromium in 1:1 nitric acid. The steep slope represents the dissolution of octahedral chromium, and the gentle slope represents the dissolution of tetrahedral chromium.

were analyzed for Si, Al, Cr, and Mg by the atomic absorption method and the wt percent cations recalculated to wt percent oxide (Table 2). A bulk fusion with $\text{NaB}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ of a 0.1 g sample of the picked, crushed k ammererite was made as a control (Table 2).

If the tetrahedral sites are assigned a value of 8 in the chlorite formula (Deer, Howie, and Zussman, 1962) with values rounded off to the nearest tenth, and the Cr is divided between the tetrahedral and octahedral sites in the ratio found analytically, the structural formula for the Day Book chrome chlorite is:



Discussion

The results indicate that virtually all the Mg is in the octahedral layer while all the Si is in the

TABLE 2. Partial Chemical Analyses of K ammererite from the Day Book Body Using the Acid Separation Technique

	HNO_3 Separation*	Fused Fraction**	Bulk Fusion**
SiO_2	Not detected	36.38	36.38
Al_2O_3	8.20	4.16	12.30
Cr_2O_3	2.92	3.47	6.30
MgO	35.99	2.70	39.50

*Dissolved in 1:1 HNO_3 for four hours.

**Fused with $\text{NaB}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and dissolved in 1:1 HCl .

tetrahedral layer (Table 2). The Cr is partitioned 55 percent in the tetrahedral layer and 45 percent in the octahedral layer (Table 2). If tetrahedral and octahedral site occupancy by Al is calculated using the values of Al in Table 2, there will be excess Al in the octahedral sites. This difference occurs because of the difference in the rate of solution of Al and Cr. It takes 4 hours to dissolve all of the octahedral chrome whereas it takes only 1/4 hours to dissolve the octahedral aluminum. Thus in the dissolution process tetrahedral aluminum is dissolving in the time span between 1/4 and 4 hours. The presence of Mg in the fused fraction is attributed to the difficulty in completely washing the Mg from the residue of the acid separation. The k ammererite used in this study does not fit in the Cr-chlorite classification scheme of Lapham (1958) as he bases the terms k ammererite and kotschubeite on whether Cr is present in the octahedral or tetrahedral layer.

Many more analyses of k ammererite from other locations would be needed to determine if the partitioning of Cr is variable or fixed. Assuming that the partitioning is variable, the author proposes that the traditional usage of k ammererite and kotschubeite be modified so that the term k ammererite is used when $\text{Cr}^{\text{VI}} \geq \text{Cr}^{\text{IV}}$ (in number of atoms) and the term kotschubeite is used when $\text{Cr}^{\text{VI}} < \text{Cr}^{\text{IV}}$ (in number of atoms). If this new use of the terms k ammererite and kotschubeite is applied to the "k ammererite" from the Day Book Body the mineral will be classified as kotschubeite.

The chemical method of determining site occupancy of Cr appears to be a rapid and simple method. A complete structural analysis of these specimens is needed, however, for comparison to assure that the chemical method is completely reliable.

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References

- BELT, C. B. (1967) Partial analysis of silicate rocks by atomic absorption. *Anal. Chem.* **39**, 676-678.
- BLAKE, W. P. (1852) Mineralogical notices. *Am. J. Sci.* **13**, 116.
- BRINDLEY, G., AND R. F. YOELL (1951) A chemical determination of tetrahedral and octahedral aluminum ions in a silicate. *Acta Crystallogr.* **4**, 495-496.
- BROWN, B. E., AND S. W. BAILEY (1960) Crystal structure of a chromium chlorite. *Geol. Soc. Am. Bull.* **71**, 1835.
- DANA, E. S. (1892) *Dana's System of Mineralogy*, John Wiley & Sons, New York, p. 643-664.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock Forming*

- Minerals*, v. 3, *Sheet Silicates*. Longmans, Green & Co., London, p. 131-162.
- GARRIDO, J. (1949) Structure cristalline d'une chlorite chromifere. *Bull. Soc. fr. Mineral. Cristallogr.* **72**, 449-470.
- GASTUCHE, M. C., AND J. J. FRIPIAT (1962) Acid solution techniques applied to the determination of the structures of clay and controlled by physical methods. *Sci. Ceram.* **1**, 121-138.
- KULP, J. L., AND D. A. BROBST (1954) Notes on the dunite and the geochemistry of vermiculite at the Day Book Deposit, Yancey County, North Carolina. *Econ. Geol.* **49**, 211-220.
- LAPHAM, D. M. (1958) Structural and chemical variation in chromium chlorites. *Am. Mineral.* **43**, 921-956.

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