

The descloizite-mottramite series of vanadates from the Otavi Mountain Land, South West Africa: an X-ray study

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ABSTRACT. Descloizite, cuprian descloizite, and mottramite from most of the known prospects and mines in the Otavi Mountain Land were sampled and subsequently analysed chemically and by X-ray diffraction. Unit cell parameters were refined with the aid of a computer program. It was found that, contrary to previous opinion, chemical parameters of these vanadates can be deduced from their X-ray powder data according to the equations (correlation coefficients in parenthesis):

$$\text{ZnO} = 75.369c - 0.119b - 31.177a - 456.512 \quad (0.9634)$$

$$\text{Zn}^{2+} = 369.568c + 236.583b - 146.42a - 3726.344 \quad (0.9642)$$

$$\text{CuO} = -74.991c + 0.086b + 29.419a + 486.204 \quad (0.9649)$$

$$\text{Cu}^{2+} = -369.568c - 236.583b + 146.420a + 3826.344 \quad (0.9642).$$

KEYWORDS: descloizite, mottramite, X-ray data, Otavi Mountain Land, South West Africa.

DESCLOIZITE was named after the French mineralogist Alfred L. O. L. Des Cloizeaux (Palache *et al.*, 1951). It was given the empirical formula $4\text{Pb}(\text{Zn}, \text{Cu})(\text{OH})(\text{V}, \text{As}, \text{P})\text{O}_4$ by Bannister and Hey (1933) after determination of its space group and unit cell dimensions. In this formula a complete isomorphous series exists between zinc and copper, the names descloizite and mottramite being applied to those end members of the series containing Zn and Cu respectively as the predominant cations. Bannister and Hey (1933) recommended that the name descloizite should be retained for the Zn-rich varieties containing up to two atoms of Cu per unit cell and mottramite for Cu-rich varieties with more than two atoms of Cu per unit cell. Verwoerd (1957) used the adjectives cuprian and zincian. Millman (1960) suggested further subdivisions, based on the ZnO content of the mineral, which may be summarized as follows:

ZnO content greater than 18 wt. %, descloizite.

ZnO content between 18 and 10 wt. %, cuprian descloizite

ZnO content between 10 and 2 wt. %, zincian mottramite.

According to Palache *et al.* (1951), descloizite crystallizes in the dipyramidal class, orthorhombic crystal system ($2/m\ 2/m\ 2/m$). The space group given by the above authors is $Pn\bar{m}$ with cell dimensions $a = 7.56$, $b = 6.05$ and $c = 9.39$ Å. However, Barnes and Quarashi (1952) suggest a space group of $Pnma$ with $a = 7.6707$, $b = 6.074$ and $c = 9.446$ Å.

Problem of determination. According to various authors (Bannister and Hey, 1933; Kingsbury and Hartley, 1956; Guillemin, 1956; Millman, 1960; and Von Rahden and Dicks, 1967), X-ray powder methods cannot differentiate satisfactorily between the different members of the descloizite-mottramite series of vanadates. In fact Bannister and Hey (1933) conducted an X-ray investigation on the descloizite series and conclude that the powder data for the descloizite-mottramite series are identical.

However, Kingsbury and Hartley (1956) described occurrences of vanadium minerals in the Caldbeck area of Cumberland in which they distinguished between descloizite and mottramite by X-ray powder photography and found that measurements of the two members showed close agreement down to 1.652 Å, but that smaller spacings differed markedly. Of the minerals investigated by them, none gave an intermediate pattern between those of descloizite and mottramite. The fact that spacings below 1.652 Å differ was also observed by Guillemin (1956) who used synthetic end-members. Although Millman (1960) also mentioned the difference in spacings below 1.652 Å, he suggested a chemical and microscopical technique to differentiate between the members of the series, stating that, for a large number of samples, chemical analyses were too tedious and X-ray powder photography too imprecise a method.

Von Rahden and Dicks (1967) determined unit cell dimensions and carried out chemical analyses on a number of samples from the Otavi Mountain Land. They conclude that cupro-descloizite cannot be satisfactorily differentiated from descloizite by X-ray diffraction methods. They favoured infra-red absorption spectroscopy to the chemical method described by Millman (1960).

During the present study, however, it was found that a very close relationship exists between the unit cell parameters and the relevant chemical composition of the isomorphous descloizite-mottramite series. The purpose of the paper is, therefore, to delineate parameters by which chemical composition, based on linear regression, can be estimated from X-ray diffraction data.

Analytical and statistical methods. Polished sections were made of all samples used in this project. These were then scanned by a Cameca electron microprobe using the automatic mode and analysed for all measurable components in order to determine the chemical homogeneity of the samples. It was found that within limits, the samples were homogeneous.

X-ray diffraction analyses of finely powdered samples were carried out with a Philips PW 1051 diffractometer. The apparatus was calibrated against a silicon standard using Ni-filtered copper radiation throughout the investigation. Calcium

fluoride (CaF₂) was used as an internal standard with the descloizite-mottramite samples. Unit cell dimensions were calculated by means of a least-squares computer program (Appleman *et al.*, 1972). The results of these calculations are given in Table I. The direct cell standard errors were in all cases very small (*a* between 0.002 and 0.004; *b* between 0.003 and 0.004; *c* between 0.001 and 0.003 Å).

The descloizite-mottramite samples were dissolved in a 10% HNO₃ solution prior to analyses with a Perkin Elmer atomic absorption spectrometer. The results (CuO, ZnO, PbO, V₂O₅, and P₂O₅) were also compared with those obtained by X-ray fluorescence spectrometry and were in excellent agreement. Results for As₂O₃ were obtained only by atomic absorption. The data are given in Table I.

To determine the relationship between the chemistry and the unit cell parameters of the descloizite-mottramite series, multiple linear regression was used, where the dependent variable is expressed as an equation containing the independent variables. The data were reduced by means of a multiple stepwise linear regression program (BMDP2R) which was developed at the Health Sciences Computing Facility at the University of Los Angeles (Dixon, 1975).

Results. Although it is known that Fe and Mn

TABLE I. Unit cell dimensions and chemical analyses of descloizite-mottramite from the Otavi Mountain Land (*a*, *b* and *c* in Å, CuO, PbO, ZnO, V₂O₅ and P₂O₅ in wt. per cent and As₂O₃ in ppm.

<i>a</i>	<i>b</i>	<i>c</i>	CuO	PbO	ZnO	V ₂ O ₅	As ₂ O ₃	P ₂ O ₅	Prospect/Mine
7.651	6.061	9.404	09.54	53.21	10.14	22.03	03446	00.12	Friesenberg
7.614	6.031	9.365	08.64	53.60	11.02	21.28	03115	00.11	Tunissen
7.640	6.080	9.458	00.50	53.43	19.16	22.09	00887	00.22	Berg Aukas (8-50)
7.628	6.076	9.446	04.44	52.64	15.16	21.87	01907	00.15	Harasib Potholes
7.619	6.083	9.436	02.21	53.73	17.42	21.63	02722	00.30	Berg Aukas
7.711	6.055	9.249	18.78	51.49	00.71	20.97	05408	00.21	Gross Otavi
7.474	6.122	9.390	01.74	53.34	17.88	21.17	02271	00.36	Auros
7.584	6.052	9.418	02.82	53.81	17.21	22.18	03313	00.12	Uitsab Opencast
7.618	6.088	9.454	00.18	54.07	19.56	21.48	01527	00.08	Berg Aukas
7.621	6.080	9.459	00.24	53.76	19.42	21.48	00931	00.24	Berg Aukas
7.620	6.079	9.456	00.40	54.08	19.51	22.37	01400	00.18	Berg Aukas (17-50)
7.660	6.066	9.384	09.26	52.46	10.31	21.29	05336	00.09	Uris
7.695	6.057	9.318	11.25	52.82	08.48	21.11	01928	00.08	Karavatu
7.623	6.066	9.417	08.12	53.44	11.63	21.91	01916	00.23	Gauss
7.628	6.085	9.459	01.24	52.93	18.61	21.48	02085	00.10	Abenab
7.698	6.056	9.332	15.27	52.31	03.51	20.96	02503	00.37	Uitsab North
7.625	6.075	9.443	02.72	52.20	17.44	20.14	09990	00.19	Baltika
7.640	6.059	9.409	09.12	52.02	10.21	20.78	01138	00.14	Röhrers
7.625	6.077	9.463	00.42	52.41	19.31	20.06	01060	00.29	Berg Aukas (6-50)
7.730	6.058	9.273	18.84	52.33	00.64	20.42	04316	00.47	Tsuneb West Vanadium
7.637	6.075	9.428	03.97	52.46	15.89	20.96	00793	00.12	Harasib I
7.625	6.071	9.431	04.86	52.84	15.13	21.81	03671	00.11	Uitsabpad
7.712	6.057	9.291	16.84	50.26	02.68	20.11	04239	00.53	Rietfontein
7.622	6.061	9.416	06.09	50.32	13.74	20.42	10830	00.22	Central Prospect
7.619	6.072	9.442	03.21	52.26	16.53	21.40	04509	00.18	Harasib II
7.735	6.059	9.456	04.38	51.50	14.82	20.08	02207	00.26	Wolkenhaben
7.697	6.067	9.294	15.77	51.66	03.83	20.71	06620	00.16	Karavatu Karst Breccia
7.619	6.083	9.436	02.06	51.79	16.38	21.66	02496	00.17	Lucas Post

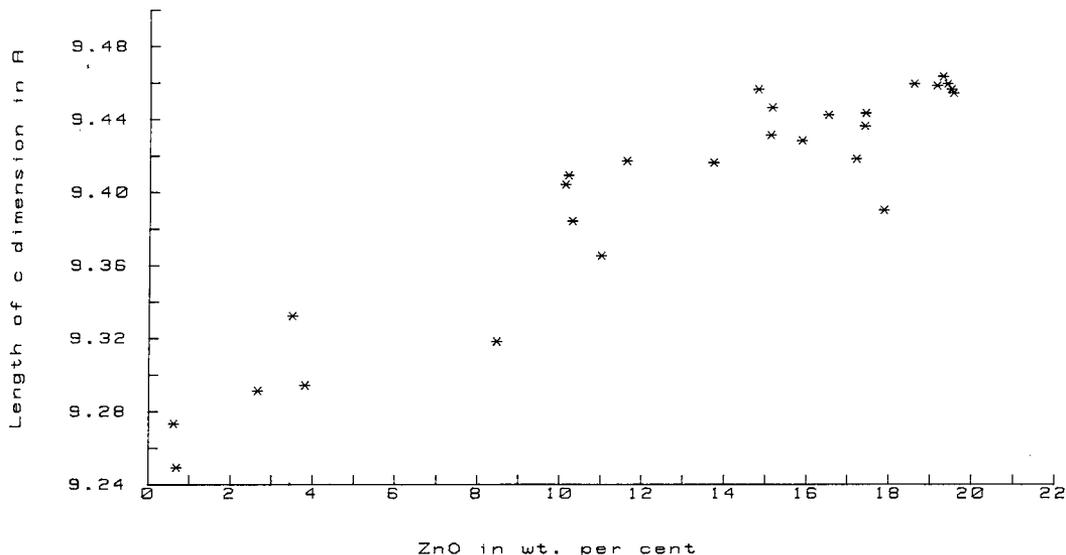


FIG. 1. The relationship between the ZnO content (in wt. %) and c cell edge (in Å) of descloizite.

substitute for Cu and/or Zn in descloizite-mottramite, very small amounts of the former elements were found in the descloizite-mottramite of the Otavi Mountain Land. The amount of Fe and Mn (as FeO and MnO) were less than 0.1 and 0.02 wt. % respectively.

Millman (1960) reported P and As substitution for V in descloizite-mottramite. These elements do not attain high concentrations in the samples studied (Table I) and exert no influence on the equation when the unit cell parameters are used as unknown variables.

ZnO was used as the first dependent variable and a , b , and c as the independent variables. The first independent variable selected was c , with a regression coefficient of 0.9367 and degrees of freedom of 1/26. The relationship between ZnO and c is illustrated in fig. 1 and can be expressed by the following equation:

$$\text{ZnO} = 89.335c - 826.75.$$

In the second step, a was selected as the independent variable, with the regression coefficient increasing to 0.9632. The relation between ZnO, c , and a can be expressed by the equation:

$$\text{ZnO} = 75.817c - 30.997a - 462.798.$$

When b is added to the independent variables in the third step, the regression coefficient increases to 0.9634. The final equation for calculating the amount of ZnO is:

$$\text{ZnO} = 75.369c - 0.119b - 31.177a - 456.512.$$

If Zn^{2+} is used instead of ZnO, the multiple regression coefficient of the final equation is 0.9642 and the equation itself is:

$$\text{Zn}^{2+} = 369.568c + 236.583b - 146.42a - 3726.344.$$

Because of the isomorphous substitution of Zn by Cu (regression coefficient of 0.985) it can be expected that the same relationship would exist between CuO and the unit cell parameters. The final equation for calculating CuO is $\text{CuO} = -74.991c + 0.086b + 29.419a + 486.204$. The multiple regression coefficient for the equation is 0.9649. The relationship between CuO and c is illustrated in fig. 2.

Again, if Cu^{2+} is used instead of CuO the multiple regression coefficient of the final equation is 0.9642 and the equation expressed as $\text{Cu}^{2+} = -369.568c - 236.583b + 146.420a + 3826.344$. The correlation between c and Zn is attributed to the difference in ionic radii of the two elements causing an expansion or contraction along the c crystallographic axes.

Discussion. The equations for the determination of zinc and copper were applied to the data presented by Von Rahden and Dicks (1967) and the results are shown in Table II. Differences between calculated and determined CuO and ZnO concentrations may be attributed to a number of factors: (a) different computer programs were used to calculate the unit cell parameters; (b) different analytical techniques for the determination of

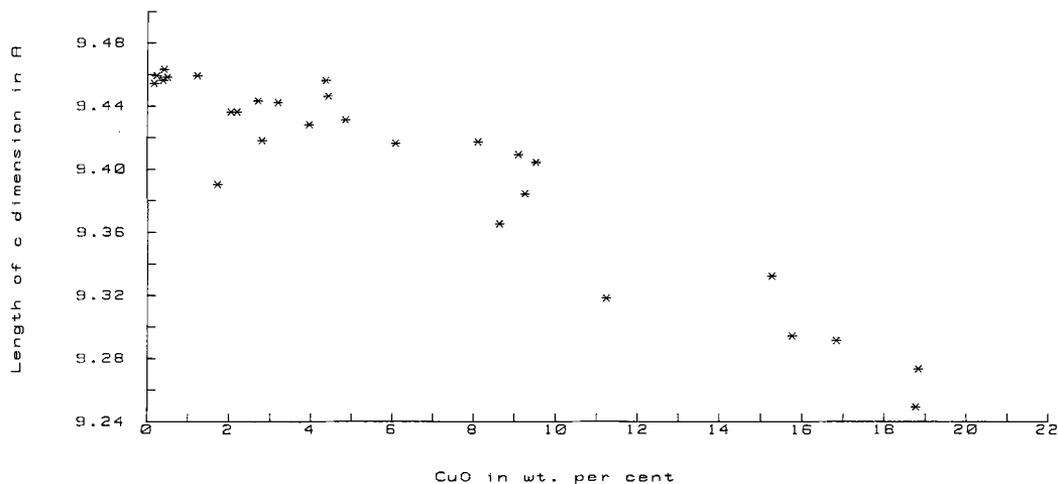


FIG. 2. The relationship between the CuO content (in wt. %) and c cell edge (in Å) of descloizite.

ZnO and CuO can also contribute to the discrepancies. Although small differences exist in the determined and calculated concentrations of these components (Table II), the overall classification remains within the limits promulgated by Millman (1960).

Table II. Unit cell dimensions (in Å) and chemical analyses (determined and calculated in wt. per cent)

a	b	c	ZnO (determined)	ZnO (calculated)	Sample No.
7.604	6.059	9.460	19.60	18.69	A
7.612	6.049	9.452	19.48	17.84	B
7.615	6.058	9.442	18.99	16.99	C
7.610	6.059	9.457	19.40	18.27	D
7.607	6.074	9.446	19.18	17.54	
			CuO (determined)	CuO (calculated)	
7.571	6.047	9.367	9.27	7.01	E
7.684	6.027	9.223	18.53	21.14	F

(Unit cell dimensions, CuO and ZnO (determined) after Von Rahden and Dicks, 1967).

A greater degree of accuracy can be expected if a calibration curve of either CuO or ZnO against c is constructed using data obtained from a single laboratory. This technique is especially applicable where only small samples are available and sophisticated analytical instruments, such as an electron microprobe, are unavailable.

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