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DESCLOIZITE, MOTTRAMITE, AND VANADINITE FROM SOUTH WEST AFRICA: AN INFRARED AND X-RAY STUDY

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ABSTRACT

Descloizite, cuprian descloizite, mottramite, and vanadinite from various localities in South West Africa were analysed chemically and by X-ray diffraction and infrared spectroscopy. The X-ray results substantiate previously determined data. The infrared method was found to offer an elegant means for the positive identification of the members of the isomorphous series, descloizite to mottramite. In addition, vanadinite can readily be distinguished from descloizite by the infrared method.

INTRODUCTION

Although the lead vanadates, descloizite, mottramite, and vanadinite, have been mined in economic quantities in South West Africa since 1914, there still appears to be a paucity of detailed mineralogical data on these minerals. Their nature and mode of occurrence were very ably described by Verwoerd (1957), but, although he presented some relevant chemical and optical data, no X-ray data were included.

In addition, the X-ray diffraction and microchemical methods currently in use for distinguishing between descloizite, cuprian descloizite, and mottramite have not proved to be satisfactory in all cases. Millman (1960) rejected the X-ray powder method as being too indefinite a means of identification, and suggested a rapid microchemical method for precise discrimination between members of the descloizite-mottramite series. In the opinion of the present authors, however, the method advocated by Millman is still too subjective for general use. Infrared spectroscopy seemed to offer a more satisfactory means of characterizing these minerals, and accordingly this technique was investigated and was found to provide a rapid and positive method of discrimination and identification.

The aim of this paper is to supplement earlier work on the lead vanadates of South West Africa with more detailed X-ray and infrared data. These data have been derived in the course of a program of infrared studies on various minerals that is currently being undertaken at the National Institute for Metallurgy, Johannesburg.

Chemistry of the descloizite-group minerals. The zinc-copper-lead hydrous vanadates known as the "descloizite-group" minerals, whose composition can be expressed by the formula (Zn, Cu)$PbVO_4OH$, were shown by Bannister and Hey (1933) to form a complete isomorphous series between the zinc and copper end-members, descloizite and mottramite respectively. Millman (1960) pointed out that the combined ZnO and CuO content approximates 20 percent throughout the series. He suggested that the name "descloizite" should be applied to that half of the series with a ZnO content exceeding 10 percent, and the name "mottramite" to the other half of the series, with a CuO content exceeding 10 percent. He suggested further subdivisons, based on the ZnO content of the mineral, which may be summarized as follows:

ZnO content greater than 18 percent—descloizite
ZnO content between 18 and 10 percent—cuprian descloizite
ZnO content between 10 and 2 percent—zincian mottramite.

Substitution in the lattice by other elements is also known to occur (Dana 1951, Millman 1960), with manganese and iron replacing zinc and copper, and arsenic, phosphorus, and molybdenum replacing vanadium.

Vanadinite, a lead chlorovanadate $Pb_5(VO_4)_3Cl$, although not a member of the descloizite group of minerals, has been included in the present investigation because its presence is so often mistakenly reported when in fact pseudomorphous replacement by descloizite, $(Zn,Cu)PbVO_4(OH)$, has occurred (Dana 1951). This replacement is well illustrated by the chromatographic print in the paper by Williams and Nakhla (1951). Examples of complete pseudomorphs of descloizite after vanadinite have also been reported by Verwoerd (1957) at the Abenab West Mine.

Earlier X-ray investigations of descloizite. Bannister and Hey (1933) obtained identical powder photographs for a group of zinc-copper-lead hydrous vanadates, namely descloizite, cuprian descloizite, psittacinite, eusynchite, dechenite, chileite, and mottramite. More recent work by Kingsbury and Hartley (1956), however, showed that although the spacings for descloizite and mottramite are similar above 1.652 Å, significant differences do occur below this value. These findings were substantiated by Guillemin (1956), who synthesized the respective end-members of the series and analysed them by X-ray diffraction. A feature common both to Guillemin's synthetically prepared mottramites and the mottramites from Angola examined by Millman (1960) was the paucity of lines below 1.38 Å.

The space group determined by Bannister and Hey (1933) for descloizite was given as

$V_h^{16}(D_{2h}^{16}$—$Pmcn)$ $Zn+Cu=4$ atoms per unit cell.

Orthorhombic $a=6.05$ Å, $b=9.39$ Å, $c=7.56$ Å.

Barnes and Qurashi (1952), however, suggested the orientation of *Pnma* for descloizite, which simply involved an interchange of the *a*, *b*, and *c* axes to *b*, *c*, and *a*, respectively. The structure was then further refined in *Pnma* by Qurashi and Barnes in 1964, and was found to consist of a three-dimensional assemblage of distorted VO_4 tetrahedra, $ZnO_4(OH)_2$ tetragonal bipyramids, and $PbO_7(OH)$ square antiprisms sharing corners and edges. Descloizite was found to be orthorhombic, with $a=7.607$ Å, $b=6.074$ Å, and $c=9.446$ Å, and $Z=4$.

Microchemical methods. Microchemical methods have been proposed for differentiating between descloizite and mottramite (Millman 1960), and between descloizite and vanadinite (Williams and Nakhla 1951, modified by Fleming 1951). By means of Millman's (1960) method, it is possible to differentiate between intermediate members of the series as well as between descloizite and mottramite, whereas the method of Williams and Nakhla (1951) can only distinguish between descloizite and vanadinite.

MATERIALS AND METHODS

Mode of occurrence of the vanadate minerals. The present samples were obtained from various localities in the Otavi Mountain Land in South West Africa: the four descloizite samples were obtained from the Berg Aukas Mine, the cuprian descloizite from Friesenberg, the mottramite from the Tsumeb Mine, and the vanadinite from Grootfontein. The genesis of these Otavi Mountain Land vanadium deposits has been discussed by Schwellnus (1945), who suggested a supergene origin for the vanadium ores.

With the exception of one of the descloizite samples that occurred as massive grains, the cuprian descloizite and descloizite occurred as subparallel or radially branching groups of pyramidal euhedral crystals, similar to those described by Verwoerd (1957). The habit of the mottramite was similar to that of the descloizite, but in hand specimen it differed in color. The vanadinite occurred as thin slender orange-brown prismatic crystals. The crystalline nature of the samples, with the exception of the one descloizite sample, indicates that the minerals probably occurred as vug infillings.

X-ray diffraction. X-ray diffraction analysis of finely powdered samples was carried out with a Philips wide-range goniometer, PW 1050/25, with an effective diameter of 170 mm, calibrated against a silicon standard. Filtered copper radiation, $\lambda=1.54050$ Å, was used throughout the investigation, which was performed at a temperature between 22°C and 25°C.

Cell constants were calculated by means of a least-squares program written for an IBM 704 computer.

Specific-gravity determinations. All specific-gravity determinations were carried out in triplicate with a Berman balance, using toluene corrected for temperature (Berman 1939). The value reported (Table 1) is the mean of three individual determinations.

Infrared analysis. Infrared analysis of the samples was carried out on a Perkin-Elmer Model 521, double-beam, grating-type, infrared spectrophotometer. The analyses were carried out on finely ground material embedded in discs made from triply recrystallized A.R. grade potassium bromide, which had been pressed at 55 tons per square inch in a die evacuated to 0.01 mm of mercury. All spectra were obtained at a temperature of 25°C, with relative humidity ranging between 30 and 40 percent. The double-beam mode of operation was used throughout, with a potassium bromide disc in the reference beam. Linear wave-number recording was used throughout the investigation.

For sharp bands, the frequencies reported are accurate to within ±2 cm^{-1}, but for broad bands the error may exceed this value.

RESULTS AND DISCUSSION

The results of the chemical, X-ray, and infrared analyses are set out in Tables 1, 2, and 3 respectively.

Chemical analyses. Since the combined ZnO and CuO content of the isomorphous descloizite-mottramite series always approximates 20 percent (Millman 1960), the data in Table 1 clearly indicate that the present samples of descloizite and mottramite from South West Africa lie close to the theoretical end-members of the series in composition. The cuprian descloizite, on the other hand, can be seen to occupy a position at roughly the midpoint of the series.

Arsenic was present in all four descloizite samples analysed, and probably replaces vanadium diadochically. The trace element content

TABLE 1. CHEMICAL ANALYSES OF DESCLOIZITE, CUPRIAN DESCLOIZITE, AND MOTTRAMITE

	A	B	C	D	E	F	G	H	I
PbO	54.66	54.77	54.43	54.22	n.d.	n.d.	54.90	51.90	54.56
ZnO	19.60	19.48	18.99	19.40	n.d.	n.d.	19.18	10.65	2.62
CuO	0.45	0.49	0.74	0.60	9.27	18.53	0.83	8.83	16.84
FeO	tr.	tr.	tr.	tr.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	tr.	tr.	tr.	tr.	n.d.	n.d.	n.d.	n.d.	n.d.
V_2O_5	20.94	21.20	21.64	21.36	n.d.	n.d.	21.07	17.38	22.73
As_2O_5	1.08	0.63	0.52	1.10	n.d.	n.d.	n.d.	tr.	n.d.
H_2O^{110}	0.10	0.01	0.08	0.06	n.d.	n.d.	n.d.	n.d.	n.fl.
H_2O^{600}	2.42	2.36	2.42	2.46	n.d.	n.d.	n.d.	n.d.	n.d.
Sp.gr.	6.200	6.197	6.132	6.075	6.181	6.144			

tr. = trace. n.d. = not detected or reported

Remainder: trace element content determined spectrographically

(d.c. arc.)

A, B, C, D: Ag, Al, Bi, Ca, Co, Cr, Fe, K, Mg, Mn, Mo, Ni, Ti, Sn.

H, I: Ag, As, Cr, Fe, Mn, Mo, Ni, Ti, Sn, P.

A, B, C, D = descloizite	Berg Aukas	South West Africa
E = cuprian descloizite	Friesenberg	South West Africa
F = mottramite	Tsumeb	South West Africa
G = descloizite	Broken Hill	N. Rhodesia Zambia
H = cuprian descloizite	Minas do Lueca	Angola
I = mottramite	Uris Mine, Tsumeb	South West Africa

All are new analyses except G, H and I, which were taken from Millman's (1960) paper.

TABLE 2. CELL DIMENSIONS FOR DESCLOIZITE, CUPRIAN DESCLOIZITE, AND MOTTRAMITE, FROM SOUTH WEST AFRICA

(Ångströms)

	A	B	C	D	E	F	G
a	7.604	7.612	7.615	7.610	7.571	7.684	7.607
b	6.059	6.049	6.058	6.059	6.047	6.027	6.074
c	9.460	9.452	9.442	9.457	9.367	9.223	9.446

A, B, C, D = descloizite Berg Aukas South West Africa
E = cuprian descloizite Friesenberg South West Africa
F = mottramite Tsumeb South West Africa
G = descloizite Los Lamentos Chihuahua, Mexico
All except G (Barnes and Qurashi, 1952) are new analyses.

of the four descloizite samples differed slightly from that reported by Millman (1960) in that phosphorus was absent but the following additional elements were found: aluminium, bismuth, calcium, cobalt, potassium, magnesium.

X-ray analyses. The cell dimensions determined for the four descloizite samples (Table 2) are in good agreement with those determined by

TABLE 3. INFRARED VIBRATION FREQUENCIES (CM^{-1}) FOR DESCLOIZITE, CUPRIAN DESCLOIZITE, MOTTRAMITE, AND VANADINITE

A	B	C	D	E	F	G
				1090		
1020	1020	1020				
				1000		
					994	
				964		
					936	
915	916	916	918	915		
854	854	853	857	850	839	
					814	803
742	745	747	746	729	738	739
					704	
		506	506	508		
					486	
453	454	453	454	450		

A, B, C, D = descloizite Berg Aukas South West Africa
E = cuprian descloizite Friesenberg South West Africa
F = mottramite Tsumeb South West Africa
G = vanadinite Grootfontein South West Africa

Barnes and Qurashi (1952). The present results bear out the finding of Kingsbury and Hartley (1956) that there are substantial differences in spacings below 1.652 Å between descloizite and mottramite.

Because of the great similarity in spacings shown by the four descloizite samples and the single cuprian descloizite sample, it was found impossible to differentiate between these two minerals by this means.

Infrared analyses. As pointed out by Adler (1964), the fundamental vibrations, and hence the corresponding absorptions, contributing to the infrared spectrum of a molecule are localized to a first approximation by the mass and internal binding energy of the functional group present. In minerals, as with other solids, the vibrational and spectral characteristics of the molecule are further influenced and altered by the particular environment to which it is attached.

Accordingly, if the premise of Bannister and Hey (1933) that a complete isomorphous series exists between descloizite and mottramite, passing through the intermediate composition of cuprian descloizite, is accepted, it is natural to expect differences between the infrared spectra of different members of the series, with the occurrence of a progressive shift in the absorption bands as the zinc is replaced by copper in the lattice.

The infrared results in Table 3 show that such a shift towards lower frequencies does in fact occur in passing from descloizite through cuprian descloizite to mottramite.

Since the functional groups present in the descloizite-mottramite series differ from those in vanadinite, differentiation between these two mineral groups by infrared spectroscopy should present no problems. Differences between their infrared spectra were in fact found and can be seen in Figure 1, where the spectra of descloizite, vanadinite, and mottramite are compared. Figure 2 shows the distinct differences between the infrared spectra of mottramite, descloizite, and cuprian descloizite; and Figure 3 shows the spectra of the four different descloizite samples.

In this investigation, no serious attempt has been made to assign the vibration frequencies to particular bonds, and accordingly it is not yet possible to suggest any reason for the nonappearance of the 1020 cm^{-1} band in descloizite *D*, shown in Figure 3. However, on the basis of the chemical analyses set out in Table 1 and of the considerably enlarged peak shown by cuprian descloizite at 508 cm^{-1}, it can be tentatively suggested that the 506 cm^{-1} band in the descloizite spectrum could possibly be assigned to a Cu—O bond.

CONCLUSIONS

1. Infrared spectroscopy offers a convenient means of differentiation between descloizite, cuprian descloizite, and mottramite.

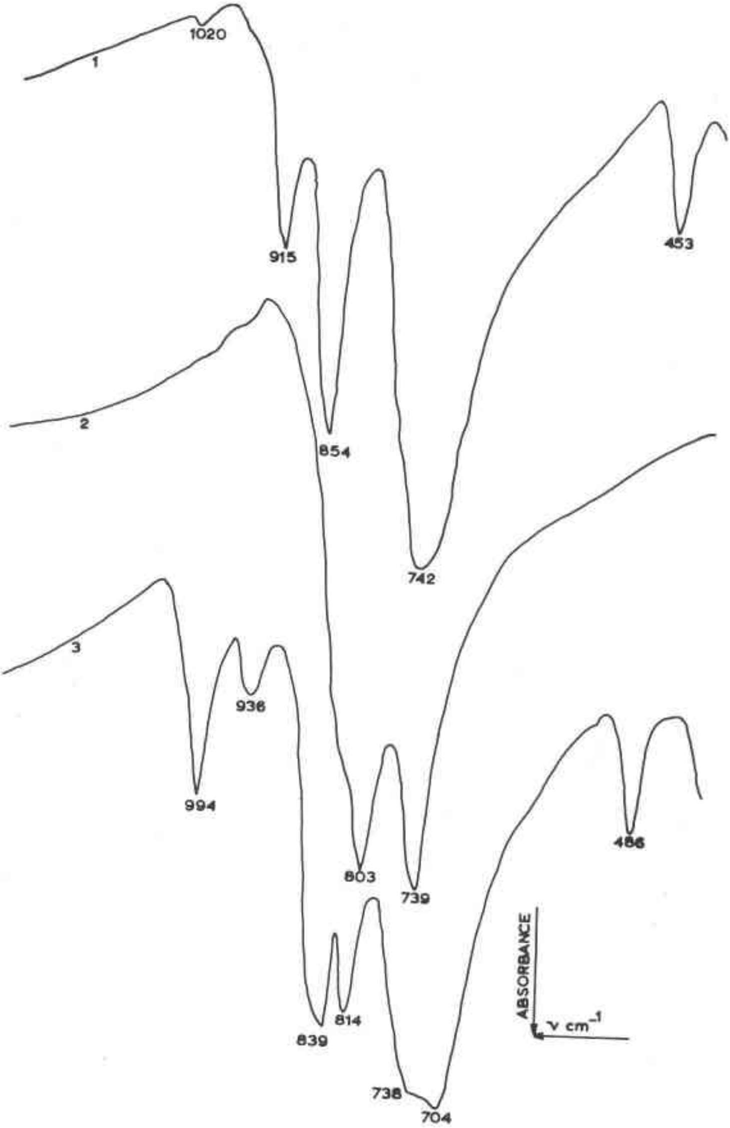

FIG. 1. Infrared spectra (1) Descloizite (2) Vanadinite (3) Mottramite.

2. Similarly, vanadinite, mottramite, and descloizite may readily be distinguished one from another by means of infrared spectroscopy.

3. From the infrared spectra, it appears that infrared spectroscopy probably offers a means of quantitatively assessing the vanadinite content of descloizite-vanadinite pseudomorphs.

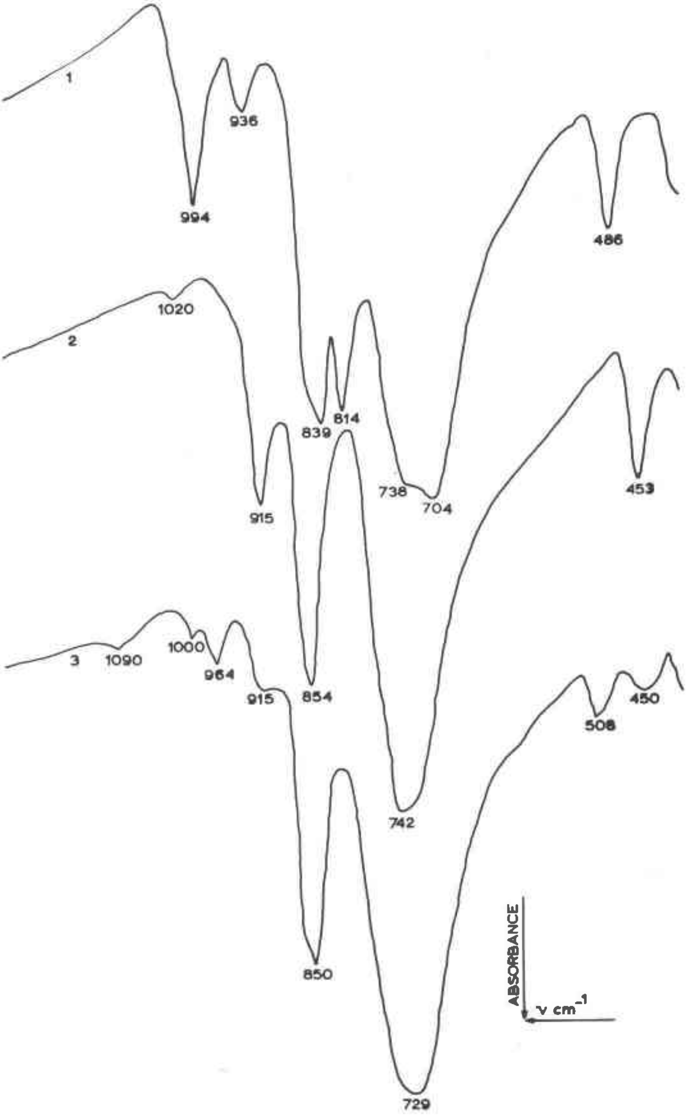

FIG. 2. Infrared spectra (1) Mottramite (2) Descloizite (3) Cuprian Descloizite.

4. The results of this study substantiate the work of Kingsbury and Hartley (1956) in showing significant differences in *d* below 1.652 Å for descloizite and mottramite.

5. Cuprian descloizite cannot be satisfactorily differentiated from descloizite by X-ray diffraction.

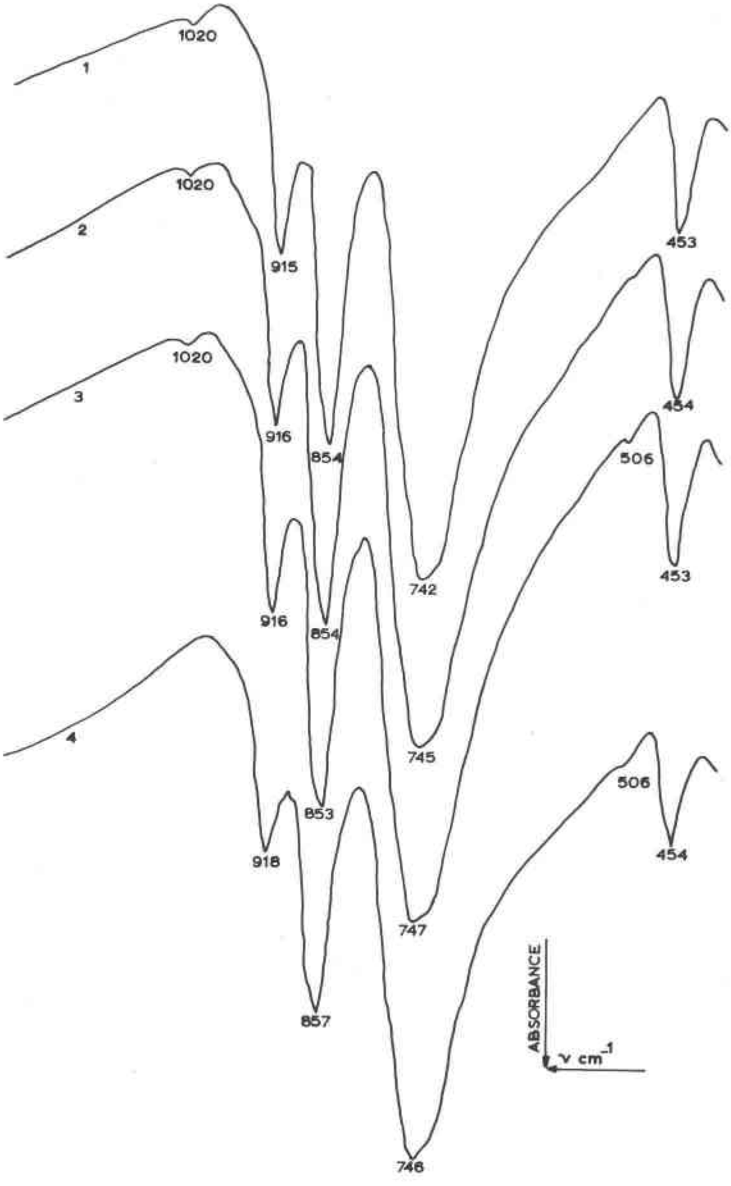

Fig. 3. Infrared Spectra (1) Descloizite A (2) Descloizite B (3) Descloizite C (4) Descloizite D.

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