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SOLID SOLUTION IN THE ADELITE GROUP OF ARSENATES

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ABSTRACT

Duftite and conichalcite specimens from Tsumeb, Namibia (South West Africa) are commonly zoned in color and composition. Microprobe analyses and X-ray powder-diffraction studies indicate extensive Cu–Zn and Pb–Ca substitutions, which represent solid solution among conichalcite ($CaCuAsO_4OH$), austinite ($CaZnAsO_4OH$) and duftite ($PbCuAsO_4OH$), all of the adelite group of arsenates. Cell dimensions of end-member duftite are *a* 7.778(4), *b* 9.207(3), *c* 6.000(5) Å, *V* 429.7 Å^3.

Keywords: adelite group, duftite, austinite, conichalcite, Tsumeb, compositional and color zoning in minerals, solid solution, X-ray powder data, cell volumes.

SOMMAIRE

Les échantillons de duftite et de conichalcite de Tsumeb, Namibie (Afrique du Sud-Ouest) montrent souvent une zonation en couleur et en composition. Les études à la microsonde et à la diffraction X sur poudres indiquent des substitutions importantes Cu–Zn et Pb–Ca, et donc des solutions solides entre la conichalcite $CaCuAsO_4OH$, l'austinite $CaZnAsO_4OH$ et la duftite $PbCuAsO_4OH$, toutes trois membres du groupe de l'adelite. Les dimensions de la maille au pôle duftite sont *a* 7.778(4), *b* 9.207(3), *c* 6.000(5) Å, *V* 429.7 Å^3.

(Traduit par la Rédaction)

Mots-clés: groupe de l'adelite, duftite, austinite, conichalcite, Tsumeb, zonation en composition et en couleur dans les minéraux, solution solide, diffraction X sur poudres, volume de la maille.

INTRODUCTION

Six members of the adelite group of arsenates are known (Table 1). Although published chemical data indicate that little solid solution occurs among members of the group, all are believed to be isostructural, with space group $P2_12_12_1$ (Radcliffe & Simmons 1971).

A specimen labeled "duftite" from the type locality, Tsumeb, Namibia (South West Africa), was examined in 1976 to obtain X-ray verification and to ascertain its possible use as a powder-diffraction standard. A microprobe analysis showed that the material varied substantially in Pb, Ca and Zn, but that Cu was fairly constant under the expanded beam used for the analysis. The material seemed to belong to the adelite group, but a precise identification could not be made. Re-examination of the above specimen, as well as others labeled "duftite", was undertaken and the results form the basis of this report. Part of the Tsumeb specimen has been deposited in the National Mineral Collection, Ottawa (*NMC* 61459).

TABLE 1. MINERALS OF THE ADELITE GROUP

Name	Composition	*a*(Å)	*b*(Å)	*c*(Å)	Reference
adelite	$CaMgAsO_4OH$	7.47	8.94	5.88	Palache *et al.* (1951)
		7.525	8.895*	5.850	PDF 24-208
austinite	$CaZnAsO_4OH$	7.43	9.00	5.90	Palache *et al.* (1951)
		7.506	9.046	5.932	Radcliffe & Simmons (1971)
conichalcite	$CaCuAsO_4OH$	7.42	9.20	5.85	Palache *et al.* (1951)
		7.393	9.220	5.830	Radcliffe & Simmons (1971)
duftite	$PbCuAsO_4OH$	7.52	9.14	5.91	Palache *et al.* (1951)
		7.51	9.14	5.9	PDF 6-0322
		7.81	9.19	6.08	PDF 14-169
gabrielsonite	$PbFeAsO_4OH$	7.86	8.62*	5.98	PDF 20-583
	$PbZnAsO_4OH$				Taggart & Foord (1980)

*b and c interchanged from the referenced setting.

ORIGINAL TSUMEB SPECIMEN

The specimen is dark green and about 3 cm in diameter. Broken and cut edges show a random oscillation of color zones, all in muted shades of green, that conform with the coarsely botryoidal surface. Microscope and microprobe examinations of a polished thin section revealed that color and composition zoning occurs on such a fine scale that areas sufficiently large and homogeneous for microprobe and X-ray powder-diffraction analyses are difficult to find.

Microprobe analyses

Analyses were performed with a Materials Analysis Company model 400 electron microprobe operated at 20 kV and a specimen current of 0.03 μA. Counting periods of 10 seconds

TABLE 2. MICROPROBE ANALYSES OF TSUMEB "DUFTITE" (NMC 61459) = PLUMBIAN, ZINCIAN CONICHALCITE

	1. Colorless			2. Medium green			3. Dark green			4. Brownish green		
	av. wt%	mol.	range, wt%	av. wt%	mol.	range, wt%	av. wt%	mol.	range, wt%	av. wt%	mol.	range, wt%
CaO	15.4	.274	12.0-17.6	14.3	.254	13.0-17.8	9.5	.170	9.1-10.5	14.7	.262	12.9-15.7
PbO	15.4	.069	8.9-22.0	15.6	.070	9.2-18.7	29.5	.132	28.1-31.4	17.6	.079	14.4-22.4
CuO	19.5	.246	16.8-21.9	20.2	.255	19.3-22.0	21.7	.272	21.0-22.4	21.5	.271	20.7-22.5
ZnO	9.1	.112	7.8-11.8	7.7	.095	6.1-8.8	3.2	.040	2.9-3.7	6.1	.075	4.9-7.5
MnO	<0.1	-		0.1	-	0.1-0.1	<0.1	-		<0.1	-	
As_2O_5	37.4	.326	36.0-39.0	37.7	.328	36.8-39.6	33.0	.287	32.1-34.4	37.9	.330	36.7-38.8
	96.9			95.6			97.0			97.9		
	av. Ca:Pb = 80:20			av. Ca:Pb = 78:22			av. Ca:Pb = 56:44			av. Ca:Pb = 77:23		
	Cu:Zn = 69:31			Cu:Zn = 73:27			Cu:Zn = 87:13			Cu:Zn = 78:22		

Second area

	Dark green			Almost colorless			Almost colorless		
	av. wt%	mol.	range, wt%	av. wt%	mol.	range, wt%	av. wt%	mol.	range, wt%
CaO	10.5	.187	10.2-10.9	10.2	.182	9.9-10.6	16.9	.301	16.6-17.2
PbO	29.0	.130	27.1-29.7	27.4	.123	26.9-27.7	12.6	.056	11.5-13.8
CuO	23.4	.294	23.0-23.7	22.7	.285	22.3-23.4	20.5	.258	19.3-21.5
ZnO	2.5	.031	2.1-2.7	3.0	.037	2.5-3.6	8.6	.106	6.8-12.8
MnO	<0.1	-		<0.1	-		<0.1	-	
As_2O_5	34.1	.296	33.4-34.8	33.9	.295	33.1-35.3	39.7	.346	39.1-40.7
	99.6			97.3			98.4		
	av. Ca:Pb = 59:41			av. Ca:Pb = 60:40			av. Ca:Pb = 84:16		
	Cu:Zn = 90:10			Cu:Zn = 89:11			Cu:Zn = 71:29		

and the following X-ray lines and standards were used: Pb $M\alpha$, galena; Ca $K\alpha$, apatite; Cu $K\alpha$, CuS; Zn $K\alpha$, ZnO; Mn $K\alpha$, rhodochrosite; As $L\alpha$, $CoAs_2$. Areas in the polished thin section of the Tsumeb specimen were selected as representative of the various color ranges.

The microprobe analyses (Table 2) show that the different color zones are variable in composition and apparently represent extensive solid solution in the adelite group. All the analyzed zones have Ca > Pb and Cu > Zn; thus the mineral is plumbian, zincian conichalcite. Although one could infer from the first four analyses in Table 2 that conichalcite becomes darker green as the copper content increases, analyses in another area of the section, consisting of numerous but narrow zones of different shades of green, do not confirm the apparent trend (Table 2). Analyses obtained from a second polished section give compositions in the same ranges as those in Table 2 and confirm the lack of correlation between color and composition. The presence of over 20% CuO in the almost colorless areas is notable.

X-ray-diffraction study

Few of the areas analyzed by microprobe were homogeneous, but the composition ranges were consistently those expected for adelite-group minerals. If the compositional heterogeneity represented physical combinations of end-member conichalcite, duftite and austinite (rather than extensive solid solution), then these mixtures should have been detectable by powder X-ray diffraction because the Ca–Pb–Cu–Zn variation is large. The cell dimensions of the relevant members of the adelite group, although similar, differ sufficiently that anomalously large diffraction-line broadening, as well as distinct lines for the individual phases, should appear on 114.6 mm films. These features are not evident on X-ray patterns of the Tsumeb material (Cu and Co radiations), but distinct diffraction-line shifts are present. These shifts are sufficiently large to indicate that the conichalcite end-member is absent in the Tsumeb material.

Powder-diffraction patterns from several of the analyzed areas were sharp even though incorporation of multiple zones, as indicated by the composition ranges in Table 2, was unavoidable. To obtain comparisons with the cell dimensions given for austinite and conichalcite by Radcliffe & Simmons (1971), MgO was added subsequently to the X-ray spindles to provide back-reflections for shrinkage corrections. Least-squares refinements were done with Cu $K\alpha_1$ radiation (λ 1.54051 Å). Although the refined parameters are near those of duftite and conichalcite, the PDF cell data for duftite differ so substantially (Table 1) that specific dimensions for the end member could not be selected.

TABLE 3. X-RAY POWDER DATA FOR DUFTITE, TSUMEB, S.W.A. (PDF 14-169)

I	d_{meas}	d_{calc}	*hkl*	*I*	d_{meas}	d_{calc}	*hkl*
40	5.03	5.00	011*	10	1.96	1.97	240
30	4.60	4.59	020*	10	1.93	1.94	013
50	4.21	4.19	111*			1.93	400
30	3.95	3.94	120*	50	1.87	1.87	331*
30	3.56	3.56	210*	10	1.85	1.84	401
100	3.26	3.24	201	10	1.82	1.82	023
40	2.99	2.98	002	10	1.81	1.82	042
80	2.85	2.84	130*	10	1.78	1.78	420
80	2.65	2.65	221*	10	1.77	1.77	142
60	2.57	2.57	131*	5	1.75	1.75	051
10	2.48	2.48	310*	30	1.71	1.71	151*
10	2.38	2.38	122	50	1.64	1.64	242
50	2.28	2.28	212*	30	1.58	1.59	412
10	2.23	2.22	231	40	1.53	1.53	060
10	2.19	2.20	140	30	1.49	1.49	004
30	2.09	2.10	222	30	1.45	1.45	252
40	2.05	2.06	132	30	1.38	1.38	403

* indices used for least-squares refinement. Original cell: *a* 7.81, *b* 9.19, *c* 6.08Å; refined cell *a* 7.716, *b* 9.178, *c* 5.954Å for CuKα_1 radiation.

Therefore, the PDF data were treated to least-squares refinement, and additional "duftite" specimens were studied.

DUFTITE

The powder data reported by Claringbull (1951, PDF 6–0322) were refined using Cu $K\alpha_1$ radiation. The cell dimensions obtained are *a* 7.51(1), *b* 9.25(2), *c* 5.920(5) Å, but discrepancies between measured and calculated *d*-values are substantial for several diffraction lines. Similar refinement of the powder data by Guillemin (1956, PDF 14–169) gave *a* 7.716 (8), *b* 9.178(8), *c* 5.954(12) Å. Guillemin's pattern, which is for duftite with Pb:Ca = 93:7 and Cu:Zn = 96:4, is considered to be the better of the two, as there are no major deviations between measured and calculated *d*-values (Table 3).

In order to obtain cell parameters for end-member duftite, it was assumed that *a* of Guillemin's mineral is slightly high because of the minor substitution of Zn for Cu. In acccordance with the trend in the conichalcite–austinite series, a correction for the Zn substitution was applied by reducing *a* from 7.716 to 7.711 Å for the copper end-member which, in this case, has the ratio Pb:Ca = 93:7. Graphical extrapolation to adjust for the calcium content leads to *a* of about 7.734 Å for pure duftite. Application of the same kind of correction leads to *b* 9.182 and c 5.958 Å, *V* 423.1 Å^3 for duftite. These extrapolations are simplistic in that the Cu–Zn and Pb–Ca substitutions are treated independently, and thus the cell volume is only approximate.

Other "duftite" specimens

Two specimens labeled "duftite" were borrowed from the Royal Ontario Museum. Both are from Tsumeb and both proved to be strongly zoned. Microprobe analysis of one specimen (*M* 29503) gave compositions that vary from calcian duftite to plumbian conichalcite (Table 4). The other specimen (*M* 34851) also proved highly variable in composition and is plumbian conichalcite with an outermost zone containing appreciable vanadium in substitution for arsenic.

TABLE 4. MICROPROBE ANALYSES OF "DUFTITE", ROM M 29503

	core			peripheral clusters		
	av. wt%	mol	range, wt%	av. wt%	mol	range, wt%
PbO	38.1	.171	34.5-39.0	19.0	.085	11.5-23.4
CaO	6.2	.110	5.5-7.6	13.5	.241	11.9-15.9
CuO	23.2	.292	22.8-24.2	26.7	.336	25.9-28.2
ZnO	0.6	.008	0.5-0.7	0.9	.012	0.9-1.1
As_2O_5	30.2	.263	29.3-31.0	37.5	.327	35.9-39.4
	av. Ca:Pb = 39:61 Cu:Zn = 97:3			av. Ca:Pb = 74:26 Cu:Zn = 97:3		

Four specimens labeled "duftite" were obtained from the Systematic Reference Series of the National Mineral Collection, Ottawa. After examination of the specimens with a binocular microscope, two were judged unsuitable because of impurities and visible zoning. The others were given a preliminary calcium analysis by means of an energy-dispersion SEM system. Material from Can Pey, France (*NMC* 13540) was found to contain abundant calcium, but the other, from Tsumeb (*NMC* 13538), proved to be mainly duftite.

Several fragments of the *NMC* duftite from

FIG. 1. End-member duftite from Tsumeb, S.W.A. (*NMC* 13538) with narrow, darker zones of calcian duftite. SEM back-scattered electron image.

TABLE 5. X-RAY POWDER DATA FOR DUFTITE FROM TSUMEB, S.W.A. (NMC 13538)

I_{est}	d_{meas}	d_{calc}	*hkℓ*
5	5.03	5.03	011
3	4.59	4.60	020
6	4.22	4.22	111
3	3.96	3.96	120
<½	3.88	3.89	200
2	3.579	3.583	210*
<<½	3.302	3.306	121
10	3.257	3.263	201
4	2.999	3.000	002
7	2.854	2.855	130*
8B	2.670	2.678	112
		2.662	221
7	2.577	2.578	131*
2	2.520	2.513	022
1	2.497	2.496	310
<½	2.409	2.409	230
5	2.298	2.300	212*
½	2.259	2.259	320*
½	2.206	2.207	140
3	2.111	2.111	222*
4	2.069	2.071	141*
½	1.982	1.981	240*
2	1.941	1.945	400
4	1.881	1.881	331*
½	1.828	1.826	042*
<<½	1.803	1.805	322
1	1.788	1.791	420
3	1.778	1.778	142
<<½	1.760	1.760	051
1	1.717	1.717	151*
6	1.653	1.653	242*
4	1.632	1.632	402*
3	1.537	1.538	422
		1.535	060
2	1.501	1.500	004
<½	1.485	1.485	440
1	1.455		
1	1.407		
2	1.389		
½	1.352		
½	1.330		

Camera diameter 114.6 mm, CuKα_1 radiation. Indices with an asterisk were used in the cell-dimension refinement (Table 6).

Tsumeb were mounted in a polished section for electron-microprobe and scanning-electron-microscope analysis. The grains are zoned, but are mainly end-member duftite with narrow bands containing small amounts of Ca and traces of Zn (Fig. 1). The bands are too small for quantitative analysis, but the broader duftite zones contain < 0.1 wt. % CaO and < 0.1 wt. % ZnO.

X-ray powder data for duftite from the polished section are given in Table 5. Shrinkage corrections and least-squares refinement were performed as outlined previously. The resultant cell volume, 429.7 Å^3, is higher than that obtained by extrapolation from Guillemin's data. The difference may be due to the simplistic nature of the extrapolation, the possibility of undetected zoning in Guillemin's material or a combination of both.

DUFTITE–CONICHALCITE SOLID SOLUTION

The *NMC* specimen, in which end-member duftite contains zones of calcian duftite, also has a narrow rind of calcian duftite with a ratio Ca:Pb = 30:70 and negligible zinc. Other analyses in this study range from plumbian conichalcite to calcian duftite (Fig. 2), thus indicating that Ca–Pb solid solution between these minerals is extensive and probably complete. Although in this study a precise correlation between axial lengths and cation solid-solution was not possible because of fine zoning, an appropriate range of cell volumes was obtained (Table 6).

Radcliffe & Simmons (1971) showed that Cu–Zn solid solution in the conichalcite–austinite series extends to at least Cu:Zn:Mg = 67:31:2, a range similar to that found here. Although the as-yet-undescribed new member of the adelite group with Pb > Ca and Zn > Cu has been mentioned (Taggart & Foord 1980), none of the analyses in the present study approaches this composition. Nevertheless, extensive solid-solution bettween Ca and Pb, and Zn and Cu in the adelite group seems to be common rather than rare.

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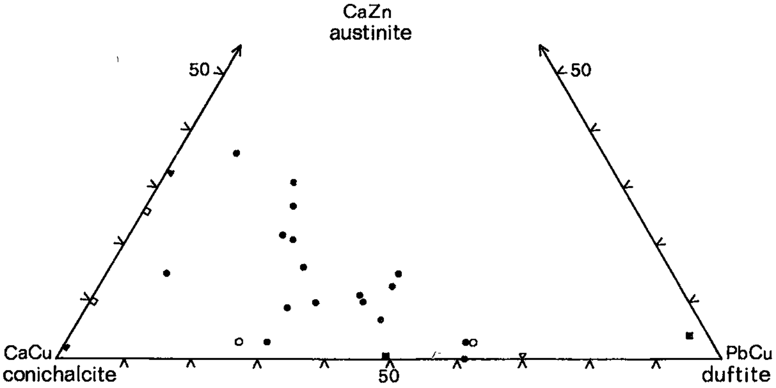

FIG. 2. Composition plot of intermediate members of the conichalcite–austinite–duftite series. Solid circles: original Tsumeb specimen, *NMC* 61459; open circles: *M* 29503; open squares: Dunin-Barkovskaya (1962); solid squares: Guillemin (1956); solid triangles: Radcliffe & Simmons (1971); open triangle: *NMC* 13538.

TABLE 6. CELL DIMENSIONS OF THE AUSTINITE-CONICHALCITE-DUFTITE SERIES

Mineral	Cu:Zn	Ca:Pb	a(Å)	b(Å)	c(Å)	V(Å^3)$_{meas}$	V(Å3)$_{calc}$*	Reference
austinite	0:100	100:0	7.506(6)	9.046(6)	5.932(6)	402.8		Radcliffe & Simmons (1971)
conichalcite	100:0	100:0	7.393(7)	9.220(15)	5.830(9)	397.4		Radcliffe & Simmons (1971)
	69:31	80:20	7.465(6)	9.185(12)	5.892(5)	404.0	405.5	Analysis 1, Table 2
	89:11	60:40	7.461(6)	9.202(11)	5.864(7)	402.6	410.9	Table 2
	90:10	59:41	7.446(7)	9.255(23)	5.881(5)	408.5	411.2	Table 2
duftite	96:4	7:93	7.716(8)	9.178(8)	5.954(12)	421.6	427.7	PDF 14-169, newly refined
	100:0	0:100	7.734	9.182	5.958		423.1	Extrapolated from PDF 14-169
	100:0	0:100	7.778(4)	9.207(3)	6.000(5)	429.7		NMC 13538 (Table 5)

*V_{meas} is that obtained from X-ray powder data; V_{calc} is that obtained by extrapolation from the cell dimensions of end-member duftite, conichalcite, and austinite.

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