

Calciodelrioite, $\text{Ca}(\text{VO}_3)_2(\text{H}_2\text{O})_4$, the Ca analogue of delrioite, $\text{Sr}(\text{VO}_3)_2(\text{H}_2\text{O})_4$

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ABSTRACT

Calciodelrioite, ideally $\text{Ca}(\text{VO}_3)_2(\text{H}_2\text{O})_4$, is a new mineral (IMA 2012-031) from the uranium-vanadium deposits of the eastern Colorado Plateau in the USA. The type locality is the West Sunday mine, Slick Rock district, San Miguel County, Colorado. The new mineral occurs on fracture surfaces in corvusite- and montroseite-impregnated sandstone and forms as a result of the oxidative alteration of these phases. At the West Sunday mine, calciodelrioite is associated with celestine, gypsum, huemulite, metarossite, pascoite and rossite. The mineral occurs as transparent colourless needles, bundles of tan to brown needles and star bursts of nearly black broad blades composed of tightly intergrown needles. Crystals are elongate and striated parallel to [100], exhibiting the prismatic forms {001} and {011} and having terminations possibly composed of the forms {100} and {61 $\bar{1}$ }. The mineral is transparent and has a white streak, subadamantine lustre, Mohs hardness of about 2½, brittle tenacity, irregular to splintery fracture, one perfect cleavage on {001} and possibly one or more additional cleavages parallel to [100]. Calciodelrioite is soluble in water. The calculated density is 2.451 g cm⁻³. It is optically biaxial (+) with $\alpha = 1.733(3)$, $\beta = 1.775(3)$, $\gamma = 1.825(3)$ (white light), $2V_{\text{meas}} = 87.3(9)^\circ$ and $2V_{\text{calc}} = 87^\circ$. The optical orientation is $X = \mathbf{b}$; $Z \approx \mathbf{a}$. No pleochroism was observed. Electron-microprobe analyses of two calciodelrioite samples and type delrioite provided the empirical formulae $(\text{Ca}_{0.88}\text{Sr}_{0.07}\text{Na}_{0.04}\text{K}_{0.01})_{\Sigma 1.00}(\text{V}_{1.00}\text{O}_3)_2(\text{H}_{2.01}\text{O})_4$, $(\text{Ca}_{0.76}\text{Sr}_{0.21}\text{Na}_{0.01})_{\Sigma 0.98}(\text{V}_{1.00}\text{O}_3)_2(\text{H}_{2.01}\text{O})_4$ and $(\text{Sr}_{0.67}\text{Ca}_{0.32})_{\Sigma 0.99}(\text{V}_{1.00}\text{O}_3)_2(\text{H}_{2.00}\text{O})_4$, respectively. Calciodelrioite is monoclinic, $I2/a$, with unit-cell parameters $a = 14.6389(10)$, $b = 6.9591(4)$, $c = 17.052(2)$ Å, $\beta = 102.568(9)^\circ$, $V = 1695.5(3)$ Å³ and $Z = 8$. The seven strongest lines in the X-ray powder diffraction pattern [listed as $d_{\text{obs}} \text{ \AA}(hkl)$] are as follows: 6.450(100)(011); 4.350(16)(013); 3.489(18)(020); 3.215(17)(022); 3.027(50)(multiple); 2.560(28)($\bar{4}15,413$); 1.786(18)(028). In the structure of calciodelrioite (refined to $R_1 = 3.14\%$ for 1216 $F_o > 4\sigma F$), V^{3+}O_5 polyhedra link by sharing edges to form a zigzag divanadate $[\text{VO}_3]$ chain along \mathbf{a} , similar to that in the structure of rossite. The chains are linked via bonds to Ca atoms, which also bond to H_2O groups, yielding $\text{CaO}_3(\text{H}_2\text{O})_6$ polyhedra. The Ca polyhedra form a chain along \mathbf{b} . Each of the two symmetrically independent VO_5 polyhedra has two short vanadyl bonds and three long equatorial bonds. Calciodelrioite and delrioite are isostructural and are the endmembers of the series $\text{Ca}(\text{VO}_3)_2(\text{H}_2\text{O})_4$ – $\text{Sr}(\text{VO}_3)_2(\text{H}_2\text{O})_4$. Calciodelrioite is dimorphous with rossite, which has a similar structure; however, the smaller 8-coordinate Ca site in rossite does not accommodate Sr.

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Introduction

THE eastern Colorado Plateau is known for mineral deposits that are rich in both uranium and vanadium. In parts of western Mesa, Montrose and San Miguel counties in Colorado and eastern Grand and San Juan counties in Utah, the mineralization is developed in bedded or roll-front deposits in sandstone of the Salt Wash member of the Jurassic Morrison Formation (Carter and Gualtieri, 1965; Shawe, 2011). This is the oldest uranium mining area in the USA and was a historically important source of uranium, vanadium and radium. It was from a deposit in this area, near Roc Creek, Montrose County, Colorado, that carnotite, $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$, was first discovered (Friedel and Cumenge, 1899). Since that time, deposits in this area have yielded more than thirty new minerals. Nearly all contain vanadium and more than one-third have been discovered in recent years as a result of the collecting efforts of one of the authors (JM). Studies of the parageneses of V-minerals in these deposits help us to understand the occurrence and formation of V-minerals in general (cf. Evans and Garrels, 1958; Hostetler and Garrels, 1962; Schindler *et al.*, 2000a).

The mineral delrioite was described by Thompson and Sherwood (1959) from the Jo Dandy mine in Montrose County, Colorado. The chemical analysis indicated virtually equal amounts of Ca and Sr. A subsequent crystallographic study by Smith (1970) showed the type material to be an intimate mixture of delrioite and metadelrioite, which exhibit a reversible hydration–dehydration relationship. Smith (1970) reported the ideal formulae for delrioite and metadelrioite to be $CaSrV_2O_6(OH)_2 \cdot 3H_2O$ and $CaSrV_2O_6(OH)_2$, respectively. Recent collecting in several currently active mines in the area by one of the authors (JM) yielded crystals of a Ca-dominant vanadate which appeared to be crystallographically equivalent to delrioite. To clarify the relation between these minerals, we have examined delrioite crystals from the type specimen of delrioite in the collection of the US National Museum of Natural History (Smithsonian Institution), catalogue number 128296.

Our study of type delrioite by electron microprobe analysis (EMPA) shows Sr to be dominant

over Ca and powder and single-crystal X-ray diffraction studies show type delrioite to be isostructural with the new Ca-vanadate. As the new mineral is the Ca analogue of delrioite, it is named calciodelrioite. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2012-031). No single specimen provided sufficient data for the complete description of the species, and therefore there is no holotype. Three cotype specimens are deposited in the collections of the Natural History Museum of Los Angeles County under catalogue numbers 63837, 63838 and 63839.

Occurrence and paragenesis

Calciodelrioite was first noted on specimens from the West Sunday mine, Slick Rock district, San Miguel County, Colorado, USA, and the characterization of the species is based on material from this mine, which is the type locality. Subsequently, it was found on specimens from the adjacent St Jude mine, from the Blue Streak mine, Bull Canyon, Montrose County, Colorado and from the Little Eva mine, Yellow Cat district, Grand County, Utah, USA.

The new mineral is moderately rare, but seems to be widespread in the U-V deposits of the area. At each of the noted localities, it occurs as crystalline crusts on fracture surfaces in corvusite- and montroseite-impregnated sandstone and forms as a result of the oxidative alteration of corvusite and montroseite. At the West Sunday mine, calciodelrioite is associated with celestine, gypsum, huemulite, metarossite, pascoite and rossite. At the St Jude mine, it is associated with delrioite, gypsum, hendersonite, metarossite, pascoite, powellite, rossite and the recently approved decavanadate mineral schindlerite (IMA2012-063). At the Blue Streak mine, it is associated with delrioite, gypsum, huemulite, hummerite, magnesiopascoite, metarossite, powellite, rossite and a K- and Mg-bearing decavanadate which is currently under study. At the Little Eva mine, it is associated with gypsum, huemulite, metarossite and rossite.

Calciodelrioite appears to be much more common than delrioite. In our study of material

from the localities noted in the foregoing text, we found that Sr was present in most crystals of calciodelrioite. Crystals with $\text{Sr} > \text{Ca}$, corresponding to compositions within the delrioite field, were found on only two specimens, one from the St Jude mine and one from the Blue Streak mine. Even in those cases, other crystals on the same specimen had compositions with $\text{Ca} > \text{Sr}$.

It is also noteworthy that in natural conditions calciodelrioite is relatively resistant to loss of H_2O . Although calciodelrioite has a structure that is very similar to rossite, with which it is commonly associated, rossite is almost always partly to completely altered to the lower hydrate, metarossite, whereas calciodelrioite exhibits no evidence of such alteration. In detailed studies (using powder X-ray diffraction and energy-dispersive spectroscopy) of specimens from these and other U-V deposits in the area, we found no natural calciodelrioite meta-phase analogous to metadelrioite.

Physical and optical properties

On the specimens examined in this study the calciodelrioite crystals have three distinct appearances: (1) transparent colourless needles typically forming parallel-to-subparallel intergrowths or divergent sprays up to about 1 mm in length (Figs 1 and 2); (2) tan to brown to reddish brown needles forming bundles of parallel crystals up to



FIG. 1. Colourless calciodelrioite needles on cotype specimen NHMLAC 63839 from the West Sunday mine, San Miguel County, Colorado. The field of view is 0.4 mm across.

about 2 mm in length (Fig. 3); (3) brownish needles intergrown very tightly to create apparently black broad blades in flat-lying 'star bursts' up to about 2 mm across (Figs 4 and 5). The relative content of Ca vs. Sr does not seem to

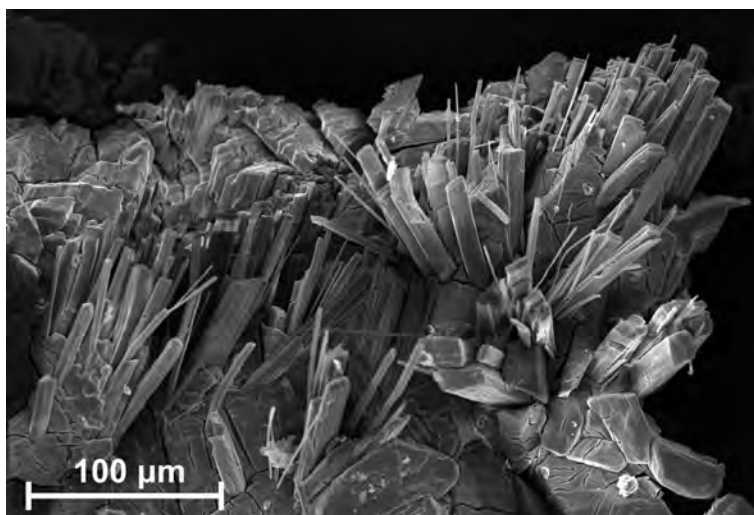


FIG. 2. A scanning electron microscope image of colourless calciodelrioite needles of the type illustrated in Fig. 1.

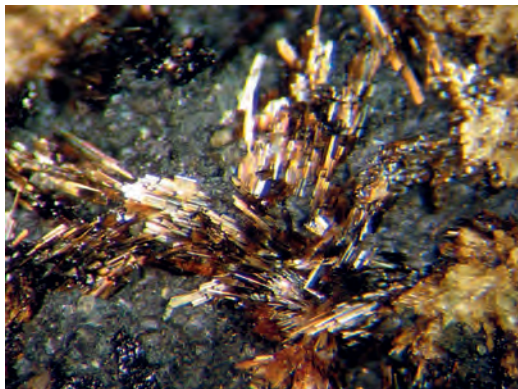


FIG. 3. Reddish brown calcicdelrioite needles on cotype specimen NHMLAC 63838 from the West Sunday mine, San Miguel County, Colorado. The field of view is 3 mm across.



FIG. 4. Blackish 'star burst' aggregate of calcicdelrioite on specimen from the St Jude mine, San Miguel County, Colorado. The field of view is 3 mm across.

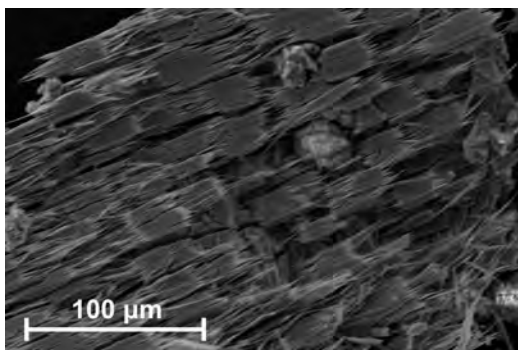


FIG. 5. A scanning electron microscope image showing a highly magnified view of tightly intergrown aggregates of calcicdelrioite needles, such as those illustrated in Fig. 4.

correlate consistently with the habit and/or colour of calcicdelrioite.

The needles or thin prisms are elongated parallel to [100] and commonly have steps and/or striations parallel to their length. The prismatic forms are {001} and {011}; terminations tend to be composed of a number of indistinct forms, which could not be measured accurately; the forms {100} and {61 $\bar{1}$ } best approximate the shape of the terminations (Fig. 6). No twinning was observed.

Calcicdelrioite has a white streak. Individual crystals are transparent with a subadamantine lustre, whereas crystal bundles are translucent with a silky lustre. Calcicdelrioite does not fluoresce in long or short wave ultraviolet light. The Mohs hardness is about 2½, the tenacity is brittle and the fracture irregular to splintery. Crystals exhibit one perfect cleavage on {001} and possibly one or more additional cleavages parallel to [100]. Calcicdelrioite is soluble in

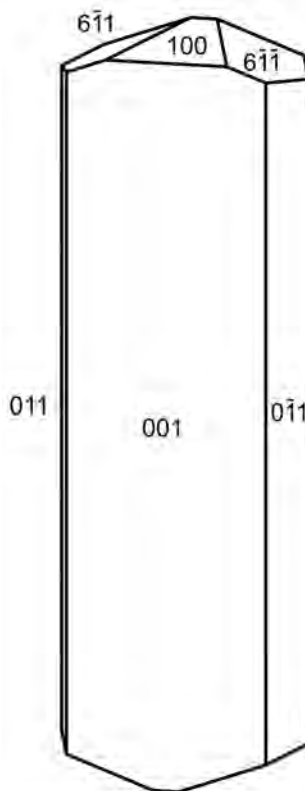


FIG. 6. Crystal drawing of calcicdelrioite (clinographic projection in non-standard orientation).

water. The mineral dissolves in available aqueous density liquids and insufficient material was available for a direct measurement; therefore the density could not be measured. The calculated densities based on the unit-cell parameters determined by single-crystal X-ray diffraction and the empirical formulae for NHMLAC 63837 and NHMLAC 63838 are 2.451 and 2.503 g cm⁻³, respectively.

Optically, calciodelrioite is biaxial positive, with $\alpha = 1.733(3)$, $\beta = 1.775(3)$ and $\gamma = 1.825(3)$, measured in white light. Conoscopic observation was impossible because of the thin prismatic habit of crystals. The 2V measured using extinction data with *EXCALIBUR* (Gunter *et al.*, 2004) is 87.3(9)°; the 2V calculated from the indices of refraction is 87°. The dispersion could not be determined. The optical orientation is $X = \mathbf{b}$; $Z \approx \mathbf{a}$. No pleochroism was observed.

Chemical composition

Electron microprobe analyses of calciodelrioite, and of the delrioite type specimen, were performed at the University of Utah on a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers. Analytical

conditions were 15 kV accelerating voltage, 10 nA beam current and a nominal beam diameter of 15 μm . Counting times were 10 s for each element. The data were corrected for matrix effects using a $\phi(\rho, Z)$ algorithm (Pouchou and Pichoir, 1991). The standards used were albite (Na), sanidine (K, Al), diopside (Ca), celestine (Sr) and V metal (V). No other elements were detected by energy-dispersive spectroscopy (EDS).

No visible damage was produced by the electron beam; however, as is typical of highly hydrated phases, calciodelrioite and delrioite partially dehydrate under the vacuum in the microprobe chamber. This H₂O loss produces higher concentrations for the non-volatile constituents in comparison to the fully hydrated phase. As insufficient material was available for a direct determination of H₂O, the H₂O content was calculated on the basis of the structure determination. It should be noted that the delrioite type material consists of crystals that are a mixture of delrioite and metadelrioite, which exhibit reversible hydration–dehydration. This does not affect the validity of basing the calculated water content on the ideal delrioite composition (and the calciodelrioite structure). Analytical data are

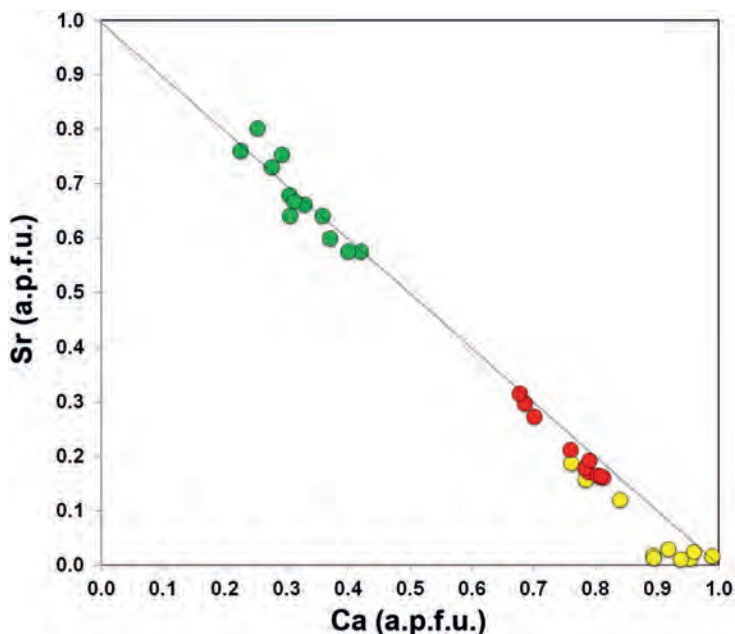


FIG. 7. Plot of the number of Ca vs. Sr atoms per formula unit for type delrioite (green circles), reddish brown needles of calciodelrioite from NHMLAC 63838 (red circles) and colourless prisms of calciodelrioite from NHMLAC 63837 (yellow circles).

TABLE 1a. Analytical results for calcicdelrioite and type delrioite.

Constituent	Calcicdelrioite NHMLAC 63837 (11 analyses)		Calcicdelrioite NHMLAC 63838 (10 analyses)		Delrioite type NMNH 128296 (12 analyses)	
	Mean (wt.%)	SD	Mean (wt.%)	SD	Mean (wt.%)	SD
Na ₂ O	0.40	0.15–0.66	0.09	0.19	0.03	0.07
K ₂ O	0.25	0.0–0.48	0.04	0.18	0.02	0.02
CaO	18.30	15.38–20.39	15.87	1.73	13.65–17.66	1.54
SrO	2.66	0.43–7.02	8.15	2.81	6.26–11.77	2.09
V ₂ O ₅	67.19	67.42–71.62	67.50	2.55	62.67–70.49	2.56
H ₂ O*	26.77		26.86			
Total	115.57		118.51		111.98	

* Water calculated on the basis of structure data.

Table 1b. Normalized analytical results for calcicdelrioite and type delrioite.

Constituent	Calcicdelrioite NHMLAC 63837		Calcicdelrioite NHMLAC 63838		Delrioite type NMNH 128296	
	Mean (wt.%)	SD	Mean (wt.%)	SD	Mean (wt.%)	SD
Na ₂ O	0.34		0.08	0.02		
K ₂ O	0.22		0.02	0.02		
CaO	15.83		13.39	5.27	18.09	
SrO	2.31		6.87	20.40		29.04
V ₂ O ₅	58.13		56.96	53.19	58.67	50.82
H ₂ O	23.16		22.66	21.09	23.24	20.14
Total	99.99 [†]		99.98 [†]	99.99 [†]	100.00	100.00

[†] These sums do not total to 100.00 due to rounding errors.

CALCIODELRIOITE, THE Ca ANALOGUE OF DELRIOITE

summarized in Table 1a and normalized analyses in Table 1b. The amount of Ca vs. Sr in atoms per formula unit (a.p.f.u.) for individual analyses is plotted in Fig. 7.

In addition to the analyses discussed in the foregoing text, supplementary quantitative

analyses were performed in the Department of Geological Sciences at the Faculty of Sciences of Masaryk University in Brno, Czech Republic using a Cameca SX100 electron microprobe in wavelength-dispersive spectrometry mode. For the purpose of confirming additional localities

TABLE 2. Powder X-ray diffraction data for calciodelrioite.

I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h k l$	I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h k l$
9	8.41(9)	8.3217	9	0 0 2			1.9032	2	0 3 5
14	7.18(4)	7.1441	17	2 0 0	4	1.905(6)	1.8987	1	$\bar{2}$ 3 5
100	6.450(14)	6.4204	100	0 1 1			1.8901	1	2 0 8
		6.1184	7	$\bar{2}$ 0 2	13	1.829(2)	1.8299	12	$\bar{8}$ 0 2
4	4.95(6)	{ 4.9880	1	$\bar{2}$ 1 1			1.7872	3	0 1 9
		4.9175	2	2 0 2	18	1.786(4)	1.7856	11	0 2 8
5	4.61(4)	4.5877	3	2 1 1			1.7846	1	2 3 5
16	4.350(15)	4.3380	15	0 1 3			1.7737	7	$\bar{4}$ 3 5
6	4.18(3)	4.1609	5	0 0 4			1.7715	6	4 3 3
5	4.02(3)	4.0241	4	$\bar{2}$ 1 3	14	1.768(6)	1.7603	3	$\bar{8}$ 1 3
		3.5766	6	$\bar{4}$ 0 2			1.7592	4	$\bar{8}$ 1 1
13	3.577(13)	3.5720	8	4 0 0			1.7526	2	$\bar{4}$ 1 9
18	3.489(10)	3.4796	20	0 2 0			1.7483	2	4 1 7
		3.4562	2	2 1 3	8	1.746(6)	1.7398	5	0 4 0
17	3.215(7)	3.2102	20	0 2 2	3	1.686(7)	1.6874	1	$\bar{8}$ 1 5
		3.1282	5	2 2 0			1.6604	2	0 3 7
		3.0592	7	$\bar{4}$ 0 4	6	1.657(3)	1.6525	2	$\bar{4}$ 0 10
		3.0506	6	4 0 2			1.6485	2	4 0 8
50	3.027(4)	3.0246	3	$\bar{2}$ 2 2	5	1.620(4)	1.6196	5	$\bar{8}$ 2 2
		3.0213	15	$\bar{4}$ 1 3	2	1.587(7)	1.5905	1	$\bar{8}$ 2 4
		3.0158	15	4 1 1			1.5889	1	8 2 0
		3.0028	12	0 1 5	4	1.563(4)	1.5645	2	$\bar{8}$ 1 7
		2.9855	3	$\bar{2}$ 1 5			1.5607	2	8 1 3
9	2.781(8)	2.7739	13	0 0 6			1.5296	1	$\bar{8}$ 0 8
28	2.560(3)	2.5593	17	$\bar{4}$ 1 5	3	1.529(8)	1.5292	1	6 3 3
		2.5526	19	4 1 3			1.5253	1	8 0 4
		2.4940	4	$\bar{4}$ 2 2	2	1.512(11)	1.5123	2	$\bar{4}$ 4 4
		2.4925	5	4 2 0			1.5113	1	4 4 2
10	2.486(6)	2.4864	2	$\bar{3}$ 1 6	5	1.490(6)	1.4927	2	$\bar{4}$ 2 10
		2.4673	2	$\bar{5}$ 1 4			1.4898	3	4 2 8
2	2.39(2)	2.3847	2	5 1 2			1.4820	2	$\bar{4}$ 1 11
7	2.293(6)	2.2975	2	0 3 1	4	1.477(6)	1.4787	2	4 1 9
		2.2897	5	1 3 0			1.4739	3	0 4 6
		2.2499	2	0 1 7			1.4275	1	$\bar{4}$ 3 9
4	2.167(14)	2.1690	4	0 2 6	4	1.424(3)	1.4252	1	4 3 7
6	2.136(9)	2.1401	7	0 3 3			1.4216	1	$\bar{8}$ 1 9
		2.1097	2	$\bar{4}$ 1 7			1.4003	1	$\bar{8}$ 2 8
5	2.091(8)	2.1041	2	4 1 5			1.3970	1	8 2 4
		2.0804	3	0 0 8	5	1.392(3)	1.3916	1	$\bar{8}$ 3 5
		2.0121	3	$\bar{4}$ 2 6			1.3900	1	8 3 1
8	2.009(4)	2.0080	3	4 2 4			1.3870	1	0 5 1
		1.9652	1	6 2 0					
3	1.957(10)	1.9521	1	6 1 3					

Only calculated lines with intensities greater than 1 are listed unless they correspond to observed lines.

for calciodelrioite and delrioite, semi-quantitative analyses were performed by energy-dispersive spectrometry using a Hitachi S-3000N variable pressure scanning electron microscope equipped with an Oxford INCA x-sight spectrometer at the Natural History Museum of Los Angeles County.

Empirical formulae (based on 10 O a.p.f.u.) are as follows: $(\text{Ca}_{0.88}\text{Sr}_{0.07}\text{Na}_{0.04}\text{K}_{0.01})_{\Sigma 1.00}(\text{V}_{1.00}\text{O}_3)_2(\text{H}_{2.01}\text{O})_4$ for NHMLAC 63837, $(\text{Ca}_{0.76}\text{Sr}_{0.21}\text{Na}_{0.01})_{\Sigma 0.98}(\text{V}_{1.00}\text{O}_3)_2(\text{H}_{2.01}\text{O})_4$ for NHMLAC 63838 and $(\text{Sr}_{0.67}\text{Ca}_{0.32})_{\Sigma 0.99}(\text{V}_{1.00}\text{O}_3)_2(\text{H}_{2.00}\text{O})_4$ for NMNH 128296. The simplified formula for calciodelrioite is $\text{Ca}(\text{VO}_3)_2(\text{H}_2\text{O})_4$, which requires CaO 18.09, V_2O_5 58.67, H_2O 23.24, total 100.00 wt.%.

The Gladstone–Dale compatibility indexes, $[1 - (K_p/K_C)]$, for calciodelrioite using the density derived from the single-crystal unit cell and the empirical formulae for NHMLAC 63837 and NHMLAC 63838 are -0.011 and -0.006 , respectively, in both cases indicating superior compatibility (Mandarino, 1981).

X-ray crystallography and structure refinement

Powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatic $\text{MoK}\alpha$ radiation. For the powder-diffraction study, the observed d -spacings and intensities were derived by profile fitting using *JADE 2010* software. The powder data presented in Table 2 show good agreement with the pattern calculated from the structure determination. Unit-cell parameters refined from the powder data using *JADE 2010* with whole-pattern fitting are as follows: $a = 14.609(7)$, $b = 6.953(7)$, $c = 17.052(7)$ Å, $\beta = 102.59(2)^\circ$ and $V = 1690(2)$ Å³.

The Rigaku *CrystalClear* software package was used to process the structure data, including the application of an empirical absorption correction. The *SHELXL-97* software package (Sheldrick, 2008) was used for the solution (by direct

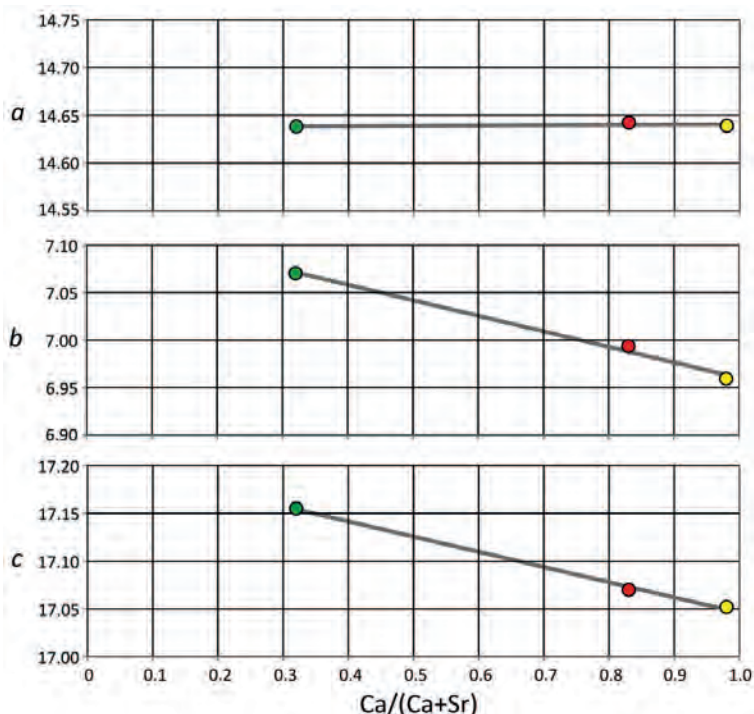


FIG. 8. Three plots showing the variation in unit-cell parameters as a function of large cation ratio $\text{Ca}/(\text{Ca}+\text{Sr})$ for type delrioite (green circles), reddish brown needles of calciodelrioite from NHMLAC 63838 (red circles) and colourless prisms of calciodelrioite from NHMLAC 63837 (yellow circles). Note that $\text{Ca}/(\text{Ca}+\text{Sr})$ for the calciodelrioite is based upon refined site occupancies.

methods) and refinement of the structure. The positions of the H atoms in the four H₂O groups were located in the difference-Fourier maps. Their positions were refined with O–H distances constrained to 0.90(3) Å and H–H distances for each H₂O group constrained to 1.45(3) Å. The isotropic displacement parameters ($\times 1.2$) were tied to those of the associated O atoms.

Structure refinements were conducted on crystals from both NHMLAC 63837 and NHMLAC 63838, and these gave almost identical results. The data presented here are for the crystal from NHMLAC 63837 because its chemistry is closer to the Ca endmember. The cell parameters for NHMLAC 63838 are $a = 14.6423(10)$, $b = 6.9935(2)$, $c = 17.070(2)$ Å and $\beta = 102.565(8)^\circ$ and the structural formula is $(\text{Ca}_{0.831}\text{Sr}_{0.169})(\text{VO}_3)_2(\text{H}_2\text{O})_4$. These values are plotted in Fig. 8, as noted in the following text.

Details of the data collection and structure refinement for the crystal from NHMLAC 63837 are provided in Table 3. Final atom coordinates and displacement parameters are provided in Table 4, selected bond distances in Table 5 and bond valence summations in Table 6. Lists of observed and calculated structure factors have been deposited with *Mineralogical Magazine* and are available at http://www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Description of the structure

The crystal structure of calciodelrioite (Fig. 9) can be considered to consist of a structural unit (polymerized polyhedra with higher bond-valence) and an interstitial unit (cations, OH and H₂O groups, which occupy the interstices between the structural units), following

TABLE 3. Data collection and structure refinement details for calciodelrioite (crystal from NHMLAC 63837).

Diffractionmeter	Rigaku R-Axis Rapid II
X-ray radiation/power	MoK α ($\lambda = 0.71075$ Å)/50 kV, 40 mA
Temperature	298(2) K
Structural Formula	$(\text{Ca}_{0.978}\text{Sr}_{0.022})(\text{VO}_3)_2(\text{H}_2\text{O})_4$
Space group	$I2/a$
Unit-cell dimensions	$a = 14.6389(10)$ Å $b = 6.9591(4)$ Å $c = 17.052(2)$ Å $\beta = 102.568(9)^\circ$
Z	8
V	$1695.5(3)$ Å ³
Density (for above formula)	2.436 g cm ⁻³
Absorption coefficient	2.953 mm ⁻¹
F(000)	1235
Crystal size	$100 \times 35 \times 20$ μm
θ range	3.26 to 25.03°
Index ranges	$-17 \leq h \leq 17$, $-8 \leq k \leq 8$, $-20 \leq l \leq 20$
Reflections collected/ unique	9941/1493 [$R_{\text{int}} = 0.0382$]
Reflections with $F_o > 4\sigma(F)$	1216
Completeness to $\theta = 25.03^\circ$	99.3%
Max. and min. transmission	0.9433 and 0.7567
Refinement method	Full-matrix least-squares on F^2
Parameters refined	143
GoF	1.053
Final R indices [$F_o > 4\sigma(F)$]	$R_1 = 0.0314$, $wR_2 = 0.0732$
R indices (all data)	$R_1 = 0.0411$, $wR_2 = 0.0784$
Largest diff. peak/hole	$+0.878/-0.615$ e Å ⁻³

$$R_{\text{int}} = \frac{\sum |F_o^2 - F_o^2(\text{mean})|}{\sum [F_o^2]}$$

$$\text{GoF} = S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n-p)} \right\}^{1/2}$$

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

$$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ where } a \text{ is } 0.0364, b \text{ is } 5.7700 \text{ and } P \text{ is } [2F_c^2 + \text{Max}(F_o^2, 0)]/3.$$

TABLE 4. Atom coordinates and displacement parameters (\AA^2) for calciodelniroite.

	x/a	y/b	z/c	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V1	0.79336(3)	-0.00857(7)	0.92497(3)	0.01287(19)	0.0080(3)	0.0192(3)	0.0116(3)	0.0000(2)	0.0026(2)	-0.0007(2)
V2	0.54422(3)	-0.01384(8)	0.92645(3)	0.01404(19)	0.0072(3)	0.0246(3)	0.0104(3)	-0.0010(2)	0.0023(2)	0.0010(2)
Ca*	0.73915(5)	-0.01650(9)	0.69610(4)	0.0238(3)	0.0264(5)	0.0222(4)	0.0216(5)	-0.0034(3)	0.0026(3)	0.0021(3)
O1	0.92778(14)	-0.0413(3)	0.95628(14)	0.0201(5)	0.0083(11)	0.0378(14)	0.0151(12)	0.0004(10)	0.0046(9)	-0.0029(10)
O2	0.67617(14)	-0.0573(3)	0.95622(13)	0.0189(5)	0.0089(11)	0.0331(13)	0.0150(12)	-0.0027(10)	0.0035(9)	-0.0002(10)
O3	0.77342(15)	-0.1365(3)	0.84035(14)	0.0230(6)	0.0176(12)	0.0283(13)	0.0239(14)	-0.0063(11)	0.0061(10)	-0.0030(10)
O4	0.78551(17)	0.2154(3)	0.89913(15)	0.0276(6)	0.0292(14)	0.0241(13)	0.0290(15)	0.0031(11)	0.0055(11)	-0.0008(11)
O5	0.51085(17)	-0.2023(4)	0.86897(16)	0.0356(7)	0.0209(13)	0.0533(17)	0.0321(16)	-0.0233(13)	0.0047(11)	-0.0045(12)
O6	0.54648(18)	0.1779(4)	0.87097(17)	0.0368(7)	0.0258(14)	0.0495(17)	0.0381(17)	0.0229(13)	0.0136(12)	0.0104(13)
OW1	0.8180(2)	-0.0315(4)	0.5851(2)	0.0480(9)	0.063(2)	0.0304(16)	0.059(2)	0.0030(15)	0.0336(18)	0.0108(15)
H1A	0.835(3)	-0.151(4)	0.574(3)	0.058						
H1B	0.833(3)	0.041(5)	0.547(2)	0.058						
OW2	0.6120(2)	-0.2827(8)	0.7546(2)	0.0860(16)	0.0322(18)	0.182(5)	0.040(2)	-0.055(3)	-0.0025(15)	0.026(2)
H2A	0.588(4)	-0.231(9)	0.795(2)	0.103						
H2B	0.566(3)	-0.285(9)	0.711(2)	0.103						
OW3	0.9065(2)	0.5369(4)	0.9048(2)	0.0534(10)	0.0385(18)	0.0294(16)	0.082(3)	-0.0022(17)	-0.0088(17)	-0.0033(13)
H3A	0.947(3)	0.439(5)	0.907(3)	0.064						
H3B	0.936(3)	0.645(4)	0.916(3)	0.064						
OW4	0.85198(16)	0.2572(4)	0.74850(15)	0.0265(6)	0.0197(12)	0.0415(15)	0.0183(14)	0.0052(12)	0.0046(10)	0.0025(11)
H4A	0.873(2)	0.292(5)	0.7063(16)	0.032						
H4B	0.899(2)	0.227(5)	0.7871(17)	0.032						

* Refined Ca occupancy: 0.978(5) Ca; 0.022(5) Sr.

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TABLE 5. Selected bond distances (Å) and angles (°) in calciodelrioite.

V1–O4	1.617(2)	V2–O6	1.640(3)	Ca–OW1	2.425(3)
V1–O3	1.666(2)	V2–O5	1.647(3)	Ca–OW3	2.435(3)
V1–O2	1.934(2)	V2–O2	1.911(2)	Ca–O3	2.491(2)
V1–O1	1.937(2)	V2–O1	1.921(2)	Ca–O3	2.542(3)
V1–O2	2.006(2)	V2–O1	1.961(2)	Ca–OW4	2.545(3)
<V1–O>	1.832	<V2–O>	1.816	Ca–OW4	2.552(3)
				Ca–OW2	2.572(4)
				Ca–O4	2.628(3)
				Ca–OW2	2.949(5)
				<Ca–O>	2.571

Hydrogen bonds (D = donor, A = acceptor)

D–H	<i>d</i> (D–H)	<i>d</i> (H···A)	<DHA	<i>d</i> (D···A)	A	<HDH
OW1–H1a	0.90(3)	2.09(3)	160(4)	2.952(4)	O2	
OW1–H1b	0.89(3)	2.80(5)	105(4)	3.147(4)	O6	104(3)
OW2–H2a	0.91(3)	1.88(4)	160(6)	2.751(4)	O5	
OW2–H2b	0.89(3)	1.93(3)	168(6)	2.807(4)	O6	107(4)
OW3–H3a	0.90(3)	2.07(3)	159(5)	2.922(4)	O5	
OW3–H3b	0.87(3)	2.29(4)	138(4)	2.998(4)	O6	110(4)
OW4–H4a	0.88(2)	1.96(3)	162(3)	2.807(3)	O6	
OW4–H4b	0.87(2)	1.91(3)	170(4)	2.774(3)	O5	109(3)

Hawthorne (1983) and as more comprehensively developed for vanadate minerals by Schindler *et al.* (2000*a,b*). The structural unit in calciodelrioite is a zigzag divanadate $[\text{VO}_3]^-$ chain along **a** consisting of edge-sharing V^{5+}O_5 polyhedra. The $[\text{VO}_3]$ chains are linked to one another via bonds to the interstitial unit, which consists of Ca^{2+} cations and H_2O groups. The Ca^{2+} is 9-coordinate, bonding to one O atom in each of three chains and to six H_2O groups. The $\text{CaO}_3(\text{H}_2\text{O})_6$ polyhedra, taken on their own, form a chain along **b**, in which the polyhedra alternately share edges and faces.

Each of the two independent VO_5 polyhedra includes two short vanadyl bonds (1.61–1.67 Å) and three longer equatorial bonds (1.91–2.01 Å) to produce a 2+3 coordination [see Schindler *et al.* (2000*a,b*) for descriptions of vanadyl, equatorial and *trans* V–O bonds and their significance]. The O atoms participating in the vanadyl bonds to V atoms are in *cis* configuration in each polyhedron (O3 and O4; O5 and O6) and each bonds to a single V. The O atoms participating in the equatorial bonds each bond to three V atoms, and hence are involved in the shared edges of the $[\text{VO}_3]$ chain.

There is no doubt that delrioite and calciodelrioite are isostructural. They have similar powder X-ray diffraction patterns and we were able to confirm from a single-crystal study of a crystal from the delrioite-metadelrioite type specimen that their unit cells and space groups correspond. Although the type delrioite-metadelrioite crystals were not suitable for structure refinement, we were able to refine the cell parameters of delrioite (see Table 7) and metadelrioite [$a = 7.324(5)$, $b = 8.357(8)$, $c = 5.085(6)$ Å, $\alpha = 111.63(8)$, $\beta = 90.63(8)$, $\gamma = 102.67(6)^\circ$] using an intergrowth of the two phases removed from the type specimen. Furthermore, the variation in the unit-cell parameters as a function of the Sr/(Sr + Ca) cation ratio is consistent with the occupation of these cations in a single site (Fig. 8). Note that the *a* parameter is essentially invariant, as it is defined by the length of the $[\text{VO}_3]$ chain, whereas the *b* and *c* parameters increase with increasing Sr content. Based upon the obvious conclusion that delrioite and calciodelrioite are isostructural and that the large cations occupy a single site in the structure, it is clear from our chemical analyses that the type material corresponds to the Sr-

TABLE 6. Bond-valence analyses for calciodelrioite and rossite. Values are expressed in valence units.

Calciodelrioite											
	O1	O2	O3	O4	O5	O6	OW1	OW2	OW3	OW4	Σ
V1	0.70	0.70 0.59	1.45	1.65							5.08
V2	0.73 0.65	0.75			1.52	1.55					5.20
Ca			0.24 0.21	0.17			0.29	0.20 0.07	0.28	0.21 0.21	1.89
H1a		0.10					0.90				1.00
H1b						0.03	0.97				1.00
H2a					0.16			0.84			1.00
H2b						0.15		0.85			1.00
H3a					0.11				0.89		1.00
H3b						0.08			0.92		1.00
H4a						0.14				0.86	1.00
H4b					0.15					0.85	1.00
Σ	2.08	2.13	1.91	1.82	1.94	1.95	2.16	1.96	2.09	2.13	
Rossite*											
	O1	O2	O7	O4	O6	O5	OW3	OW8	OW9	OW10	Σ
V2	0.81	0.85 0.34	1.47	1.59							5.06
V1	0.70 0.61	0.77			1.52	1.57					5.17
Ca			0.31	0.31	0.25		0.28	0.20 0.18	0.25	0.27	2.05
H3a		0.17					0.83				1.00
H3b							0.83		0.17		1.00
H8a						0.18		0.82			1.00
H8b						0.15		0.85			1.00
H9a					0.19				0.81		1.00
H9b			0.16						0.84		1.00
H10a				0.19						0.81	1.00
H10b							0.17			0.83	1.00
Σ	2.12	2.13	1.94	2.09	1.96	1.90	2.11	2.05	2.07	1.91	

* Note that the atoms in the rossite structure have been labelled to facilitate comparison with calciodelrioite. Bond-valence parameters were taken from Brown and Altermatt (1985); for calciodelrioite hydrogen-bond strengths are based on H...O bond lengths and for delrioite they are based on O...O bond lengths, also from Brown and Altermatt (1985). The bond strengths for the Ca site in calciodelrioite are based upon the refined Ca/Sr occupancy.

dominant member of a series between $\text{Ca}(\text{VO}_3)_2(\text{H}_2\text{O})_4$ (calciodelrioite) and $\text{Sr}(\text{VO}_3)_2(\text{H}_2\text{O})_4$ (delrioite).

Calciodelrioite is dimorphous with rossite (Ahmed and Barnes, 1963) and the two minerals are quite similar in structure (Fig. 9). The rossite structural unit is also an edge-sharing divanadate $[\text{VO}_3]$ chain, which is topologically identical to that in calciodelrioite; however, the $[\text{VO}_3]$ chain

in the rossite structure is geometrically 'twisted' relative to that in calciodelrioite, as can be seen looking down the chains in Fig. 9. The linkages between the structural and interstitial units in the structures of calciodelrioite and rossite are quite similar. In both cases, the $[\text{VO}_3]$ chains are linked to one another via bonds to Ca atoms and each Ca atom bonds to one O atom in each of three chains, although there are some differences in the bonds

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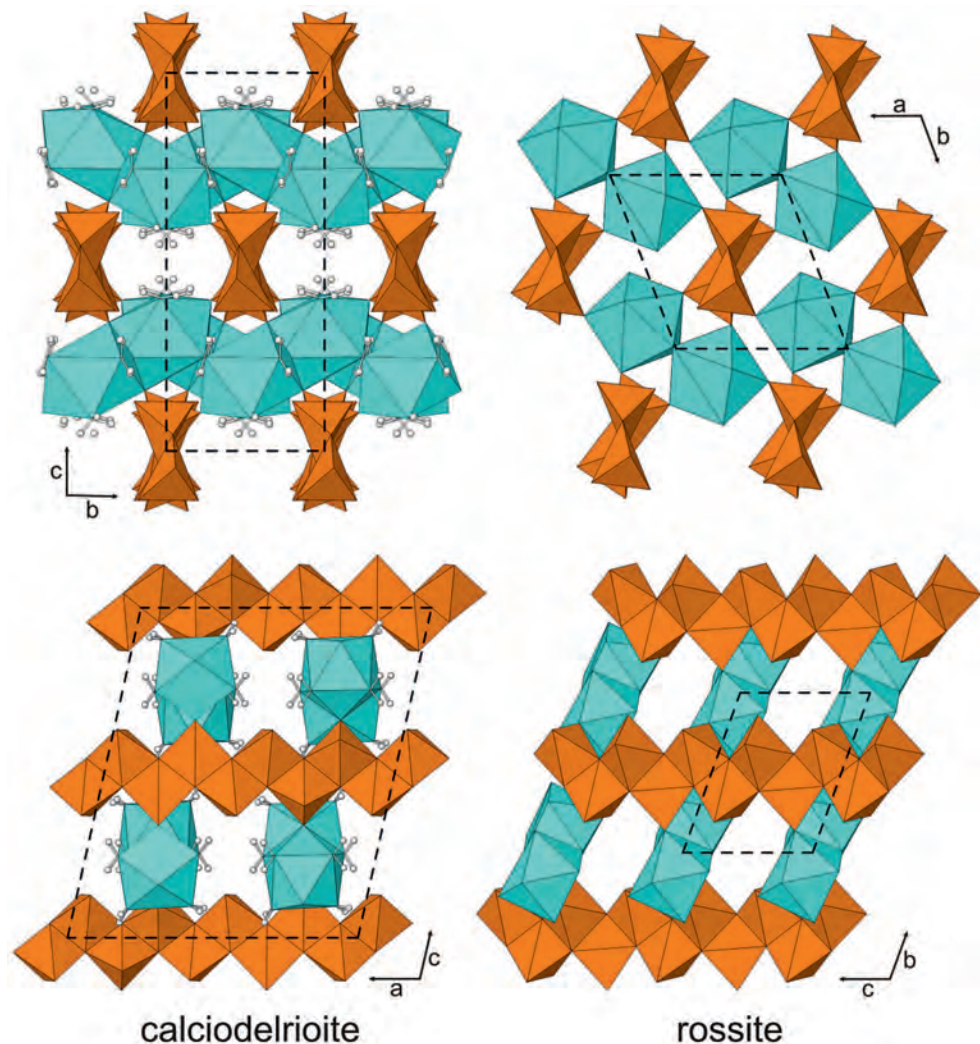


FIG. 9. Comparison of the crystal structures of calciodelrioite and rossite. The VO_5 polyhedra are orange and the CaO_8 and CaO_9 polyhedra blue. The H atoms in calciodelrioite are shown as small white spheres.

from Ca and H received by O atoms of the VO_5 groups (Table 6).

It is noteworthy that one of the two symmetrically independent VO_5 groups in rossite includes a much longer *trans* V–O bond (V2-O2) of 2.19 Å, and that the VO_5 group has a 2+2+1, rather than a 2+3 coordination geometry. A bond-valence analysis for the rossite structure (Table 6) clearly demonstrates that the long *trans* V2–O2 bond, which provides a bond valence of only 0.34 vu, is necessary to balance the bond-valence sum to the O2 atom. There does not

appear to be any direct correlation between the different coordination geometry for the V2 polyhedron in rossite and the differences in bonding between the structural unit and the interstitial unit in the rossite and calciodelrioite structures; however, the 2+2+1 coordination geometry of the V2 polyhedron may be related to the more ‘twisted’ configuration of the $[\text{VO}_3]$ chain in the rossite structure.

The most interesting contrast between the calciodelrioite and rossite structures is seen in the coordination of the Ca atoms and the linkages

between them. In calciodelrioite Ca is 9-coordinate and the CaO_9 polyhedra form a chain in which the polyhedra alternately share edges and faces. In the rossite structure, Ca is 8-coordinate and the CaO_8 polyhedra link to one another by a single shared edge, forming dimers rather than chains. The mean Ca–O bond length is considerably longer in near-endmember ($\text{Ca}_{0.978}\text{Sr}_{0.022}$) calciodelrioite (2.571 Å) than in rossite (2.478 Å). The steady increase in the *b* and *c* parameters with increasing Sr content in the calciodelrioite–delrioite series, indicates that the Ca/Sr–O bond lengths increase as well. It seems reasonable to infer that the differences in size and coordination number of the Ca site in the two structures are in some way related to the geometric configuration of the $[\text{VO}_3]$ chain structural units and how that, in turn, relates to the manner in which they link to the interstitial unit.

Calciodelrioite and rossite are commonly associated and appear to have formed contemporaneously, so differing conditions of formation cannot be the explanation for the dimorphism. The key factor appears to be the difference between the cation sites of the interstitial units in the two structures. The larger 9-coordinate cation site in the calciodelrioite structure is clearly able to better accommodate Sr and, in this regard, it is noteworthy that all of our chemical analyses of calciodelrioite contain some Sr, whereas those of rossite do not. Furthermore, even accounting for the small Sr occupancy in the Ca site in near-endmember calciodelrioite, the bond-valence sum incident at the site is only 1.89 vu, compared to 2.05 vu for the Ca site in the rossite structure; this implies that in calciodelrioite the Ca site is inherently larger than necessary for Ca alone. It, therefore,

TABLE 7. Comparison of unit-cell parameters, optical properties and densities for delrioite, calciodelrioite and rossite.

	Delrioite*	Calciodelrioite	Rossite [§]
Ideal Formula	$\text{Sr}(\text{VO}_3)_2(\text{H}_2\text{O})_4$	$\text{Ca}(\text{VO}_3)_2(\text{H}_2\text{O})_4$	$\text{Ca}(\text{VO}_3)_2(\text{H}_2\text{O})_4$
Crystallography*			
Space group	<i>I</i> 2/a	<i>I</i> 2/a	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.638(5)	14.6389(10)	8.534
<i>b</i> (Å)	7.070(8)	6.9591(4)	8.556
<i>c</i> (Å)	17.155(6)	17.052(2)	7.105
α (°)	90	90	101.53
β (°)	102.37(8)	102.568(9)	114.97
γ (°)	90	90	103.77
<i>V</i> (Å ³)	1734(2)	1695.5(3)	425.3
<i>Z</i>	8	8	2
Optics			
Optical class	Biaxial (–)	Biaxial (+)	Biaxial (–)
α	1.783(3)	1.733(3)	1.710
β	1.834(3)	1.775(3)	1.770
γ	1.866(3)	1.825(3)	1.840
$2V_{\text{meas}}$ (°)	medium to large	87.3(9) ^o	60(15) ^o
Density			
D_{meas} (g cm ^{–3})	3.1(1)	n.d.	2.45
D_{calc} (g cm ^{–3})	2.620	2.451	2.42

* The delrioite unit-cell parameters are based on our single-crystal study of a crystal from the type specimen. The *a* and *c* parameters are reversed in comparison to those reported by Smith (1970). The optical properties and measured density are from Thompson and Sherwood (1959) based on intimate intergrowths with metadelrioite. The calculated density is based upon our cell and EMPA of the type material.

[§] The rossite unit-cell parameters are from Ahmed and Barnes (1963). The optical properties and densities are from Palache *et al.* (1951, pp. 1053–1054).

seems reasonable to conclude that the dimorphism is driven by the presence of Sr. We suggest that in the absence of Sr only rossite is likely to form, if Sr is present at a relatively low abundance both calciodelrioite and rossite are likely to form and if Sr is sufficiently abundant only delrioite is likely to form.

Finally, it is worth noting that the chemical composition of the inadequately described and questionable mineral 'pintadoite', $\text{Ca}_2\text{V}_2\text{O}_7 \cdot 9\text{H}_2\text{O}$ (Hess and Schaller, 1914), is similar to those of calciodelrioite and rossite; however, as noted by Thompson and Sherwood (1959), "available specimens of pintadoite seem to be nothing more than faintly stained sandstone so that it has not been possible to compare the two minerals directly." As the reported chemical analysis of pintadoite includes no Sr, if pintadoite does correspond to either of these species, it is more likely that it is equivalent to rossite than to calciodelrioite.

A comparison of unit-cell parameters, optical properties and densities of delrioite, calciodelrioite and rossite is provided in Table 7.

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References

- Ahmed, F.R. and Barnes, W.H. (1963) The crystal structure of rossite. *The Canadian Mineralogist*, **7**, 713–726.
- Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters from a systematic analysis of the inorganic crystal structure database. *Acta Crystallographica*, **B41**, 244–247.
- Carter, W.D. and Gualtieri, J.L. (1965) *Geology and uranium-vanadium deposits of the La Sal quadrangle, San Juan County, Utah, and Montrose County, Colorado*. US Geological Survey Professional Paper, **508**. US Geological Survey, Reston, Virginia, USA, 82 pp.
- Evans, H.T. and Garrels, R.M. (1958) Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits. *Geochimica et Cosmochimica Acta*, **15**, 131–149.
- Friedel, C. and Cumenge, E. (1899) Sur un nouveau minéral d'urane, la carnotite. *Comptes rendus de l'Académie des sciences*, **128**, 532–534.
- Gunter, M.E., Bandli, B.R., Bloss, F.D., Evans, S.H., Su, S.C. and Weaver, R. (2004) Results from a McCrone spindle stage short course, a new version of EXCALIBUR, and how to build a spindle stage. *The Microscope*, **52**, 23–39.
- Hawthorne, F.C. (1983) Graphical enumeration of polyhedral clusters. *Acta Crystallographica*, **A39**, 724–736.
- Hess, F.L. and Schaller, W.T. (1914) Pintadoite and uvanite, two new vanadium minerals from Utah: a preliminary note. *Journal of the Washington Academy of Science*, **4**, 576–579.
- Hostetler, P.B. and Garrels, R.M. (1962) Transportation and precipitation of uranium and vanadium at low temperatures, with special reference to sandstone-type uranium deposits. *Economic Geology*, **57**, 137–167.
- Mandarino, J.A. (1981) The Gladstone–Dale relationship: part IV. The compatibility concept and its application. *The Canadian Mineralogist*, **19**, 441–450.
- Palache, C., Berman, H. and Frondel, C. (1951) *Dana's System of Mineralogy*, 7th edition, volume II. John Wiley and Sons, New York.
- Pouchou, J.-L. and Pichoir, F. (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model 'PAP'. Pp. 31–75 in: *Electron Probe Quantitation* (K.F.J. Heinrich and D.E. Newbury, editors). Plenum Press, New York.
- Schindler, M., Hawthorne, F.C. and Baur, W.H. (2000a) A crystal-chemical approach to the composition and occurrence of vanadium minerals. *The Canadian Mineralogist*, **38**, 1443–1456.
- Schindler, M., Hawthorne, F.C. and Baur, W.H. (2000b) Crystal-chemical aspects of vanadium: polyhedral geometries, characteristic bond valences, and polymerization of (VO_n) polyhedra. *Chemistry of Materials*, **12**, 1248–1259.
- Shawe, D.R. (2011) *Uranium-vanadium deposits of the Slick Rock district, Colorado*. US Geological Survey Professional Paper, **576-F**. US Geological Survey, Reston, Virginia, USA, 80 pp.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.
- Smith, M.L. (1970) Delrioite and metadelrioite from Montrose County, Colorado. *American Mineralogist*, **55**, 185–200.
- Thompson, M.E. and Sherwood, A.M. (1959) Delrioite, a new calcium strontium vanadate from Colorado. *American Mineralogist*, **44**, 261–264.