Dollaseite-(Ce) (magnesium orthite redefined): Structure refinement and implications for $F + M^{2+}$ substitutions in epidote-group minerals

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ABSTRACT

The crystal structure of dollaseite-(Ce) $[a = 8.934(18), b = 5.721(7), c = 10.176(22) \text{ Å}, \beta = 114.31(12)^{\circ}$, space group $P2_1/m]$ has been refined, giving rise to the ideal formula CaREE³⁺Mg₂AlSi₃O₁₁(OH)F with Z = 2. Formerly known as "magnesium orthite," it has been renamed dollaseite-(Ce) in honor of Dr. Wayne Dollase of UCLA. Dollaseite-(Ce) represents the probable limit of substitution of octahedrally coordinated M²⁺ cations in members of the epidote group. Mg is ordered over two equipoints, Ca and the REEs are each ordered over two different sites, and F and OH are each ordered over two different sites. The heretofore unrecognized substitution of Mg + F in dollaseite-(Ce) for M³⁺ + O of allanite suggests that such substitutions may occur commonly in other members of the epidote group.

INTRODUCTION

The mineral described herein was first reported by Geijer (1927) from the Ostanmossa mine, Norberg district, Sweden. It was named "magnesium orthite" by him on the basis of an apparent relation to orthite, the new phase having Mg dominant, whereas orthite has Fe dominant. The orthite vs. allanite nomenclatural ambiguity was decided by the Commission on New Minerals and Mineral Names, IMA, in favor of allanite, in 1986. However, as we show below, this phase is not the Mg analogue of allanite. Its formula may be written CaREEMg₂Al-Allanite has the formula Ca- $Si_3O_{+1}F(OH)$. REEFe²⁺(Al,Fe³⁺)₂Si₃O₁₁O(OH). It can be derived from the formula of clinozoisite by the coupled substitution REE + Fe^{2+} = Ca + Al, where REE or Ca occupy site A(2) and Al or Fe^{2+} occupy M(3). This new mineral has two paired substitutions relative to clinozoisite: REE + Mg = Ca + Al, and Mg + F = Al + O. Because it is not directly analogous to allanite, it should not have a name that implies that it is the Mg equivalent of Fe2+-containing allanite, as was inherent in the original appelation, "magnesium orthite." We therefore proposed the alternative name dollaseite-(Ce), in honor of Professor Wayne Dollase of UCLA, who has carried out the definitive research on the crystal chemistry of the epidote group. This redefinition and the revised name were approved by the Commission on New Minerals and Mineral Names, IMA, prior to publication. Geijer did not designate a type specimen (pers. comm.: Bengt Lindqvist). Accordingly, we have designated a neotype, (NMNH no. R6505), which is on deposit at the Smithsonian Institution.

DESCRIPTION

Dollaseite-(Ce) occurs as massive brown material, intimately associated with tremolite, norbergite, and calcite. Additional accessory phases, found by utilizing backscattered-electron and energy-dispersive X-ray analysis on a scanning electron microscope, include a Ca-REE mineral [bastnäsite-(Ce)?] and a Ca-Sr-REE-silicate [cerite-(Ce)?]. At the contact with calcite, dollaseite-(Ce) forms subhedral 0.3-mm-diameter crystals, which were utilized for single-crystal X-ray diffraction studies. Calculation of the Gladstone-Dale relationship for dollaseite-(Ce), using the chemical data presented herein, and the density (3.9 g/cm³) and indices of refraction ($\alpha = 1.715$, $\beta = 1.718$, and $\gamma = 1.733$) of Geijer (1927), yields a compatibility index in the "superior" category (Mandarino, 1981).

CHEMICAL COMPOSITION

Dollaseite-(Ce) was analyzed using electron-microprobe procedures. Operating conditions included operating voltage of 15 kV, sample current of $0.025 \ \mu$ A, measured on brass, 10-s counting times, and data correction employing a modified version of the MAGIC-4 program. The standards used were hornblende (Si, Al, Fe, Mg), wollastonite (Ca), fluorite (F), and the Drake REE glasses for REE elements. A wavelength-dispersive microprobe scan showed no detectable elements with atomic number greater than 8, except those reported here.

The resultant analysis yielded SiO_2 32.4, Al_2O_3 8.9, FeO 3.3, MgO 13.1, CaO 9.2, La_2O_3 6.0, Ce_2O_3 13.2, Pr_2O_3

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2.6, Nd₂O₃ 6.0, Sm₂O₃ 2.4, Gd₂O₃ 2.1, F 3.0, H₂O (from Geijer, 1927) 2.02, less $O \equiv F 1.3$, sum = 102.9 wt%. Calculated on the basis of 3 Si, this analysis yields the empirical formula $(Ca_{0.91} Ce_{0.45} La_{0.20} Nd_{0.20} Pr_{0.09} Sm_{0.08}-Gd_{0.06})_{21.99}(Mg_{1.81}Fe_{0.25})_{22.07}Al_{0.97}Si_{3,00}(OH)_{1.25}F_{0.88}O_{10.99}$. Ideally, this is Ca(REE)Mg₂AlSi₃O₁₁(OH)F. Adopting the Levinson rules for naming of REE minerals (Levinson, 1966), the name is suffixed to reflect the dominant REE: dollaseite-(Ce).

X-RAY CRYSTALLOGRAPHY

Weissenberg and precession photographs show that dollaseite-(Ce) has space group $P2_1/m$ or $P2_1$. By analogy with members of the epidote family, $P2_1/m$ was assumed to be the correct space group, and this assumption was borne out by the results of the structure refinement described below. Lattice parameters were refined by leastsquares, utilizing data from a powder photograph. Refined parameters are a = 8.934(18), b = 5.721(7), c = 10.176(22)Å, $\beta = 114.31(12)^\circ$. The powder diffraction data are listed in Table 1. They were obtained with a 114.6-mm-diameter Gandolfi camera, Cu $K\alpha$, Ni-filtered radiation, and Si as an internal standard.

STRUCTURE REFINEMENT

The crystal structure of epidote (Dollase, 1971; Carbonin and Molin, 1980) and that of the isostructural minerals clinozoisite (Dollase, 1968) and piemontite (Dollase, 1969) contain two large sites, A(1) and A(2), which are usually occupied by Ca, three tetrahedral sites occupied only by Si, and three octahedrally coordinated sites M(1), M(2) and M(3), principally occupied by cations of charge +3 such as Al, Fe³⁺, or Mn³⁺. This gives rise to the formula Ca₂M₃³⁺Si₃O₁₁O(OH). In hancockite (Dollase, 1971; Dunn, 1985), Pb and Sr substitute in A(2). Allanite has REE³⁺ ordered in A(2), with charge balance maintained by substitution of Fe²⁺ for M³⁺, principally in site M(3) (Dollase, 1971).

The analytical data for dollaseite-(Ce) lead to the apparent formula CaREE³⁺Mg₂AlSi₃O₁₁(OH)F, with two cations of charge +2 and Al occupying the three octahedrally coordinated sites; the resulting charge imbalance is made up by substitution of REE^{3+} for Ca as in allanite. and by substitution of OH or F for the O atom not coordinated to Si. Because the amounts of Ca, REEs, Al, (Mg + Fe) and F pfu are near the integer values required for ordering in the available equipoints, ordered substitution was implied, but not proven. We therefore carried out a refinement of the structure in order to determine the cation and anion distributions, which involve the substitution of F (which is generally not recognized in epidotegroup minerals) and the substitution of Mg + (OH,F) for M^{3+} + O, which also has not been considered. Because these substitutions may also occur in ordinary rock-forming members of the epidote group, this refinement was undertaken, in part, to assess the implications of the substitutions in such phases.

Intensity data were measured using a subhedral crystal

TABLE 1. Powder-diffraction data for dollaseite-(Ce)

I/ I ₀ *	$d_{\rm obs}$	d_{calc}^{\dagger}	hkl	// / ₀ *	$d_{\rm obs}$
20	9.29	9.27	001‡	5	1.887
10	8.25	8.14	100‡	2	1.756
10	5.13	5.16	101‡	1	1.730
5	4.87	4.87	011‡	2	1.702
10	4.65	4.68	110	5	1.659
		4.64	111	10	1.601
		4.64	002‡	5	1.567
5	3.77	3.77	112	1	1.483
20	3.52	3.52	211‡	2	1.465
15	3.26	3.27	201	5	1.430
		3.27	212	2	1.418
100	2.915	2.916	113‡	2	1.404
		2,925	302	2	1.386
30	2.852	2.861	020‡	5	1.302
		2.836	211	1	1.283
70	2.709	2,714	300	2	1.229
		2.699	120‡	2	1.200
	2.624	2.624	311±	2	1.164
5	2.576	2.578	202±	2	1.130
2	2.503	2.507	204		
		2.501	121		
2	2.403	2.409	221		
		2,405	313‡		
2	2.323	2.322	222±		
		2.318	004		
10	2.185	2.186	123		
		2,185	401		
		2,179	311		
20	2,150	2.156	403		
0.000		2,152	221±		
		2,149	014		
5	2,124	2,125	314		
		2,124	223±		
2	2.089	2.100	023		
-		2.083	203		
		2.080	412		
1	2.046	2.055	321		
		2.045	322±		
		2.042	411		
		2.036	400		
		2.000			

* Intensities visually estimated utilizing a Gandolfi photograph obtained with 114.6-mm-diameter camera, $CuK\alpha$ radiation, and Si as an internal standard.

† *d* values calculated with unit-cell parameters a = 8.934, b = 5.721, c = 10.176 Å, β = 114.31°.

‡ Reflections used in least-squares refinement of lattice parameters. Where two or more d_{cate} match a d_{obs}, indices were chosen on the basis of intensities observed by single-crystal diffraction.

with dimensions $0.20 \times 0.24 \times 0.06$ mm, an automated Supper Weissenberg-geometry diffractometer system and graphite-monochromated MoK α radiation. The intensities of 1367 reflections in a single asymmetric unit were measured for which $\sin \theta \ge 0.5$, utilizing two background counts of 25 s and scan rates of 2° or 4°/min. Intensities were corrected for Lorentz-polarization and absorption (Burnham, 1962) ($\mu_1 = 71.0 \text{ cm}^{-1}$; $T_{\text{max}} = 0.64$; $T_{\text{min}} =$ 0.26). The final data set contained 60 reflections for which $|F|_{\text{obs}} < 3\sigma(|F|_{\text{obs}})$. Refinement was carried out with the program SHELX-76 (Sheldrick, 1976) using neutral-atom scattering factors and anomalous scattering coefficients (*International Tables for X-ray Crystallography*, 1974). Weights were computed as the reciprocal variances of values of $|F|_{\text{obs}}$.

The refinement converged rapidly, starting with coordinates for epidote (Carbonin and Molin, 1980) and in-

TABLE 2. Atom coordinates and site occupancies for dollaseite-(Ce)

TABLE 5. Selected interatomic distances (A)	for	dollaseite-(Ce)	
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Atom	×	У	z	Refined occupancy
A(1)	0.7627(2)	3/4	0.1480(1)	0.943(3)Ca + 0.057Ce
A(2)	0.5932(1)	3/4	0.4261(1)	0.020(6)Ca + 0.980Ce
Si(1)	0.3439(2)	3/4	0.0427(2)	
Si(2)	0.6912(2)	1/4	0.2784(2)	
Si(3)	0.1877(2)	3/4	0.3220(2)	
M(1)	0	0	0	1.005(1)Mg - 0.005Fe
M(2)	0	0	1/2	0.985(7)AI + 0.015Fe
M(3)	0.3155(2)	1/4	0.2127(2)	0.872(8)Mg + 0.128Fe
O(1)	0.2450(4)	0.9917(5)	0.0369(3)	
O(2)	0.3120(4)	0.9743(5)	0.3615(3)	
O(3)	0.8020(4)	0.0153(5)	0.3336(3)	
O(4)	0.0607(5)	1/4	0.1457(4)	0.87(9)F + 0.13O
O(5)	0.0455(5)	3/4	0.1564(5)	
O(6)	0.0768(6)	3/4	0.4172(5)	
O(7)	0.5174(5)	3/4	0.1806(5)	
O(8)	0.5474(6)	1/4	0.3324(5)	
O(9)	0.6154(6)	1/4	0.1008(5)	
O(10)	0.0917(6)	1/4	0.4342(5)	
н`́	0.068(10)	1/4	0.333(10)	

2.334(3) 2.348(6) 2.371(3) 2.493(7)	A(2)–O(7) -2O(2) -O(10) -2O(2')	2.204(7) 2.524(3) 2.579(7) 2.652(3)
2.375 1.607(5) 1.629(4)	-20(3) -20(8) Avg.*	2.849(5) 2.990(4) 2.523
1.644(7) 1.627	M(1)–2O(4) –2O(5) –2O(1)	1.969(4) 2.052(5) 2.063(4)
1.592(7) 1.625(4) 1.648(6) 1.623	Avg. M(2)–2O(3) –2O(10)	2.028 1.881(5) 1.902(5)
1.635(4) 1.640(6)	–20(6) Avg.	1.924(5) 1.902
1.646(7) 1.639	M(3)–O(8) O(4) -2O(2)	1.952(7) 2.056(7) 2.185(4)
0.96(10) 1.88(10) 2.833(9)	-20(1) Avg.	2.205(5) 2.131
	2.334(3) 2.348(6) 2.371(3) 2.493(7) 2.375 1.607(5) 1.629(4) 1.644(7) 1.627 1.592(7) 1.625(4) 1.648(6) 1.623 1.635(4) 1.648(6) 1.646(7) 1.639 0.96(10) 1.88(10) 2.833(9)	$\begin{array}{ccccc} 2.334(3) & A(2)-O(7) \\ 2.348(6) & -2O(2) \\ 2.371(3) & -O(10) \\ 2.493(7) & -2O(2') \\ 2.375 & -2O(3) \\ 1.607(5) & Avg.^* \\ 1.629(4) & Avg.^* \\ 1.644(7) & M(1)-2O(4) \\ 1.627 & -2O(5) \\ 1.592(7) & Avg. \\ 1.648(6) & M(2)-2O(3) \\ 1.623 & -2O(1) \\ 1.623 & -2O(10) \\ 1.635(4) & Avg. \\ 1.648(6) & M(2)-2O(3) \\ 1.639 & -2O(6) \\ 1.640(6) & Avg. \\ 1.646(7) & M(3)-O(8) \\ 1.639 & -O(4) \\ 0.96(10) & -2O(2) \\ 1.88(10) & Avg. \\ 2.833(9) & Avg. \\ \end{array}$

cluding refinement of site-occupancy factors modeled with form factors for Ce^{3+} and Ca applied both to A(1) and A(2), with Fe and Mg both applied to the three sites M(1), M(2), and M(3). Ce was used as representative of REE, as Ce is dominant in this mineral, and its form factor serves as a reasonable average of those of the remaining REEs. The form factor for Mg was used in part because it also served as a good approximation to the form factor for Al. Following refinement to $R \simeq 6\%$ with isotropic temperature factors, calculation of interatomic distances showed that the mean M(2)-O distance (1.90 Å) was considerably smaller than mean values for M(1)-O or M(3)-O (see Table 5 for final distances). In addition, calculation of empirical bond valences with Al ordered in M(2) (Table 6) gave more reasonable values than for Al in M(1) or M(3). M(2) was therefore assumed to be occupied prin-

TABLE 3. Anisotropic temperature factors for dollaseite-(Ce)

cipally by Al, with minor Fe³⁺, and form factors were accordingly applied and refined.

Form factors for the two anions not coordinated to Si, O(4) and O(10), had initially been set to that for oxygen. However, the anisotropic temperature factors for O(4) refined to a non-positive-definite value, implying that the site is occupied by an atom of greater electron density. Calculation of an electron-density synthesis showed a peak in the approximate position inferred by Dollase (1968) to correspond to a H atom bonded to O(10). As bond-valence sums (Table 6) implied that these anions [O(4) and O(10)] have a charge of -1 and because charge balance for the formula requires two such anions, they were assumed to be (OH, F). Because the H–O(10) bond distance corresponded to a hydrogen bond, O(4) was assumed to be occupied by F and O(10) by OH. Subsequent refinement

	<i>U</i> ₁₁	U ₂₂	U ₃₃	U ₂₃	<i>U</i> ₁₃	U ₁₂
A(1)	0.0142(6)	0.0100(6)	0.0110(6)	0	0.0086(5)	0
A(2)	0.0072(2)	0.0134(2)	0.0073(2)	0	0.0018(1)	0
Si(1)	0.0058(9)	0.0083(8)	0.0069(9)	0	0.0019(7)	0
Si(2)	0.0069(9)	0.0087(8)	0.0079(9)	0	0.0036(7)	0
Si(3)	0.0064(9)	0.0072(8)	0.0067(9)	O	0.0034(7)	0
M(1)	0.0044(10)	0.0049(10)	0.0063(10)	-0.0004(8)	0.0024(8)	-0.0005(8)
M(2)	0.0057(9)	0.0077(9)	0.0069(9)	0.0001(7)	0.0022(7)	0.0005(7)
M(3)	0.0045(9)	0.0074(8)	0.0057(9)	0	-0.0009(7)	0
O(1)	0.0082(16)	0.0084(15)	0.0087(16)	0.0010(12)	0.0022(13)	0.0011(13)
0(2)	0.0104(16)	0.0104(16)	0.0078(16)	-0.0012(12)	0.0028(13)	-0.0016(13)
O(3)	0.0109(17)	0.0079(16)	0.0108(17)	-0.0008(12)	0.0004(13)	0.0008(13)
O(4)	0.0084(20)	0.0111(19)	0.0074(19)	0	0.0023(16)	0
O(5)	0.0061(23)	0.0122(22)	0.0044(21)	0	0.0004(18)	0
0(6)	0.0106(25)	0.0099(21)	0.0141(23)	0	0.0080(20)	0
0(7)	0.0053(23)	0.0152(23)	0.0088(23)	0	-0.0006(19)	0
O(8)	0.0050(24)	0.0306(29)	0.0147(26)	0	0.0038(20)	0
O(9)	0.0098(25)	0.0267(27)	0.0050(23)	0	0.0025(20)	0
O(10)	0.0069(22)	0.0123(21)	0.0085(22)	0	0.0040(18)	0
Н	0.02					

Note: Temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}hla^*c^*\cos\beta^* + 2U_{23}klb^*c^*\cos\alpha^*).$ † Isotropic temperature factor, U, unrefined.

TABLE 6. Empirical bond-valence sums (v.u.) for dollaseite-(CE)

of the H-atom position with a fixed isotropic temperature factor was successful. Refinement of the occupancy factor for O(4), with O and F form factors, is consistent with an occupancy of 1.74 F, whereas the chemical analysis shows 1.76 F per unit cell. The ordered distribution of F in O(4) and OH in O(10) was therefore considered to be verified. The *R* factor converged to a value of 3.2% (unweighted) and 2.5% (weighted) with full-matrix refinement of form factors, coordinates, and anisotropic temperature factors. Coordinates and occupancy factors are listed in Table 2, temperature factors in Table 3, structure factors in Table 4¹ and selected interatomic distances in Table 5. Empirical bond valence sums (Table 6) were calculated according to the method of Brown (1981).

DISCUSSION

The crystal structure displays only minor shifts from atomic positions of the isostructural phases epidote (Ito, 1950; Belov and Rumanova, 1953; Belov, 1954; Ito et al., 1954; Dollase, 1971; Carbonin and Molin, 1980), piemontite (Dollase, 1969), and allanite and hancockite (Dollase, 1971). The detailed pattern of adjustments in positions and bond lengths are compatible with the changes in bond valences due to substitutions of atoms of different charge (e.g., Mg for Al) and radius and so will not be described in detail.

The substitution of REEs into A(2) duplicates the equivalent substitution of REEs in allanite. Although the siteoccupancy values indicate some minor mutual substitution of Ca and REEs on A(1) and A(2), ordering is nearly complete. Dollase (1971) pointed out that REE substitution occurs in A(2) rather than A(1) because that site has the larger radius in epidote-type structures that contain only Ca. Another, perhaps more significant reason, is that A(2) and M(3) are linked through O(8) and particularly O(2), as shown in Table 6. As Fe²⁺ substitutes in M(3) of allanite and that substitution is balanced by that of REE³⁺ for Ca, substitution of REEs in A(2) provides a more satisfactory local charge balance for O(2) and O(8).

The M(1), M(2), and M(3) distances (Table 5) are compatible with nearly complete ordering of Mg in M(1), Al in M(2) and Mg + Fe²⁺ in M(3). The site occupancies (Table 2) likewise are compatible with a lack of Fe in M(1), a trace of Fe in M(2) and Mg plus substantial Fe in M(3). Taken in sum, these data are consistent with complete order of Mg in M(1), Al (and, presumably Fe³⁺) in M(2) and Mg + Fe²⁺ in M(3). As noted above, this distribution also gives rise to the most satisfactory local charge balance (Table 6). It is also in agreement with the preferred distribution of Al in M(2), other cations in M(1) and M(2), and Fe²⁺ in M(3) as found by Dollase for other members of the epidote group.

O(4) is coordinated only to 2M(1) and M(3). Therefore, even in structures where all octahedrally coordinated cat-

					Sum
O(1)	Si(1) 1.01	M(1) 0.35	M(3) 0.26	A(1) 0.32	1.94
O(2)	Si(3) 0.99	M(3) 0.27	A(2) 0.26	A(2) 0.36	1.88
O(3)	Si(2) 1.01	M(2) 0.53	A(1) 0.35	A(2) 0.16	2.05
O(4)	2M(1) 2(0.46)	M(3) 0.36			1.28
O(5)	Si(3) 0.97	2M(1) 2(0.37)	A(1) 0.23		1.94
O(6)	Si(3) 0.95	2M(2) 2(0.47)	A(1) 0.09		1.98
O(7)	Si(1) 1.03	A(1) 0.33	A(2) 0.65		2.01
O(8)	Si(2) 1,08	M(3) 0.48	2A(2) 2(0.12)		1.80
O(9)	Si(1) 0.95	Si(2) 0.95	2A(1) 2(0.07)		2.04
O(10)	2M(2) 2(0.51)	A(2) 0,30			1.32

ions are trivalent, it is severely undersaturated. In allanite, where considerable Fe^{2+} occurs in M(3) as a charge balance for REE³⁺ occupancy of A(2), an even more severe charge imbalance occurs. Any additional substitution of M²⁺ for M³⁺ in M(1) must therefore be coupled by OH or F substitution for O on this site. The substitution of Mg in M(1) and M(3) results in charge deficiencies for other oxygen atoms bonded to the atoms M(1) and M(3) [O(1), O(2), O(5), and O(8), as shown in Table 6], but these are small and adjustments are apparently readily made.

The anion O(4) plays a crucial role in the above substitution pattern. In allanite, it is so severely undersaturated that the possibility that some F or OH substitutes for it in combination with Mg + Fe²⁺ on M(1) should be considered. Indeed, the substitution relations in dollaseite-(Ce) imply that there may be a coupled substitution of (F,OH) + Mg²⁺ for O(4) + Al³⁺_{M(1)}. In any event, these relations imply that F should be routinely sought in analyses of members of the epidote group. When found, its presence would be particularly significant in estimating the Fe²⁺:Fe³⁺ ratio when Fe is present on the M sites and when, as with electron-microprobe analyses, valences are not directly determinable.

Lastly, it is of interest that the species F and OH are ordered on sites O(4) and O(10), respectively. The location of the H atom (occupying approximately the same position between the O(4) and O(10) sites as it does in epidote and clinozoisite) indicate a hydrogen bond of the type O- $H \cdots F$. The existence of F-H-O bonds such as occur here has been cited by Cotton and Wilkinson (1980). The bond distances [H-O(10) = 0.96 Å, H-O(4) = 1.88 Å] are typical of such hydrogen-bonding geometry when oxygen is involved.

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¹ A copy of Table 4 may be ordered as Document AM-88-381 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

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