# CRYSTAL STRUCTURE AND CATION ORDERING OF PIEMONTITE

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ABSTRACT

The crystal structure of the Mn^{3+}-bearing epidote, piemontite, has been refined. For a crystal of composition, $Cz_{65}Pm_{24}Ps_{11}$, refinement of the occupancies cf the two large, nominally calcium sites and the three non-equivalent octahedral sites, gives:

$$(Ca_{1.00})(Ca_{0.87}Sr_{0.13})(Al_{0.80}M_{0.20})(Al_{1.00})(Al_{0.17}M_{0.83})Si_3O_{12}OH,$$
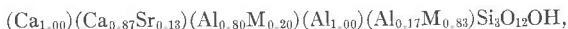
where $M = Mn_{0.7}Fe_{0.3}$. All of the (Mn, Fe) substitution for Al occurs in one of the two non-equivalent chains of edge-sharing octahedra. In the substituted chain, which is topologically identical with that found in the olivine structure, the larger $M(3)$ site (symmetry-m) lying on the edge of the chain, contains most of the (Mn,Fe) with lesser amounts in the smaller $M(1)$ site (symmetry-$\bar{1}$) which forms the core of the chain.

INTRODUCTION

The common, rock-forming epidote group minerals $Ca_2M_3Si_3O_{12}OH$, are members of a ternary system with M consisting of the trivalent, octahedral cations, Al,Fe^{3+},Mn^{3+}. The respective ideal end member compositions are commonly given mnemonics Cz, Ps, and Pm (see *e.g.* Strens, 1964). The isostructural allanites are related to the group by substitution of lanthanides for calcium and concomitant replacement of an octahedral trivalent cation by a divalent cation.

Although several members of the epidote group have been studied[1] by single-crystal X-ray diffraction methods, little attention was paid to cation ordering except for the general supposition that only one of the three octahedral sites accepted the Fe^{3+},Mn^{3+} ions substituting for Al. This assignment, apparently initially made on bond length and/or electron density map criteria (Ito, 1950), puts the Fe^{3+} and Mn^{3+} ions in the $M(3)$ site and places a compositional limit on the group although members with $(Fe+Mn)/(Al+Fe+Mn)$ well above on-third are known (Strens, 1966).

Recently, other methods have been applied to the question of cation distribution in this mineral group including measurements of indices of refraction by Strens (1964), optical absorption spectra by Burns and Strens (1967), and Mössbauer effect by Bancroft *et al.*, (1967). In these investigations a number of high-iron epidotes and piemontites, for which microprobe analyses were available, were examined and all three studies have suggested octahedral ordering, with Fe and Mn substituting mainly

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[1] See Dollase (1968) for listing of previous epidote-group structural studies.

into the M(3) site. In addition, the first two studies have suggested significant occupation by Fe and/or Mn in the other two octahedral sites for appropriate bulk compositions.

As part of a structural study of the epidote group, a crystal structure analysis of piemontite was undertaken and the results are presented here. The geometric structural details will be compared to those of other monoclinic epidotes elsewhere.

Material and Refinement

Piemontite from St. Marcel, Italy, was obtained from the University of California collection at Berkeley (UC 13612). A microprobe analysis for Mn and Fe by Dr. B. W. Evans, on material from the same specimen has been published (Strens, 1966). The reported composition is $Cz_{65}Pm_{24}Ps_{11}$. An earlier analysis of material from the same locality (Malmqvist, 1929) leads to the formula:

$$(Ca_{1.78}Mn^{2+}_{0.13}Na_{0.10}K_{0.03})(Al_{1.73}Mn^{3+}_{0.76}Fe^{3+}_{0.51})Si_3O_{12.45}(OH)_{0.08}$$
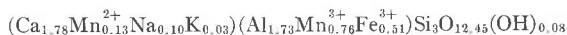
(analyst: J. Jakob), which corresponds to $Cz_{58}Pm_{25}Ps_{17}$.

Cell dimensions, measured from precession photographs are: $a = 8.878 \pm 0.010$ $b = 5.692 \pm 0.005$, $c = 10.201 \pm 0.010$ Å and $\beta = 115.40 \pm 0.2°$. The a and b dimensions of St. Marcel piemontite are given by Strens (1966) and agree within one standard deviation.

The experimental methods employed in the data collection and refinement are the same as those used in a study of clinozoisite (Dollase, 1968), where more details are given. From a nearly equidimensional crystal of about 0.15 mm diameter, a total of 865 independent, nonzero, reflections were measured on a single crystal diffractometer. Molybdenum radiation was used and the data are essentially complete up to sin $°\theta/\lambda = 0.7$ Å^{-1}. The variation of transmission factors over this range, for the crystal employed, was considered negligible and no absorption correction was made.

The least-squares refinement of the data started with the epidote parameters of Ito *et al.* (1954). Unit weighting was used consistent with the observation that the absolute agreement of observed and calculated structure factors was independent of the magnitude of the structure factor. Only the heaviest atoms, or those most likely to vibrate anisotropically, were refined with anisotropic temperature factors in order to conserve a high ratio of observations to variables.

The greatest anomaly in the difference map, computed before the last stage of refinement, was taken as the hydrogen atom although the very large standard errors of its parameters, furnished in the subsequent refinement, indicate that this location must be considered tentative. The final refined positional and thermal parameters are given in Table 1. The anisotropic temperature factors are in the form exp-$(h_2\beta_{11} + \cdots 2hk\beta_{12} + \cdots)$. The final R-factor for all reflections is 3.5 percent.

Site Occupancy Calculations

The multipliers of the scattering curves of the three octahedral and two nominally calcium sites were refined as least-squares variables. The multipliers and thermal parameters are sufficiently independent to allow refinement of both as the maximum correlation coefficient of these parameters is 0.51 for atoms with anisotropic temperature factors and 0.78 for isotropic cases. The results are listed and interpreted in Table 2.

TABLE 1. PIEMONTITE POSITIONAL AND THERMAL PARAMETERS
Standard errors, in parentheses, refer to last digit

Atom	x	y	z	$B(Å^2)$
Ca (1)	0.7574 (2)	0.75	0.1533 (2)	0.77[a]
Ca (2)	.5979 (2)	.75	.4250 (1)	.81[a]
Si (1)	.3410 (2)	.75	.0448 (2)	.52 (3)
Si (2)	.6846 (2)	.25	.2745 (2)	.51 (3)
Si (3)	.1855 (2)	.75	.3197 (2)	.35 (3)
M (1)	0	0	0	.47 (5)
M (2)	0	0	.5	.56 (3)
M (3)	.2957 (1)	.25	.2216 (1)	.39[a]
O (1)	.2330 (4)	.9912 (7)	.0356 (3)	.81 (6)
O (2)	.3058 (4)	.9795 (7)	.3550 (3)	.80 (6)
O (3)	.7963 (4)	.0163 (7)	.3378 (3)	.81 (5)
O (4)	.0588 (6)	.25	.1318 (5)	.59 (8)
O (5)	.0424 (6)	.75	.1473 (5)	.70 (8)
O (6)	.0686 (6)	.75	.4091 (5)	.62 (8)
O (7)	.5145 (6)	.75	.1805 (5)	.80 (8)
O (8)	.5276 (6)	.25	.3140 (5)	.92 (9)
O (9)	.6208 (7)	.25	.0986 (6)	.99[a]
O (10)	.0868 (6)	.25	.4330 (6)	.60 (8)
H	.04 (1)	.25	.36 (1)	0 (2)

Anisotropic Temperature Factors

	$\beta 11$	$\beta 22$	$\beta 33$	$\beta 12$	$\beta 13$	$\beta 23$
Ca (1)	0.0044 (2)	0.0065 (5)	0.0025 (2)	0	0.0025 (2)	0
Ca (2)	.0029 (2)	.0104 (6)	.0014 (2)	0	.0005 (1)	0
M (3)	.0009 (2)	.0036 (4)	.0014 (1)	0	.0004 (1)	0
O (9)	.0057 (8)	.015 (2)	.0023 (6)	0	.0030 (6)	0

[a] Equivalent isotropic temperature factors.

The interpretation assumes that the site is fully occupied by "two" atomic species whose combined scattering curve is equivalent to the product of the multiplier and the scattering curve actually employed in the refinement. The very small difference in scattering power of the manganese and iron atoms necessitates considering them together in the ratio determined from the proble analyses. The standard errors of the subscripts given in the "indicated occupancy" column of Table 2 are estimated as 0.02. This value includes the random error in the least-squares estimate of the occupancy factor, the effect of possible differential ordering of the Mn and Fe atoms between the sites and the difference in shape of the assumed scattering curve times the occupancy factor and the ac-

TABLE 2. SITE POPULATIONS IN PIEMONTITE

Site notation			Scattering curve, Z_0	Multiplier, s	Indicated occupancy,[a] $Z_{a(x)} Z_{b(1-x)}$
This paper	Ito *et al.* 1954	Burns and Strens 1967			
M (1)	Al (1)	AlO	Al	$1.189 \pm .012$	$Al_{0.80}M^*_{0.20}$
M (2)	Al (2)	AlOH	Al	$0.985 \pm .013$	$Al_{1.00}$
M (3)	Al(Fe)	Al	M*	$0.920 \pm .007$	$Al_{0.17}M^*_{0.83}$
Ca (1)	Ca (1)	—	Ca	$0.974 \pm .010$	$Ca_{1.00}$
Ca (2)	Ca (2)	—	Ca	$1.113 \pm .009$	$Ca_{0.87}Sr_{0.13}$

$M^* = Mn_{0.7}Fe_{0.3}$.

[a] Assuming $s Z_0 = xZ_a + (1-x) Z_b$.

tual scattering curve. If, in addition, the Mn/Fe ratio is far different from that given by the probe analysis, the M(3) proportions would be slightly affected.

DISCUSSION OF THE STRUCTURE REFINEMENT

Peimontite is isostructural with epidote (Ito *et al.*, 1954). This structure type has been further discussed and illustrated for the case of clinozoisite (Dollase, 1968) and only the difference, relative to the Al end member, will be emphasized here. The pertinent interatomic distances and angles are listed in Table 3.

The octahedral M-O bond length differences between piemontite and clinozoisite roughly reflect the cation substitution and ordering. For clinozoisite the mean M-O distances, in their sequential order, are 1.906, 1.878, and 1.978 Å, compared to mean values of 1.933, 1.891, and 2.062 Å in piemontite. Note that the main substitution of the larger Mn^{3+} and Fe^{3+} ions is into a site that is already significantly larger than the other sites in the unsubstituted end member.

The degree of distortion of the octahedra is of interest in relation to the ordering. For comparison purposes the degree of distortion of a specific octahedron is defined as the rms-deviation of its fifteen bond angles from their ideal octahedral values. In clinozoisite these distortion indices are 3.8, 2.5, and 7.9° for the three octahedra, while in piemontite they are 3.8, 4.1, and 9.2°. The extreme distortion of the M(3) octahedron in piemontite is probably due in part to the Jahn-Teller effect which is characteristic of the Mn^{3+} ion.

Two of the edges of the M(3) octahedron are shared with the M(1) octahedron and although these edges expand with substitution from

TABLE 3. PIEMONTITE INTERATOMIC DISTANCE AND ANGLES

Multiplicity	Bond	Length	σ	Bond	Angle ($\sigma = 0.4°$)
2	Ca(1)-O(1)	2.456 ± 0.005 Å		O(1)-Si(1)-O(1)'	112.2°
2	-O(3)	2.324	.005	O(1)-Si(1)-O(7)	112.1
	-O(5)	2.557	.006	O(1)-Si(1)-O(9)	106.7
	-O(6)	2.873	.006	O(7)-Si(1)-O(9)	106.7
	-O(7)	2.288	.006		
	(next nearest:	3.05)		O(3)-Si(2)-O(3)'	110.5
				O(3)-Si(2)-O(8)	110.4
2	Ca(2)-O(2)	2.711	.004	O(3)-Si(2)-O(9)	107.6
2	-O(2)'	2.548	.004	O(8)-Si(2)-O(9)	110.3
2	-O(3)	2.745	.004		
	-O(7)	2.277	.006	O(2)-Si(3)-O(2)'	106.8
	-O(10)	2.541	.007	O(2)-Si(3)-O(5)	111.3
	(next nearest:	3.03)		O(2)-Si(3)-O(6)	112.8
				O(5)-Si(3)-O(6)	102.0
2	Si(1)-O(1)	1.654	.005		
	-O(7)	1.569	.007	O(1)-M(1)-O(4)	86.5
	-O(9)	1.638	.007	O(1)-M(1)-O(5)	90.1
				O(4)-M(1)-O(5)	95.6
2	Si(2)-O(3)	1.619	.005		
	-O(8)	1.608	.007	O(3)-M(2)-O(6)	89.8
	-O(9)	1.634	.007	O(3)-M(2)-O(10)	91.9
				O(6)-M(2)-O(10)	96.9
2	Si(3)-O(2)	1.627	.005		
	-O(5)	1.671	.007	O(1)-M(3)-O(1)'	80.7
	-O(6)	1.649	.007	O(1)-M(3)-O(2)	89.6
				O(1)-M(3)-O(4)	76.9
2	M(1)-O(1)	1.941	.004 Å	O(1)-M(3)-O(8)	104.1
2	-O(4)	1.872	.005	O(2)-M(3)-O(2)'	98.6
2	-O(5)	1.985	.005	O(2)-M(3)-O(4)	92.6
				O(2)-M(3)-O(8)	86.5
2	M(2)-O(3)	1.857	.004		
2	-O(6)	1.934	.005	Si(1)-O(9)-Si(2)	151.0
2	-O(10)	1.881	.006		
2	M(3)-O(1)	2.274	.005		
2	-O(2)	2.031	.005		
	-O(4)	1.900	.006		
	-O(8)	1.861	.006		

2.54 Å in clinozoisite to 2.61 Å in piemontite, the M(1) octahedron does not become more distorted. This is partly due to the additional substitution that occurs in the M(1) site and is perhaps related to why substitution occurs here but not in the M(2) site which shares no edges with the M(3) octahedron.

DISCUSSION OF THE SITE POPULATIONS

The (Mn, Fe) total taken from the values given in Table 2, is in almost exact agreement with the independently determined microprobe total. The distribution of the transition metals among the sites is reasonably similar to that reported for an epidote, $Cz_{69}Ps_{31}$, by Burns and Strens (1967). From a refinement of the two dimensional X-ray data of Ito *et al.* (1954) these authors report the "best fit" is obtained for a distribution of 0.10, 0.00, and 0.87 Fe atoms in the M(1), M(2), and M(3) sites, respectively.

Whether the Mn:Fe ratio is the same in the M(1) and M(3) sites of the St. Marcel piemontite, or whether ordering of these two species occurs, is undetermined by this study. Some evidence on this point is furnished by other studies of piemontites although the conclusions reached are not all in accord with each other or with this study. The lack of agreement may reflect real differences in the ordering schemes of compounds of similar bulk compositions. Mössbauer measurements on two epidotes ($Cz_{71}Ps_{29}$ and $Cz_{72}Ps_{28}$) and a piemontite ($Cz_{68}Pm_{21}Ps_{11}$) have been reported (Bancroft *et al.*, 1967). The spectra were interpreted to mean that the iron atoms are restricted to one, rather distorted site, this being the same site in all samples. (It was estimated that contributions to the spectrum of less than 5 percent of the total intensity would not be resolved.) As the X-ray studies are in agreement that the high-Fe site in epidote is the M(3) site, this would also put the iron in this particular piemontite into the M(3) site.

Burns and Strens (1967) in their optical absorption spectra study assign the bulk of the Fe and Mn atoms to the acentric M(3) site, in preference to the two centric sites, on the basis of the magnitude of the extinction coefficients. In addition, for the Cz-Ps series, they conclude, "constancy of the extinction coefficient over the whole range of Fe^{3+} concentrations implies that contributions from Fe^{3+} ions in other positions . . . (than M(3)) . . . are negligible." Whereas, for the Cz-Ps-Pm series, "the variability of the extinction coefficient indicates the absorption is due to Mn^{3+} being present in more than one position." For the Mn distribution they assign the additional position as the M(2) site on the basis that in the Ito epidote model this site is more distorted than the M(1) site and that due to the Jahn-Teller effect, the Mn^{3+} ion would

prefer the more distorted site. Their final site preference order for the Mn^{3+} ion is $M(3) \geq M(2) \gg M(1)$. In the St. Marcel piemontite the $M(2)$ site is also slightly more distorted than the $M(1)$ site (as discussed above). However, there is no substitution of Mn (or Fe) into this site.

The $Ca(2)$ occupancy factor indicates the presence of some heavy atom substituents in this site. This is somewhat speculatively assigned to strontium substitution on the basis of a qualitative microprobe study of this material which indicated a significant amount of Sr (and no lanthanides). Deer *et al.* (1962) list piemontites with up to 0.06 Sr atom per formula unit and the variety hancockite with 0.21 Sr atom.

In the earlier Jakob analysis of St. Marcel piemontite, Sr was not reported but an 0.22 Ca atom deficiency per formula unit, was made up mainly by substitution of Mn^{2+} and Na. (See formula reported above). Such substitution would not account for the observed occupancy factor and is not thought to occur in the crystals studied here on the additional grounds: (a) the 1.04 total $(Mn+Fe)$ reported in the microprobe analysis is accounted for in the octahedral sites, leaving no excess, (b) an additional 0.44 (Mn,Fe) atom would be required to account for the observed occupancy factor (any Na present would have to be counterbalanced by further substitution of atoms heavier than Ca), (c) the substituting atoms occupy the larger, 8-fold coordinated $Ca(2)$ site in preference to the smaller, 7-fold coordinated $Ca(1)$ site (mean $Ca(1)$-$O = 2.47$ Å, mean $Ca(2)$-$O = 2.60$ Å) suggesting that the substituting atoms are as large as, or larger than, the Ca atoms. This supposition is supported by the structure of allanite (Rumanova and Nikolaeva, 1959) which shows the larger lanthanide atoms preferentially occupying the $Ca(2)$ site.

THERMAL VIBRATION ELLIPSOIDS

The elements of the thermal vibration ellipsoids–obtained from the anisotropic temperature factors given in Table 1–are listed in Table 4. The oxygen atom is that shared between silica tetrahedra in the Si_2O_7 group. The magnitude of its thermal motion is greater than for any other atom and the orientation of its vibration ellipsoid appears controlled by the bonds it forms to the silicon atoms. Thus the angle between the shortest vibration axis and the Si-Si axis is only $18 \pm 6°$ and the longest vibration axis is perpendicular to the Si-O-Si plane. Similarly in the case of the markedly flattened $M(3)$ octahedron, the shortest vibration direction of the $M(3)$ atom lies at an angle of $6 \pm 3°$ with the shortened O-$M(3)$-O octahedral axis.

TABLE 4. PIEMONTITE THERMAL VIBRATION ELLIPSOIDS

Atom	Ellipsoid axis	rms amplitude	ϕ_a[a]	ϕ_b	ϕ_c
Ca(1)	1	0.074 ± 0.004 Å	$43 \pm 3°$	$90°$	$158 \pm 3°$
	2	$.104 \pm .004$	90	0	90
	3	$.125 \pm .002$	47 ± 3	90	68 ± 3
Ca(2)	1	$.104 \pm .003$	8 ± 4	90	123 ± 4
	2	$.131 \pm .003$	90	0	90
	3	$.078 \pm .004$	82 ± 4	90	33 ± 4
M(3)	1	$.055 \pm .005$	23 ± 3	90	92 ± 3
	2	$.077 \pm .005$	90	0	90
	3	$.081 \pm .004$	113 ± 3	90	2 ± 3
O(9)	1	$.139 \pm .008$	39 ± 6	90	77 ± 6
	2	$.157 \pm .011$	90	0	90
	3	$.063 \pm .017$	129 ± 6	90	13 ± 6

[a] The ϕ's are the angles between the axes of the ellipsoid and the crystallographic axes.

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