Structure refinements of two natural pyromorphites, $Pb_5(PO_4)_3Cl$, and crystal chemistry of chlorapatite group, $M_5(PO_4)_3Cl$

H. Hashimoto* and T. Matsumoto

Kanazawa University, Faculty of Science, Department of Earth Sciences, Kakuma-machi, Kanazawa, Ishikawa, 920-1192, Japan

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Abstract. X-ray single-crystal structure analyses of green and brown pyromorphites, $Pb_5(PO_4)_3Cl$, from Kamioka Mine and Mikura Mine both in Japan, respectively, were performed at room temperature. They are hexagonal, $P6_3/m$, and the cell dimensions are 10.022(3) Å and 9.993(2) Å for a axis, and 7.348(9) Å and 7.334(6) Å for c axis for green and brown ones, respectively. The structures were refined to R's of 0.031 for green and 0.029 for brown ones. No significant difference was observed between their structures. In both of the pyromorphites, the site occupancies of Pb atoms which have two crystallographically independent sites, M(1) and M(2), are slightly larger at M(2) than at M(1), and those of impurities (minor cations) are slightly larger at M(1) than at M(2).

The thermal ellipsoids of the Cl atoms in the two pyromorphites were nearly isotropic. In the chlorapatite group, $M_5(PO_4)_3Cl$, the amplitude along [001] of the thermal ellipsoid of Cl atom becomes quantitatively large with decreasing the value of the ionic radius of M atom, $r_{M^{2+}}$.

Introduction

Mineral pyromorphite $\{Pb_5(PO_4)_3Cl\}$ generally occurs in green, brown or yellow [2], and belongs to the chlorapatite group, $M_5(PO_4)_3Cl$ (M = Cd, Ca, Sr, Pb, Ba, etc.). Here M atom has two crystallographycally different sites M(1) and M(2). The chlorapatite group crystallizes in hexagonal or monoclinic structures; i.e. cadmium chlorapatite, M = Cd, [3], strontium chlorapatite, M = Sr, [4] and barium chlorapatite, M = Ba, [1] crystallize in hexagonal, $P6_3/m$, and stoichiometric chlorapatite, M = Ca, [5] crystallizes in a monoclinic, $P2_1/b$, but strongly pseudo-hexagonal structure ($b = 2a$, $\gamma = 120°$) which is closely related to the structures of the former three. Pyromorphite is isostructural with strontium and barium chlorapatites.

The chlorapatite group has three crystallographycally different sites for Cl atoms on the 3-fold axis (where the space group $P2_1/b$ of chlorapatite is treated as $P6_3/m$). The first site is position 0, 0, 0 with site symmetry $\bar{3}$ (when M is Ba or Sr), the second site is 0, 0, 1/4 with site symmetry $\bar{6}$ (when M is Cd), and the last site is 0, 0, 0.06 with site symmetry 3 (when M is Ca). The relation between the sites of Cl atoms and the kind of M atoms was summarized by Hata et al. [1] as follows. In the structure of $M_5(PO_4)_3Cl$, the location of Cl^- ion depends on the value of $r_{M^{2+}}$. In short, if the value of $r_{M^{2+}}$ is larger than that of $r_{Ca^{2+}}$, the Cl^- ion occupies the position 0, 0, 0, and if the value of $r_{M^{2+}}$ is smaller than that of $r_{Ca^{2+}}$, the Cl^- ion occupies the position 0, 0, 1/4. The position of the Cl^- ion, in $Ca_5(PO_4)_3Cl$, is intermediate between 0, 0, 0 and 0, 0, 1/4.

Structure refinement of pyromorphite was reported by Akao, Aoki, Innami, Minamikata and Yamada, 1989, [6] and Dai, Hughes, 1989, [7]. However the application of the absorption correction seems to be unsuitable in the former report [6] (for synthetic pyromorphite), and the anisotropic temperature factors of anions were not determined in the latter report [7] (for natural green one). In short, there are no well-refined structural data on pyromorphite. Therefore, as a part of study of the chlorapatite group, we refined the crystal structures of two natural pyromorphites with different colors from two localities.

Present results are also compared with the structures of other members of the chlorapatite group, $M_5(PO_4)_3Cl$ (M = Cd, Ca, or Sr), and we report the crystal chemistry of the chlorapatite group.

Experimental

Specimens

Experiments were performed on the two natural pyromorphites from Kamioka Mine, Gifu Pref., Japan and Mikura Mine, Shizuoka Pref., Japan (University Museum of University of Tokyo, No. MI-90463). The pyromorphite from Kamioka Mine occurs as euhedral hexagonal crystals, green in color and rarely with pyramidal faces $\{10\bar{1}1\}$. Their sizes are less than 0.3 mm along the c axis. The other pyromorphite from Mikura Mine occurs as euhedral hexagonal crystals, pale brown in color and usually with pyramidal faces. The sizes are less than 1.5 mm along the c axis.

The chemical compositions of the green and brown pyromorphites obtained by electron microprobe analyses (EPMA) are shown in Table 1. Ca, K, Fe, Zn, Si, Al

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* Correspondence author

Present address: Room No. 205, 64 Kohama-machi, Ohmuta, Fukuoka, 836-0034, Japan

Table 1. EPMA data for the two natural pyromorphites from Kamioka Mine (Green) and Mikura Mine (Brown).

	Green	Brown
PbO (wt%)	79.79	80.73
CaO	0.26	0.09
ZnO	0.27	0.02
K_2O	0.01	<0.01
FeO	<0.01	<0.01
P_2O_5	16.14	16.50
SiO_2	0.28	0.03
Al_2O_3	0.15	n.d.
Cl	2.60	2.80
F	0.03	0.02
Total	99.53	100.19
Atomic proportions[a]		
Pb	4.72	4.78
Ca	0.06	0.02
Zn	0.04	0.00
K	0.00	0.00
Fe	0.00	0.00
P	3.00	3.07
Si	0.06	0.01
Al	0.04	n.d.
Cl	0.99	0.99
F	0.01	0.01

n.d. is not detected.

a: Atomic proportions are calculated on the basis of 12 oxygen atoms combined with one Cl(F) atom per formula unit.

and F were detected as impurities. Especially, the amounts of Ca, Zn, Al and Si were much higher in the green one than in the brown one (Al was not detected in the brown one). The total amounts of impurities included in the green and brown ones were approximately 1.0 wt% and 0.2 wt%, respectively. The chemical formulae calculated on the basis of 12 oxygen atoms combined with one Cl(F) atom per formula unit are, $Pb_{4.72}Ca_{0.06}Zn_{0.04}P_{3.00}Si_{0.06}Al_{0.04}O_{12}Cl_{0.99}F_{0.01}$ for the green and $Pb_{4.78}Ca_{0.02}P_{3.07}Si_{0.01}Al_{0.04}O_{12}Cl_{0.99}F_{0.01}$ for the brown pyromorphites.

Space groups of the two pyromorphites were confirmed to be $P6_3$ or $P6_3/m$ from Weissenberg photographs. No reflection was observed to show the monoclinic superstructure, the systematic absences for $00l$ being consistent with 6_3 screw axis. The $P6_3/m$ was employed in the structure refinements, since most members of the chlorapatite group are known to belong to this space group. The specimens were ground, using the Bond method, into approximate spheres with mean diameters of 0.113 mm [0.110 mm ($\perp c$ axis) and 0.118 mm ($//c$ axis)] for the green one and 0.089 mm [0.088 mm ($\perp c$ axis) and 0.092 mm ($//c$ axis)] for the brown one.

Collections of diffraction intensities

The diffraction data of the green pyromorphite were collected at room temperature (297 K) on a Rigaku AFC-6 automated four-circle diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71069$ Å), using the $\omega - 2\theta$ scan method with scan width $1.4° + 0.35° \tan\theta$ and scan speed 4° per minute. During the data collection, three standard reflections were monitored every 100 reflections. 1550 reflections in one sixth of the reciprocal space with the conditions $0 \le h \le 11$, $0 \le k \le 11$, $-10 \le l \le 0$ and $-11 \le h \le 0$, $-11 \le k \le 0$, $-10 \le l \le 0$ were measured up to $2\theta = 60°$.

The data collection for the brown pyromorphite was performed on a Rigaku AFC7-R. The measurement conditions were almost the same as those for the green one except a few points. The scan speed was 16° per minute and the standard reflections were monitored every 200 reflections. 6292 reflections in one third of the reciprocal space with the conditions $0 \le h \le 15$, $0 \le k \le 15$, $-13 \le l \le 13$ and their Friedel pairs were measured up to $2\theta = 80°$.

Crystal structure refinements

The structure refinements of the two natural pyromorphites with different colors were performed using their chemical formulae derived by EPMA. In the refinements, their chemical formulae were assumed to be $(Pb_{4.72}M_{G0.20} \cdot \square_{G0.08})_{\Sigma=5.00}P_3O_{12}(Cl_{0.99}F_{0.01})_{\Sigma=1.00}$ for the green and $(Pb_{4.78}M_{B0.10}\square_{B0.12})_{\Sigma=5.00}P_3O_{12}(Cl_{0.99}F_{0.01})_{\Sigma=1.00}$ for the brown ones, where $M_{G0.20} = Ca_{0.06} + Zn_{0.04} + Si_{0.06} + Al_{0.04}$ and $M_{B0.10} = Ca_{0.02} + P_{0.07} + Si_{0.01}$, and the atomic scattering factors of M_G and M_B were estimated as weighted means of the scattering factors of impurity atoms. Here, $\square_G$ and $\square_B$ are the vacancies of the M sites for the green and brown ones, respectively, and in each refinement, the vacancies were equally allotted to M(1) and M(2), and the total amounts were fixed to the initial values. The intensities were corrected for Lp and absorption factors ($\mu R = 3.57$ for the green and $\mu R = 2.88$ for the brown ones). Averages of equivalent reflections with $|F_o| > 4\sigma|F_o|$ were used for structure refinements, where $\sigma|F_o|$ was the standard deviation estimated from counting statistics. The numbers of unique reflections for the green and brown ones were 365 and 556, respectively. The respective refinements were started from the parameters given by Dai et al. [7], using the program SHELXL-93 [8]. In the refinements, the atomic parameters of [$M_G(1)$ and $M_B(1)$], [$M_G(2)$ and $M_B(2)$] and F atoms were assumed to be equal to those of the Pb(1), Pb(2) and Cl atoms, respectively. The neutral atomic scattering factors and anomalous dispersion factors were taken from International Tables for X-ray Crystallography, Vol. C [9]. The final atomic coordinates and the site occupancies of the M sites were given in Table 2[1] for the two specimens, and the anisotropic temperature factors were given in Table 3[1]. The refinements of the green and brown ones finally converged to give the R values of 0.031 and 0.029, and R_w of 0.057 and 0.053, respectively. The weighting scheme

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[1] The crystal structure refinements were also performed using the intensity data corrected for the maximum and minimum absorption factors ($\mu R_{max} = 3.70$ and $\mu R_{min} = 3.45$ for the green and $\mu R_{max} = 2.94$ and $\mu R_{min} = 2.81$ for the brown pyromorphites). The atomic coordinates and anisotropic temperature factors are in good agreement with a discrepancy of the order of ±0.001 in both of the specimens.

Table 2. Fractional atomic coordinates and equivalent isotropic mean square displacements for the two natural pyromorphites from Kamioka Mine (Green) and Mikura Mine (Brown) and synthetic pyromorphite (Synthetic).[a] Standard deviations, in the last significant digit, are given in parentheses.

Site	Atom	Position[b]	x	y	z	U_{eq}	Occupancy
Green ($R = 0.031$)							
M(1)	Pb(1)	4*f*3	1/3	2/3	0.00463(5)	0.0190(3)	0.931(4)
	$M_G(1)^c$						0.053(4)
	$\square_G(1)^d$						0.016
M(2)	Pb(2)	6*hm*	0.25467(9)	0.00605(9)	1/4	0.0201(2)	0.952(3)
	$M_G(2)^c$						0.032(3)
	$\square_G(2)^d$						0.016
P		6*hm*	0.4106(5)	0.3790(6)	1/4	0.0162(9)	
O(1)		6*hm*	0.3477(19)	0.4924(18)	1/4	0.028(3)	
O(2)		6*hm*	0.5893(15)	0.4736(18)	1/4	0.028(3)	
O(3)		12*i*1	0.3588(12)	0.2728(11)	0.0819(4)	0.027(2)	
Cl	Cl	2*b*3	0	0	0	0.026(2)	0.99
	F						0.01
Brown ($R = 0.029$)							
M(1)	Pb(1)	4*f*3	1/3	2/3	0.00461(10)	0.0170(2)	0.947(2)
	$M_B(1)^c$						0.029(2)
	$\square_B(1)^d$						0.024
M(2)	Pb(2)	6*hm*	0.25489(6)	0.00606(6)	1/4	0.01796(13)	0.962(2)
	$M_B(2)^c$						0.014(2)
	$\square_B(2)^d$						0.024
P		6*hm*	0.4104(4)	0.3789(4)	1/4	0.0120(5)	
O(1)		6*hm*	0.3452(14)	0.4892(13)	1/4	0.025(2)	
O(2)		6*hm*	0.5884(10)	0.4738(10)	1/4	0.021(2)	
O(3)		12*i*1	0.3612(9)	0.2732(9)	0.0800(11)	0.028(2)	
Cl	Cl	2*b*3	0	0	0	0.0153(8)	0.99
	F						0.01
Synthetic[a] ($R = 0.058$)							
M(1)	Pb(1)	4*f*3	1/3	2/3	0.0051(2)	0.0148	
M(2)	Pb(2)	6*hm*	0.2547(1)	0.0060(2)	1/4	0.0153	
P		6*hm*	0.4102(9)	0.3790(8)	1/4	0.0095	
O(1)		6*hm*	0.3402(40)	0.4893(30)	1/4	0.025	
O(2)		6*hm*	0.5871(28)	0.4735(29)	1/4	0.016	
O(3)		12*i*1	0.3593(29)	0.2738(23)	0.0848(25)	0.025	
Cl	Cl	2*b*3	0	0	0	0.0177	

a: Synthetic pyromorphite was analized by Akao, et al. [6] and the values of synthetic pyromorphite are transformed to compare with the values of this study.

b: Position indicates a multiplicity, Wyckoff letter and site symmetry.

c: M_G and M_B are impurities of the M sites for the green and brown pyromorphites, respectively. Here, $M_G = 0.06Ca + 0.04Zn + 0.06Si + 0.04Al$ and $M_B = 0.02Ca + 0.07P + 0.01Si$.

d: $\square_G$ and $\square_B$ are vacancies of the M sites for the green and brown pyromorphites, respectively. These were equally allotted to M(1) and M(2), and the total amounts were fixed to the initial values.

adopted in the calculations are: $w = 1/(\sigma^2|F_o|^2 + 0.0087P)$, where $P = (|F_o|^2 + 2|F_c|^2)/3$. The list of F_o/F_c-data is available from the author up to one year after the publication has appeared.

Discussions

Crystal structures of pyromorphites

As seen in Table 2, most of the atomic coordinates of the two natural pyromorphites are in good accordance with each other. The discrepancies are within 1σ except a few parameters. The values are also in good agreement with those of the synthetic one [6], the discrepancies being less than 1σ. In the two pyromorphites, the site occupancy of Pb atom is slightly larger at M(2) than at M(1), while those of the impurities, M_G and M_B, are slightly larger at M(1) than at M(2). As seen in Table 3 most of the anisotropic temperature factors are slightly larger for the green pyromorphite than for the brown one, and those for the two natural pyromorphites are slightly larger than those for the synthetic one [6].

Selected interatomic distances and bond angles of the green and brown ones are given in Table 4. There are two crystallographycally independent Pb atoms in the structure of pyromorphite: Pb(1) atom is surrounded by nine O atoms [three O(1), three O(2) and three O(3) atoms], and Pb(2) atom is surrounded by six O atoms [one O(1), one O(2) and four O(3) atoms] and two Cl atoms. P atom is surrounded by four O atoms [one O(1), one O(2) and two O(3) atoms]. As seen in Table 4, the bond distances and angles of the two pyromorphites are in good agreement within 1σ except a few distances, and those of the two pyromorphites and the synthetic one are also in good agreement within 1σ. Whereas the PO_4 tetrahedron in the

Table 3. Anisotropic temperature factors for the two natural pyromorphites from Kamioka Mine (Green) and Mikura Mine (Brown) and synthetic pyromorphite (Synthetic).[a]
The temperature factor is in the form $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2c^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.
Standard deviations, in the last significant digit, are given in parentheses.

Site	Atom	Position[b]	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
				Green (R = 0.031)				
M(1)	Pb(1) $M_G(1)^c$	4*f*3	0.0224(3)	U_{11}	0.0122(4)	$U_{11}/2$	0	0
M(2)	Pb(2) $M_G(2)^c$	6*hm*	0.0147(4)	0.0175(4)	0.0271(4)	0.0074(3)	0	0
P		6*hm*	0.015(2)	0.014(2)	0.020(2)	0.007(2)	0	0
O(1)		6*hm*	0.042(9)	0.033(9)	0.029(8)	0.035(8)	0	0
O(2)		6*hm*	0.010(7)	0.021(7)	0.038(9)	−0.003(5)	0	0
O(3)		12*i*1	0.039(6)	0.026(5)	0.021(5)	0.021(4)	−0.019(4)	−0.011(4)
Cl	Cl F	$2b\bar{3}$	0.024(2)	U_{11}	0.030(4)	$U_{11}/2$	0	0
				Brown (R = 0.029)				
M(1)	Pb(1) $M_B(1)^c$	4*f*3	0.0189(2)	U_{11}	0.0131(3)	$U_{11}/2$	0	0
M(2)	Pb(2) $M_B(2)^c$	6*hm*	0.0120(2)	0.0148(2)	0.0266(3)	0.0063(2)	0	0
P		6*hm*	0.0121(13)	0.0136(13)	0.0101(13)	0.0064(11)	0	0
O(1)		6*hm*	0.039(6)	0.030(6)	0.016(5)	0.026(5)	0	0
O(2)		6*hm*	0.013(4)	0.007(4)	0.039(6)	0.002(3)	0	0
O(3)		12*i*1	0.030(4)	0.028(3)	0.031(4)	0.019(3)	−0.012(3)	−0.012(3)
Cl	Cl F	$2b\bar{3}$	0.0166(11)	U_{11}	0.013(2)	$U_{11}/2$	0	0
				Synthetic[a] (R = 0.058)				
M(1)	Pb(1)	4*f*3	0.0177	U_{11}	0.0092	$U_{11}/2$	0	0
M(2)	Pb(2)	6*hm*	0.0101	0.0125	0.0228	0.0050	0	0
P		6*hm*	0.0098	0.0125	0.0107	0.0087	0	0
O(1)		6*hm*	0.0337	0.0186	0.0361	0.0220	0	0
O(2)		6*hm*	0.0137	0.0221	0.0158	0.0111	0	0
O(3)		12*i*1	0.0434	0.0198	0.0172	0.0205	−0.0140	−0.0011
Cl	Cl	$2b\bar{3}$	0	U_{11}	0.0172	$U_{11}/2$	0	0

a: Synthetic pyromorphite was analized by Akao, et al. [6] and the values of synthetic pyromorphite are transformed to compare with the values of this study.
b: Position indicates a multiplicity, Wyckoff letter and site symmetry.
c: M_G and M_B are impurities of the M sites for the green and brown pyromorphites, respectively. Here, $M_G = 0.06Ca + 0.04Zn + 0.06Si + 0.04Al$ and $M_B = 0.02Ca + 0.07P + 0.01Si$.

synthetic one is more distorted than those in other members of apatite group, the distortions of PO_4 tetrahedra in the two natural ones are approximately in the same degree as those in other members. The structure of the brown one projected along the c axis on (001) by ORTEP II [10] is shown in Fig. 1. Although the chemical composition of the brown one is purer than that of the green one, the structures of the two pyromorphites seem to have no significant difference.

Crystal chemistry of chlorapatite group, $M_5(PO_4)_3Cl$

1. Position of Cl atom

As mentioned before, it has been reported that the chlorapatite group, $M_5(PO_4)_3Cl$, has an approximately the same structure, though it has three crystallographycally different positions for the Cl atoms depending on the value of $r_{M^{2+}}$ [1]. In this study, the crystal structures of the two natural pyromorphites were refined by using their chemical formulae derived by EPMA. However, in this section, we assume the ideal chemical formula, $Pb_5(PO_4)_3Cl$, to that of the brown one, whose formula is nearly ideal: the amount of impurities included in the brown one is less than 0.2 wt%. We also assume the space group $P6_3/m$ to $Ca_5(PO_4)_3Cl$, of which real symmetry is $P2_1/b$.

Some crystallographic data for the chlorapatite group, $M_5(PO_4)_3Cl$, where M = Cd, Ca, Sr or Pb, are given in Table 5. The arrangements of the Cl and M(2) atoms in the chlorapatite group along the c axis, looked down [210], are shown in Fig. 2. As seen in Table 5, almost all values increase qualitatively with the value of $r_{M^{2+}}$, but a few values do not. The Cl atoms occupy the position 0, 0, 0 with site symmetry $\bar{3}$ in $Pb_5(PO_4)_3Cl$ and $Sr_5(PO_4)_3Cl$ [4], where $r_{Pb^{2+}} = 1.18$ Å and $r_{Sr^{2+}} = 1.16$ Å [11]. On the other hand, they occupy the position 0, 0, 0.06 with site symmetry 3 in $Ca_5(PO_4)_3Cl$ ($r_{Ca^{2+}} = 1.00$ Å) [5, 11], and the position 0, 0, $^1/_4$ with site symmetry $\bar{6}$ in $Cd_5(PO_4)_3Cl$ ($r_{Cd^{2+}} = 0.95$ Å) [3, 11]. (Although the values of ionic radii of six-coordination are indicated for all M atoms, the M(2) atoms are seven-coordination in $Cd_5(PO_4)_3Cl$ and $Ca_5(PO_4)_3Cl$, and eight-co-

Table 4. Selected interatomic distances (Å) and bond angles (°) for the two natural pyromorphites from Kamioka Mine (Green) and Mikura (Brown) and synthetic pyromorphite (Synthetic).[a] Standard deviations, in the last significant digit, are given in parentheses.

Pb(1) Polyhedra	(sc)	Green	Brown	Synthetic[a]
Pb(1)–O(1)	(1)	2.564(10)	2.571(8)	2.55(3)
Pb(1)–O(1)	(2)	2.564(10)	2.571(8)	2.55(3)
Pb(1)–O(1)	(3)	2.564(10)	2.571(8)	2.55(3)
Pb(1)–O(2)	(4)	2.677(13)	2.677(7)	2.69(2)
Pb(1)–O(2)	(5)	2.677(13)	2.677(7)	2.69(2)
Pb(1)–O(2)	(6)	2.677(13)	2.677(7)	2.69(2)
Pb(1)–O(3)	(4)	2.902(11)	2.869(8)	2.90(2)
Pb(1)–O(3)	(5)	2.902(11)	2.869(8)	2.90(2)
Pb(1)–O(3)	(6)	2.902(11)	2.869(8)	2.90(2)
Pb(2) Polyhedra				
	(sc)			
Pb(2)–O(1)	(3)	3.14(2)	3.108(12)	3.07(5)
Pb(2)–O(2)	(2)	2.373(15)	2.364(9)	2.37(3)
Pb(2)–O(3)	(1)	2.641(11)	2.641(8)	2.63(3)
Pb(2)–O(3)	(5)	2.646(10)	2.636(8)	2.66(2)
Pb(2)–O(3)	(8)	2.646(10)	2.636(8)	2.66(2)
Pb(2)–O(3)	(10)	2.641(11)	2.641(8)	2.63(3)
Pb(2)–Cl	(1)	3.121(2)	3.1143(11)	3.115(1)
Pb(2)–Cl	(10)	3.121(2)	3.1143(11)	3.115(1)
Pb(2)–Pb(2)	(2)	4.369(2)	4.3603(13)	4.359(2)
P Tetrahedra				
	(sc)			
P–O(1)	(1)	1.552(14)	1.536(11)	1.57(3)
P–O(2)	(1)	1.551(14)	1.541(10)	1.53(3)
P–O(3)	(1)	1.541(10)	1.547(8)	1.53(3)
P–O(3)	(10)	1.541(10)	1.547(8)	1.52(2)

atom2	(sc)	atom1	atom3	(sc)	Green	Brown	Synthetic[a]
O(1)	(1) –	P –	O(2)	(1)	108.6(10)	109.4(6)	110(2)
O(1)	(1) –	P –	O(3)	(1)	112.7(5)	112.7(4)	112(1)
O(2)	(1) –	P –	O(3)	(1)	108.0(6)	107.2(4)	108(2)
O(3)	(1) –	P –	O(3)	(10)	106.6(8)	107.4(6)	106(2)

(sc) is symmetry codes.
1: x, y, z; 2: $-y, x-y, z$; 3: $y-x, -x, z$; 4: $-x, -y, -z$; 5: $y, y-x, -z$;
6: $x-y, x, -z$; 7: $-x, -y, z+0.5$; 8: $y, y-x, z+0.5$; 9: $x-y, x, z+0.5$;
10: $x, y, -z+0.5$; 11: $-y, x-y, -z+0.5$; 12: $y-x, -x, -z+0.5$
a: Synthetic pyromorphite was analized by Akao, et al. [6].

ordination in $Sr_5(PO_4)_3Cl$ and $Pb_5(PO_4)_3Cl$.) In short, the position of the Cl atom depends on the value of $r_{M^{2+}}$, as suggested by Hata et al. [1].

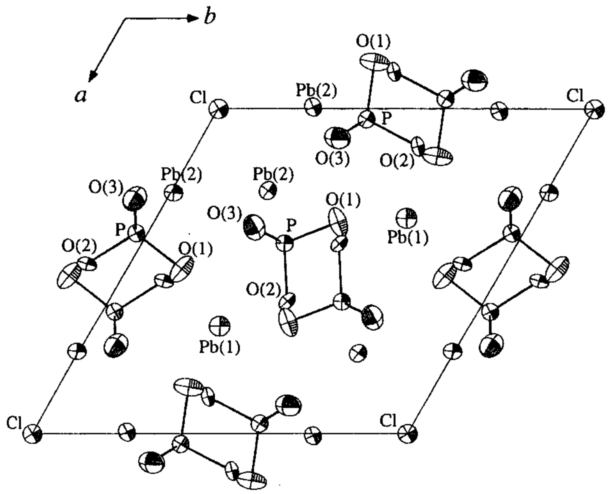

Fig. 1. The structure of the brown pyromorphite projected along the c axis on (001) by ORTEP II. The thermal ellipsoids are shown at the 70% probability.

2. Thermal ellipsoid of Cl atom

It is noticeable that the amplitude along [001] of the thermal ellipsoids of the Cl atoms in the chlorapatite group also depends on the value of $r_{M^{2+}}$. As seen in Fig. 2, the thermal ellipsoids of the Cl atoms in $Sr_5(PO_4)_3Cl$, $Ca_5(PO_4)_3Cl$ and $Cd_5(PO_4)_3Cl$ are clearly anisotropic with the largest amplitude along [001], while that in $Pb_5(PO_4)_3Cl$ is nearly isotropic. In short, as the value of $r_{M^{2+}}$ decreases, the amplitude along [001] of the thermal ellipsoids of the Cl atoms becomes qualitatively large. This tendency may be explained as follows. When the value of $r_{M^{+2}}$ is small such as Cd, the Cl atoms occupy the position $0, 0, {}^1/_4$ and are connected to three M(2) atoms lying at the same height ($z = {}^1/_4$). That is, the Cl atoms exist in the center of the triangle of the three M(2) atoms, therefore the amplitude along [001] of the thermal ellipsoids of the Cl atoms becomes large. In contrast, when the value of $r_{M^{2+}}$ is large such as Pb, the Cl atoms occupy the position 0, 0, 0 and are connected to six M(2) atoms, which are at a different height ($z = \pm{}^1/_4$) from that of Cl. Namely the Cl atoms exist in the center of the octahedron of the six M(2) atoms, therefore the amplitude along [001] of the thermal ellipsoids of the Cl atoms becomes small.

Table 5. Some crystallographic data for the chlorapatite group, $M_5(PO_4)_3Cl$ (M = Pb, Sr, Ca or Cd).

$M_5(PO_4)_3Cl$	$Pb_5(PO_4)_3Cl$	$Sr_5(PO_4)_3Cl$	$Ca_5(PO_4)_3Cl^a$	$Cd_5(PO_4)_3Cl$
Cell constants				
a, c (Å)	9.993, 7.334	9.859, 7.206	9.628, 6.7646	9.633, 6.484
Ionic radii of M^{2+} (Å)	1.18	1.16	1.00	0.95
$r_{M^{2+}} + r_{Cl^-}$ (Å)	2.99	2.91	2.81	2.76
$r_{M^{2+}} + / r_{Cl^-}$ ratio	0.65	0.64	0.55	0.52
M(2)–O(1) (Å)	3.108	2.847	2.973	3.157
M(2)–O(2) (Å)	2.364	2.437	2.295	2.253
M(2)–O(3) (Å)	2.640	2.696	2.539	2.203
M(2)–O(3)′ (Å)	2.636	2.510	2.336	2.465
M(2)–M(2) (Å)	4.360	4.340	4.191	4.116
M(2)–Cl (Å)	3.114	3.086	2.630	2.545
Coordinates of Cl	0, 0, 0	0, 0, 0	0, 0, 0.06	0, 0, $^1/_4$
U_{33} of Cl (Å^2)	0.013	0.022	0.022	0.046
References	This study	[4]	[5]	[3]

a: $Ca_5(PO_4)_3Cl$ is treated as hexagonal symmetry, $P6_3/m$.
The values of ionic radii of six-coordination are indicated for all atoms.
A single primed symbol (O(3)′) designates an atom with coordinates y, $y-x$, $-z$ where x, y, z are those of the atom designated by an unprimed symbol (O(3)).

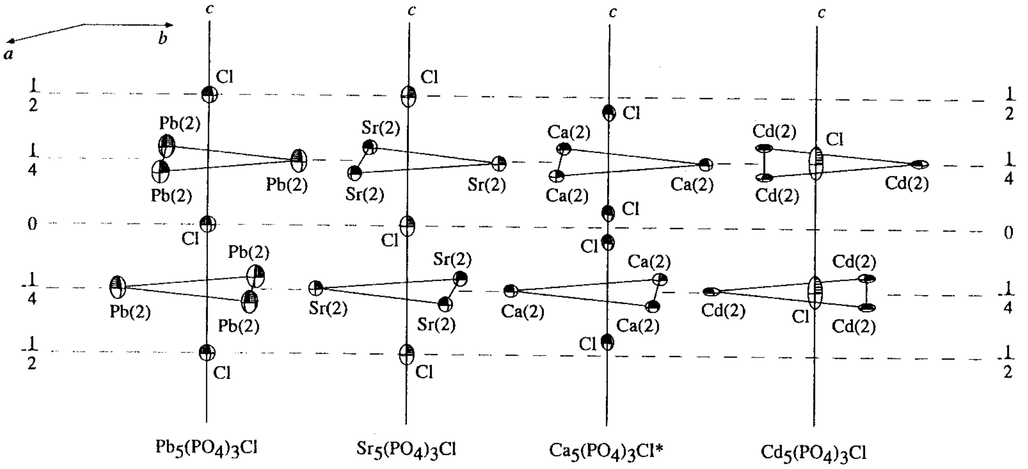

Fig. 2. Perspective view, looked down [210], of the c axis arrangements for $Pb_5(PO_4)_3Cl$, $Sr_5(PO_4)_3Cl$ [4], $Ca_5(PO_4)_3Cl$ [5] and $Cd_5(PO_4)_3Cl$ [3]. These plots are drawn by ORTEP II. The thermal ellipsoids are shown at the 70% probability. $Ca_5(PO_4)_3Cl$ is treated as hexagonal symmetry, $P6_3/m$. The Cl atoms are statistically distributed with half weight.

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