

Alforsite, a new member of the apatite group: the barium analogue of chlorapatite¹

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Abstract

Alforsite, ideally $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$, is a new member of the apatite group occurring in contact metamorphosed evaporitic rocks from Fresno and Mariposa counties, California, associated with fluorapatite and many other rare barium minerals previously described by Alfors *et al.* (1965). It is optically uniaxial, negative, with $\omega, \epsilon = 1.70(1)$. The density is calculated to be $4.83(2) \text{ gm/cm}^3$ for the end member composition. It is hexagonal, space group $P6_3/m$, with $a = 10.25(1)$ and $c = 7.64(2) \text{ \AA}$. The strongest lines in the powder pattern are $3.06(100)$, $2.95(30)$, $2.13(30)$, $2.03(30)$, and $1.928(30)$. The associated assemblage of witherite, quartz, and sanbornite buffers the CO_2 fugacity at metamorphic pressures and temperatures. The name is in honor of Dr. John T. Alfors of the California Division of Mines and Geology in recognition of his contributions to the study of barium minerals.

Introduction

The sanbornite deposits of eastern Fresno and Mariposa counties, California, contain many rare barium minerals, principally silicates (Rogers, 1932). The metamorphic sanbornite-quartz rock and foliated quartzite, both of which contain the new mineral, are described by Matthews and Alfors (1962), Stinson and Alfors (1963, 1964), Alfors and Putman (1964), Alfors and Stinson (1965), and by Alfors *et al.* (1965). The sanbornite rocks appear to be metasedimentary rocks, presumably meta-evaporites. The regional geology of the area is described by MacDonald (1941) and by Krauskopf (1953). All the sanbornite localities are within a few hundred meters of granodiorite intrusions and it will be assumed below that the rocks last equilibrated in a contact metamorphic event producing hornblende- and pyroxene-hornfels facies conditions at pressures of 1-3 kbar.

Alforsite was first discovered in samples from the Big Creek locality during qualitative electron microprobe analysis of what appeared in thin-section to be ordinary apatite. A distinctive reddish-violet cathodoluminescence and EDA observations showing major levels of barium, chlorine, and phosphorus were noticed in several grains selected for further

study. The phase was found to have the structural and physical characteristics of apatite, and determined to be the barium analogue of chlorapatite. As the natural phase is rare and very fine-grained even at the type locality, studies were supplemented by work on a synthetic end-member barium chlorapatite supplied by Dr. Charles Prewitt of the State University of New York at Stony Brook. Alforsite was subsequently found in samples from the Incline locality where it is, as at Big Creek, associated with fluorapatite and many barium minerals.

We have named this mineral for Dr. John T. Alfors of the California Division of Mines and Geology in recognition of his extensive studies of the type locality of the mineral and his descriptions of the other associated rare and new minerals. The name and mineral have been approved by the IMA Commission on New Minerals and New Mineral Names. Type material, designated to be that of the Big Creek locality, is preserved in the mineral collections of the University of Michigan and the National Museum of Natural History, Smithsonian Institution under catalogue number NMNH 147511.

X-ray diffraction

Single crystals of alforsite were separated by meticulously scratching exceptionally small (approximately 0.02 mm diameter) crystals from thin sections

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where it had been identified and differentiated from the more common fluorapatite using optical and electron microprobe methods. Therefore, space group and unit cell parameters were determined by standard Weissenberg and precession X-ray diffraction methods on the synthetic material. Precession photographs of the natural material, although yielding very weak reflections, duplicated those of the synthetic material, confirming that alforsite has the apatite structure. Due to the rarity of alforsite grains, powder diffraction data were also obtained using the synthetic barium chlorapatite. These data were used to refine unit cell parameters by least-squares methods. Powder diffraction data for the synthetic phase are listed in Table 1. Alforsite is hexagonal, with space group $P6_3/m$, analogous to apatite. Unit cell parameters are $a = 10.25(1)$ and $c = 7.64(2)\text{\AA}$.

Extremely long X-ray exposures of Weissenberg and precession photographs of the synthetic apatite failed to reveal the superstructure reflections which occur in X-ray photographs of pure or nearly pure chlorapatites and other members of the apatite group. If present, these reflections would indicate that the true structure is monoclinic, pseudo-hexagonal, with one a -translation doubled relative to an hexagonal unit cell (Mackie *et al.*, 1972). The synthetic alforsite shows no evidence of monoclinic character, but we cannot be absolutely sure about the natural phase.

Chemical analysis

Analyses of alforsite were made with the University of Michigan ARL-EMX electron microprobe with three wavelength-dispersive crystal spectrometers and an Ortec current digitizer to compensate for beam current fluctuations during data collection. The analyses were taken at an excitation potential of 12 kV and a specimen current of $0.02\ \mu\text{a}$ with LiF, PET and TAP crystal spectrometers. Standards used were fluorapatite for F and Ca; synthetic barium chlorapatite for Ba, Cl, and P; and strontianite for Sr. Analyses for Mn, Si, Pb, and S using synthetic Mn_2SiO_4 , SiO_2 , and PbS standards showed these appeared in minor amounts. Careful tests were made to insure that no damage to or volatilization of the sample occurred during analysis. Drift, atomic number, absorption, and fluorescence corrections were made using the program EMPADR VII (Rucklidge and Gasparrini, 1969). Analyses of the apatite from the Incline and Big Creek localities are listed in Table 2. These analyses result in formulae, calculated on the basis of $\text{O} + \text{Cl} + \text{F} = 13$, of $(\text{Ba}_{4.68}\text{Sr}_{0.19}\text{Ca}_{0.13})(\text{P}_{2.98}$

Table 1. Powder diffraction data for synthetic $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$. $\text{CuK}\alpha$ radiation, 114.6 mm diameter camera

d(Obs)	d(calcd)	hkl	I/I ₀	d(Obs)	I/I ₀
5.68	5.79	101	5	1.615	20
5.17	5.13	110	5	1.600	20
4.41	4.44	200	5	1.566	30
4.25	4.26	111	10	1.511	2
3.85	[3.84	201	5	1.477	2
	3.82	002		1.453	2
3.52	3.51	102	5	1.423	2
3.37	3.36	120	20	1.398	10
3.06	[3.07	121	100	1.366	20
	3.06	112		1.336	30
2.95	2.96	300	30	1.286	2
2.45	[2.46	130	2	1.262	2
	2.45	103		1.242	1
2.36	[2.34	131	2	1.227	2
	2.34	302		1.207	2
2.13	[2.13	401	40	1.181	2
	2.13	222		1.144	2
2.07	2.07	132	10	1.125	1
2.03	[2.04	230	30	1.107	20
	2.03	123		1.077	30
1.971	1.968	231	20	1.067	30
1.928	1.931	303	30	1.042	10
1.734	[1.730	501	5	1.026	10
	1.728	142		1.005	20
1.672	[1.674	403	5		
	1.667	331			
1.638	1.639	241	2		

$\text{Si}_{0.01}\text{O}_{11.96}(\text{Cl}_{0.99}\text{F}_{0.05})$ and $(\text{Ba}_{4.05}\text{Ca}_{0.75}\text{Sr}_{0.24}\text{Pb}_{0.03})(\text{P}_{2.94}\text{Si}_{0.01})\text{O}_{11.93}(\text{Cl}_{0.93}\text{F}_{0.14})$, respectively. The F + Cl in excess of 1.00 and the slight deficiency of Si + P is consistent with a minor $\text{CO}_3 \cdot \text{F}$ substitution for PO_4 similar to some carbonate-fluorapatites (McConnell, 1973) although deviation from the ideal formula is within the precision of the analysis for P and Cl. The ideal formula is $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ and alforsite is the barium analogue of chlorapatite.

Physical properties

Alforsite occurs as isolated small subhedral grains, generally less than 0.05 mm in diameter but rarely up to 0.2 mm. These colorless grains resemble typical fluorapatite, exhibiting low birefringence and high relief. This makes it difficult to distinguish alforsite from fluorapatite and from many of the associated high-relief barium minerals except by using the electron microprobe. Alforsite is identifiable through an intense violet fluorescence in the 10–15 kV electron beam of a luminoscope or electron microprobe. This fluorescence is more intense and redder than the violet color exhibited by other apatites, and is very distinctive. No fluorescence appears under short- or long-wavelength ultraviolet light. Alforsite is uniaxial, negative with extremely low birefringence and

Table 2. Electron microprobe analyses of alforsite

oxide wt. %	Big Creek, Fresno, Co.	Incline, Mariposa, Co.
SiO ₂	0.1	<0.05
MnO	<0.1	<0.1
CaO	4.6	0.7
SrO	2.7	2.0
BaO	67.7	>1.3
PbO	0.8	<0.1
P ₂ O ₅	22.7	21.0
Cl	3.6	3.5
F	0.7	<0.1
sum	102.6	98.9
O=F,Cl	-0.9	-0.8
sum	101.7	98.1
mole ratios*		
P	2.94	2.98
Si	0.01	<0.01
Mn	<0.01	<0.01
Ca	0.75	0.13
Sr	0.24	0.19
Ba	4.05	4.68
Pb	0.03	<0.01
Cl	0.93	0.99
F	0.14	0.05
O	11.93	11.96
%Ba ₅ (PO ₄) ₃ (Cl,F)	79	93
%Sr ₅ (PO ₄) ₃ (Cl,F)	5	4
%Ca ₅ (PO ₄) ₃ (Cl,F)	15	3
%Pb ₅ (PO ₄) ₃ (Cl,F)	1	<1

*atoms normalized to O + Cl + F = 13

high relief. The refractive indices were determined as carefully as possible on small grains removed from a thin section of the Big Creek sample and are ω , $\epsilon = 1.70(1)$. It was possible to determine the refractive indices to a higher degree of accuracy on the larger grains of the synthetic analogue using crushed grain mounts, and these are $\epsilon = 1.694(3)$, $\omega = 1.696(3)$. The density of alforsite was calculated to be 4.73(2) gm/cm³ and 4.80(2) gm/cm³ for Big Creek and Incline localities, respectively, assuming cell contents of 2 formula units and the formulae given above. The density calculated for the end-member composition is 4.83(2) gm/cm³. Since the grains of both the natural and synthetic samples are very small, surface tension effects prohibited measurement of actual density for comparison.

Occurrence

Alforsite occurs as an accessory mineral in samples from both the Incline, Mariposa County, and Big Creek, Fresno County, localities as described by Alfors, *et al.* (1965). Big Creek samples are from the sites in Section 27, Township 11 S, Range 25 E on their sketch map and were provided by Alfors. The samples from the Incline locality were obtained from the University of Michigan Mineralogical Collection and more specific information on sample sites was not available.

Alforsite is, in both cases, .05 mm or smaller grains disseminated in fine-grained metamorphic sanbornite-quartz rock. The alforsite-bearing samples are massive grey rocks with gneissic banding due primarily to segregations of quartz. In samples from Incline, prominent bands of pink gillespite occur and here alforsite is associated with sanbornite, witherite, and celsian in quartz-rich and gillespite-rich bands. Fresnoite, walstromite, tourmaline, and pyrite though less abundant are disseminated throughout the rock. The lighter grey samples from Big Creek, which contain alforsite, are quartz-rich and contain no gillespite. The alforsite and fluorapatite are scattered within different fine-grained bands which contain a high proportion of quartz and alternate with bands bearing quartz in lesser amounts. Both bands contain abundant celsian, witherite, and sanbornite with accessory, disseminated fresnoite, walstromite, tourmaline, and pyrite.

Nearly pure fluorapatite is also common in these

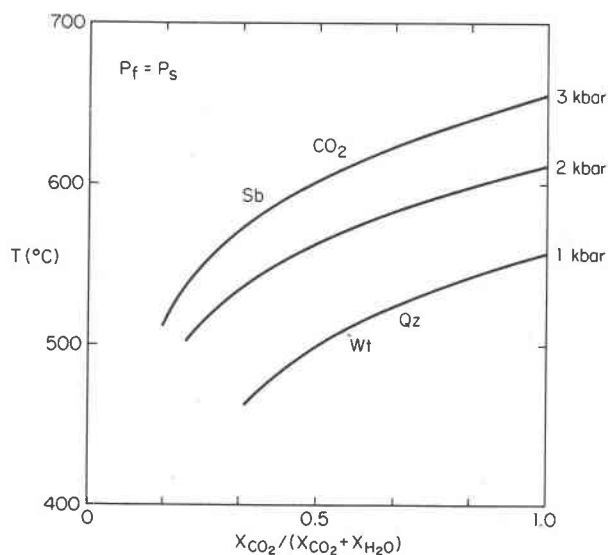


Fig. 1. Calculated decarbonation equilibria for the reaction: Witherite (Wt) + Quartz (Qz) = Sanbornite (Sb) + CO₂.

samples, perhaps suggesting a solvus gap between Ba-Cl and Ca-F end-member apatites, but more data would be necessary to evaluate this possibility. The two apatites have not been found touching one another in thin section and are generally in different bands in the rocks. The coexistence of these apatites probably reflects a difference in bulk sediment layer composition, and may not indicate a solvus gap in the system. Apatites typically form complete solid solutions between end-members, but a solvus is possible on crystal-chemical grounds as the difference in ionic radii between Ca and Ba atoms is quite large (Shannon and Prewitt, 1969).

Alforsite occurs in a univariant assemblage of sanbornite-quartz-witherite. Energy dispersive analysis of these phases indicates that they are >95% of the end-member components. CO₂ fugacity is buffered at a given *P-T* by the reaction:



Although thermodynamic data are incomplete for sanbornite, Kelley (1962) estimated ΔG_T° data for sanbornite allowing calculation of the reaction using standard thermodynamic data for the other phases (Robie *et al.*, 1978). The results are given in Figure 1 for 1, 2, and 3 kbar at variable $X_{\text{CO}_2}/(X_{\text{CO}_2} + X_{\text{H}_2\text{O}})$. No quantitative *P-T* information are available for the contact metamorphism limiting the usefulness of the calculation for determining X_{CO_2} . However, it can be seen from Figure 1 that temperatures of 500–600°C are required for the witherite-sanbornite-quartz assemblage over a wide range of X_{CO_2} . If the thermodynamic data for sanbornite are correct, adjacent wollastonite rocks (Alfors *et al.*, 1965) require higher *T* or lower X_{CO_2} (Greenwood, 1967). A more precise interpretation of the *P-T-X* data depends on more accurate geothermometry and on better thermodynamic data for sanbornite.

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