

The structure and composition of the mineral pharmacosiderite

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Dedicated to Prof. Dr. G. Menzer on the occasion of his 70th birthday

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Auszug

Eine Struktur von Pharmakosiderit wurde von ZEMANN 1947 vorgeschlagen. An einem Pharmakosiderit von Cornwall untersuchten wir die Struktur von neuem. Obwohl die starken Reflexe mit $P\bar{4}3m$ bei $a = 7,98 \text{ \AA}$ im Einklang sind, in Übereinstimmung mit ZEMANNs Ergebnissen, verlangen doch einige schwächere Reflexe eine größere Elementarzelle, was zusammen mit einer schwachen Doppelbrechung auf eine geringere Symmetrie hinweist. Wegen der Inhomogenität des Materials mußten wir uns auf die Untersuchung einer gemittelten Struktur, bezogen auf eine isometrische Zelle mit $a = 7,98 \text{ \AA}$, beschränken. Wir konnten die Struktur bis zu $R = 6\frac{1}{2}\%$ verfeinern. Unsere Untersuchung bestätigt das von ZEMANN vorgeschlagene Strukturgerüst, ändert jedoch etwas an der Ausfüllung der offenen Räume, an der keine Alkaliatome beteiligt sind. Wenn die Struktur auf die isometrische Zelle mit $a = 7,98 \text{ \AA}$ bezogen wird, so können die Wassermoleküle nur teilweise die Punktlagen besetzen, denen sie zugeordnet sind. Wir schließen daraus, daß das Pharmakosiderit-Gerüst kontinuierlich ist, das Wasser in den Hohlräumen jedoch die Symmetrie verringert, und daß sich der einheitlich erscheinende Kristall in Wirklichkeit aus Bereichen zusammensetzt, in denen die Anordnung der Wassermoleküle einheitlich ist, aber an den Bereichsgrenzen Zwillingsorientierungen aufweist.

Es wird gezeigt, daß bei Behandlung von Pharmakosiderit mit Alkalihydroxyd-Lösungen Alkaliatome in die Struktur eindringen. Wir untersuchten Pharmakosiderit, der von CsOH durchtränkt worden war, und fanden, daß die Reflexintensitäten sich am besten durch die Annahme erklären ließen, daß Cs sich in $\frac{1}{2}\frac{1}{2}0$ befindet.

Abstract

A structure for pharmacosiderite was proposed by J. ZEMANN in 1947. We have reinvestigated the structure using the Cornwall pharmacosiderite. Although all strong reflections conform to $P\bar{4}3m$ with $a = 7.98 \text{ \AA}$, in accordance with

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ZEMANN's results, some weaker reflections require a larger cell, which, taken together with the weak birefringence, indicate a lower symmetry. Because of the inhomogeneity of our material we had to limit ourselves to investigating the average structure referred to an isometric cell of $a = 7.98 \text{ \AA}$. We were able to refine this structure to $R = 6\frac{1}{2}\%$. This work confirms ZEMANN's framework but modifies the filling of its open spaces somewhat. No alkali atoms are present in the filling. If the structure is referred to an isometric cell with $a = 7.98 \text{ \AA}$, the water molecules occupy only partially the equivalent positions to which they are assigned. We conclude that, in the true pharmacosiderite structure, the framework is continuous, but that the water which fills its cavities degrades the symmetry, and that, what appears to be an individual crystal is actually composed of regions in which the arrangement of the water molecules is uniform and that the arrangements of molecules in adjacent regions are in twinned orientation.

It is shown that when pharmacosiderite is treated with alkali hydroxide solution, the alkali atoms enter the structure. We investigated pharmacosiderite which had been soaked in CsOH and found that if the Cs is placed at $\frac{1}{2}\frac{1}{2}0$ the intensities are best explained.

Background

Pharmacosiderite is a hydrated iron arsenate mineral which has been known since 1790. DANA's System¹ gives its chemical composition as $\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$, and assigns it to space group $P\bar{4}3m$ with $1\frac{1}{2}$ formula units to a unit cell whose edge is $a = 7.94 \text{ kX}$. Although the structure of this mineral has been proposed by J. ZEMANN^{2,3}, there still seems to be some doubt about its symmetry, cell and composition. In this paper we report our investigation of the structure, and give some comments on the interesting features of this mineral.

The structure proposed by ZEMANN is defined by the equipoints and parameters in Table 1. The first four atoms listed in the table comprise a skeleton framework or rigid scaffolding within whose interstices the other atoms are housed. ZEMANN's framework, illustrated in Fig. 1, has a composition which can be represented by $[\text{Fe}_4(\text{OH})_4(\text{AsO}_4)_3]^{-1}$ per cell. This consists of bulky clusters having tetrahedral symmetry and located at the cell origins, bonded together to translation-equivalent clusters in the directions of the cell axes. The clusters have composition $\text{Fe}_4(\text{OH})_4\text{O}_{12}$, and consist of four

¹ CHARLES PALACHE, HARRY BERMAN and CLIFFORD FRONDEL, The system of mineralogy of JAMES DWIGHT DANA and EDWARD SALISBURY DANA. Vol. 2, seventh edition. John Wiley, New York (1963) 995—997.

² J. ZEMANN, Über die Struktur des Pharmakosiderits. *Experientia* **3** (1947) 452.

³ J. ZEMANN, Formel und Strukturtyp des Pharmakosiderits. *Mineralog. Mitt.* **1** (1948) 1—13.

Table 1. Atom location in pharmacosiderite, from ZEMANN³

Atom	Equipoint in $P43m$	Representative coordinates	Parameters	
			x	z
Framework	Fe	$4e$.131	.375
	As	$3d$	$\frac{1}{2}00$	
	O(1)	$12i$	xxx	
	O(2) = OH	$4e$	xxx	
	O(3) = H ₂ O	$3e$	$0\frac{1}{2}\frac{1}{2}$	
	O(4) = H ₂ O	$4e$	xxx	
K	not exactly placed			

octahedra of oxygens about the iron atoms, each octahedron sharing one edge with each of the three other octahedra. These clusters are bonded together at the middle of the cell edges by As atoms. This

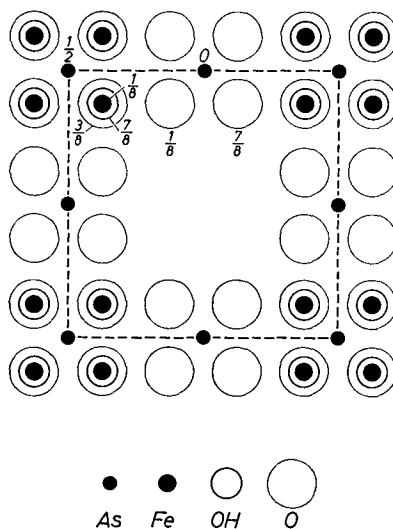


Fig. 1

scaffolding has large channels through the middles of the cell faces and parallel to the cell edges. These channels have a minimum free diameter of about 3.5 Å, which is about that found in the more open zeolites. The channels intersect at the centers of the cells where they produce large cavities. In these channels and cavities are located the water molecules indicated in Table 1, and one K atom in an unspecified location.

Our involvement with the structure of pharmacosiderite began by accident. We started to study the crystals of a mineral specimen, but after a few x-ray photographs it became evident that it had been mislabeled and that we were actually dealing with pharmacosiderite. On looking into what was known of the structure of this mineral, we found that ZEMANN³ had proposed one for it nearly twenty years ago, so we decided to at least refine his structure, and probably also settle the nature of the non-framework atoms, about which there still appeared something to be done.

New data

Symmetry and cell. Pharmacosiderite has an isometric appearance, commonly displaying a cubic or cubo-tetrahedral habit. LAUE photographs are reported^{3,4} to show symmetries consistent with an isometric crystal; if isometric, the presence of the tetrahedral form development would require class $\bar{4}3m$. On the other hand, crystals examined with the polarizing microscope show optical anomalies^{5,6} which have been ascribed to tensional origin¹. HEIDE⁵ found pharmacosiderite crystals to have a zoned structure in which the zones were marked out by different optics.

Our own examination of some crystals from Cornwall which were small enough to be suitable for structural study, confirms that they were not homogeneous, but the inhomogeneities were on such a minute scale that we were unable to break off fragments we considered homogeneous. On the other hand, the inhomogeneity consisted of differences in the very small birefringence displayed in zones and irregular areas. In this sense our single-crystal specimens were inhomogeneous, probably twinned.

We examined our material by the precession method and, if some weak spots noted later are ignored, its diffraction symbol was found to be $m3mP---$. Taken together with the tetrahedral faces present in

⁴ G. HÄGELE und F. MACHATSCHKI, Synthese des Alumopharmakosiderits; Formel und Struktur des Pharmakosiderits. Fortschr. Mineralog. **21** (1937) 77–78.

⁵ F. HEIDE, Über eine hydrothermale Paragenesis von Quarz und Arsenmineralien im veränderten Quarzporphyr vom Saubach i. V. und über einige Eigenschaften des Pharmakosiderits und des Symplesits. Z. Kristallogr. **67** (1928) 33–90.

⁶ RAYMOND HOCART, Contribution à l'étude de quelques cristaux à anomalies optiques. Bull. Soc. franç. Minéralog. **57** (1934) 5–127, especially 74–89, 124.

the form development, the space group, if isometric, would be $P\bar{4}3m$ with $a = 7.99 \text{ \AA}$. Data from a back-reflection Weissenberg photograph permitted refining this value to $a = 7.9816 \pm 0.0005 \text{ \AA}$. These results are in agreement with HÄGELE and MACHATCHKI'S⁴ value of 7.94 kX (= 7.96 Å) and ZEMANN'S³ 7.91 kX (= 7.93 Å), both based upon powder photographs, the latter determined on material, like ours, from Cornwall.

The density of the Cornwall mineral is given by DANA'S System¹ as 2.797 g/cm³. For ZEMANN'S formula, $[\text{Fe}_4(\text{OH})_4(\text{AsO}_4)_3] \text{K} \cdot 6-7\text{H}_2\text{O}$, this would³ give 1.001 formula weights for 6H₂O, or 0.980 for 7H₂O.

Careful examination of our precession photographs revealed some very weak additional reflections. The relative intensities of these reflections differed for different specimens. Referring these reflections to an isometric cell with $a = 7.98 \text{ \AA}$, they had indices described by either

$$h + \frac{1}{2} \quad k + \frac{1}{2} \quad l,$$

or

$$h + \frac{1}{2} \quad k + \frac{1}{2} \quad l + \frac{1}{2}.$$

We confirmed the existence of such fractional indices by finding a few weak reflections on rotating-crystal photographs which, based on a cell with $a = 7.98 \text{ \AA}$, would have to be indexed on layers with indices $l + \frac{1}{2}$.

The additional reflections show less-than-isometric symmetry and strong evidences of twinning. They thus confirm what was suggested by the birefringence: that pharmacosiderite is not truly isometric. Accordingly, with the inhomogeneous, probably twinned, material at our disposal, we could only hope to investigate the average structure of pharmacosiderite, that is, the structure of a set of subcells whose contents are all translated to a single subcell whose symmetry is isometric and whose edge is $a = 7.98 \text{ \AA}$.

Intensity measurement. For measurement of the diffracted intensities we chose a small specimen of approximately cubic shape having edge dimensions of about 0.17 mm. Our measurements were made with an automated single-crystal diffractometer based upon equi-inclination geometry. Filtered Cu radiation was used, and the diffracted intensities were collected with an argon-filled proportional counter. For each measurement the photons were counted as the crystal was rotated through the orientation for reflection; this count was corrected by subtracting an average background as determined

by a fixed-time count in an orientation just before and just after collecting the reflection. The intensities so determined were corrected for Lorentz-polarization factors, and also for absorption by the specimen. The absorption correction was carried out with the aid of a computer program written by CHARLES W. BURNHAM.

Since all our material was somewhat inhomogeneous, and since our crystal showed an optical departure from pure isometric symmetry, we were forced to treat the crystal as an isometric average structure. Accordingly, we collected 567 intensity data corresponding to an octant of reciprocal space. From this larger set, reflections symmetrical by $P\bar{4}3m$ were averaged to produce a set of isometric averaged intensities. There are 128 reflections in this set, all of which were measured as nonzero.

Preliminary structure examination

Our study of the literature and abstracting sources gave us the impression that the heavy atoms of the scaffolding of ZEMANN's structure were probably correctly placed, but that there was some doubt about the locations of the atoms filling the interstices of the framework, and possibly of the oxygen atoms of the framework. Accordingly we began by computing structure factors for the reflections but based only on the 4 Fe and 3 As atoms of the framework. For our observed $|F|$'s these gave a discrepancy of $R = 30\%$.

We computed a difference electron density based upon the phases determined by the 4 Fe and 3 As atoms in the framework, and using as ΔF the difference between observed F and that expected due to 4 Fe + 3 As. This Fourier synthesis returned the original 4 Fe and 3 As atoms and, in addition, the oxygen atoms of ZEMANN's framework and the water oxygen O(4). The water oxygen O(3), however, which ZEMANN had placed in $3c$ at $0\frac{1}{2}\frac{1}{2}$, appeared separated into the $6g$ positions at $\pm x\frac{1}{2}\frac{1}{2}$ with $x \approx .07$. The short distance between split atoms precludes full occupancy of the two separated parts, and on the basis of the height of the peak in the difference Fourier, a partial occupancy of 0.5 was assigned this atom. No alkali atom was found, and, in particular, there was no K atom in either of the two possible one-fold positions, $1a$ and $1b$ of $P\bar{4}3m$.

Since we could not find any indication of an alkali atom in the difference map, and since absence of such an atom would appear to leave the composition of pharmacosiderite with a net negative charge, we felt it desirable to check the absence of alkali by an independent

method. A spectroscopic analysis, however, confirmed our finding; only traces of alkali were indicated.

A structure-factor calculation incorporating these changes resulted in an R value of 22%. Least-squares refinement was then begun; by allowing ZEMANN's parameters and isotropic temperature factors to vary, the R value was reduced to 12%. During the refinement the temperature factor of O(4) (representing the water molecule near the cell center) became anomalously large ($> 10 \text{ \AA}^2$), suggesting that this equipoint also was only partially occupied. An attempt to refine the occupancy of O(4) failed due to the high correlation between this parameter and the atomic temperature factor (about 0.8). As a result, O(4) was arbitrarily assigned an occupancy of $\frac{1}{2}$ atom per average cell in order to reduce its temperature factor to a credible value. In addition, since there is considerable anomalous dispersion of $\text{CuK}\alpha$ radiation by both arsenic and iron, this effect was incorporated in the refinement program. With these changes, and maintaining isotropic temperature factors, continued refinement brought the R value down to 6.6%. The parameters of this final model and their standard deviations are listed in Table 2. In Fig. 2 is shown the electron density of the framework of this structure. Table 3 shows the agreement between the observed and computed F 's.

To obtain a more detailed picture of the distribution of water molecules in the channels, a difference Fourier synthesis was made using as coefficients the difference between the observed F 's and those calculated for the framework atoms only. The result is added in broken contour lines to Fig. 2. This clearly displays the statistical

Table 2. *Final positional and thermal parameters of the atoms in the Cornwall pharmacosiderite, described as an average structure based on an isometric cell with $a = 7.98 \text{ \AA}$*

Atom	Equipoint in $P\bar{4}3m$	Fraction of site occupied	Repre- senta- tive coordi- nates	Parameters		
				x	z	B
Fe	$4e$	} Frame- work	xxx	$.1426 \pm .0007$	$.3787 \pm .0022$	$1.1 \pm 0.2 \text{ \AA}^2$
As	$3d$		$\frac{1}{2}00$			1.5 ± 0.1
O(1)	$12i$		xxz	$.1223 \pm .0015$		1.8 ± 0.3
O(2)	$4e$		xxx	$.8847 \pm .0027$		1.2 ± 0.8
O(3) = H_2O	$6g$	$\frac{1}{2}$	$x\frac{1}{2}\frac{1}{2}$	$.068 \pm .005$		3.3 ± 1.0
O(4) = H_2O	$4e$	$\frac{1}{2}$	xxx	$.694 \pm .005$		2.5 ± 1.3

distribution of channel waters O(3) and O(4). It is evident that O(3) is continuously distributed along the channel in the neighborhood of $x = 0$. Thus the model of Table 2, which has two half-molecules of water at $x_{\frac{1}{2}}$ and $\bar{x}_{\frac{1}{2}}$, is only an approximation to the apparent distribution, and is only a slightly better approximation than ZEMANN's model, in which the distribution is represented by a single water molecule at $x = 0$. The heights of the peaks corresponding to the

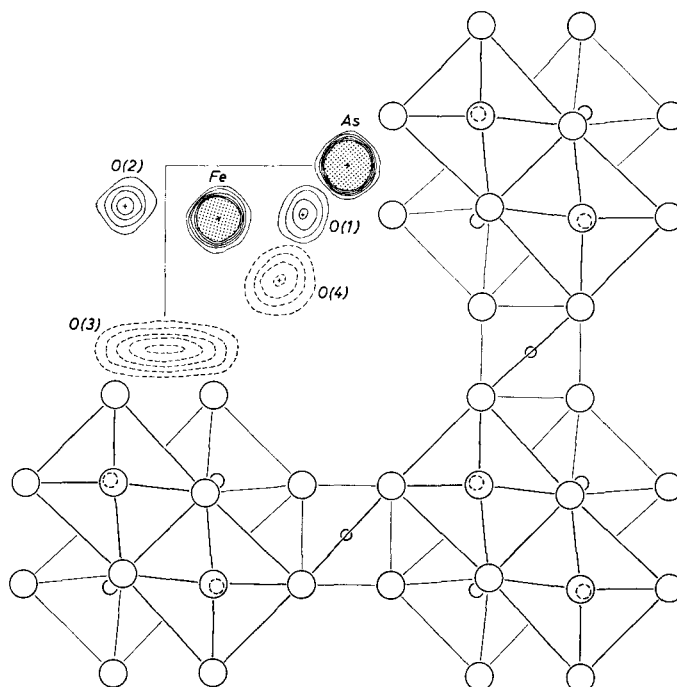


Fig. 2

water molecules, when compared with other features in the final electron-density map, are consistent with their assigned occupancies of $\frac{1}{2}$.

As can be appreciated from a comparison of Tables 1 and 2, our refined coordinates do not differ greatly from those of ZEMANN, and thus the general geometry of his proposed structure is confirmed. Table 4 lists the pertinent interatomic distances, angles, and their estimated standard deviations. The distances involving O(3) take into account its apparent disordered distribution in the channels at $x_{\frac{1}{2}}$, $x \approx -0.1$ to $+0.1$.

Table 3
Comparison of observed and calculated F 's for the Cornwall pharmacosiderite

$h k l$	F_o	F_c	$h k l$	F_o	F_c
1 0 0	*		5 5 0	*	
2 0 0	75.56	83.55	6 5 0	6.43	7.89
3 0 0	80.78	80.85	7 5 0	19.37	16.24
4 0 0	65.70	64.67	8 5 0	3.80	2.03
5 0 0	36.19	33.45			
6 0 0	84.14	80.12	6 6 0	45.89	45.02
7 0 0	62.58	64.10	7 6 0	23.14	25.42
8 0 0	87.97	81.99			
9 0 0	9.35	11.36	1 1 1	80.89	82.95
			2 1 1	86.53	73.40
1 1 0	15.29	5.95	3 1 1	87.68	87.71
2 1 0	24.68	18.38	4 1 1	63.47	62.84
3 1 0	73.00	76.01	5 1 1	67.14	70.74
4 1 0	45.72	45.74	6 1 1	29.55	28.71
5 1 0	26.63	26.26	7 1 1	29.70	31.30
6 1 0	32.54	33.08	8 1 1	18.81	14.66
7 1 0	13.38	13.56	9 1 1	36.22	36.22
8 1 0	36.68	36.69			
9 1 0	17.34	11.15	2 2 1	44.29	40.95
			3 2 1	23.06	23.66
2 2 0	108.16	107.32	4 2 1	36.53	34.02
3 2 0	17.82	23.96	5 2 1	52.71	51.34
4 2 0	80.13	79.10	6 2 1	17.66	18.32
5 2 0	14.81	18.21	7 2 1	20.62	17.51
6 2 0	42.92	40.93	8 2 1	30.23	27.88
7 2 0	6.41	1.69	9 2 1	22.02	20.47
8 2 0	33.77	32.48			
9 2 0	5.68	9.32	3 3 1	42.28	41.76
			4 3 1	17.64	13.66
3 3 0	37.17	41.60	5 3 1	58.06	59.40
4 3 0	88.18	88.10	6 3 1	30.14	36.88
5 3 0	8.85	8.00	7 3 1	53.42	53.37
6 3 0	8.17	7.52	8 3 1	23.47	24.42
7 3 0	46.61	42.65	9 3 1	19.85	19.58
8 3 0	16.28	17.33			
9 3 0	6.19	3.27	4 4 1	69.35	67.50
			5 4 1	17.01	16.61
4 4 0	143.94	150.12	6 4 1	20.60	20.03
5 4 0	34.59	38.95	7 4 1	33.26	30.39
6 4 0	27.32	24.49	8 4 1	7.39	10.51
7 4 0	32.58	29.54			
8 4 0	7.87	10.24	5 5 1	51.17	53.66
			6 5 1	23.14	24.64
			7 5 1	30.86	31.62
			8 5 1	22.15	23.57

Table 3. (Continued)

<i>h k l</i>	F_o	F_c	<i>h k l</i>	F_o	F_c
6 6 1	28.52	25.99	3 3 3	92.34	87.86
7 6 1	5.17	2.49	4 3 3	53.40	56.92
			5 3 3	50.81	54.05
2 2 2	100.29	93.75	6 3 3	10.55	9.57
3 2 2	28.52	25.35	7 3 3	12.83	14.50
4 2 2	66.71	68.47	8 3 3	10.38	3.84
5 2 2	35.95	36.13			
6 2 2	42.56	39.77	4 4 3	33.86	32.03
7 2 2	14.06	16.39	5 4 3	22.71	22.96
8 2 2	49.44	47.31	6 4 3	30.91	31.27
9 2 2	24.35	25.96	7 4 3	13.77	15.91
			8 4 3	29.31	28.63
3 3 2	39.81	36.40			
4 3 2	20.08	16.07	5 5 3	34.25	36.37
5 3 2	25.75	26.63	6 5 3	10.68	12.26
6 3 2	16.39	15.14	7 5 3	26.54	27.61
7 3 2	6.55	4.66			
8 3 2	22.00	21.33	6 6 3	3.65	4.98
9 3 2	14.46	13.67	7 6 3	22.36	21.65
4 4 2	48.69	48.62	4 4 4	23.04	25.10
5 4 2	27.57	26.02	5 4 4	11.44	10.54
6 4 2	48.03	47.96	6 4 4	41.99	43.72
7 4 2	13.73	15.22	7 4 4	36.08	39.09
8 4 2	29.60	28.40			
			5 5 4	19.32	21.80
5 5 2	35.99	38.79	6 5 4	15.50	15.45
6 5 2	26.13	27.74	7 5 4	5.84	3.22
7 5 2	10.37	5.43			
8 5 2	23.87	21.35	5 5 5	46.19	50.37
			6 5 5	26.40	25.91
6 6 2	33.02	32.76			
7 6 2	7.46	9.28			

* Not measured.

Discussion of the structure

For the atoms listed in Table 2, the formula for pharmacosiderite would be $\text{Fe}_4\text{As}_3\text{O}_{16} \cdot 5\text{H}_2\text{O}$. HEIDE⁵ gives the water content as about $14\frac{1}{2}$ weight per cent, which would correspond to 6 or 7 water molecules per formula. This discrepancy may be due to a different degree of hydration of the channels in different specimens, or, since our water

Table 4. *Interatomic distances and bond angles in pharmacosiderite*

<i>Metal—oxygen</i>					
	distance	σ			
As — O (1)	1.69 Å	.01			
Fe — O (1)	1.90	.02			
Fe — O (2)	2.08	.02			
<i>Metal—metal</i>					
Fe — Fe	3.22 Å	.01			
Fe — As	3.28	.01			
<i>Oxygen—oxygen ($\sigma = .04$)</i>					
	O (1)	O (2)	O (3)	O (4)	
Framework	{ O (1)	2.89 Å	2.83 Å	> 3.17 Å	3.26 Å
	{ O (2)		2.60	> 4	2.63
	O (3)			—	2.85–2.95
	O (4)				4.38
<i>Bond angles ($\sigma = 1^\circ$)</i>					
O (1) — As — O (1)'	110°		Fe — O (1) — As	132°	
O (1) — As — O (1)''	109°		Fe — O (2) — Fe	101°	
O (2) — Fe — O (2)	77°				
O (1) — Fe — O (1)'	99°				
O (1) — Fe — O (2)	91°				
O (1) — Fe — O (2)'	165°				

occupancy was determined essentially by a criterion of reasonable temperature factors, a higher water content is possible if one accepts higher temperature factors. From Table 4 it can be seen that the individual O(4) water molecules are too widely separated to be hydrogen-bonded to each other, but are probably bonded to the O(2) oxygen atoms of the framework by relatively strong hydrogen bonds. The O(3) water molecules appear to be too far from the framework to be bonded to it, but are probably weakly bonded to O(4) water molecules.

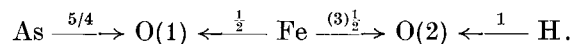
If the highest normal valence states are assigned to the remaining atoms, which form the framework, a net charge deficit of +5 results. HEIDE⁵ gives an additional weight loss, above the "zeolitic" dehydration, corresponding presumably to 4 or 5 hydroxyl hydrogen atoms, which would balance the charge in the case of 5 hydrogen atoms, or leave a deficit of +1 if there are four hydrogen atoms. Unfortunately

the light hydrogen atoms were not located in either ZEMANN's or our study. In his model, ZEMANN assumes that there are four additional hydrogen atoms, and that they are bound as hydroxyls to O(2), and that the remaining charge of $+1$ is contributed by a K atom which occurs at an unspecified location in the channels.

If the hydrogen atoms are not to be disordered, and if a normal O(2)—H bond (1 Å) is assumed, this choice of a hydrogen position corresponds to placing it in a $4e$ position at xxx , with $x = .812$. Such a location appears very reasonable in that:

- (1) It gives oxygen O(2) an almost exact tetrahedral coordination.
- (2) It provides the hydrogen for a linear O(2)—H \cdots O(4) bond whose length is consistent with an hydroxyl nature for O(2).
- (3) It leads to an almost exact local charge balance on both O(2) and O(1).

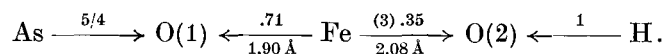
This achievement of local charge balance brings out several interesting features of this structure and thus is worth considering in more detail. If the Fe were exactly in the center of its coordinating octahedron we could represent the electrostatic-valence bonds schematically as



In this case the bond strength reaching O(1) is 1.75, while that reaching O(2) is 2.5, as opposed to the expected bond strengths to these oxygen atoms of 2. To compensate for this it appears that the iron atom is displaced towards O(1) and away from O(2). The resulting asymmetric bond-strength contributions by the iron atom may be recalculated taking into account the bond distances by means of PAULING's formula,

$$n = e^{(D_1 - D_n)/0.26},$$

where n is the bond order, and D_1 and D_n are the ideal single-bond distance and the observed bond distance, respectively. If D_1 is taken as the mean Fe—O distance found in pharmacosiderite, the observed bonding may then be schematically represented as;



This scheme gives total bond strengths to the oxygen atoms of 1.96 for O(1) and ~ 2.06 for O(2) which are fair approximations to 2; nevertheless this scheme should not be taken too literally since it ignores the net charge on the iron atom, the shorter-than-expected As—O distance,

and the effects of long hydrogen bonds to and from the channel water molecules.

In regard to the remaining imbalance of charge, our investigation shows that there is no more than a trace of potassium or other alkali metal, at least in our specimens. Early workers also reported that some, but not all, pharmacosiderites showed no more than traces of alkali metals^{7,5}. These same investigators, and others also, noted remarkable color changes from green to red, and back to green, when pharmacosiderite fragments were treated with basic and then acidic solutions. These changes in color probably represent sorption of alkali-metal cations from basic solutions, and exchange of these for hydrogen ions (or hydronium ions) in acidic solutions. If so, the charge in our pharmacosiderite could be balanced by an (as yet, unlocated) hydrogen ion.

It is interesting that, in the charge-balance calculations, it was unnecessary to account for the "remaining" charge, that is for the K^+ of ZEMANN, or our proposed H^+ . This is equivalent to saying that this formal charge appears to be dispersed over the atoms of the framework rather than localized, and this may account for the ease of exchange in solution that has been noted.

Cesium-exchanged pharmacosiderite

To substantiate the contention of base exchange and, if possible, to subsequently locate the exchanged heavy atom, we treated a sample of the natural green pharmacosiderite from Cornwall with an aqueous solution of CsOH at room temperature. We noted a relatively rapid color change of the crystals to a brilliant red within a day's time, and there was no further change apparent even with crystals kept in such solutions for up to six months. The red crystals remained weakly birefringent.

Several of these red crystals were examined by single-crystal x-ray methods. It was found that the treatment with CsOH had caused no loss of crystallinity. The diffraction patterns of these crystals were generally similar to those of the untreated pharmacosiderite. Within the error of measurement of precession films, the cell edges of both types of crystal were identical. On close examination, however, individual reflections were seen to have markedly different intensities, and indeed the violation of FRIEDEL's law due to anomalous dispersion

⁷ E. G. J. HARTLEY, Ueber die Zusammensetzung der natürlichen Arsenate und Phosphate. *Z. Kristallogr.* **32** (1900) 220—226.

with Cu radiation was very much more obvious in the case of the treated crystals. Since Cs has an imaginary scattering component of 8 electrons, we can conclude that the treated crystals contain at least some Cs. Accordingly we refer hereafter to the red, treated compound, as Cs pharmacosiderite.

Careful examination of photographs of Cs pharmacosiderite made with long exposures failed to reveal any of the extra reflections found in the natural pharmacosiderite, although it should be noted that the background was higher in the case of the Cs pharmacosiderite, which would make the detection of such weak reflections even more difficult. Furthermore, in spite of the birefringence, the photographs of the Cs pharmacosiderite showed no obvious departure from $\bar{4}3m$ symmetry. We were thus forced to deal with the structure of Cs pharmacosiderite by using the same isometric averaging approximations as with the natural pharmacosiderite structure.

Location of the cesium

The independent $hk0$ reflections of a Cs pharmacosiderite crystal were measured under the same experimental conditions as outlined above. After the usual corrections, the 40 total F 's were compared with those calculated from the framework of the natural pharmacosiderite model. The agreement, in terms of the usual R value, was 40%, which indicated the magnitude of the change of diffraction pattern due to treatment with CsOH.

On the basis of the charge-balance arguments given above, there would be one Cs atom per unit cell. Trial structure-factor calculations were made for a structure in which this one atom was placed at the only one-fold position in the channels, namely in $1b$ at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. For this placement the R value dropped only to 29%. A second trial was made in which one Cs atom was divided among the positions of next greater multiplicity, that is with $\frac{1}{3}$ Cs occupying each of the $3c$ positions at $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, and $0\frac{1}{2}\frac{1}{2}$. The R value for this model was 18%. The R value of neither trial model could be improved by adding water molecules to the channels. Any further trials with the Cs atom in the channels would require splitting this atom into six or more parts, and this was not attempted.

The observed F 's and those calculated for the model of best agreement are listed in Table 5. Because of the failure to bring the disagreement of calculated and observed F 's below 18%, this model cannot be considered as more than a rough approximation, although

Table 5. Comparison of observed and calculated F 's for Cs pharmacosiderite

$h k l$	F_o	F_c	$h k l$	F_o	F_c
1 0 0	*		6 0 0	1030	936
1 1 0	*		6 1 0	230	180
			6 2 0	687	617
2 0 0	1184	1187	6 3 0	110	167
2 1 0	62	49	6 4 0	437	423
2 2 0	1282	1222	6 5 0	0	29
			6 6 0	440	564
3 0 0	887	906			
3 1 0	679	710	7 0 0	370	499
3 2 0	93	162	7 1 0	*	
3 3 0	242	223	7 2 0	156	48
			7 3 0	378	457
4 0 0	276	266	7 4 0	413	315
4 1 0	528	555	7 5 0	119	190
4 2 0	920	1016	7 6 0	91	172
4 3 0	489	654			
4 4 0	1173	1598	8 0 0	1055	920
			8 1 0	364	238
5 0 0	571	297	8 2 0	500	438
5 1 0	327	335	8 3 0	194	202
5 2 0	74	54	8 4 0	0	66
5 3 0	0	114	8 5 0	106	81
5 4 0	162	276			
5 5 0	*		9 0 0	80	69
			9 1 0	79	140
			9 2 0	68	45
			9 3 0	45	67

* Not measured.

it should be noted that this particular Cs location leads to an acceptable Cs—O distance of about 3.3 Å, which is about the same as that found in rhodizite⁸, namely 3.24 Å.

Conclusions

We feel that we have carried our investigation of the structure of pharmacosiderite as far as can be justified by the study of the inhomogeneous material at our disposal. Because of the small scale of the inhomogeneity, which appeared to consist of both twinning and zoning, we were forced to treat our birefringent material as

⁸ MARTIN J. BUERGER and KARLHEINZ TAXER, Rhodizite, structure and composition. *Science* **151** (1966) 500–502.

isometric, and its cell as if it did not show faint evidence of a multiple volume. We therefore had to study the average structure of a non-isometric crystal as if it were isometric.

In spite of this drawback, we have been able to advance our understanding of pharmacosiderite somewhat. We have confirmed ZEMANN's general structure proposal and, with minor modifications, refined its average structure to about $6\frac{1}{2}\%$. ZEMANN's framework is certainly correct. Table 2 shows that the atoms of the framework have higher temperature coefficients than the ordinary dense inorganic structures. This is not surprising, for high temperature coefficients are known to occur in other framework structures such as the zeolites. Nevertheless, the possibility should not be overlooked that, since the symmetry of pharmacosiderite is not isometric, the framework may not be as ideal as it appears in the average structure, and that parts of it may depart from true translation equivalence within our inhomogeneous sample, thus giving rise to what appears in the structure as slight disorder, and in the refinement as high temperature coefficients.

In spite of possible small distortions, the framework is essentially isometric, and its continuity throughout the crystal and across inhomogeneities is responsible for the pseudo-isometric character of pharmacosiderite. We believe that the departure of pharmacosiderite from isometric symmetry is to be accounted for by the distribution of atoms in the open spaces of the framework. The key to this is to be found in the water oxygen atoms, O(3) and O(4), which have only fractional occupancy when referred to the 7.98 Å isometric cell. The true cell, which has some lower symmetry⁹, must be made up of several subcells, the average of which is our pseudoisometric cell. Within the true cell the several component subcells may differ in respect to the number and position of the O(3) and O(4) atoms each contains. On the basis of the optics it is known that regions large enough to be visible with the polarizing microscope are homogeneous, and so correspond to true single crystals. Adjacent regions are known to be in twinned orientation. Across these twin boundaries the framework is continuous, and only the arrangement of water molecules presumably changes.

In addition to these regions which differ in orientation, pharmacosiderite also contains regions which correspond to zoning. This

⁹ Early optical studies suggested monoclinic symmetry^{5,6}.

kind of inhomogeneity almost certainly is caused by changes in composition, most probably of the channel fillings rather than of the framework.

From the discussion given it appears obvious that if the detailed arrangement of the atoms filling the framework of the pharmacosiderite structure is to be found, the experimental work must be based upon optically homogeneous crystals. Such further study is quite worthwhile, for it should settle the details of the hydrogen bonding among the oxygen atoms within the open spaces of the framework, and incidentally cast light on the charge balance within the framework.

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