THE CRYSTAL STRUCTURE OF CERVANDONITE-(Ce), AN INTERESTING EXAMPLE OF As³⁺ → Si DIADOCHY

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ABSTRACT

Cervandonite-(Ce), a unique arsenosilicate from Alpine fissures at Pizzo Cervandone (Scherbadung) in the Central Alps between the Binn Valley (CH) and Ossola (I), has proven to be a problem in view of the extreme scarcity of single crystals suitable for the determination of its complex structure. The monoclinic supercell (Z = 6) originally described by the discoverers is confirmed; we have established the crystal structure of a trigonal subcell, with space group $R3m$ and a 6.508(1), c 18.520(3) Å, V 679.4(2) Å³ and Z = 3, to a final R(F) = 0.0380 for 441 observed independent reflections [$I > 2\sigma(I)$]. The mechanism of the very unusual As³⁺ → Si (not As⁵⁺ → Si) diadochy is accounted for by considering the presence in two different sites of sorosilicate anions $Si_2O_7^{6-}$, which are statistically replaced by arsenite [AsO_3^{3-}] anions and minor amounts of OH⁻; the positions of the oxygen atoms common to these anions are the same. The asymmetric unit also contains one eight-coordinated atomic site occupied by Ce and other REE lying on the three-fold axis; a bipyramidal six-coordinated site (of symmetry .m) occupied by Fe, Ti, or Al also is present. The originally proposed chemical formula $(Ce,Nd,La)(Fe^{3+},Fe^{2+},Ti^{4+},Al)_3SiAs(Si,As)O_{13}$ is accordingly revised to $(Ce,Nd,La)(Fe^{3+},Fe^{2+},Ti^{4+},Al)_3O_2(Si_2O_7)_{1-x+y}(AsO_3)_{1+x-y}(OH)_{3x-3y}$, where x and y are 0.47 and 0.31, respectively, in the sample here examined.

Keywords: cervandonite-(Ce), crystal structure, arsenites, arsenosilicates, As³⁺ → Si diadochy, Alpine minerals, Cervandone, Scherbadung, Binn Valley, Switzerland, Ossola, Italy.

SOMMAIRE

La cervandonite-(Ce), arsenosilicate unique provenant des fissures alpines à Pizzo Cervandone (Scherbadung) dans les Alpes centrales entre la vallée de Binn (CH) et Ossola (I), s'est avérée un problème à cause de l'extrême rareté de monocristaux convenables à la détermination des complexités de sa structure. Nous pouvons confirmer la supermaille monoclinique (Z = 6) décrite par ceux qui ont découvert l'espèce; aussi, nous avons pu établir la structure de la sous-maille trigonale, dans le groupe spatial $R3m$, avec a 6.508(1), c 18.520(3) Å, V 679.4(2) Å³ et Z = 3, jusqu'à un résidu final R(F) de 0.0380 pour 441 réflexions indépendantes observées [$I > 2\sigma(I)$]. Le mécanisme de la substitution très inhabituelle de As³⁺ (et non de As⁵⁺) au Si s'explique en considérant la présence de deux sites distincts des anions de groupes sorosilicatés $Si_2O_7^{6-}$, qui sont statistiquement remplacés par des groupes arsenite [AsO_3^{3-}] et des quantités mineures de OH⁻; les positions des atomes d'oxygène communs à ces anions sont les mêmes. L'unité assymétrique contient aussi un site à coordinence huit où logent le Ce et les autres terres rares, sur un axe de rotation 3; un site bipyramidal à coordinence six (de symétrie .m) contenant Fe, Ti, ou Al est aussi présent. La formule chimique proposée antérieurement, $(Ce,Nd,La)(Fe^{3+},Fe^{2+},Ti^{4+},Al)_3SiAs(Si,As)O_{13}$, se voit donc révisée pour lire $(Ce,Nd,La)(Fe^{3+},Fe^{2+},Ti^{4+},Al)_3O_2(Si_2O_7)_{1-x+y}(AsO_3)_{1+x-y}(OH)_{3x-3y}$, dans laquelle x et y sont 0.47 et 0.31, respectivement, dans l'échantillon examiné ici.

(Traduit par la Rédaction)

Mots-clés: cervandonite-(Ce), structure cristalline, arsenites, arsenosilicates, substitution As³⁺ → Si, minéraux alpins, Cervandone, Scherbadung, vallée de Binn, Suisse, Ossola, Italie.

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INTRODUCTION

Cervandonite-(Ce), an arsenosilicate from Alpine fissures first described by Armbruster *et al.* (1988), was discovered in the two-mica gneisses of the Monte Leone Nappe at Pizzo Cervandone or Scherbadung, from which the species took its name. This mountain is well known to both Alpine excursionists and mineral collectors, and is situated on the Italian–Swiss border between the Binn Valley in Wallis (Valais) (CH) and Val Devero in Ossola (I). In the area, there are other world-famous localities, such as for instance that at Lengenbach, Switzerland. Since 1965, a series of interesting arsenic-containing minerals, some of which are entirely new or at least new for the Alps, have been discovered in such gneisses (Graeser 1965, 1966, Graeser *et al.* 1973, 1994, Graeser & Roggiani 1976, Graeser & Schwander 1987, Demartin *et al.* 1994, Krzemnicki & Reusser 1998). Cervandonite-(Ce), a very unusual mineral and one of the latest discoveries, had long been overlooked because of its appearance, which led to easy confusion at first sight with hematite or other oxides. This mineral is especially interesting because of the very unusual replacement of silicon by arsenic, which was already noted by Armbruster *et al.* (1988), who proposed the formula (Ce,Nd,La)$(Fe^{3+},Fe^{2+},Ti^{4+},Al)_3SiAs(Si,As)O_{13}$, with arsenic in the 5+ state. However, the lack of suitable crystals prevented the possibility of documenting the details of such As $\rightarrow$ Si substitution using X-ray diffraction data. This situation has now been remedied.

STRUCTURE DETERMINATION

A single-crystal fragment of type cervandonite-(Ce) measuring $0.08 \times 0.03 \times 0.02$ mm afforded a promising diffraction pattern with a precession camera (Graeser 1989: specimen #S101, Cervandone/I). The same fragment was re-examined with MoKα radiation ($\lambda = 0.71073$ Å) using a BRUKER Apex II diffractometer equipped with a 2K CCD detector. A one-minute frame-time and 0.3° frame width were used. A complete Ewald sphere up to $2\theta = 57.74°$ was measured, resulting in a total of 1963 reflections. Using 1130 of these reflections with $I > 5\sigma$, a monoclinic cell with *a* 11.289(4), *b* 6.514(2), *c* 7.238(3) Å, β 121.36(1)°, *V* 454.5(5) Å^3, *Z* = 2 was obtained. If our value of *b* is tripled, these parameters closely correspond to those of the supercell defined by Armbruster *et al.* (1988) (*a* 11.3, *b* 19.5, *c* 7.2 Å, β 121°, *Z* = 6). The very weak supercell reflections were also observed by us, but after having attempted to use them in the structure determination without significant results, we decided not to consider such data in this work.

Our monoclinic subcell can be transformed into a trigonal *R*-centered cell, with *a* 6.508(1), *c* 18.520(3) Å, *V* 679.4(2) Å^3, and *Z* = 3 using the transformation matrix [0 $\bar{1}$ 0 / ½ ½ 0 / 1 0 3]. The transformation matrix from our rhombohedral cell to the supercell of Armbruster *et al.* (1988) is: [1 2 0 / $\bar{3}$ 0 0 / $\overline{1/3}$ $\overline{2/3}$ $^1/_3$]. In Table 1, the X-ray powder-diffraction patterns from two additional samples (P5757 and P4300, in the collection of Naturhistorisches Museum, Basel) are reported. The unit-cell values derived from a least-squares fit according to the approach of Holland & Redfern (1997) show minor but significant differences, very probably related to the variable composition.

After a multi-scan absorption correction using the SADABS program (Sheldrick 2000), a comparison of the possible equivalent reflections in the Ewald sphere gave R$_{int}$ in the range 0.034–0.035 for the following space-groups: *R*3, *R*$\bar{3}$, *R*3*m*, *R*32 and *R*$\bar{3}$*m*. The distribution of *E*-values suggested the mineral to be non-centrosymmetric ($E^2 - 1 = 0.702$), and the structure solution has shown the attribution to the non-chiral *R*3*m* group to be correct. The structure was solved by direct methods with SIR97 (Altomare *et al.* 1999) and refined with the SHELXL97 program (Sheldrick 1997) implemented in the WINGX suite (Farrugia 1999). A total of 441 reflections with $I > 2\sigma(I)$ were used for the structure refinement. Since the structure solution had indicated that even the crystal used was a "racemic" twin, a [$\bar{1}$ 0 0 / 0 $\bar{1}$ 0 / 0 0 $\bar{1}$] twin matrix was applied, and the relative percentage of the twins was refined [to 0.62(5) : 0.38(5)]. On applying the program PLATON (ADDSYM module) (Le Page 1987, 1988) after the final refinement, no obvious additional symmetry was suggested. Further details concerning the data collection and refinement are reported in Table 2.

The possibility for the real symmetry of the subcell to be monoclinic was also considered by solving the crystal structure anew in the monoclinic system, space group *Cm* (a subgroup of *R*3*m*). The result was practically the same as that obtained in the trigonal case, including the As–Si disorder, and the R factor was not significantly lowered.

The solution of the structure immediately revealed the presence of one eight-coordinated REE-containing site *M*(1) lying on the threefold axis (Wyckoff position *a* of symmetry *3m*); a bipyramidal six-coordinated site *M*(2) (Wyckoff position *b* of symmetry .*m*) containing Fe, Ti, or Al, was also evident. The other most intense peaks were less straightforward to interpret, and can be referred to partly overlapping As and Si atoms belonging to disordered sorosilicate and arsenite groups (see below). The partial disorder might also account for the weak superstructure reflections. Owing to this situation and considering steric hindrance (see Fig. 1), the following constraints relative to site populations *m* were introduced in the least-squares refinement:

a) *m* As(1) = 1–*m* Si(1) = *x*
b) *m* Si(2) = *m* Si(1) = 1–*x*
c) *m* Si(3) = *m* Si(4) = *y*
d) *m* As(2) = 1–*m* Si(4) = 1–*y*
e) *m* O(6) = *m* Si(1) = *m* Si(2) = 1–*x*
f) *m* O(7) = *m* Si(3) = *m* Si(4) = *y*

FIG. 1. A view of the two disordered orientations of the anions. The Si–O bonds in the Si_2O_7 group are shown in light gray, the As^{3+}–O bonds are represented in black. The bonds in the prevailing orientation are represented as solid lines.
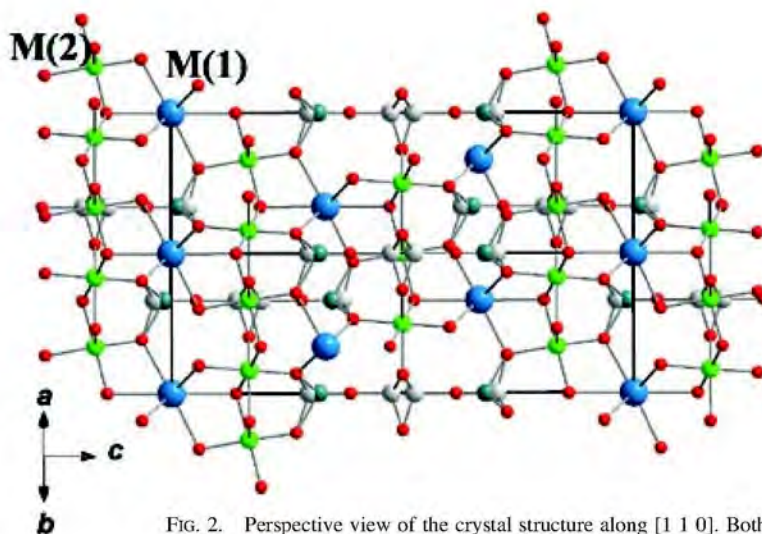

FIG. 2. Perspective view of the crystal structure along [1 1 0]. Both the disordered orientations of the anions are represented; the pseudo-centrosymmetric arrangement of atoms is evident. The $M(1)$ sites are represented in blue, the $M(2)$ sites in green, the silicon atoms in light gray, the arsenic atoms in blue-gray ("teal"), and the oxygen atoms in red.
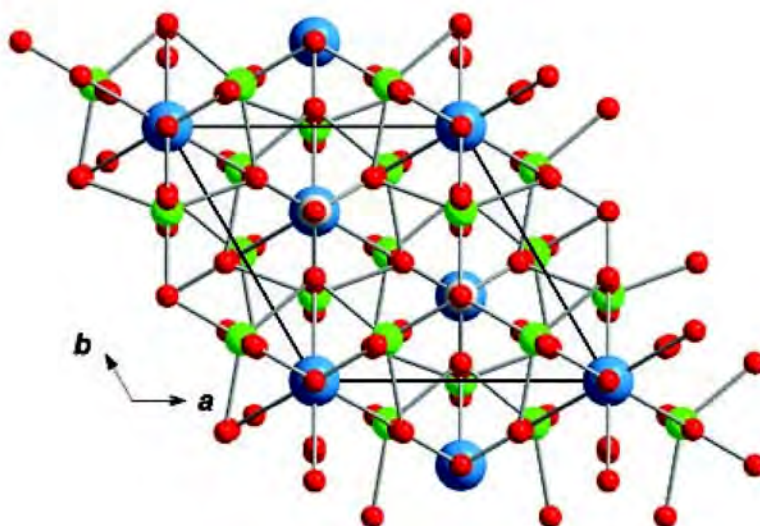

FIG. 3. Perspective view of the crystal structure along [0 0 1].

At the end of the refinement, the values of x and y in the present sample were found to be 0.474(4) and 0.313(4), respectively; however, these values of the esd are too optimistic, and the third decimal will not be considered from this point on. The scattering factors of neutral atoms were used in the refinement.

The occupancy of the $M(1)$ and $M(2)$ sites was also refined using the scattering factors of Ce and Fe atoms for $M(1)$ and $M(2)$ sites, respectively: the values obtained [0.948(2) for $M(1)$ and 0.850(2) for $M(2)$] account for the partial replacement of Ce and Fe by the other substituents and are compatible with the compositional range indicated by Armbruster *et al.* (1988). Refinement of the extinction parameter did not provide a significant result. The final coordinates and displacement parameters of the atoms are reported in Table 3. Most displacement parameters of the lighter atoms have been considered to be isotropic; although the R index could be further lowered (to just below 3%),

the corresponding ellipsoids were not fully plausible otherwise.

Selected interatomic distances are shown in Table 4. Views of the crystal structure are reported in Figures 2–5. A table of observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, on the Mineralogical Association of Canada web site [document Cervandonite-(Ce) CM46_423].

RESULTS AND DISCUSSION

Our detailed interpretation reported below (see also Fig. 1) has been derived by refining the site populations as the most plausible hypothesis, considering the possible effects of steric hindrance and the chemical composition. Owing to the present limits of accuracy of crystallographic refinement of disordered structures, minor deviations from this model cannot be excluded.

The unique sample used here for crystallographic purposes could not be adequately polished and sacrificed for chemical analysis; for this reason, in view of the consistent number of points analyzed by Armbruster *et al.* (1988), who indicated a marked variability taking place even within the same crystal, the compositional ranges of these authors were considered to be fundamental in our discussion. The values of the site-population parameters x and y obtained from the refinement and taking disorder into consideration exclude steric hindrance between Si(2) and Si(3) $(1 - x + y \leq 1)$, and correspond to an atom ratio As/Si of 0.69, and to As + Si = 2.84 *apfu*; such values lie within the ranges reported by Armbruster *et al.* (1988) [As/Si in the range 0.60–1.13; As+Si in the range 2.80–3.09].

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR CERVANDONITE-(Ce)

		Sample P5757 Gorb, Binntal, Switzerland			Sample P4300 Cervandone, Italy		
$h\,k\,l$	d (Å)$_{obs}$	d (Å)$_{calc}$[**]	I/I_0[§]	d (Å)$_{obs}$	d (Å)$_{calc}$[***]	I/I_0[§§]	I calc[*]
1 0 1	5.397	5.385	70	5.394	5.391	65	13
1 0 4	3.580	3.576	30	3.569	3.582	30	5
1 1 0	3.255	3.249	100	3.255	3.253	87	72
1 1 2	3.071	3.066	40	3.071	3.070	57	15
1 1 3	2.872	2.876	90	2.877	2.879	100	100
2 0 1	2.784	2.782	50	2.787	2.785	39	16
2 0 2	2.699	2.693	60	2.707	2.696	27	14
0 2 4	2.400	2.405	40	2.397	2.408	35	17
1 1 6	2.233	2.238	40	2.238	2.242	35	25
2 1 1	2.115	2.113	40	2.116	2.116	<10	14
3 0 0	1.878	1.876	20	1.876	1.878	10	7
3 0 3	1.795	1.795	30	1.798	1.797	38	23
2 0 9	1.664	1.661	20				16
2 2 0	1.627	1.625	40	1.629	1.626	31	34
0 0 12	1.545	1.544	10	1.549	1.547	12	16
2 2 6	1.433	1.438	20	1.439	1.440	10	26

Debye–Scherrer camera, 90 mm Ø, FeKα radiation.
[*] Calculated from the crystal structure; [**] calculated values from the least-squares unit-cell parameters a 6.4986(5), c 18.528(3) Å. [***] Calculated values from the least-squares unit-cell parameters a 6.5059(5), c 18.565(3) Å.
[§] Intensities visually estimated from the measured peaks; [§§] intensities determined densitometrically.

TABLE 2. CERVANDONITE-(Ce): SINGLE-CRYSTAL DATA

Crystal system	trigonal	Scan mode	ω
Space group	$R3m$ (no.160)	θ max (°)	28.87
a (Å)	6.508(1)	Measured reflections	1963
c (Å)	18.520(3)	Independent reflections	490
V (Å³)	679.4(2)	Observed reflections [$I > 2\sigma(I)$]	441
Z	3		
Minimum transmission-factor	0.587		
Parameters refined	60		
Final R and wR2 [§]	0.0380, 0.0887		
Largest diffraction peak and hole (e Å⁻³)	1.52, -1.36		

[§] R = Σ||Fo| – |Fc|| / Σ|Fo|; wR2 = {Σ[w(Fo² – Fc²)²] / Σ[w(Fo²)²]}^{½}.

TABLE 3. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN CERVANDONITE-(Ce)

Atom	X/a	Y/b	Z/c	U_{eq}/U
$M(1)$	0	0	0	0.0203(1)
$M(2)$	0.1682(3)	0.3365(7)	-0.1661(1)	0.0309(2)
As(1)	1/3	2/3	0.3470(1)	0.0183(6)
As(2)	1/3	2/3	-0.0156(1)	0.0311(6)
Si(1)	1/3	2/3	0.3698(4)	0.0291(11)
Si(2)	1/3	2/3	0.1928(3)	0.0188(7)
Si(3)	1/3	2/3	0.1424(6)	0.0188(7)
Si(4)	1/3	2/3	-0.0355(9)	0.0291(11)
O(1)	0	0	-0.1404(9)	0.0710(40)
O(2)	0	0	0.1400(5)	0.0720(50)
O(3)	0.2024(5)	0.4048(10)	0.1673(3)	0.0291(11)
O(4)	0.0608(11)	0.5304(6)	0.3926(3)	0.0349(13)
O(5)	0.1926(5)	0.3853(10)	-0.0638(3)	0.0237(11)
O(6)	1/3	2/3	0.2824(11)	0.0380(50)
O(7)	1/3	2/3	0.0532(16)	0.0230(60)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$M(1)$	0.0225(1)	0.0225(1)	0.0159(2)	0	0	0.0113(1)
$M(2)$	0.0286(3)	0.0585(6)	0.0157(4)	0.0040(4)	0.0020(2)	0.0292(3)
As(1)	0.0232(7)	0.0232(7)	0.0084(9)	0	0	0.0116(4)
As(2)	0.0400(8)	0.0400(8)	0.0133(9)	0	0	0.0200(4)

The anisotropic displacement factor exponent takes the form:
$-2\pi^2(U_{11}h^2(a^*)^2 + ... + 2U_{12}hka^*b^* + ...)$; Ueq = 1/3 $(U_{11} + U_{22} + U_{33})$.

An important result of our structure determination is the presence of Si as a part of a sorosilicate $Si_2O_7^{6-}$ anion, which is statistically distributed over two partly overlapping different $3m$ positions with occupancy $1 - x$ and y, respectively. One Si atom in each $Si_2O_7^{6-}$ position [Si(1) and Si(4), respectively] can be replaced with As^{3+} atoms belonging to arsenite AsO_3^{3-} ions [As(1) with occupancy x and As(2) with occupancy $1 - y$]; here the Si and As atoms only partly overlap, whereas the overlap of the corresponding oxygen atoms is complete. This disordered As → Si replacement is in agreement with Figure 6 in Armbruster et al. (1988), which shows a negative correlation to exist between the continuously variable As and Si contents of the mineral (see also their Table 3). Further evidence for compositional variation is provided by the significant differences observed in some cases in the unit-cell parameters reported for various crystals [see Table 2 of Armbruster et al. (1988)]. As $1 - x + y = 0.84$, the difference from unity can be ascribed to the presence of OH^- groups, so that O(3) remains fully occupied, as is suggested by the structure refinement (see below). This substitution with OH^- groups is similar to the $4 OH^- \rightarrow SiO_4^{4-}$ replacement occurring in several silicates such as hydrogarnets (see, for instance, Basso et al. 1981) and is in agreement with the IR-spectroscopic measurements by Armbruster et al. (1988), who do not exclude the presence of "low H_2O/OH concentrations in cervandonite-(Ce)".

The partial occupancy of the O(6) and O(7) sites might involve the presence of vacancies, a questionable point for such structures where the energy of formation of structural "voids" would be too high; for this reason, we assume the sites of O(3), O(4) and O(5) to be fully occupied. For the O(6) and O(7) sites, which are vacant if the corresponding sorosilicate ion is absent, such "voids" are at least in part occupied by the lone pairs of the arsenite groups.

On looking at Figures 1 and 2, the overall arrangement of the sorosilicate and the arsenite groups along the c axis appears to be nearly centrosymmetric, and such a marked pseudo-centrosymmetry extends all over the structure. For this reason, in spite of strong statistical evidence such as the distribution of E values (see above), the values of the occupancy parameters x and y for which $1 - x$ is significantly different from y (contrary to the centrosymmetric case) and the results from PLATON (see above), we reconsidered the possible of existence of a center of symmetry. Such a precaution was taken also remembering the case of parwelite, another arsenosilicate where the existence of the center of symmetry was first overlooked (Moore & Araki 1977, Marsh & Schomaker 1979). However, if the space group would be assumed to be $R\bar{3}m$, the final R in the refinement would not drop below 10%. In any case, the presence of a center of symmetry, instead of simplifying matters, would involve additional disorder of the O(3) atoms between two main positions rotated by 60% about the threefold axis, contrary to the difference-Fourier

evidence and to the absence of a substantial deviation of the U values from the average for the other oxygen atoms.

The $Si_2O_7^{6-}$ ion is linear, as in thortveitite (Bianchi et al. 1988), in spite of some theoretical predictions of general character (Meagher et al. 1979, Gibbs et al. 1981, and references therein). Apart from the high accuracy of the structure of thortveitite, unquestionable confirmation of the possibility of Si–O–Si angles being really linear and not apparently so owing to a toroidal distribution of the atoms has been provided by lattice-dynamics calculations for coesite (Pilati et al. 1998, and references therein).

Lacking crystal-structure information, Armbruster et al. (1988) used IR spectroscopic data to deduce the oxidation state of As in the mineral, and they concluded it to be 5+ instead of 3+. Such a conclusion is questionable, because the higher-frequency IR absorption bands observed for some arsenites [e.g., fetiasite, magnussonite and asbecasite: see Figure 3 in Graeser et al. (1994) and the supplementary Fig. S1 deposited in document Cervandonite-(Ce) CM46_423] are in the same range as those reported for cervandonite. In general, in analogy with organic crystals, where in most cases isolated molecules only connected by van der Waals bonds are present, the observed IR- and Raman-active lower frequencies in minerals are too often ascribed to some well-defined vibrational modes involving bond bending, etc. of isolated ions such as SiO_4^{4-}, $Si_2O_7^{6-}$, AsO_4^{3-}, CO_3^{2-}, etc. which are treated like molecules. Such an approximation is unjustified for these ionic crystals, owing to very strong interaction with other ions in the structure, which may

TABLE 4. INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN CERVANDONITE-(Ce)

$M(1)O_8$ polyhedron, $M(1)$ = Ce, Nd, La ...

M(1)-O(1)	2.600(9)	M(1)-O(4) × 3	2.478(6)
M(1)-O(2)	2.593(9)	M(1)-O(5) × 3	2.472(6)
M(1)-O(average)	2.505		

$M(2)O_6$ polyhedron, $M(2)$= Fe^{3+}, Fe^{2+}, Ti^{4+}, Al

M(2)-O(1)	1.955(6)	M(2)-O(4)	2.032(6)
M(2)-O(2)	1.929(6)	M(2)-O(5)	1.914(5)
M(2)-O(3) × 2	2.103(4)	M(2)-O(average)	2.006

SiO_4 tetrahedra

Si(1)-O(4) × 3	1.594(7)	Si(2)-O(3) × 3	1.550(6)
Si(1)-O(6)	1.62(2)	Si(2)-O(6)	1.66(2)
O(4)-Si(1)-O(4) × 3	113.2(3)	O(3)-Si(2)-O(3) × 3	111.2(3)
O(4)-Si(1)-O(6) × 3	105.4(4)	O(3)-Si(2)-O(6) × 3	107.7(3)
Si(3)-O(3) × 3	1.546(6)	Si(4)-O(5) × 3	1.671(8)
Si(3)-O(7)	1.65(3)	Si(4)-O(7)	1.64(3)
O(3)-Si(3)-O(3) × 3	111.5(4)	O(5)-Si(4)-O(5) × 3	110.6(5)
O(3)-Si(3)-O(7) × 3	107.3(4)	O(5)-Si(4)-O(7) × 3	108.3(6)

$As^{3+}O_3$ trigonal pyramids

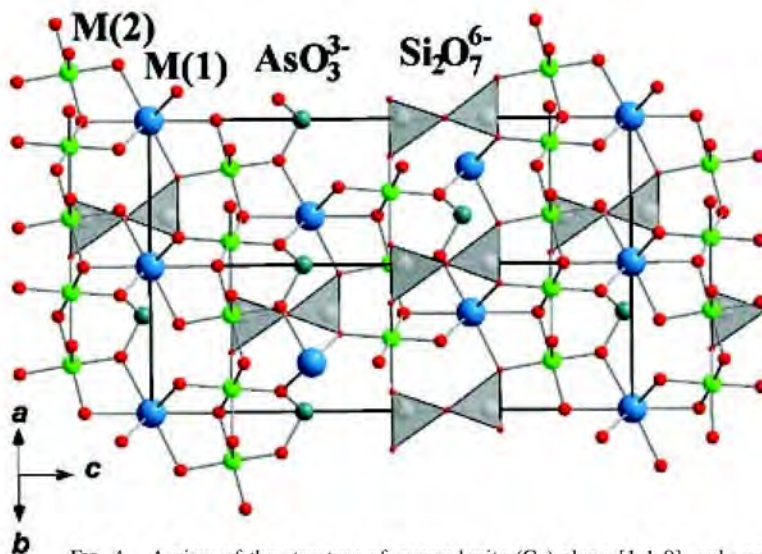|			
As(1)-O(4) × 3	1.753(6)	As(2)-O(5) × 3	1.820(6)
O(4)-As(1)-O(4) × 3	98.7(2)	O(5)-As(2)-O(5) × 3	98.0(2)

FIG. 4. A view of the structure of cervandonite-(Ce) along [1 1 0]; only one configuration of the disorder is shown. The tetrahedra of the sorosilicate anion are evident.
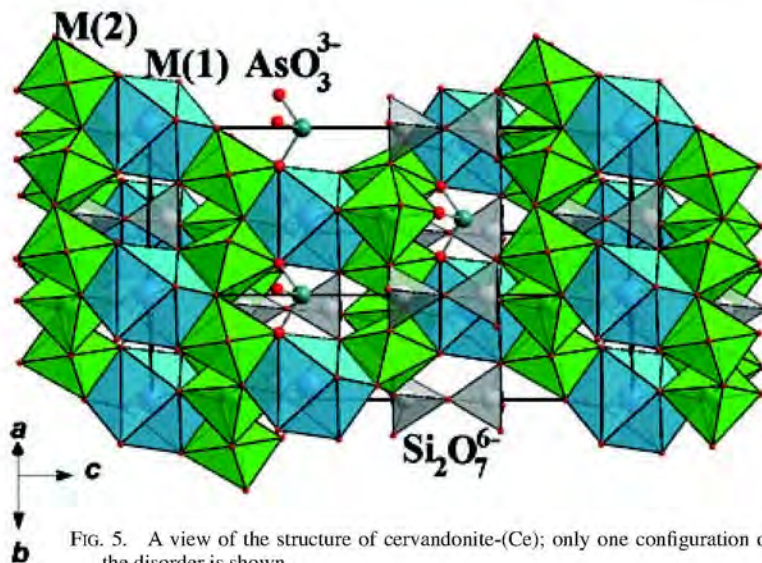

FIG. 5. A view of the structure of cervandonite-(Ce); only one configuration of the disorder is shown.

radically alter the interpretation. This effect becomes particularly notable where strongly charged atoms are present, owing to the intensity of the Coulombic fields, which is not negligible even at large distances. For this reason, the interpretation of such spectra using symmetry-unlabeled data and the avoidance of detailed lattice-dynamics calculations should always be taken with much caution (Gramaccioli 2002), in spite of its wide use in the spectroscopy of minerals.

There are further arguments supporting our attribution of most of the arsenic to the presence of arsenite and not of arsenate ions. a) The occupancy of O(6) and O(7) derived from the refinement is consistently less than one, therefore excluding the presence of a fourth oxygen atom bonded to As; moreover, such an absence is strongly supported by the unconstrained refined values of the corresponding U values, which do not differ appreciably from those of the other oxygen

atoms. b) The O(6) and O(7) atoms would be too close to As(1) and As(2), respectively [As(1)–O(6) = 1.20(2); As(2)–O(7) = 1.27(3) Å]. c) The geometry of the As(1)O(4)$_3$ and As(2)O(5)$_3$ groups is much closer to that of arsenites than that of the AsO$_4$ group in arsenates. The As(1)–O(4) and As(2)–O(5) distances are in fact 1.753(6) Å and 1.820(6) Å, respectively, and are sufficiently distinct from the average value for the As–O bond lengths in arsenates (1.686 Å according to Ferraris 1970), but is reasonably close to the grand average of 1.776 (± 0.012) Å reported by Hawthorne (1985) for a significantly large group of natural arsenites (see also Ghose et al. 1987). Moreover, our values for the O–As(1)–O and O–As(2)–O angles are about 10% smaller than the ideal value, 109°28', for the O–As–O angles in arsenates. Our values are instead near the average (97.2°: see Table 7 in Hawthorne 1985) in natural arsenites, and account for the presence of the lone pair, in agreement with the VSEPR theory (Gillespie & Hargittai 1991).

The presence of most of the arsenic as As^{3+} instead of As^{5+} is not surprising, in view of the profusion in the same environment of other arsenites, such as cafarsite, fetiasite, and graeserite, and even arsenite-silicates such as asbecasite (Graeser 1966, Cannillo et al. 1969, Edenharter et al. 1977, Graeser et al. 1994, Krzemnicki & Reusser 1998, Berlepsch & Armbruster 1998).

The positions of the silicon atoms in cervandonite-(Ce) are sufficiently distinct from those of their immediate neighbors to afford reasonable details concerning the bond geometry. For instance, the average of the Si–O distances (1.603 Å) is not far from that observed for thortveitite (1.623 Å), especially if the high uncertainty and the strong interference of As–Si disorder are considered.

CONCLUSIONS

We have explored the unusual nature of the As → Si substitution in cervandonite-(Ce), and found the arsenic to be present as As^{3+} instead of As^{5+}; the presence of sorosilicate Si$_2$O$_7^{6-}$ anions has also been established. Accordingly, the chemical formula (Ce,Nd,La)(Fe^{3+},Fe^{2+},Ti^{4+},Al)$_3$SiAs(Si,As)O$_{13}$ in the original description should be revised to: (Ce,Nd,La) (Fe^{3+},Fe^{2+},Ti^{4+},Al)$_3$O$_2$(Si$_2$O$_7$)$_{1-x+y}$(AsO$_3$)$_{1+x-y}$(OH)$_{3x-3y}$, where x and y are 0.47 and 0.31 in our sample, respectively. Although it is derived from a refinement of the occupancies in a disordered crystal, this new formula reasonably matches the charge balance [13 negative versus 12.75 positive charges for the average chemical composition of the M(1) + M(2) sites given by Armbruster et al. (1988)]. The presence of As in the 3+ state emphasizes the reducing environment in the positive arsenic anomaly in the Cervandone area where, away from the rock surface, in lieu of arsenates, arsenites are formed instead wherever their crystal structure is sufficiently stable.

In the literature, a few As-containing silicates, none of which containing the Si$_2$O$_7$ group, or arsenic in the 3+ state, were considered to be possible examples of As → Si diadochy [e.g., parwelite, first described as (Mn,Mg)$_5$Sb(Si,As)$_2$O$_{10-11}$ (Moore 1968)]. However, for this mineral, after accurate determination of the crystal structure (Moore & Araki 1977, Marsh & Schomaker 1979), the As and Si atoms were shown instead to occupy distinct sites, and a similar conclusion has been attained for the other cases for which accurate crystal-structure information is available. Therefore, at least so far, As–Si disorder seems to be unique for cervandonite-(Ce) and accounts for its variable As:Si ratio. This very unusual diadochy, the variable composition and the presence of superstructures suggest that a crystal of cervandonite-(Ce) might indeed consist of an assembly of more or less twinned microdomains with an ordered structure in different proportions; there also is the possibility of existence of a series of "cervandonites" with different values of As/Si and unit-cell parameters, although until now only one type of superstructure has been observed. For this reason, if a suite of better crystals with different As/Si values were available, so that the supercell reflections could be accurately measured, the model shown here might be improved. Furthermore, another example of a linear configuration of the sorosilicate group Si$_2$O$_7$ is also provided.

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