Cervandonite-(Ce), (Ce,Nd,La)(Fe3+,Fe2+,Ti4+,Al)3SiAs(Si,As)O13, a new alpine fissure mineral

Cervandonite-(Ce),
(Ce,Nd,La)(Fe^{3+},Fe^{2+},Ti^{4+},Al)$_3$SiAs(Si,As)O$_{13}$,
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Abstract

Cervandonite-(Ce), (Ce,Nd,La) (Fe^{3+}, Fe^{2+}, Ti^{4+}, Al)$_3$ SiAs(Si,As)O$_{13}$, is a new fissure mineral in the two-mica-gneisses of the mountain Pizzo Cervandone (Swiss synonymous name: Scherbadung) in the Central Alps. The crystals form black saddle-like aggregates up to 4 mm in diameter. The mineral is monoclinic with the space group C2 or Cm or C2/m and lattice parameters a = 11.3 Å, b = 19.5 Å, c = 7.2 Å, β = 121°, Z = 6, D_{calc}: 4.9 g/cm^3. Reflectance values in air were measured between 440 and 660 nm and range from 8 to 12%. The mineral is pleochroic. In one direction the crystals are black (refractive index n = 2.0), along another direction (n = 1.99) they appear yellowish-reddish-brown. Chemical analyses were carried out by an electron microprobe. The Fe^{3+}/Fe^{2+}-ratio of 3/1 was determined by Mössbauer spectroscopy.

Introduction

The new alpine fissure mineral cervandonite-(Ce) was found east and west of Pizzo Cervandone (Italian name) also called Scherbadung (Swiss synonymous name). The mountain ridge, elevation 3155 m, extends from southwest to northeast and forms the Italian-Swiss border line. Thus, cervandonite-(Ce) was discovered in Italy (east of Pizzo Cervandone) and in Switzerland (west of Pizzo Cervandone). The name cervandonite was chosen after the locality and points at the high Ce concentration. To be in accordance with the Levinson convention and with a recent decision of the IMA Commission on New Minerals and Mineral Names the complete name is cervandonite-(Ce) which has been accepted by the above IMA commission.

All cervandonite-(Ce) findings were made in the region of the two-mica-gneisses of the Monte Leone Nappe. A more detailed geological description of the area is given by BADER (1934) and GRAESER and SCHWANDER (1987). The region is characterized by a striking positive arsenic anomaly (GRAESER, 1965). Already two arsenites: cafarsite and asbecasite, (GRAESER, 1966, CANILLO et al., 1969, EDENHARTER et al., 1977) and one arsenate: gasparite-(Ce) (GRAESER and SCHWANDER, 1987) have been reported as new minerals in this setting. Chernovite-(Y) (GRAESER et al., 1973), tilasite (GRAESER and ROGGIANI, 1976) and As-bearing davidite (STALDER and BÜHLER, 1987) are additional minerals indicating high arsenic concentrations. All minerals occur within the steep NW–SE extending narrow fissures, which often contain a variety of mineral assemblages. The composition of the assemblages changes from fissure to fissure. However, almost all

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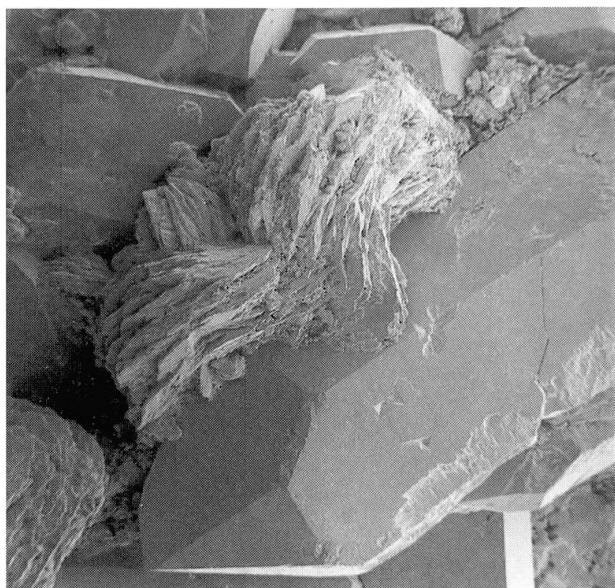
Fig. 1 SEM micrograph of saddle-like aggregates of cervandonite-(Ce) grown on a quartz crystal (sample NMBE-B4880). Edge-length of the photograph is about 2 mm.

contain As-rich minerals as listed above. Cervandonite-(Ce) ist not a rare mineral in this region. It has already been collected years before but considered as small hematite rosettes (Fig. 1).

Occurrences

East flank of Pizzo Cervandone, Alpe Devero (Italy). Finder: F. Parani, Montecrestese (Italy). Date of finding: summer 1981 (NMBE-B3953) and summer 1985 (NMBE-B4695). Mineral paragenesis: Cervandonite-(Ce) aggregates up to 3 mm in diameter, quartz, albite, white mica.

West flank of Pizzo Cervandone, Binn Valley, VS. (Switzerland). Finder Th. Mumenthaler (Zürich), A. Frey (Estavayer), and Chr. Margot (Lausanne). Date of finding: summer 1985 and summer 1986 (NMBE-B4880). Mineral paragenesis: Saddle-like aggregates up to 4 mm in diameter of cervandonite-(Ce), quartz, rutile, anatas, white mica, chlorite, albite, tourmaline, senaite, hematite, magnetite, chernovite. Neighboring fissures contain assemblages without cervandonite-(Ce) but with asbecasite or monazite. Fissures a little further away are characterized by cafarsite and asbecasite.

At the east flank of Pizzo Cervandone (Italy), cervandonite-(Ce) was found in three different fissures, all in the same zone at a height of about 2800 m. The country rock is a light coloured two-mica-gneiss. First samples of cervandonite-(Ce) from this locality were found in 1974 by G. Gaspari, Crodo (Italy) but mistaken for hematite roses. Finally, in 1985 they were studied in Basel and found to be the new mineral species (M30802). Mineral paragenesis: rounded and radial aggregates of cervandonite-(Ce) up to 4 mm in diameter, red translucent rutile, muscovite, albite, quartz, and sometimes synchisite.

General Appearance

Saddle- or rosette-like aggregates of cervandonite-(Ce) are megascopically black with adamantine lustre, brittle tenacity, poor cleavage parallel (001), conchoidal fracture, and a brownish-black streak. The Vickers hardness was determined with a 50 g load yielding a mean value of 450 which corresponds to a Mohs' hardness of about 5. The crystals are only translucent in very thin splinters.

X-ray Crystallography

SINGLE-CRYSTAL EXPERIMENTS

Two cervandonite-(Ce) samples (NMBE-B4880 and M30802) were investigated using precession and Weissenberg single-crystal techniques with filtered $MoK\alpha$ or $CuK\alpha$ radiation. The results indicate cervandonite-(Ce) to be monoclinic with approximate cell dimensions a = 11.3 Å, b = 19.5 Å, c = 7.2 Å, β = 121° with h k l: h+k = 2n (possible space groups: C2, Cm, C2/m). However, reflections of the type hkl with k = 3n are very weak and can only be seen in over-exposed photographs. Thus, the tripling of the b-axis possesses superstructure character.

A selected single-crystal (NMBE-B4880) was subsequently transferred to an Enraf Nonius CAD4 single-crystal diffractometer with graphite filtered Mo-radiation. Cell dimensions were refined from 22 automatically centered reflections with 16° > Θ > 6° yielding a = 11.235(4) Å, b = 6.501(5) Å, c = 7.201(3) Å, β = 121.22(3)°. Superstructure reflections along the b-axis could not be recorded with the diffractometer, thus b/3 was refined.

POWDER-EXPERIMENTS

For sample NMBE-B3953, a guinier camera with $FeK\alpha_1$ radiation was employed to collect an X-ray powder diffractogram. 12 reflections were measured with Si as internal standard. Starting values as obtained from single-crystal experiments were used for the refinement (Tab. 1 and 2) (program INDLSQ: APPLEMAN and EVANS, 1973). If multiple indexing of reflections was possible, only those indices of reflections was possible, only those indices

were applied for which single-crystal experiments revealed high diffraction intensities. Powder intensities reported in Table 1 are estimated by eye.

A powder photograph comprising 14 reflections of sample M30802 was recorded with a Bradley camera ($FeK\alpha$-radiation), reflection intensities were measured with a densitometer (Tab. 1). Cell dimensions (Tab. 2) are refined with the same method as for sample NMBE-B3953.

Tab. 1 X-ray powder data of cervandonite-(Ce).

| h k l | NMBE-B3953* | | | M30802** | |
	d-calc	d-obs	I/I_1	d-obs	I/I_1
1 3 0	5.392	5.390	80	5.403	65
1 3 1	3.5766	3.5750	40	3.592	30
0 6 0	3.2546	3.2530	90	3.255	87
-3 3 1	3.2534				
0 0 2	3.0854	3.0847	80	3.096	57
0 6 1	2.8788	2.8785	100	2.874	100
3 3 0	2.8775				
-3 3 2	2.8784				
-2 6 1	2.7862	2.7867	60	2.792	39
2 6 0	2.6959	2.6964	50	2.707	27
-2 0 3	2.3946	2.3939	30	2.403	35
1 3 2	2.3941				
4 0 0	2.4060				
-2 6 2	2.4074				
0 6 2	2.2392	2.2400	30	2.244	35
-3 3 2	2.2393				
-1 9 0	2.1166	2.1165	30		
-4 6 1	2.1160				
-5 3 2	2.1159				
-3 9 2	1.7975	1.7982	30	1.7938	38
				1.7379	10
-6 6 2	1.6267	1.6261	40	1.6268	31
				1.5460	12
				1.4400	10

Note: Reflections of the type hkl with k ≠ 3*n are weak and could only be found on overexposed single-crystal photographs. Powder data would also satisfy a unit cell with $b/3 \approx 6.509$ Å.

* Guinier camera $FeK\alpha_1$-radiation, intensities estimated by eye from the film.

** Bradley camera $FeK\alpha$-radiation, intensities measured by densitometer.

Tab. 2 Cell dimensions of cervandonite-(Ce)

Sample No.	a [Å]	b [Å]	c [Å]	β	V [Å³]
NMBE-B4880	11.235(4)	19.50(2)	7.201(3)	121.22(3)	1349
NMBE-B3953	11.269(2)	19.527(3)	7.226(1)	121.35(1)	1358
M30802	11.26(2)	19.54(2)	7.250(6)	121.31(7)	1362

Optical Properties

Sample M30802 was studied in transmitted light. Two extreme refractive indices were estimated $n = 2.0$ parallel to a direction where the crystal appears black, and $n = 1.99$ parallel to a direction where the crystal appears yellowish-reddish-brown.

Polished sections of saddle-like aggregates of cervandonite-(Ce) reveal high concentrations of irregular pores. The shape of the aggregates is caused by stilbite-like bundles associated with lateral whirls of crystals, resembling a pattern characteristic of force lines of magnets (Fig. 2).
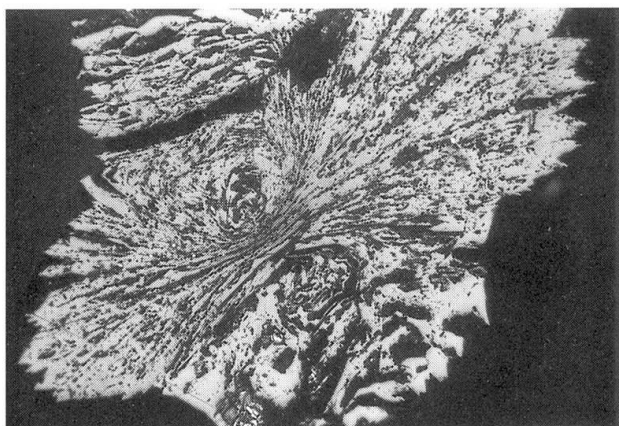

Fig. 2 Micrograph of a polished section of cervandonite-(Ce) aggregates under reflected light (sample NMBE-B3953). The aggregate has a maximum diameter of approximately 3 mm. The three -dimensional saddle-like shape is formed by bundles of fanlike arranged plates associated with lateral whirls of crystals, resembling force lines of a magnet.

Fig. 3 Section of Fig. 2 but viewed under oil immersion. Oriented unidentified exsolutions with slightly lower reflectance become visible within the cervandonite-(Ce) matrix (maximum dimension of the photograph is approximately 100 μm).

Optical reflectance in air was measured between 440 nm and 660 nm in steps of 20 nm using WC as standard. Reflectance values varied between 8 and 12% without specific absorptions within the range investigated. When using oil immersion for reflected light microscopy sample NMBE-B3953 appeared to be inhomogeneous, displaying partly oriented domains of exsolutions with slightly lower reflectance (Fig. 3). In air these domains were not detected. Sample NMBE-B4880 appeared homogeneous even in oil immersion.

Chemical Composition

Electron microprobe analyses were performed on all three samples using TiO_2, $CaSiO_3$, $PbCl(VO_4)_2$, U_3P_4, ThO_2, $AlAsO_4$, SnO_2, natural spinel for Al and Fe, and the rare earth element glasses of DRAKE and WEILL (1972) as standards. In addition, the mineral was analyzed for Mg, Cr, Sr, Mn, Nb, Zn, Re, Pr, Ba, K, Cu, V, Sm, Yb, Lu. However, these elements were not found in significant concentrations (Tab. 3).

The inhomogeneities observed in oil immersion under reflected light for sample NMBE-B3953 could not be relocated on the electron microprobe. However, few individual electron microprobe analyses of this sample (not displayed in Tab. 3) yielded significantly higher UO_2- but lower REE- and SiO_2-concentrations which are probably related to the exsolutions.

To determine the valence of iron in cervandonite-(Ce) Mössbauer spectra (Fig. 4) of sample NMBE-B4880 at liquid nitrogen (80K) and room (295K) temperature were taken using a conventional Mössbauer spectrometer (source 25 mCi ^{57}Co/Rh; multichannel analyzer with 1024 channels; electromechanical drive, symmetric triangular velocity shape). Two doublets were fitted to the experimental data of both spectra. The doublet with the large quadrupole splitting QS = 2.60(1) mm/s at 80K and QS = 2.45(1) mm/s at 295K, respectively, and the large isomer shift IS = 1.081 mm/s at 80K and 0.90(1) mm/s at 295K, respectively, is assigned to Fe^{2+}. The doublet with the small quadrupole splitting QS = 1.13(1) mm/s at 80K and QS = 1.11(1) mm/s at 295K, respectively, and the small isomer shift IS = 0.51(1) mm/s at 80K and 0.41(1) mm/s at 295K is assigned to Fe^{3+}. The half widths HW of the Fe^{2+}- and

Tab. 3 Electron microprobe analyses of cervandonites. The Fe^{3+}/Fe^{2+} was fixed at 3/1 according to the Mössbauer results.

	3953 1	3953 2	3953 3	4880 1	4880 2	4880 3	4880 4	4880 5	4880 6	30802 1	30802 2	30802 3
Ce_2O_3	10.00	9.97	10.60	11.63	12.65	12.08	12.45	11.23	12.12	9.94	10.23	10.35
Nd_2O_3	5.16	5.17	5.30	6.01	6.61	6.32	6.45	6.64	6.32	4.85	4.40	4.65
La_2O_3	5.14	4.83	6.09	5.65	5.43	5.66	5.65	5.04	5.49	4.25	4.50	3.88
Y_2O_3	0.94	1.05	1.05	0.86	0.48	0.62	0.57	0.66	0.72	0.00	0.00	0.00
ThO_2	2.34	2.86	2.13	1.92	2.04	2.11	2.31	2.61	2.10	2.19	2.33	2.30
UO_2	1.35	1.77	1.45	0.33	0.38	0.35	0.44	0.65	0.42	0.00	0.29	0.47
CaO	0.25	0.40	0.19	0.25	0.11	0.32	0.16	0.13	0.19	0.18	0.16	0.13
PbO	0.17	0.04	0.00	0.16	0.25	0.11	0.11	0.21	0.10	0.00	0.00	0.00
Fe_2O_3	15.03	13.99	15.32	15.53	15.17	16.27	15.81	14.89	15.87	16.12	16.82	16.64
FeO	4.51	4.20	4.60	4.67	4.55	4.88	4.74	4.47	4.76	4.83	5.05	4.99
TiO_2	11.67	11.57	10.83	11.42	10.90	11.95	11.98	11.56	12.02	12.52	12.02	12.17
Al_2O_3	3.60	4.07	3.74	2.95	2.40	2.14	2.82	3.05	2.50	3.15	2.92	3.10
SnO_2	1.24	0.89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO_2	17.65	17.76	16.76	15.17	13.23	11.97	12.07	15.58	12.11	15.22	14.05	13.60
As_2O_5	20.41	21.93	22.76	24.18	25.66	25.50	26.07	25.23	24.35	23.34	23.84	24.14
Σ	99.47	100.48	100.81	100.72	99.84	100.28	101.62	101.93	99.07	96.59	96.60	96.41

mineral formula on the basis of 13 oxygen atoms

|												
Ce^{3+}	0.39	0.39	0.41	0.46	0.52	0.49	0.50	0.44	0.50	0.40	0.41	0.42
Nd^{3+}	0.20	0.20	0.20	0.23	0.26	0.25	0.25	0.25	0.25	0.19	0.17	0.18
La^{3+}	0.20	0.19	0.24	0.23	0.22	0.23	0.23	0.20	0.23	0.17	0.18	0.16
Y^{3+}	0.05	0.06	0.06	0.05	0.03	0.04	0.03	0.04	0.04	0.00	0.00	0.00
Th^{4+}	0.06	0.07	0.05	0.05	0.05	0.05	0.06	0.06	0.05	0.05	0.06	0.06
U^{4+}	0.03	0.04	0.03	0.01	0.01	0.01	0.01	0.02	0.01	0.00	0.01	0.01
Ca^{2+}	0.03	0.05	0.02	0.03	0.01	0.04	0.02	0.01	0.02	0.02	0.02	0.02
Pb^{2+}	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Σ	0.97	0.98	1.02	1.05	1.11	1.12	1.11	1.02	1.11	0.83	0.86	0.84
Fe^{3+}	1.21	1.11	1.23	1.26	1.27	1.36	1.31	1.19	1.34	1.32	1.40	1.39
Fe^{2+}	0.40	0.37	0.41	0.42	0.42	0.46	0.44	0.40	0.45	0.44	0.47	0.46
Ti^{4+}	0.94	0.92	0.87	0.93	0.91	1.00	0.99	0.93	1.02	1.03	1.00	1.02
Al^{3+}	0.46	0.51	0.47	0.38	0.32	0.28	0.37	0.38	0.33	0.41	0.38	0.41
Sn^{4+}	0.05	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Σ	3.06	2.95	2.98	2.97	2.92	3.10	3.10	2.90	3.14	3.20	3.24	3.27
Si^{4+}	1.89	1.88	1.79	1.64	1.47	1.34	1.33	1.66	1.36	1.66	1.55	1.51
As^{5+}	1.14	1.21	1.27	1.36	1.49	1.49	1.50	1.40	1.43	1.33	1.38	1.40
Σ	3.03	3.09	3.05	3.00	2.97	2.82	2.82	3.06	2.80	2.99	2.93	2.91
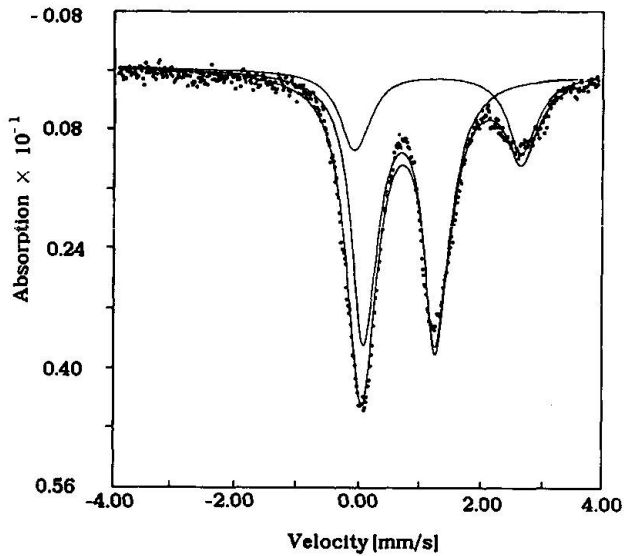
Fig. 4 ^{57}Fe Mössbauer spectrum of cervandonite taken at liquid nitrogen absorber temperature. The solid line represents a two doublet fit of the experimental data (black points). The doublet with the smaller area A = 26(1)% and the large quadruple splitting QS = 2.60(1) mm/s is assigned to Fe^{2+}, the doublet with the larger area A = 74(1)% and the smaller quadruple splitting QS = 1.13(1) mm/s is assigned to Fe^{3+}.

Fe^{3+}-lines are broad [HW (Fe^{2+}) = 0.50(1) mm/s at 195 K; HW(Fe^{3+}) = 0.49(1) mm/s at 295K] indicating that more than one crystallographic position may be occupied by iron. However, because the crystal structure of cervandonite is not known, no further evaluation attempts were performed. According to the isomer shift Fe^{3+} is most probably coordinated by six oxygen. The isomer shift of Fe^{2+} seems to be a little bit too small for octahedral Fe^{2+}. From the areas of doublets in the liquid nitrogen spectrum an Fe^{2+} content of 26(1)% and Fe $^{3+}$ content of 74(1)% was determined.

IR-powder spectra using the KBr-pellet technique for samples M30802 and NMBE--B4880 indicate a weak broadened absorption band at ca. 3440 cm^{-1} (Fig. 5). It is not clear wheter this absorption indicates low H_2O/OH concentrations in cervandonite-(Ce) or whether the absorption band is caused by a weathered surface on the sample and/or humidity in the KBr-pellet.

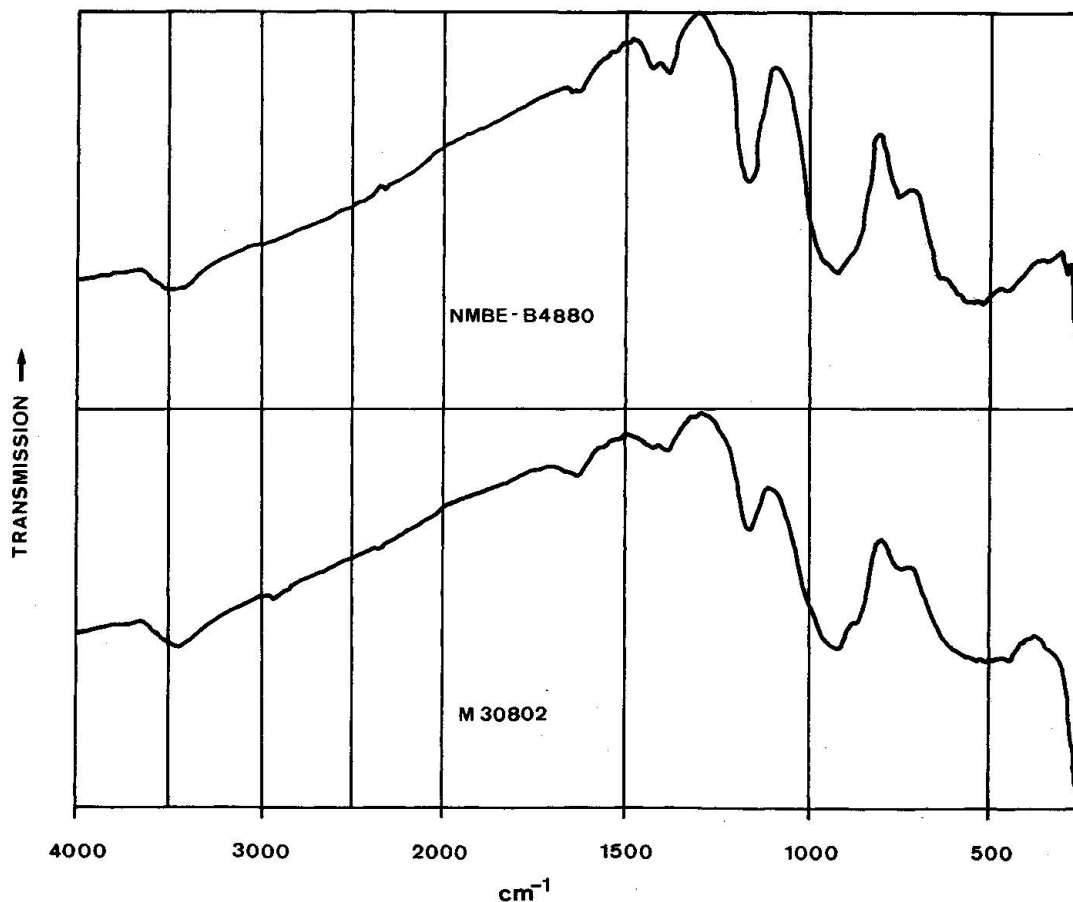Microprobe analyses were recalculated in order to satisfy a Fe^{3+}/Fe^{2+} ratio of 3/1

Fig. 5 IR-powder spectra of cervandonite-(Ce) samples M30802 and NMBE-B4880 (KBr-pellet technique).

(Tab. 3). The valence of As in all analyses was assumed to be As^{5+} because of various reasons:

a) Assumption of As^{3+} results in low oxide sums (ca. 97 wt.%), compared to about 100 wt.% if assuming As^{5+}.

5) No simple stoichiometric formula could be found if assuming As^{3+}.

c) Microprobe analyses (Tab. 3) indicate that there is a partial substitution of As for Si.

d) The IR spectra of cervandonite-(Ce) are clearly in favour of As^{5+} instead of As^{3+}. As^{3+}-pyramids produce merely uncharacteristic absorption spectra similar to those of oxides and hydroxides. In contrast, As^{5+} tetrahedra display always uniform, characteristic absorption bands in the region of 800 cm^{-1}, very similar to those of (neso-)silicate minerals. Actually, before the high As content was known, the IR spectrum of cervandonite-(Ce) was erroneously interpreted as that of a pure silicate mineral. All IR-spectroscopic evidence supports an arsenate-silicate mineral.

Assuming a unit cell volume of 1349 Å^3 (Tab. 2), a formula weight of 668 and Z=6, the calculated density of cervandonite-(Ce) is 4,9 g/cm^3. An experimental density determination was not successful because of the numerous pores within the crystal aggregates (Fig. 2).

vestigation of manganostibite (DUNN, 1987) revealed even higher Si substitutions.

A group of very complex arsenosilicates contains simultaneously As^{3+} in form of AsO_3 trigonal pyramids, and tetrahedral As^{5+}. One member of this group with a known crystal structure is dixenite, $Cu^{1+} Mn^{2+}_{14} Fe^{3+} (OH)_6 (As^{3+} O_3)_5 (SiO_4)_2(As^{5+}O_4)$, (ARAKI and MOORE, 1981). In dixenite As^{5+} and Si form a solid solution in tetrahedral oxygen coordination, thus mean (Si,As)-O distances of 1.636, 1.667 and 1.676 Å were found in the three different tetrahedra. Kraisslite (MOORE and ITO, 1978) and mcgovernite (WUENSCH, 1960) are additional members of this mineral group.

To our knowledge, asbecasite, $Ca_3(Ti,Sn) [(As^{3+}_3 SiBeO_{10})_2]$, (GRAESER, 1966, CANILLO et al., 1969) is the only arsenosilicate with all As in form of $As^{3+}O_3$ pyramids.

On the basis of this knowledge about arsenosilicates and our chemical analyses on cervandonite-(Ce) (Tab. 3), it seems probable that dominantly As^{5+} is present in the new mineral. Furthermore, Fig. 6 displays a negative correlation between (As-1) and (Si-1) calculated per formula unit which indicates a tetrahedral Si-As^{5+} solid solution range similar as in manganostibite or dixenite. Charge balance may be obtained by variations in the Fe^{3+}/Fe^{2+} ratio.

Valence of As in Arsenosilicates

Several minerals in this group possess only As in form of As^{5+}. Ardennite, $Mn^{2+}_2(Mn,Ca)_2 (AlOH)_4 [(Mg,Al,Fe^{3+})OH]_2 (As,V) O_4 Si_3 O_{10} (SiO_4)_2$ (DONNAY and ALLMANN, 1968), parwellite, $(Mn,Mg,Ca)_5SbAsSiO_{12}$, (MOORE and ARAKI, 1977a, MARSH and SCHOMAKER, 1979), tiragalloite, $Mn_4(AsSi_3O_{12}(OH))$, (GRAMACCIOLI et al., 1979, 1980), holdenite, $(Mn,Mg)Zn_3 (OH)_8(AsO_4)_2(SiO_4)$, (MOORE and ARAKI, 1977b), and kolicite, $Mn_7(OH)_4 [As_2Zn_4Si_2O_{16}(OH)_4]$, (PEACOR, 1980) show Si and As^{5+} in distinct tetrahedra without significant (Si, As) mixing on the same position. In these structures the mean Si-O distances vary between 1.622–1.638 Å and the mean As-O distances are about 1.69 Å long. Manganostibite, $Mn^{2+}_7Sb^{5+}As^{5+}O_{12}$, (MOORE, 1970) is not an arsenosilicate but MOORE (1970) noticed that in the crystal used for structure analysis 20% of As^{5+} is replaced by Si leading to a mean (As,Si)-O distance of 1.666 Å. A chemical rein-
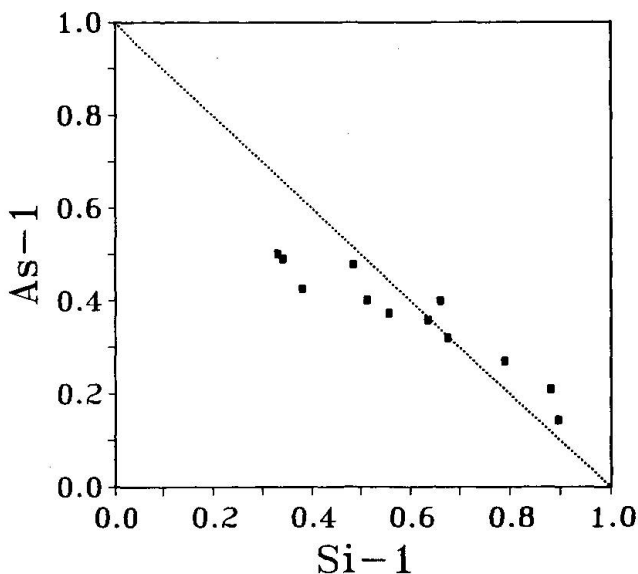

Fig. 6 Correlation between (As-1) and (Si-1) as obtained from formula units of electron microprobe analyses in Table 3. The negative correlation indicates partial Si-As substitution.

The final decision whether additional $As^{3+}O_3$-pyramids and/or OH-groups are part of the cervandonite-(Ce) structure must be left for a crystal structure determination, currently under study.

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