Paraniite-(Y), a new tungstate arsenate mineral from Alpine fissures

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Abstract

Paraniite-(Y) has been found in the Alpine fissures of the Italian side of Scherbadung (Pizzo Cervandone, Ossola), as a unique specimen bearing only a few creamy-yellow crystals up to 3 mm, having an elongated bipyramidal tetragonal habit. From microprobe analyses and from a single crystal X-ray structure determination the following chemical formula has been derived: $[Ca_{1.64}(Y,REE)_{0.36}]_{\Sigma = 2.00}(Y,REE)[(As_{0.96},W_{0.04})_{\Sigma = 1.00}O_4][(W_{0.89},As_{0.11})_{\Sigma = 1.00}O_4]_2$. The mineral is tetragonal, space group $I4_1/a$ with $a = 5.135(1)$ Å, $c = 33.882(5)$ Å, $V = 893.4(4)$ Å^3, $Z = 4$. The structure was refined to $R = 0.024$ for 840 observed reflections. The unit-cell parameters and the symmetry of the mineral are strictly related to those of scheelite, the c parameter being approximately three times the corresponding value for scheelite. The structure conforms to the scheelite type and consists of layers with composition near to $CaWO_4$ and $(Y,REE)AsO_4$, respectively, stacked along [001] with a molar ratio of 2 : 1.

Keywords: Paraniite-(Y), new mineral, rare earth mineral, crystal structure refinement, Penninic Alps, Northern Italy.

Riassunto

Il nuovo minerale paraniite-(Y) è stato rinvenuto al Pizzo Cervandone (Alpe Devero, Ossola) come specie tipica delle fessure alpine, su un unico campione che presenta soltanto alcuni cristalli della dimensione massima di 3 mm, con abito bipiramidale tetragonale allungato, di colore giallo crema. Dalla composizione chimica, determinata mediante microsonda elettronica a dispersione di lunghezza d'onda (WDS) e dai dati strutturali ottenuti tramite diffrazione di raggi X su cristallo singolo, si può scrivere la formula della paraniite-(Y) come $[Ca_{1.64}(Y,REE)_{0.36}]_{\Sigma = 2.00}(Y,REE)[(As_{0.96},W_{0.04})_{\Sigma = 1.00}O_4][(W_{0.89},As_{0.11})_{\Sigma = 1.00}O_4]_2$. La simmetria è tetragonale, gruppo spaziale $I4_1/a$ con parametri della cella elementare $a = 5.135(1)$ Å, $c = 33.882(5)$ Å, $V = 893.4(4)$ Å^3, e $Z = 4$. Il raffinamento finale ha portato ad un valore di $R = 0.024$ per 840 riflessi osservati. I dati strutturali del minerale sono strettamente correlati a quelli della scheelite, con il parametro c circa il triplo di quello della scheelite. Rispetto a questa, la struttura del nuovo minerale può essere descritta come derivante dall'impilamento lungo [001] di strati di composizione circa $CaWO_4$ e $(Y,REE)AsO_4$ in rapporto molare 2 : 1, il che porta appunto ad un triplicamento del parametro di cella c.

Introduction

The region of Pizzo Cervandone (Swiss name: Scherbadung), situated at the Swiss-Italian border (the famous Binn Valley is on the Swiss side), is characterized by a striking positive arsenic anomaly (GRAESER, 1965). In the gneiss fissures, this anomaly gives origin to a number of characteristic As-rich minerals: some of them are exclusive of this area in the Alpine region, and a few were discovered here for the first time in the world. Among the species for which this region is the type locality, gasparite-(Ce) (GRAESER and SCHWANDER, 1987) is an arsenate, cervandonite-(Ce) (Armbruster et al., 1988) also apparently contains As in the (+V) state, whereas cafarsite, asbecasite (GRAESER, 1966), and fetiasite (GRAESER et al., 1994), contain As exclusively in the

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Tab. 1   Electron microprobe analyses results.

CONSTI-TUENT	wt%	range	e.s.d.	calc*	Probe Standard
CaO	12.35	12.12–12.59	± 0.06	11.50	scheelite
Y_2O_3	16.15	15.43–16.80	± 0.39	16.20	synth. glass
Gd_2O_3	0.70	0.51– 0.91	± 0.15	0.72	synth. glass
Dy_2O_3	1.87	1.64– 2.14	± 0.08	1.86	synth. glass
Er_2O_3	1.37	1.28– 1.46	± 0.08	1.34	synth. glass
Yb_2O_3	0.81	0.64– 0.98	± 0.15	0.79	synth. glass
UO_2	0.25	0.21– 0.32	± 0.05	0.27	synth. UO_2
WO_3	51.61	50.84–52.19	± 0.32	52.74	scheelite
As_2O_5	16.92	16.44–17.88	± 0.24	14.57	adamite
Total	102.03 ± 0.61			100.00	

Other elements detected: Nb, Th (0.x %). Not detected P, Mo, Ce, Nd (below 0.1 %).
* The calculated values are those corresponding to the empirical formula reported below.
Empirical formula: (based on 12 oxygens)
$[Ca_{1.64}(Y,REE)_{0.36}]_{\Sigma = 2.00}(Y,REE)[(As_{0.96},W_{0.04})_{\Sigma = 1.00}O_4]$
$[(W_{0.89},As_{0.11})_{\Sigma=1.00}O_4]_2$.

Tab. 2   Summary of crystallographic data.

Crystal system:	tetragonal
Space group:	$I4_1/a$
	$a = 5.135(1)$ Å
	$c = 33.882(5)$ Å^3
	$V = 893.4(4)$ Å^3
	$Z = 4$

Data collected with MoKα radiation up to $2\Theta = 70°$

Variable scan speed with maximum 90 sec. for each reflection

Reflections measured:	4281
Independent reflections:	1405
Observed reflections with $I > 3\sigma(I)$:	840
R on eq. reflections (R_{int}):	0.027
Final R [$]:	0.024
Final R_w [$]:	0.027
N. of parameters refined:	46
S [&]:	1.088

[$] $R = [\Sigma(|Fo|-k|Fc|)/\Sigma|Fo|]$
$Rw = [\Sigma w(|Fo|-k|Fc|)^2/\Sigma w|Fo|^2]^{1/2}$

[&] $S = [\Sigma w(|Fo|-k|Fc|)^2/(N_{observations} - N_{variables})]^{1/2}$

(+III) state. Recently, an additional new mineral, paraniite-(Y), a tungstate arsenate of calcium and yttrium, was discovered in the same area (Alpe Devero, Ossola), and its crystal structure determined (DEMARTIN et al., 1992); the present paper concerns the description and complete crystal-chemical characterization of the mineral.

A single specimen, bearing only a few crystals of the new mineral paraniite-(Y) was found in 1990; this sample, which remains the only one known so far, has been deposited at the Museum of the Centro Studi "P. Ginocchi" (Crodo, Ossola Valley – Italy). The mineral was named in honour of the discoverer, the non-professional mineral collector Fausto Parani from Montecrestese (Ossola Valley – Italy), who provided it for investigation. The mineral and the mineral name have been accepted by the Commission on New Minerals and Mineral Names I.M.A. (proposal 92–018).

Experimental

PHYSICAL PROPERTIES

Paraniite-(Y) appears as creamy-yellow crystals up to 3 mm in length, with elongated bipyramidal tetragonal habit, closely resembling scheelite. The crystal faces are not measurable on the goniometer. The lustre is vitreous inclining to adamantine. The cleavage is distinct along {001}; the parting is uneven to subconchoidal. The fluorescence is moderately strong, orange-yellow at short wave UV radiation (254 nm); no fluorescence at 366 nm.

Owing to the lack of material, no attempt was made to determine the density experimentally; from the crystal-structure data and the chemical analysis the calculated value is 5.95 g/cm^3.

For the same reasons, only a very small fragment of the crystal used for the structure determination was available to determine the optical properties: from this fragment, an estimate of ω was tentatively obtained by immersion and ε was deduced by measuring the birefringence at the microscope. The results are the following: uniaxial(+) with ω = 1.87(1) and ε = 1.92(1). However, the values obtained here are not in satisfactory agreement with the corresponding estimate ($n_{aver.} = 2.018$) from the Gladstone-Dale rule (MANDARINO, 1981) and the compatibility index is poor (0.128); this is almost surely due to the poor quality of these optical measurements.

Tab. 3 Fractional atomic coordinates with e.s.d.'s.

Atom	Mult	x	y	z	$U_{eq}(Å^2)$
Y	0.275(1)	0.000	0.250	0.125	0.00919(8)
As	0.264(1)	0.500	−0.250	0.125	0.00887(9)
W	0.469(1)	0.000	−0.250	0.04678(1)	0.01037(4)
Ca	0.603(2)	0.500	0.250	0.04167(3)	0.0130(3)
O(1)	1.00	0.2437(8)	−0.1148(8)	0.0160(1)	0.0149(8)
O(2)	1.00	0.1557(7)	0.4784(7)	0.0705(1)	0.0137(6)
O(3)	1.00	0.3224(9)	−0.0343(8)	0.0977(1)	0.0181(8)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i a_j$$

Tab. 4 Anisotropic thermal parameters – U's.

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Y	0.0110(2)	U(1,1)	0.0055(2)	0	0	0
As	0.0108(2)	U(1,1)	0.0051(3)	0	0	0
W	0.01111(9)	0.00956(9)	0.01044(8)	0.0015(1)	0	0
Ca	0.0140(4)	0.0153(4)	0.0097(4)	0.0034(5)	0	0
O(1)	0.017(2)	0.018(2)	0.009(1)	0.001(1)	0.002(1)	−0.001(1)
O(2)	0.013(1)	0.017(1)	0.011(1)	0.000(1)	0.000(1)	0.002(1)
O(3)	0.022(2)	0.021(2)	0.011(1)	0.007(2)	0.000(2)	0.002(1)

The form of the temperature factor is:
$\exp[-2\pi^2\{h^2a^{*2}U(1,1) + kb^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)\}]$ where a^*, b^*, and c^* are the reciprocal lattice constants.

CHEMICAL ANALYSIS

A preliminary EDS qualitative analysis obtained via SEM techniques revealed the presence of W, Ca, As, Y as the major constituents. A quantitative wavelength-dispersion microprobe analysis was subsequently performed on a polished grain, using the ARL-SEMQ instrument of the Italian National Research Council (C.N.R.) at the Centro Studi per la Stratigrafia e la Petrografia delle Alpi Centrali, Milan. The series of natural and synthetic standards reported in table 1 was employed. Operating conditions: accelerating voltage 20 kV; sample current on brass 0.01 μA; beam spot diameter about 0.15 μm. The results of the microprobe chemical analysis are reported in table 1.

CRYSTAL STRUCTURE DETERMINATION

Most experimental details concerning the determination of the crystal structure have already

been reported (DEMARTIN et al., 1992); a summary of the crystallographic data is given in table 2. In agreement with the results of chemical analysis, the possibility of non negligible substitution in all the metal atom sites was considered and the relative occupancy factors were refined. Initially, due to strong correlation between these parameters, the occupancy of the As site was kept at the fixed value of 0.25, which corresponds to the exclusive presence of this element, and the occupancy of the W atom site was refined in view of possible partial replacement by As; this assumption is in agreement with the chemical analysis results, since the occupation of the As site is still insufficient to account for the total.

The results of this stage of the refinement have already been reported (DEMARTIN et al., 1992); later on, it was noticed that the final least-squares cycles showed no convergence problems even allowing all the occupancies to vary. For this reason the final results here reported (see tables 3 and 4) are slightly different from our previous paper, in particular the occupation and thermal parame-

Tab. 5 X-ray powder diffraction pattern for paraniite-(Y).

h	k	l	d_{obs}	d_{calc}	I/I_o
0	1	1	5.073	5.077	6
0	1	3	4.674	4.674	18
0	0	8	4.240	4.235	1
0	1	5	4.096	4.093	8
1	1	6	3.059	3.054	100
0	1	9	3.039	3.036	8
0	0	12	2.827	2.823	13
0	1	11	2.644	2.641	3
0	2	0	2.571	2.567	19
1	2	1	2.296	2.291	2
1	2	3	2.255	2.250	5
1	1	12	2.235	2.229	2
0	2	8	2.196	2.195	1
1	2	5	2.179	2.175	3
1	1	14	2.018	2.014	2
1	2	9	1.964	1.960	2
0	2	12	1.901	1.899	32
0	1	17	1.862	1.858	2
1	2	11	1.842	1.841	4
2	2	0	1.818	1.816	16
1	1	18	1.674	1.671	17
0	2	16	1.635	1.634	1
1	2	15	1.612	1.610	3
1	3	6	1.562	1.560	32
2	2	12	1.530	1.527	13
1	2	17	1.509	1.505	3
0	3	11	1.501	1.496	1

ters. Different projections of the crystal structure are shown in figures 1 and 2. A list of the observed and computed structure factor moduli is available from the authors on request.

In order to provide a readily available identification reference for the new mineral, the calculated pattern from the final crystal structure data, using the program POWLS80 (WILL, 1979), is reported (fifth column of table 5). Although a diffraction pattern directly obtained from the powder is preferred by some mineralogists for these purposes, we decided to follow the above procedure to preserve the only few crystals available of the mineral. In the fourth column of table 5, the observed values obtained from reelaboration of experimental data from the single crystal are also reported.

Discussion

The unit-cell parameters are strictly related to those of scheelite ($a = 5.2429(3)$, $c = 11.3737(6)$ Å, in HAZEN et al., 1985); with respect to this mineral, the c parameter is approximately three times as large and the a parameter is almost the same, with
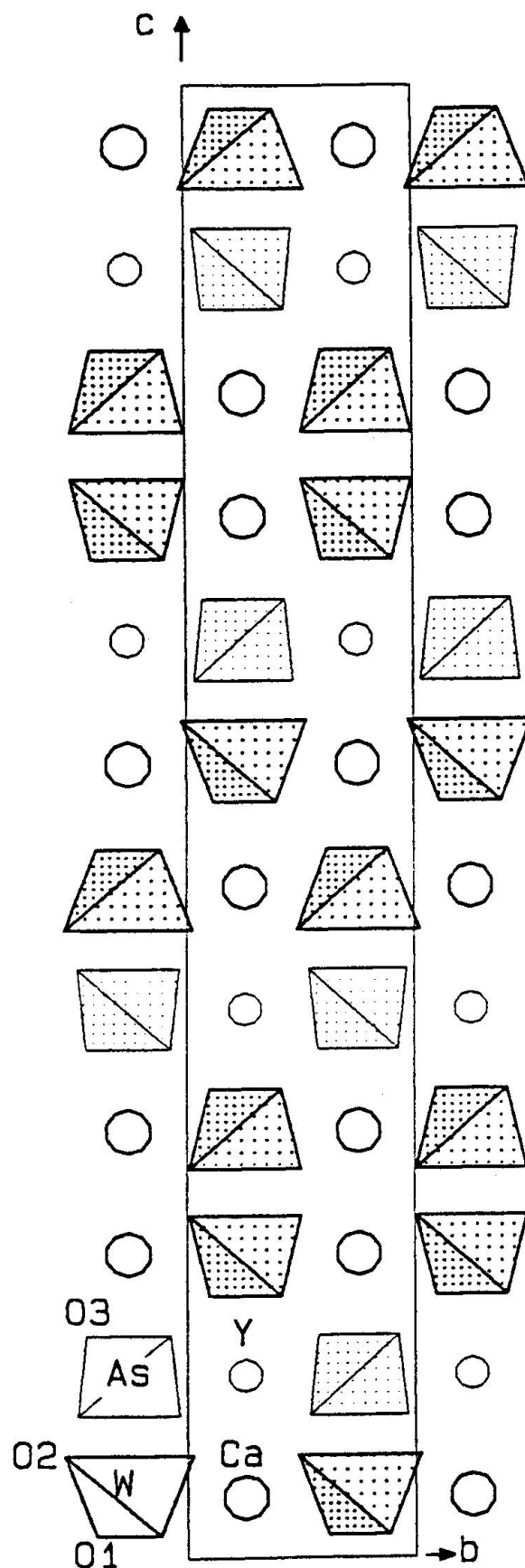

Fig. 1 Projection of the crystal structure of paraniite-(Y) along [100] obtained by program POLIEDRI (PILATI, 1990).
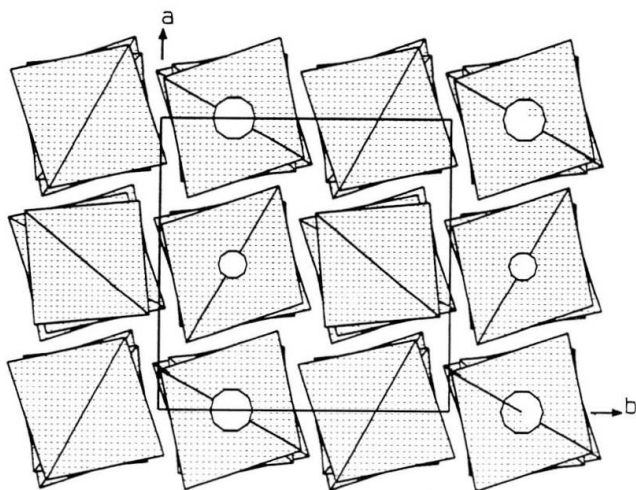
Fig. 2 Projection of the crystal structure of paraniite-(Y) along [001] obtained by program POLIEDRI (PILATI, 1990).

a small contraction; the space group, $I4_1/a$, is the same for both minerals.

The structure may be envisioned as deriving from that of scheelite, with different layers containing either Ca and W or Y and As atoms stacked along [001] in 2 : 1 molar ratio for the ideal compound with formula $Ca_2(Y,REE)(AsO_4)(WO_4)_2$: this explains why the unit-cell parameter c is a multiple of that of scheelite. However ca. 15% of the layers containing Ca and W are statistically replaced by Y and As; this partial replacement is confirmed by chemical analysis (see tables 1 and 3); a limited replacement of As by W has also been found in the final cycles of the refinement (see below).

In view of all these possible replacements, the problem of establishing the crystal-chemical formula of the mineral was considered. First of all, assuming the REE and Y (plus U) distribution provided by the chemical analysis to be correct, the average number of electrons (43) correspond-

Fig. 3 Picture of a crystal of paraniite-(Y) (size 3 mm).

ing to the mixture of Y+REE's in the mineral was deduced. On this basis, assuming no other substitution in the Y site to be present, the occupation factor of 1.11 for this site was calculated, in excellent agreement with the crystallographic result [1.100(1)]. Using this average number of electrons for Y+REE, the crystallographic occupation parameter for the Ca site [1.206(2)] corresponds to the presence of 82% (atomic) of Ca and 18% of Y (+REE). The crystallographic occupation factor for W [0.938(1)] corresponds to the presence in this site of 88.8% W and 11.2% As; in turn, the occupation factor of the As site shows the presence of 4.5% W. This is slightly different from our previous assumption of the exclusive presence of As in this site (DEMARTIN et al., 1992); however, this present interpretation is also favoured on the grounds of entropy of mixing. From all the above considerations, the following crystal-chemical formula has been derived: $[Ca_{1.64}(Y,REE)_{0.36}]_{\Sigma=2.00}$ $(Y,REE) [(As_{0.96},W_{0.04})_{\Sigma=1.00}O_4] [(W_{0.89},As_{0.11})_{\Sigma=1.00}O_4]_2$. The calculated chemical composition according to this formula is reported in table 1 together with the results of the microprobe analysis. The number of oxygen atoms required by charge balance, assuming the oxidation state of W and As to be +VI and +V, respectively, is 12.09, in satisfactory agreement with the theoretical value of 12.

The As–O distance [1.708(4) Å] is slightly but significantly larger than the average As–O distance in arsenates [1.684 Å, FERRARIS (1970)]. This confirms the partial replacement by W found in the last stage of the refinement. Conversely the average W–O distance [1.785(3) Å] remains practically the same as in pure scheelite [1.782(5) Å in HAZEN et al., 1985], in spite of the extensive substitution by As. It should also be noticed that the average As–O distance, although larger than usual, does not correspond to the weighted average of the As–O and W–O distance [1.688 Å].

The average Y–O distance [2.362(3) Å] is close to the corresponding value for chernovite-(Y) from the same area [2.358(1) Å in DEMARTIN et al., in preparation]. The average Ca–O distance [2.450(3) Å] is comparable to the corresponding value for scheelite [2.460(3) Å in HAZEN et al., 1985].

It was recently found that, under high pressure, zircon ($ZrSiO_4$) undergoes a phase transition to a scheelite-type modification; this also happens for other substances with the same structure, e.g. for wakefieldite (YVO_4) and the corresponding synthetic REE vanadates (KNITTLE and WILLIAMS, 1993, and references therein). On these grounds, a similar transformation can be expected to occur for xenotime (YPO_4) and chernovite

Tab. 6 Selected interatomic distances (Å) and angles (deg.).

W–O(1)x2	1.772(4)	O(1)–W–O(1)[b]	107.8(2)
W–O(2)[a]x2	1.797(4)	O(1)–W–O(2)[a]x2	104.7(2)
		O(1)–W–O(2)[c]x2	105.9(2)
		O(2)[a]W–O(2)[c]	127.0(2)
As–O(3)x4	1.708(4)	O(3)–As–O(3)[d]x4	107.1(1)
		O(3)–As–O(3)[e]x2	114.3(3)
Y–O(2)x4	2.330(4)		
Y–O(3)x4	2.394(4)		
Ca–O(1)x2	2.449(4)		
Ca–O(1)[f]x2	2.455(4)		
Ca–O(2)x2	2.335(4)		
Ca–O(3)x2	2.561(4)		

Symmetry codes:

$a = x, y-1, z; b = -x, -1/2-y, z; c = -x,1/2-y, z;$

$d = 3/4+y, 1/4-x, 1/4-z; e = 1-x, -1/2-y, z; f = 1-x, -y, -z.$

$(YAsO_4)$, which also have a zircon-type structure. Therefore, the new mineral might be considered as an intermediate between scheelite and the corresponding modification of chernovite (as yet unknown), stabilized by the presence of scheelite layers.

As for all the metal atoms in scheelite, the site symmetry of Y and As is 4 here but the site symmetry of Ca and W is 2; both Y and Ca are in eightfold bidisphenoidal coordination. Selected interatomic distances and angles are reported in table 6.

Acknowledgements

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