Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen =

Bulletin suisse de minéralogie et pétrographie

Band: 74 (1994)

Heft: 2

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

Autor: Demartin, Francesco / Gramaccioli, Carlo M. / Pilati, Tullio

DOI: https://doi.org/10.5169/seals-56338

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Mehr erfahren

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. En savoir plus

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. Find out more

Download PDF: 22.11.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

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

by Francesco Demartin¹, Carlo M. Gramaccioli² and Tullio Pilati³

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 I4₁/a with a=5.135(1) Å, c=33.882(5) Å, V=893.4(4) Å³, 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) ų, 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

¹ Istituto di Chimica Strutturistica Inorganica, Università degli Studi, Via Venezian, 21, I-20133 Milano, Italy.

² Dipartimento di Scienze della Terra and Centro C.N.R., Università degli Studi, Via Botticelli 23, I-20133 Milano, Italy.

³ Centro C.N.R. per lo Studio delle Relazioni tra Struttura e Reattività Chimica, Via Golgi 19, I-20133 Milano, Italy.

Tab. 1 Electron microprobe analyses results.

CONSTI	- 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 ₂ O 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	1	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)

 $\begin{array}{l} [Ca_{1.64}(Y,REE)_{0.36}]_{\Sigma=2.00}(Y,REE)[(As_{0.96},W_{0.04})_{\Sigma=1.00}O_4] \\ [(W_{0.89},As_{0.11})_{\Sigma=1.00}O_4]_2. \end{array}$

(+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 paranilte-(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

Tab. 2 Summary of crystallographic data.

Crystal system:	tetragonal				
Space group:					
	a = 5.135(1) Å				
	$c = 33.882(5) \text{ Å}^3$				
	$V = 893.4(4) \text{ Å}^3$				
	Z = 4				
Data collected w	ith MoKα radiation	up to $2\Theta = 70^{\circ}$			
Variable scan speed with maximum 90 sec. for each reflection					
Reflections measured: 4281					
Independent ref	lections:	1405			
Observed reflect	840				
R on eq. reflections (R_{int}) : 0.027					
Final R \$:	0.024				
Final R _w \$:	0.027				
N. of parameters	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 = $[\Sigma w(Fo -k)]$	$(Fc)^2/(N_{observations} - N_s)$	variables)] ^{1/2}			

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/cm³.

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 $\omega=1.87(1)$ and $\varepsilon=1.92(1)$. However, the values obtained here are not in satisfactory agreement with the corresponding estimate ($n_{\text{aver.}}=2.018$) 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.

Atom	Mult	X	y	Z	$\mathrm{U_{eq}}(\mathrm{\AA^2})$
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)

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

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-

<i>Tab.</i> 5	X-ray powder diffraction pattern for paraniite-
(Y).	

h k 1 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 1 2.296 2.291 2 1 1 12 2.235 2.250 5 1 1 12 2.235 2.229 2 0 2							
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<	h	k	1	d_{obs}	$d_{\rm calc}$	I/I _o	
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 4 2.018 2.014 2 1 2 9 </th <th>0</th> <th>1</th> <th>1</th> <th></th> <th>5.077</th> <th>6</th> <th></th>	0	1	1		5.077	6	
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 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 4 2.018 2.014 2 1 2 9 <th>0</th> <th>1</th> <th>3</th> <th>4.674</th> <th>4.674</th> <th>18</th> <th></th>	0	1	3	4.674	4.674	18	
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 1 1.842 1.841 4 2 2 0 1.818 <		0	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 1 1.842 1.841 4 2 2 0 1.818 <		1	5	4.096	4.093		
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 1 1.842 1.841 4 2 2 0 1.818 1.816 16 1 1 18 1.674 1.671 17	1	1		3.059	3.054		
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 1 1.842 1.841 4 2 2 0 1.818 1.816 16 1 1 18 1.674 1.671 17	0	1	9	3.039	3.036		
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	0	12				
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 1 1.842 1.841 4 2 2 0 1.818 1.816 16 1 1 18 1.674 1.671 17	0	1	11	2.644	2.641		
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 1 1.842 1.841 4 2 2 0 1.818 1.816 16 1 1 18 1.674 1.671 17	0	2	0	2.571	2.567	19	
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	1	2	1 .	2.296	2.291	2	
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 1 1.842 1.841 4 2 2 0 1.818 1.816 16 1 1 18 1.674 1.671 17	1	2	3	2.255	2.250	5	
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 1 1.842 1.841 4 2 2 0 1.818 1.816 16 1 1 18 1.674 1.671 17	1	1	12			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	8	2.196			
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	1	2	5	2.179	2.175	3	
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	1	1	14	2.018	2.014	2	
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	1	2	9	1.964	1.960	2	
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	12	1.901	1.899	32	
2 2 0 1.818 1.816 16 1 1 18 1.674 1.671 17	0	1	17	1.862	1.858	2	
1 1 18 1.674 1.671 17	1	2	11	1.842	1.841		
	2	2	0				
0 2 16 1.635 1.634 1		1	18			17	
1 4 4 4 16 16 16 16 16 16 16 16 16 16 16 16 16	0	2	16	1.635			
1 2 15 1.012 1.010 3	1	2	15	1.612	1.610	3	
1 3 6 1.562 1.560 32	1	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	2	2			1.527		
1 2 17 1.509 1.505 3		2				3	
0 3 11 1.501 1.496 1	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

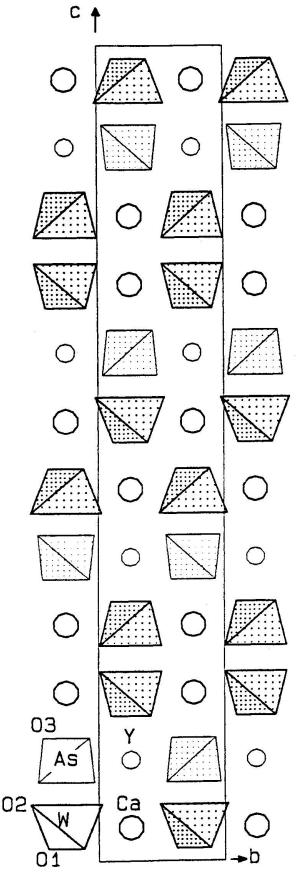


Fig. 1 Projection of the crystal structure of paramite-(Y) along [100] obtained by program POLIEDRI (PILATI, 1990).

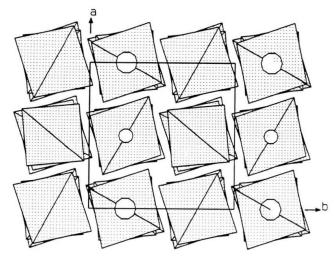


Fig. 2 Projection of the crystal structure of paraniite-(Y) along [001] obtained by program POLIEDRI (PILATI, 1990).

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 Ca₂(Y,REE) (AsO₄)(WO₄)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 (ZrSiO₄) undergoes a phase transition to a scheelite-type modification; this also happens for other substances with the same structure, e.g. for wakefieldite (YVO₄) 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 (YPO₄) and chernovite

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

	# 100 CONTRACT OF THE PARTY OF		26 60 70 30 30 30 400
W-O(1)x2 W-O(2)ax2		O(1)-W-O(1) ^b O(1)-W-O(2) ^a x2 O(1)-W-O(2) ^c x2 O(2) ^a W-O(2) ^c	107.8(2) 104.7(2) 105.9(2) 127.0(2)
As-O(3)x4	1.708(4)	O(3)-As-O(3) ^d x4 O(3)-As-O(3) ^e x2	107.1(1) 114.3(3)
Y-O(2)x4 Y-O(3)x4	2.330(4) 2.394(4)		
Ca-O(1)x2 Ca-O(1) ^f x2 Ca-O(2)x2 Ca-O(3)x2	2.335(4)		

Symmetry codes:

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

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

(YAsO₄), 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

The courtesy of Fausto Parani in providing us with the unique sample of the mineral is gratefully acknowledged. Financial support from the Italian C.N.R. is also acknowledged. We also thank Roberto Appiani for the photograph of figure 3.

References

Mitt., 68, 125-132.

DEMARTIN, F., GRAMACCIOLI, C.M. and PILATI, T. (1992): Structure of a new natural tungstate arsenate, [Ca₂Y(AsO₄)(WO₄)₂], structurally related to scheelite. Acta Cryst., C48, 1357–1359.

FERRARIS, G. (1970): Considerazioni sulla configurazione del gruppo (AsO₄H)²-. Rend. Soc. Ital. Mineral. Petr., 26, 589-598.

Graeser, S. (1965): Die Mineralfundstellen im Dolomit des Binnatales. Schweiz. Mineral. Petrogr. Mitt., 45,

Graeser, S. (1966): Asbecasit und Cafarsit, zwei neue Mineralien aus dem Binntal (Kt. Wallis). Schweiz. Mineral. Petrogr. Mitt., 46, 367-375.

Graeser, S. and Schwander, H. (1987): Gasparite-(Ce) and monazite-(Nd): two new minerals to the monazite group from the Alps. Schweiz. Mineral, Petrogr. Mitt., 67, 103–113.

Graeser, S., Schwander, H., Demartin, F., Gramaccioli, C.M., Pilati, T. and Reusser, E. (1994): Fetiasite (Fe²⁺,Fe³⁺,Ti)₃O₂As₂O₅, a new arsenite mineral: its description and structure determination. Am. Mineral. (in press)

HAZEN, R.M., FINGER, L.W. and MARIATHASAN, J.W.E. (1985): High-pressure crystal chemistry of scheelitetype tungstates and molybdates. J. Phys. Chem. of Solids, 46, 253–263.

KNITTLE, E. and WILLIAMS, Q. (1993): High-pressure Raman spectroscopy of ZrSiO₄: observation of the zircon to scheelite transition at 300 K. Am. Mineral.,

Mandarino, J.A. (1981): The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. Can. Mineral., 19, 441–450. PILATI, T. (1990): POLIEDRI: A Fortran program de-

signed for plotting any kind of convex polyhedron. Acta Cryst., A46 C-69. WILL, G. (1979): POWLS: A powder least-squares pro-

gram. J. Appl. Cryst., 12, 483-485.

Manuscript received November 14, 1993; accepted January 22, 1994.