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Paganoite, NiBi^{3+}As^{5+}O$_5$, a new mineral from Johanngeorgenstadt, Saxony, Germany: description and crystal structure

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Abstract: Paganoite, ideally NiBi^{3+}As^{5+}O$_5$, triclinic space group $P\bar{1}$, $a = 6.7127(8)$, $b = 6.8293(8)$, $c = 5.2345(6)$ Å, $\alpha = 107.625(2)°$, $\beta = 95.409(2)°$, $\gamma = 111.158(2)°$, $V = 207.62$ Å^3, a:b:c: = 0.9829:1:0.7665, Z = 2, is a new mineral found on a single nickeline-veined quartz specimen from Johanngeorgenstadt, Saxony, Germany. The strongest seven lines of the X-ray powder-diffraction pattern [d in Å (I) (hkl)] are: 5.943 (100) (010); 3.233 (100) (011); 3.067 (60) (0$\bar{2}$1); 3.047 (50) (200); 2.116 (50) ($\bar{1}$12, 0$\bar{3}$1, 311, $\bar{1}$22, 231); 2.095 (40) ($\bar{2}$30, 102); 1.659 (40) ($\bar{4}$20). It occurs as isolated orange-brown to deep-golden-brown crystals and crystal aggregates which are always intimately associated with aerugite; additional associations include bunsenite, xanthiosite, rooseveltite, native bismuth and two undefined arsenates. Individual prismatic crystals are subhedral to euhedral, elongate along [010] with a length-to-width ratio of 3:1, and average 0.3 mm in longest dimension. Forms observed are {100} major, {010} minor, {001} minor and perhaps {$h0l$} minor. Crystals possess a very pale orange-brown streak, are transparent (crystals) to translucent (aggregates), brittle, adamantine (almost gemmy), and do not fluoresce under ultraviolet light. The mineral shows neither twinning nor cleavage, has an uneven fracture, and the calculated density (for the empirical formula) is 6.715 g/cm^3. Electron-microprobe analyses yielded NiO 15.37, CoO 2.05, Bi$_2$O$_3$ 55.06, As$_2$O$_5$ 28.0, total 100.48 wt. %. The empirical formula, derived from the crystal-structure analysis and electron-microprobe analyses, is (Ni$^{2+}_{0.86}$Co$^{2+}_{0.11}$)$_{\Sigma 0.97}$Bi$^{3+}_{0.99}$As$^{5+}_{1.02}$O$_5$, based on O = 5. In reflected plane-polarized light in air, it is grey with no obvious internal reflections, bireflectance or pleochroism. Measured reflectance values, in air and in oil, are tabulated: indices of refraction calculated from these at 589 nm are 2.07 and 2.09. The name honours Renato and Adriana Pagano for their long-standing service to the European mineralogical community.

The crystal structure of paganoite has been solved by direct methods and refined on the basis of F^2 using 977 unique reflections measured with Mo$K\alpha$ X-radiation on a diffractometer equipped with a CCD-based detector. The final $R1$ was 4.4%, calculated for the 926 observed reflections. The structure contains AsO$_4$ tetrahedra and distorted Ni^{2+}O$_6$ octahedra, as well as one-sided Bi^{3+}O$_5$ polyhedra due to the presence of an s^2 lone pair of electrons on the Bi^{3+} cation. The structure is an open framework composed of dimers of edge-sharing NiO$_6$ octahedra that are linked by vertex-sharing with AsO$_4$ tetrahedra. Bi^{3+} cations occur within voids in the framework, and bond only to framework elements. The structure of paganoite is very closely related to that of jagowerite, BaAl$_2$P$_2$O$_8$(OH)$_2$, which possesses an identical framework of octahedra and tetrahedra.

Key-words: paganoite, new mineral, NiBi^{3+}As^{5+}O$_5$, crystal structure, Johanngeorgenstadt (Saxony, Germany).

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Introduction

The pedigree of this particular specimen, containing the new mineral described herein, paganoite, is somewhat shrouded in mystery. Undoubtedly mined in the mid-1800's, nothing was preserved of its previous history until it was located in 1981 by the American mineral dealer David New in the back of a drawer in an old mineral shop in Germany. The identities of the minerals present on the specimen were unrecognized at that time. Somewhat later on, one of us (MNF) megascopically identified both bunsenite, NiO, crystals and the Ni-bearing arsenates aerugite, $Ni_{17}As_6O_{32}$, and xanthiosite, $Ni_3(AsO_4)_2$, on the sample in association with nickeline, NiAs, and native bismuth, and purchased the specimen from Mr. New in March, 1988. This association is unique to only one known mineral locality – Johanngeorgenstadt, Saxony, Germany. Although there was no geographic information provided with the sample, we are quite confident that this is the correct locality where the sample was collected, since bunsenite, aerugite and xanthiosite are quite rare, and the megascopic appearance of specimens from Johanngeorgenstadt is quite distinct from that of specimens from the only other known locality for this assemblage – South Terras Mine, St. Stephen-in-Brannell, Cornwall, England (Davis *et al.*, 1965).

Further detailed binocular study revealed the presence of four additional unknowns on the hand sample; colourless to white adamantine crystals, deep-golden-brown crystals, deep-blue microcrystalline crusts intimately associated with quartz, and deep-red crystalline masses. Subsequent routine X-ray powder-diffraction studies, coupled with SEM energy-dispersion analyses, have shown that the colourless to white crystals are rooseveltite, Bi AsO_4, but also that the other three phases are new to science. Searches of various national mineral collections in both Europe and North America have failed to uncover additional examples of these particular unknowns on specimens labelled as bunsenite, aerugite or xanthiosite from Johanngeorgenstadt, Saxony, Germany. Mineralogical and crystal-structure data for the first of these, the deep-golden-brown crystals now known as paganoite, are given below.

The mineral name honours both Renato (b. 1938) and Adriana (b. 1939) Pagano of Cinisello, Milan, Lombardy, Italy. They are very competent amateur mineralogists who have contributed significantly to the advancement of specimen mineralogy within Europe for over thirty-five years. They have authored several articles on both historical and locality subjects and continue to support both mineralogists and museum curators in their research and acquisition projects. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA. The holotype specimen still resides within the mineral collection of one of us (MNF) and will remain so until the other two undefined phases are fully characterized. Small fragments (of paganoite with aerugite) in a gelatin capsule, a SEM stub (with paganoite and aerugite crystals), and several powder and single-crystal mounts of paganoite have been deposited in the Systematic Reference Series of the National Mineral Collection of Canada, housed within the Geological Survey of Canada, Ottawa, Canada, under catalogue number NMCC 68083. The polished section used for both the electron-microprobe and reflectance studies will be deposited in the mineral collections at The Natural History Museum, London, UK.

Occurrence and associated minerals

The bulk of the specimen, which measures 7x5x4 cm, consists of a fine-grained quartz matrix with several veins of nickeline up to 4 mm thick, dispersed throughout. The nickeline veinlets are rimmed by native bismuth which, in turn, is rimmed by intergrown very dark-green crystals of bunsenite, up to 1 mm in size. Significant areas of the sample are richly covered by a number of colourful secondary minerals. These include: grass-green aerugite crystals and crystal aggregates, with euhedral crystals up to 1 mm in size; yellow crystalline xanthiosite, with rare euhedral crystals up to 0.5 mm in size; colourless to white adamantine crystals of rooseveltite, up to 1 mm in size in several vugs; deep-blue crusts of an undefined phase, intimately associated with quartz, which may be the Ni-Co analogue of alarsite; and an undefined deep-red crystalline phase that is a probable new Ni-Co arsenate. Paganoite is found intimately associated with the aerugite and most likely formed from the breakdown of primary nickeline and native bismuth. However, it is tempting to speculate that it might also be formed by the reaction of bunsenite and rooseveltite, since the following reaction fits perfectly:

$$\underset{\text{bunsenite}}{NiO} + \underset{\text{rooseveltite}}{BiAsO_4} \rightarrow \underset{\text{paganoite}}{NiBiAsO_5}$$

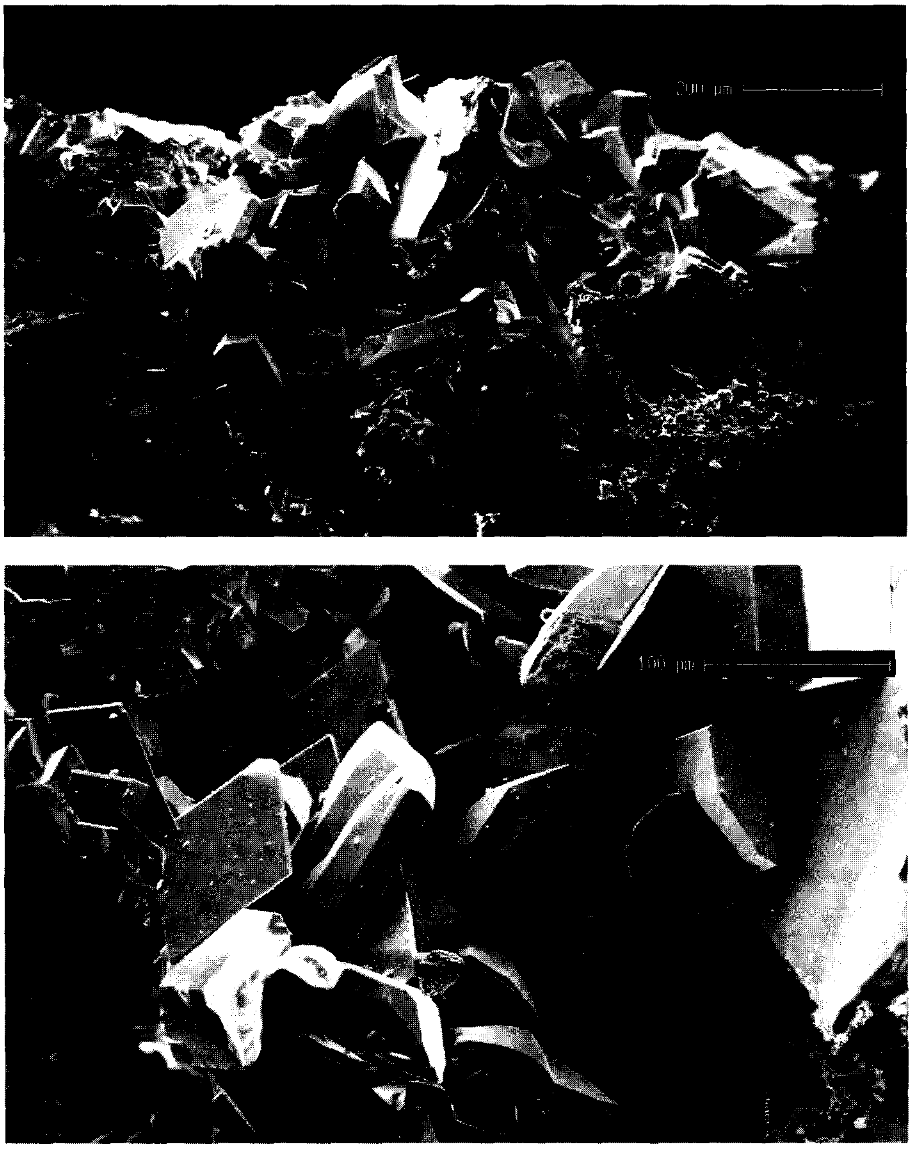

Fig. 1. SEM photomicrograph of a typical paganoite-aerugite assemblage. a) General view. Large subhedral to euhedral crystals are paganoite and more fine-grained mottled material is aerugite. b) Close up view of a paganoite crystal aggregate.

Physical properties

Paganoite occurs as both individual crystals and crystalline aggregates that are sparsely scattered in several areas of a few centimetres across the specimen and, as previously mentioned, are always intimately associated with aerugite. A SEM photomicrograph of a typical paganoite-aerugite assemblage is given in Fig. 1a and a closeup of a paganoite aggregate is given in Fig. 1b. Individual prismatic subhedral to euhedral crystals average 0.3 mm in size, but may reach to 1 mm in maximum length, are elongate along [010], and have a length-to-width ratio of approximately 3:1. These crystals are too small to determine crystal forms by optical goniometry; single-crystal precession studies indicate that the dominant form is {100} with minor {010}, {001} and perhaps a minor {*h*0*l*} face. Twinning was not observed megascopically nor in X-ray single-Crystal Studies. Crystals are orange-brown to deep-golden-brown, and the streak is very pale orange-brown. The lustre is adamantine, almost gemmy, and crystals are transparent, whereas aggregates are translucent. Paganoite is brittle, with an uneven fracture, no observable cleavage, and is nonfluorescent under both long- and short-wave ultraviolet radiation. The density could not be measured because of the small size of available crystals and dearth of material. The calculated density, on the basis of the empirical formula and unit-cell parameters derived from the crystal structure, is 6.715 g/cm^3; the idealized formula and same set of unit-cell parameters gives a calculated density of 6.760 g/cm^3. Crystals are too small to properly ascertain hardness, but the mineral is soft since grains are easily crushed between two glass slides.

Reflectance studies

In plane-polarized reflected light, paganoite is grey with no perceptible bireflectance, no pleochroism and no obvious internal reflections. However, under crossed polars the mineral shows dark-orange internal reflections. Reflectance measurements, in both air and oil, were made relative to a Zeiss silicon carbide standard, SiC no. 472, and are presented in Table 1. The oil index of refraction (N_D) is 1.515. The COM wavelengths are listed in bold face within the table. Refractive indices calculated from the air reflectances at 589 nm are 2.07 and 2.09. Vikkers micro-hardness was not attempted because the material available for study was but a single grain mount; VHN values obtained would not be reliable.

Table 1. Reflectance data for paganoite.

λ nm	R_1	R_2	$^{im}R_1$	$^{im}R_2$
400	13.8	14.0	3.27	3.38
420	13.35	13.6	3.09	3.24
440	13.05	13.3	2.94	3.12
460	12.9	13.2	2.88	3.02
470	12.85	13.1	2.84	2.99
480	12.75	13.0	2.80	2.95
500	12.6	12.85	2.74	2.91
520	12.5	12.7	2.69	2.88
540	12.4	12.65	2.64	2.82
546	12.35	12.6	2.63	2.80
560	12.25	12.55	2.61	2.79
580	12.2	12.5	2.58	2.78
589	12.15	12.5	2.57	2.77
600	12.1	12.45	2.56	2.76
620	12.15	12.4	2.57	2.77
640	12.1	12.4	2.54	2.74
650	12.0	12.35	2.52	2.73
660	12.0	12.3	2.50	2.72
680	11.95	12.3	2.48	2.72
700	11.95	12.35	2.48	2.73

Chemical composition

Paganoite crystals were analyzed with a JEOL 733 electron microprobe (using Tracor Northern 5500 and 5600 automation), utilizing an operating voltage of 15 kV, a beam current of 20 nA, and a beam 20 μm in diameter. Data reduction was performed with a PAP routine in XMAQNT (pers. comm. C. Davidson, CSIRO). The following standards were employed: synthetic cochromite (Co *K*α), synthetic $NiTa_2O_6$ (Ni *K*α), natural mimetite (As *L*α), and synthetic bismutotantalite (Bi *M*α). A 100s energy-dispersion scan showed no other elements other than those reported. Valency states for Ni, Bi and As, as well as the number of O atoms, were determined by crystal-structure analysis prior to final interpretation of the electron-microprobe results. The average of two determinations (and range) gave NiO 15.37 (15.03 – 15.71), CoO 2.05 (2.01 – 2.08), Bi_2O_3 55.06 (55.00 – 55.12), As_2O_5 28.00 (27.87 – 28.13), total 100.48 wt. %. With O = 5, the empirical formula is $(Ni^{2+}_{0.86}Co^{2+}_{0.11})_{\Sigma 0.97}Bi^{3+}_{0.99}As^{5+}_{1.02}O_5$. Thus the analyzed material is a slightly cobaltian paganoite. The idealized formula, $NiBiAsO_5$, requires NiO 17.67, Bi_2O_3 55.13, As_2O_5 27.19, total 100.00 wt. %.

The physical refractive energy (K_P) value is 0.1608 and is derived from the average refractive index ($\bar{n}$) of 2.08 and the calculated density of 6.715 g/cm^3. The chemical refractive energy (K_C) value is 0.1596 and is based on the empirical formula given above. The compatibility index ($1 - K_P/K_C$) is – 0.008 which is rated as superior based on the classification scheme of Mandarino (1981).

X-ray crystallography

Preliminary single-crystal precession photos of a paganoite crystal showed that the symmetry is tri-

Table 2. Miscellaneous information pertaining to the structure determination of paganoite.

a (Å)	6.7127(8)	Crystal size (mm)	0.12 x 0.12 x 0.04
b (Å)	6.8293(8)	D_{calc} (g/cm^3)	6.760
c (Å)	5.2345(6)	μ (mm^{-1})	54.7
α (°)	107.625(2)	Total ref.	1851
β (°)	95.409(2)	Unique ref.	977
γ (°)	111.158(2)	Unique $\|F_o\| \geq 4\sigma_F$	926
V (Å^3)	207.62	Final R* (%)	4.4
Space Group	$P\bar{1}$	S†	1.10
F(000)	368		
Unit-cell contents: 2(NiBiAsO$_5$)			

*$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

†$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for m observations and n parameters

clinic with space group choices $P1$ or $P\bar{1}$. The crystal-structure determination indicated that $P\bar{1}$ is the correct space group and the cell parameters derived from the structure determination and other pertinent information are given in Table 2. The unit-cell parameters, given below, are for the same orientation as those derived from the structural study.

Unit-cell parameters, $a = 6.709(2)$, $b = 6.820(3)$, $c = 5.229(2)$ Å, $\alpha = 107.63(3)°$, $\beta = 95.43(3)°$, $\gamma = 111.13(3)°$, $V = 207.0(1)$ Å^3, $a{:}b{:}c = 0.9837{:}1{:}0.7667$, were refined from 29 powder reflections representing d values between 3.233 and 1.436 Å for which unambiguous indexing was possible on the basis of the calculated intensities derived from the crystal structure. A fully indexed and shrinkage-corrected powder pattern is presented in Table 3. The powder data are not similar to any other inorganic phase listed in the Powder Diffraction File up to and including Set 49. Paganoite diffracts exceedingly well; all diffraction lines in the front reflection region on the powder film are very clean and sharp.

Crystal-structure refinement

A euhedral crystal with superior optical properties was mounted on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector and a crystal-to-detector distance of 5 cm. A discussion of the application of CCD detectors to the analysis of crystal structures is provided by Burns (1998). A sphere of data was collected using monochromatic Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω, with 20s used to acquire each frame. Several hundred frames of data were analyzed to locate diffraction maxima for the determination of the unit-cell parameters. The data were consistent with a triclinic unit cell which was refined using least-squares techniques (Table 2). Data were collected for $3° \leq 2\theta \leq 56.7°$ in approximately 17 hours; comparison of the intensities of identical reflections collected at different times during the data collection showed no evidence of significant decay. The three-dimensional data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption correction based upon the intensities of equivalent reflections was applied using the program SADABS (G. Sheldrick, unpublished), and the data were further corrected for Lorentz, polarization, and background effects. A total of 1851 reflections was collected; merging of equivalent reflections gave 977 unique reflections ($R_{INT} = 4.5\%$) with 926 classed as observed ($|F_o| \geq 4\sigma_F$).

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from International Tables for X-Ray Crystallography, Vol. IV (Ibers & Hamilton, 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure.

Reflection statistics indicated the space group $P\bar{1}$, with verification provided by the successful solution of the structure by direct methods. The structure was refined on the basis of F^2 using all unique reflections. Following refinement of the atomic positional parameters and isotropic-displacement parameters for all atoms, the agreement factor ($R1$) was 6.4% for observed reflections. The displacement parameters for all atoms were then converted to anisotropic forms and were further refined to-

Table 3. X-ray powder-diffraction data for paganoite.

	$I_{est.}$	dÅ$_{(meas.)}$	dÅ$_{(calc.)}$	*hkl*
	100	5.943	5.928	010
	20	5.546	5.531	$\bar{1}10$
	25	4.854	4.851	001
	30	4.689	4.677	$0\bar{1}1$
	30	4.306	4.306	$\bar{1}01$
	10	3.913	3.908	$1\bar{1}1$
	30	3.434	3.432	$\bar{1}11$
			3.431	101
	5	3.315	3.318	$\bar{2}10$
*	100	3.233	3.224	011
*	15	3.117	3.118	$1\bar{2}1$
*	60	3.067	3.074	$0\bar{2}1$
*	50	3.047	3.046	200
*	15	2.970	2.964	020
*	30	2.895	2.896	$\bar{2}01$
*	25	2.800	2.800	$\bar{2}11$
*	25	2.766	2.765	$\bar{2}20$
*	30	2.678	2.681	$2\bar{1}1$
*	25	2.605	2.600	$0\bar{1}2$
*	15	2.547	2.550	$2\bar{2}1$
	10	2.486	2.489	111
			2.479	$\bar{1}\bar{2}1$
	15	2.450	2.455	$\bar{1}02$
			2.450	$\bar{1}\bar{1}2$
*	10	2.403	2.406	$\bar{1}21$
	20	2.342	2.346	210
			2.336	$1\bar{1}2$
*	10	2.319	2.317	120
	5	2.259	2.262	$1\bar{2}2$
			2.252	$1\bar{3}1$
	3	2.199	2.199	021
	50	2.116	2.122	$\bar{1}12$
			2.118	$0\bar{3}1$
			2.113	$\bar{3}11$
			2.112	$\bar{1}\bar{2}2$
			2.106	$2\bar{3}1$
	40	2.095	2.096	$\bar{2}30$
			2.094	102
*	20	2.044	2.045	$\bar{2}\bar{1}2$
	1	2.024	2.030	300
*	10	2.003	2.003	$\bar{2}12$
*	20	1.975	1.976	030
	15	1.936	1.937	$\bar{3}21$
			1.936	$3\bar{1}1$
*	30	1.912	1.912	$\bar{2}\bar{2}1$
*	10	1.889	1.888	211
*	10	1.842	1.842	121
*	20	1.801	1.801	$2\bar{3}2$
	3	1.780	1.782	$\bar{2}31$
			1.774	$\bar{1}31$
*	20	1.770	1.769	$\bar{2}\bar{2}2$
	30	1.741	1.742	112
			1.740	$\bar{3}12$
			1.737	301
*	20	1.719	1.719	$\bar{1}\bar{1}3$
*	10	1.681	1.681	$2\bar{4}1$
*	40	1.659	1.659	$\bar{4}20$
	5	1.635	1.637	$1\bar{2}3$
	5b	1.615	1.618	$3\bar{2}2$
			1.617	003
			1.612	022
			1.610	$1\bar{1}3$
	10	1.599	1.600	$1\bar{4}2$
			1.598	$\bar{1}40$
	10	1.586	1.587	$0\bar{4}1$
			1.585	$\bar{3}22$
	5	1.570	1.570	$3\bar{3}2$
*	20	1.559	1.559	$\bar{4}01$
*	20	1.549	1.549	$1\bar{3}3$
*	10	1.534	1.533	$\bar{3}40$
	1	1.522	1.523	400
	5	1.514	1.515	$\bar{2}\bar{3}1$
			1.514	221
	3	1.501	1.502	$4\bar{3}1$
			1.500	$\bar{1}13$
*	10	1.494	1.494	$4\bar{1}1$
	15b	1.480	1.485	311
			1.481	$\bar{2}13$
			1.481	103
			1.480	$\bar{2}\bar{3}2$
			1.474	$\bar{1}\bar{3}3$
	10	1.459	1.461	$\bar{3}\bar{2}2$
			1.457	$\bar{4}31$
*	20	1.436	1.436	131
	5	1.425	1.425	320
	5	1.415	1.415	$\bar{1}\bar{4}1$
			1.414	230
	20	1.406	1.407	$\bar{1}32$
			1.405	$\bar{3}\bar{1}3$
	15b	1.382	1.383	$\bar{3}32$
			1.378	$4\bar{4}1$

114,6 mm Debye-Scherrer powder camera; Cu radiation, Ni filter (λ Cu*K*α = 1.54178 Å)
– Intensities estimated visually; * = lines used for unit-cell refinement
– Corrected for shrinkage and no internal standard; b = broad line
– Indexed on a = 6.709, b = 6.820, c = 5.229 Å, α = 107.63°, β = 95.43°, γ = 111.13°

Table 4. Atomic-position parameters and equivalent isotropicdisplacement parameters for paganoite.

	x	y	z	$*U_{eq}$
Ni	0.3634(3)	0.7345(3)	0.8307(3)	133(6)
Bi	0.23608(7)	0.96812(7)	0.40945(9)	127(3)
As	0.1864(2)	0.3875(2)	0.1578(3)	108(5)
O(1)	0.501(2)	0.050(2)	0.770(2)	118(18)
O(2)	0.228(2)	0.628(2)	0.416(2)	119(17)
O(3)	0.235(2)	0.423(2)	0.864(2)	167(20)
O(4)	-0.083(2)	0.202(2)	0.084(2)	145(19)
O(5)	0.347(2)	0.275(2)	0.268(2)	163(20)

$*U_{eq} = U_{eq}$ Å^2 x 10^4

Table 5. Anisotropic-displacement parameters for the structure of paganoite.

	$*U_{11}$	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	99(10)	170(10)	129(10)	49(7)	23(6)	57(7)
Bi	77(4)	183(4)	134(4)	55(2)	36(2)	67(2)
As	72(8)	144(8)	108(8)	38(5)	15(5)	51(5)
O(1)	70(44)	237(47)	70(38)	47(33)	24(33)	95(38)
O(2)	122(47)	149(41)	128(42)	65(34)	48(35)	87(37)
O(3)	176(54)	148(41)	194(48)	51(35)	34(39)	97(39)
O(4)	111(46)	166(44)	160(47)	61(36)	45(37)	55(37)
O(5)	87(47)	204(47)	237(53)	103(40)	48(40)	80(41)

$*U_{ij} = U_{ij}$ x 10^4

gether with the positional parameters and a weighting scheme of the structure factors. The final model resulted in a $R1$ index of 4.4% for 926 unique observed reflections ($|F_o| \geq 4\sigma_F$) and a goodness-of-fit (S) of 1.10. In the final cycle of refinement the average parameter shift/esd was 0.000 and the largest peaks in the final difference-Fourier maps were 2.73 and -2.81 e/Å^3. The final atomic-position parameters and anisotropic-displacement parameters are given in Tables 4 and 5, respectively, and selected interatomic distances and angles are given in Table 6.

Description of the structure

All atoms in the structure are on general positions in space group $P\bar{1}$. Anion bond-valence sums are met (Table 7), thus there is no evidence of H atoms in the structure. Inspection of the atom list in Table 4 results in the formula $NiBiAsO_5$, $Z = 2$.

There is only one symmetrically distinct site for each cation in the structure. The Ni^{2+} cation is coordinated by six atoms of O arranged at the corners of a distorted octahedron, with a <Ni-O> bond length of 2.087 Å. The As^{5+} cation is tetrahedrally coordinated by O atoms, with an <As-O> bond length of 1.687 Å. The Bi^{3+} cation occupies a distinctly one-sided coordination polyhedron (Fig. 2) composed

Table 6. Selected interatomic distances (Å) and angles (°) for paganoite.

Bi-O(1)a	2.101(9)	Ni-O(1)e	2.04(1)
Bi-O(1)b	2.246(9)	Ni-O(3)	2.02(1)
Bi-O(2)	2.317(9)	Ni-O(2)	2.06(1)
Bi-O(5)b	2.33(1)	Ni-O(5)a	2.08(1)
Bi-O(4)c	2.43(1)	Ni-O(4)f	2.14(1)
<Bi-O>	2.285	Ni-O(1)b	2.150(9)
		<Ni-O>	2.087
As-O(3)d	1.69(1)		
As-O(5)	1.68(1)		
As-O(2)	1.688(9)		
As-O(4)	1.71(1)		
<As-O>	1.687		

a = 1-x, 1-y, 1-z; b = x, y+1, z; c = -x, 1-y, -z; d = x, y, z-1; e = 1-x, 1-y, 2-z; f = -x, 1-y, 1-z.

Table 7. Bond-valence* analysis (*vu*) for paganoite.

	Bi	Ni	As	Σ
O(1)	0.97 0.66	0.35 0.26		2.25
O(2)	0.54	0.33	1.24	2.13
O(3)		0.34	1.30	1.64
O(4)	0.40	0.27	1.17	1.84
O(5)	0.52	0.32	1.27	2.12
Σ	3.09	1.87	4.98	

*parameters from Brese & O'Keefe (1991)

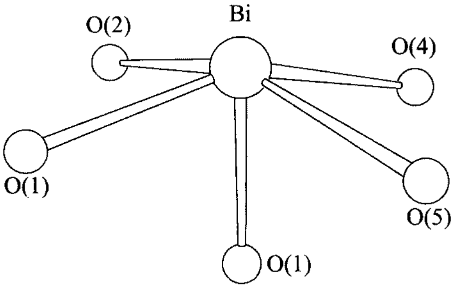

Fig. 2. The coordination polyhedron about Bi^{3+} in the structure of paganoite.

of five O atoms, with a mean <Bi-O> bond length of 2.285 Å. The distortion of the BiO_5 polyhedron is presumably due to the presence of a s^2 lone pair of electrons on the Bi^{3+} cation.

The structure is shown projected along [001] and [010] in Fig. 3. Symmetrically equivalent NiO_6 octahedra share the O(1)-O(1) edge, forming a dimer of composition Ni_2O_{10}. With the exception of the common O(1)-O(1) edge, all vertices of the NiO_6 octahedra are shared with AsO_4 tetrahedra, and all vertices of the AsO_4 tetrahedra are also elements of NiO_6 octahedra. This linkage results in a framework that contains large voids (Fig. 3a). The Bi^{3+} cations occur in the voids, with all five of their coordinating ligands being framework elements. The s^2 lone pair of electrons associated with the Bi^{3+} cation presumably project approximately along [110], into the voids in the framework (Fig. 3a).

The structure of paganoite is very closely related to that of jagowerite, $BaAl_2P_2O_8(OH)_2$ (Meagher, 1974). Both structures are shown projected along [100] in Fig. 4. Each involves an identical framework of edge-sharing dimers of octahedra linked by vertex sharing with tetrahedra. In paganoite, the framework has the composition $[NiAsO_5]^{-3}$, whereas the framework of jagowerite has the composition $[AlPO_4(OH)]^{-1}$. Thus, the voids in the frameworks contain twice as many Bi^{3+} cations in paganoite as Ba^{2+} cations in jagowerite. In jagowerite, the large Ba^{2+}

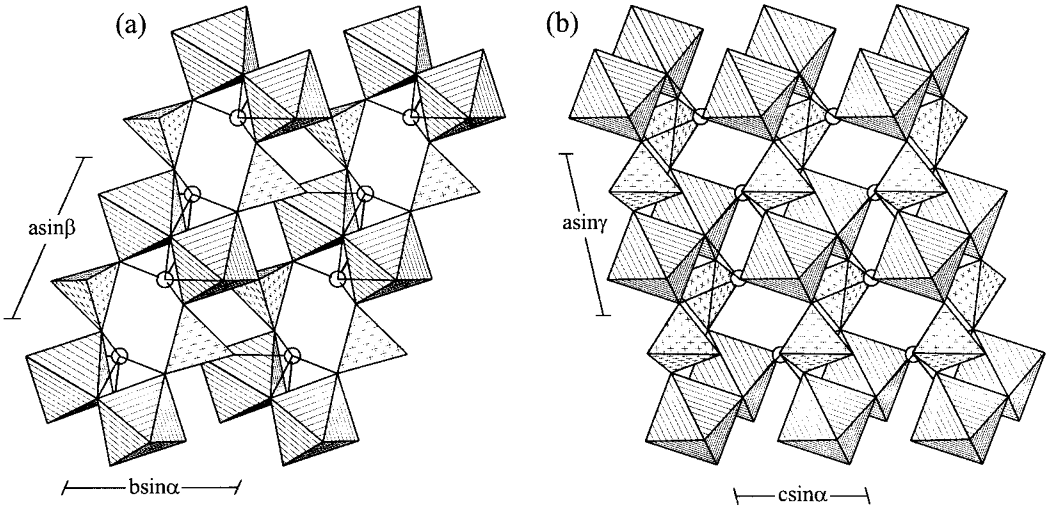

Fig. 3. Polyhedral representations of the structure of paganoite projected along (a) [001] and (b) [010]. NiO_6 octahedra are shown shaded with parallel lines, AsO_4 tetrahedra are shown shaded with crosses, and Bi^{3+} cations are represented by open circles.

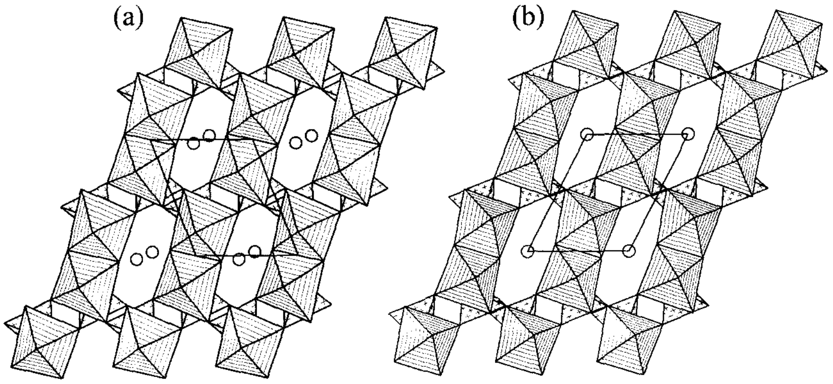

Fig. 4. Polyhedral representation of the structures of (a) paganoite and (b) jagowerite projected along [100]. The unit cells are outlined. In each case, octahedra are shaded with parallel lines and tetrahedra with crosses.

cations are located at the centers of the structural voids, on the center of symmetry. In the case of paganoite, the Bi^{3+} cations are located off-center, with the s^2 lone electron pair projecting towards the center of the void (Fig. 3a).

The structures of both paganoite and jagowerite may be classed as structures involving frameworks with edge-sharing between octahedra, and corner-sharing between octahedra and tetrahedra in the structural hierarchy of $M^{[6]}T^{[4]}\varphi_n$ minerals proposed by Hawthorne (1990).

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