Bianchiniite, Ba$_2$(Ti$^{4+}$V$^{3+}$)(As$_2$O$_5$)$_2$OF, a new diarsenite mineral from the Monte Arsiccio mine, Apuan Alps, Tuscany, Italy

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Abstract

The new mineral bianchiniite, Ba$_2$(Ti$^{4+}$V$^{3+}$)(As$_2$O$_5$)$_2$OF, has been discovered in the Monte Arsiccio mine, Apuan Alps, Tuscany, Italy. It occurs as brown [001] tabular crystals, up to 1 mm across, with a vitreous lustre. It is brittle, with a perfect [001] cleavage. Streak is brownish. In reflected light, bianchiniite is grey, with orange-yellow internal reflections. It is weakly bireflectant, with a very weak anisotropy in shades of grey. Minimum and maximum reflectance data for COM wavelengths \([R_{\min}/R_{\max}] (\%, \phi, nm)\) are: 5.0/5.8 (470), 5.7/6.5 (546), 5.7/7.0 (589) and 5.2/6.3 (650). Electron microprobe analyses gave (wt.\% – average of 10 spot analyses): TiO$_2$ 10.34, V$_2$O$_3$ 3.77, Fe$_2$O$_3$ 3.76, As$_2$O$_3$ 44.36, Sb$_2$O$_3$ 0.22, SrO 0.45, BaO 34.79, PbO 0.28, F 1.77, sum 99.74, \(-O=F\) = F – 0.75, total 98.99. On the basis of 12 anions per formula unit, the empirical formula of bianchiniite is \([\text{Ba}_2.00\text{Sr}_0.04\text{Pb}_0.02\text{As}_3.98\text{Sb}_0.02\text{O}_{10.18}\text{F}_{0.82}]\). Bianchiniite is tetragonal, space group \(I4/mcm\), with unit-cell parameters \(a = 8.7266(6), c = 15.6777(7) \text{\AA}, V = 1193.91(12) \text{\AA}^3\) and \(Z = 8\). Its crystal structure was refined from single-crystal X-ray diffraction data to \(R_w = 0.0134\) on the basis of 355 unique reflections with \(F_0 > 4o(F_0)\) and 34 refined parameters. The crystal structure shows columns of corner-sharing \([\text{Ti}/(\text{V,Fe})]\)-centred octahedra running along \(c\), connected along \(a\) and \(b\) through \((\text{As}_2\text{O}_5)\) dimers. A [001] layer of Ba-centred \([10\times 2]\)-coordinated polyhedra is intercalated between \((\text{As}_2\text{O}_5)\) dimers. Bianchiniite has structural relations with fresnoite- and melilite-group minerals. The name honours the two mineral collectors Andrea Bianchini (b. 1959) and Mario Bianchini (b. 1962) for their contribution to the knowledge of the mineralogy of pyrite ± baryte ± iron-oxide ore deposits from the Apuan Alps.

Keywords: bianchiniite, arsenite, barium, titanium, vanadium, new mineral, crystal structure, Monte Arsiccio, Apuan Alps, Italy

Introduction

Arsenic mineralogy is a very interesting topic, owing to the complex crystal-chemistry of this element, occurring in more than 400 mineral species, and its environmental significance (e.g. Majzlan et al., 2014). Usually, arsenic occurs in arsenates as \(\text{As}^{5+}\), forming the oxy-anion \((\text{As}^{5+}_n\Phi_m)\), where \(\Phi\) is a ligand \(\text{[e.g. O}_2^{2-}, \text{(OH)}^-\ldots]\); the oxy-anion \((\text{As}^{5+}_n\Phi_m)\) is definitely rarer, occurring in only a few minerals. As the Pauling’s bond strength for each bond in an \((\text{As}^{5+}_n\Phi_m)\) group is 1 valence unit (vu), such groups can be polymerised, giving rise to different possible configurations. Consequently, in addition to isolated \((\text{As}^{5+}_n\Phi_m)\) groups, \((\text{As}_2\text{O}_3)\) dimers, \((\text{As}_3\text{O}_5)\) tetratramers and \((\text{As}_5\text{O}_{11})\) pentamers are known in minerals. In addition, infinite chains have been observed.

Tetratramers, pentamers and infinite chains are rare, having been found in only four mineral species. Rings formed by four \((\text{As}_3\text{O}_5)\) groups occur in stenhuggarite, ideally \(\text{CaFeSbAs}_2\text{O}_7\) (Coda et al., 1977), whereas pentamers were observed in ludlockite, \(\text{PbFe}_5\text{As}_5\text{O}_{22}\) (Cooper and Hawthorne, 1996). Infinite chains have been reported in trippkeite, \(\text{CuAs}_2\text{O}_4\) (Pertlik, 1975) and leiteite, \(\text{ZnAs}_2\text{O}_4\) (Ghose et al., 1987). Species containing \((\text{As}_3\text{O}_5)\) dimers are relatively more common. Table 1 lists the minerals characterised by this structural feature. In schneiderhönmites, \(\text{Fe}^{2+}\text{Fe}^{3+}_2\text{As}_2\text{O}_{13}\), \((\text{As}_3\text{O}_5)\) dimers occur along with isolated \((\text{As}_5\text{O}_8)\) groups (Hawthorne, 1985; Cooper and Hawthorne, 2016), whereas karibibite displays \((\text{As}_5\text{O}_8)\) dimers and \((\text{As}_2\text{O}_4)\) chains (Colombo et al., 2017).

During the investigation of the mineralogy of the Monte Arsiccio mine in the Apuan Alps, northern Tuscany, Italy, the arsenite mineral graeserite was identified in veins hosted in metadolomite (Biagioni et al., 2020a). This mineral is sometimes associated with square tabular crystals, usually deeply altered to an earthy X-ray amorphous compound. Some relics of the original mineral were eventually found at the core of one of these altered crystals and some unaltered individuals were collected. This made it possible to obtain some material for the mineralogical investigation that led to recognition of this phase as a new mineral species, bianchiniite. The mineral and its name have been approved by
Bianchiniite Ba$_2$(TiV)(As$_2$O$_5$)$_2$OF 8.79 8.79 15.64 90 90 90

The Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) under the number IMA2019-022 (Biagioni et al., 2019c). The holotype material, represented by the grain used for the collection of all the mineralogical data, is deposited in the collection of the Museo di Storia Naturale, Università di Pisa, Via Roma 79, Calci, Pisa, Italy, with catalogue number 19892. The name honours the mineral collectors Andrea Bianchini (born 5th September 1959) and Mario Bianchini (born 28th August 1962) (no relationship between them) for their contribution to the knowledge of the mineralogy of As-rich hydrothermal fluids during the Alpine tectono-metamorphic event, under specific O$_2$ conditions, within the north-eastern sector of the Sant’Anna tectonic window, in the eastern part of the Monte Arsiccio mine; several phases identified in the same occurrence are sphalerite, derblite, siderite, dolomite,ankerite and quartz. Usually, crystals of bianchiniite are deeply altered to an X-ray amorphous earthy material (Fig. 1), in some cases admixed with microcrystalline rutile; in the second additional identified specimen, a relict of bianchiniite was observed at the core of a deeply altered crystal, confirming the identity of the original pseudomorphosed mineral. The crystallisation of bianchiniite is probably related to the circulation of As-rich hydrothermal fluids during the Alpine tectono-metamorphic event, under specific fO$_2$ conditions, within the

**Occurrence and mineral description**

**Occurrence and physical properties**

Bianchiniite was found in only a few samples collected in the Sant’Olga level, Monte Arsiccio mine (43°58′N, 10°17′E), near Sant’Anna di Stazzema, Stazzema, Apuan Alps, Tuscany, Italy. The Monte Arsiccio mine exploited a pyrite ± baryte ± iron-oxide ore deposit located in the southern Apuan Alps. A review on its geological setting can be found in Biagioni et al. (2015) and references therein.

In type material, bianchiniite is associated with baryte, ‘hyalophane’ and ‘chlorite’, in a fracture of metadolostone (Fig. 1). After the first finding, which provided the material used for the type description, two additional specimens of bianchiniite were identified. The first one has the same associated minerals as observed in type material, plus galena in cuboctahedral crystals. Other phases identified in the same occurrence are sphalerite, derblite, siderite, dolomite, ankerite and quartz. Usually, crystals of bianchiniite are deeply altered to an X-ray amorphous earthy material (Fig. 1), in some cases admixed with microcrystalline rutile; in the second additional identified specimen, a relict of bianchiniite was observed at the core of a deeply altered crystal, confirming the identity of the original pseudomorphosed mineral. The crystallisation of bianchiniite is probably related to the circulation of As-rich hydrothermal fluids during the Alpine tectono-metamorphic event, under specific fO$_2$ conditions, within the

**Table 1.** Minerals characterised by the occurrence of (As$_2$O$_5$) dimers.

| Mineral       | Chemical formula | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) | Space group | Reference                                      |
|---------------|------------------|-------|-------|-------|-------|-------|-------|-------------|------------------------------------------------|
| Bianchiniite  | Ba$_2$(TiV)(As$_2$O$_5$)$_2$OF | 8.79  | 8.79  | 15.64 | 90    | 90    | 90    | I4/mcm     | This work                                      |
| Fetiasite     | (Fe$^{3+}$,Fe$^{4+}$,Ti$^{4+}$)$_2$(As$_2$O$_5$)$_2$ | 10.61 | 3.25  | 8.94  | 90    | 108.8 | 90    | P2$_1$/m    | Graeser et al. (1994)                          |
| Gebhardite    | Pb$_2$(As$_2$O$_5$)$_2$ | 6.72  | 11.20 | 34.19 | 90    | 85.2  | 90    | P2$_1$/c    | Klaska and Gebert (1982)                       |
| Karibibite    | Fe$_2$(As$_2$O$_5$)$_2$(As$_3$O$_5$)(OH) | 7.26  | 27.99 | 6.52  | 90    | 90    | 90    | Pmma       | Colombo et al. (2017)                          |
| Paulmooreite  | Pb$_2$(As$_2$O$_5$)$_2$ | 13.58 | 5.65  | 8.55  | 90    | 108.8 | 90    | P2$_1$/a    | Araki et al. (1980)                            |
| Prachalfite   | CaSb$_2$(As$_2$O$_5$)$_2$O$_2$ | 13.95 | 13.95 | 19.90 | 90    | 90    | 120   | P3$_1$c     | Kolitsch et al. (2018)                         |
| Schneiderhöhnite | Fe$_2$Fe$^{3+}$As$_2$O$_3$ | 8.94  | 10.02 | 9.16  | 62.9  | 116.1 | 81.7  | P1          | Cooper and Hawthorne (2016)                    |
| Vajdakite     | (MoO$_3$)$_3$(H$_2$O)$_2$As$_2$O$_5$H$_2$O | 7.05  | 12.09 | 12.22 | 90    | 101.3 | 90    | P2$_1$/c    | Ondrus et al. (2002)                           |

**Fig. 1.** (a) A loose aggregate of tabular crystals of bianchiniite, associated with ‘hyalophane’ and ‘chlorite’. Holotype material was sampled from this specimen. (b) Deeply altered earthy tabular crystals of bianchiniite associated with rhombohedral crystals of siderite and whitish microcrystalline fibrous aragonite. Both specimens from the Sant’Olga level, Monte Arsiccio mine, Stazzema, Apuan Alps, Tuscany, Italy (in a private collection).
metadolostone rock body embedded in the Monte Arsiccio ore deposit. The alteration affecting the large majority of the observed crystals of bianchinite may suggest a successive alteration by low-T fluids, during the final stages of the evolution of the Monte Arsiccio mineral assemblages.

Bianchinite occurs as square tabular {001} crystals, up to 1 mm across. The colour is brown and the streak is brownish. The mineral is transparent, with a vitreous lustre. Owing to the small size of the grains available for the collection of mineralogical data, hardness was not measured. Bianchinite is brittle, with a perfect {001} cleavage; fracture is irregular. Density was measured; on the basis of the empirical formula and unit-cell volume refined from single-crystal X-ray diffraction data, the calculated density is 4.863 g/cm³.

The holotype material was embedded in epoxy and subsequently optical properties were determined on the polished crystal using reflected light microscopy. Reflectance was measured using an AVASPEC-UL2048×16 spectrometer attached to a Zeiss Axiositron UV-microscope (Swedish Museum of Natural History, Stockholm, Sweden), using a halogen lamp (100 W), with a measured field of 30 μm in diameter. In plane-polarised light, bianchinite is grey in colour, non-pleochroic, with orange-yellow internal reflections. Between crossed polars, this mineral is weakly bireflectant, with a very weak anisotropy in shades of grey.

Reflectance values (SiC as standard), measured in air, are given in Table 2. Mean refractive index, calculated according to the Gladstone–Dale relationship (Mandarino, 1979, 1981), is 2.044.

### Chemical and micro-Raman data

Quantitative chemical data were collected using a Cameca SX50 electron microprobe at the Istituto di Geologia Ambientale e Geoingegneria, CNR, Rome, Italy. The following analytical conditions were used: wavelength dispersive mode, accelerating voltage = 15 kV, beam current = 15 nA and beam size = 1 μm. Standards (element, emission line) were: rutile (TiKα), vanadinite (VKα), magnetite (FeKα), GaAs (AsLα), InSb (SbLα), celestine (SrLα), baryte (BaLα), galena (PbMα) and fluorophlogopite (FKα). Chromium and Cl were sought but were below the detection limit. Chemical data are given in Table 3. Vanadium, Fe and As were considered as V⁴⁺, Fe³⁺ and As³⁺, respectively, on the basis of the crystal structure refinement (see below). On the basis of 12 anions per formula unit, the empirical formula of bianchinite is (Ba₂₋₀₀Sr₀.₀₄Pb₀.₀₂)₂₋₀₀[Ti₁₀⁺V₁⁴⁺O₄₋₀₀F₀.₅₂₋₀₂O₁₋₀₂][As₂₋₀₀₁₉Sb₀.₀₂₋₀₂]₀.₉₈O₁₀₋₀₂(O₁₋₀₂F₀.₅₂₋₀₂), corresponding to the end-member formula Ba₄(Ti₄⁺V₁⁴⁺)(As₂O₅)₂OF, in accordance with the CNMNC-IMA guidelines (Bosi et al., 2019). This latter formula corresponds to (in wt.%) TiO₂ 9.20, V₂O₅ 8.63, As₂O₃ 45.57, BaO 35.32, F 2.19, sum 100.92, -O = F -0.92, total 100.

Micro-Raman spectra of bianchinite were collected in near back-scattered geometry with a Horiba Jobin-Yvon Xplora Plus apparatus, equipped with a motorised x–y stage and an Olympus BX41 microscope with a 100x objective (Dipartimento di Scienze della Terra, Università di Pisa). The 532 nm line of a solid-state laser was used. The minimum lateral and depth resolution was set to a few μm. The system was calibrated using the 520.6 cm⁻¹ Raman band of Si before each experimental session. Spectra were collected through multiple acquisitions (3) with single counting times of 60 s, with the laser power filtered at 50% (i.e. 12.5 mW). No thermal damage was observed. Back-scattered radiation was analysed with a 1200 gr/mm grating monochromator. The Raman spectrum of bianchinite in the region between 100 and 1200 cm⁻¹ is shown in Fig. 2. The interpretation of the Raman bands is not straightforward, as very few Raman spectroscopic studies on diarsenites are available (e.g. Čejka et al., 2008; Bahfenne et al., 2012). Bands between 750 and 850 cm⁻¹ may be related to As–O₅ₖ stretching modes, where subscript ‘nbr’ indicates ‘non-bridging’ oxygen atoms in the (As₂O₅) groups, in agreement with Bahfenne et al. (2012) and the theoretical calculations of Tossell (1997). In particular, the band at 766 cm⁻¹ seems to be the most probable candidate for this assignment, as it is very close to the value observed in fetsiasite (770 cm⁻¹; Graeser et al., 1994) and interpreted by Tossell (1997) as due to the As–O₅ₖ stretching vibrations. Other bands in this range, as well as the bands at 892 cm⁻¹ can be also related to other M–O modes, where M can be Ba or (Ti,V,Fe). Bands in the range between 480 and 660 cm⁻¹ are attributed to the As–O₅ₖ stretching mode, where subscript ‘br’ indicates ‘bridging’ oxygen atoms. More questionable is the correct attribution of the strong band at 658 cm⁻¹.

### Table 2

| λ (nm) | R_min (%) | R_max (%) | λ (nm) | R_min (%) | R_max (%) |
|-------|-----------|-----------|-------|-----------|-----------|
| 400   | 6.6       | 7.7       | 560   | 5.7       | 6.8       |
| 420   | 5.8       | 6.5       | 580   | 5.7       | 7.1       |
| 440   | 5.0       | 5.8       | 589   | 5.7       | 7.0       |
| 460   | 4.9       | 5.7       | 600   | 5.6       | 6.8       |
| 470   | 5.0       | 5.8       | 620   | 5.5       | 6.8       |
| 480   | 5.0       | 5.9       | 640   | 5.3       | 6.5       |
| 500   | 5.2       | 6.1       | 650   | 5.2       | 6.3       |
| 520   | 5.5       | 6.3       | 660   | 5.2       | 6.3       |
| 540   | 5.6       | 6.6       | 680   | 5.1       | 6.3       |
| 546   | 5.7       | 6.5       | 700   | 5.0       | 6.3       |

*The reference wavelengths required by the Commission on Ore Mineralogy (COM) are given in bold.

### Table 3

| Constituent | Mean | Range | S.D. [σ] |
|-------------|------|-------|----------|
| TiO₂        | 10.34| 9.75–10.82 | 0.36     |
| V₂O₅        | 3.77 | 3.11–5.22  | 0.75     |
| Fe₂O₃       | 3.76 | 2.89–4.64  | 0.54     |
| As₂O₅       | 44.36| 43.43–45.03 | 0.53     |
| Sb₂O₅       | 0.22 | 0.07–0.33  | 0.09     |
| SrO         | 0.45 | 0.28–0.57  | 0.09     |
| BaO         | 34.79| 34.01–35.42 | 0.47     |
| PbO         | 0.28 | 0.09–0.42  | 0.11     |
| F           | 1.77 | 1.66–2.02  | 0.13     |
| O=F         | -0.75|         |         |
| Total       | 98.99| 98.73–101.21| 0.81     |

Atoms per formula unit on the basis of O+F = 12:

| Ti   | 1.14 | 1.06–1.20 | 0.04   |
| V   | 0.44 | 0.36–0.60  | 0.08   |
| Fe  | 0.42 | 0.32–0.52  | 0.06   |
| As  | 3.96 | 3.92–4.00  | 0.02   |
| Sb  | 0.02 | 0.00–0.02  | 0.02   |
| Sr  | 0.04 | 0.02–0.04  | 0.02   |
| Ba  | 2.00 | 1.96–2.04  | 0.02   |
| Pb  | 0.02 | 0.00–0.02  | 0.02   |
| F   | 0.82 | 0.78–0.92  | 0.06   |
| O   | 35.42| 34.65–36.21 | 0.06   |
| (Fe+V)| 0.86 | 0.80–0.94  | 0.06   |

| (Ba+Sr+Pb) | 2.06 | 2.02–2.10 | 0.02   |

S.D. – standard deviation
Indeed, this band is similar to the one reported in the infrared spectrum of fetasite (at 660 cm\(^{-1}\); Graeber et al., 1994) and interpreted by Tossell (1997) as due to the As–O\(_{br}\) stretching mode. However, these values do not match with the experimental data given for paulmooreite, with bands at 562 and 503 cm\(^{-1}\), and with the theoretical ones reported by Tossell (1997), who calculated stretching wavenumbers at 554 and 496 cm\(^{-1}\). Consequently, the strong band at 658 cm\(^{-1}\) could have another interpretation; for instance, it may be due to (Ti, V, Fe)\(_{br}\)–O vibrations. The band at 295 cm\(^{-1}\) may be due to deformations of the As–O\(_{lab}\) bonds (e.g. Bahfenne et al., 2012). Other bands below 300 cm\(^{-1}\) can be probably attributed to lattice or M–O bonds. In paulmooreite, bands at 186 and 138 cm\(^{-1}\) were observed (Bahfenne et al., 2012), comparable to those at 178 and 140 cm\(^{-1}\) measured in bianchiniite. No spectral features were observed in the range 2800–4000 cm\(^{-1}\), thus supporting the absence of (OH\(^{-}\)) and H\(_2\)O groups in bianchiniite.

### Crystallography

Powder X-ray diffraction data of bianchiniite were collected using a 114.6 mm Gandolfi camera and Ni-filtered CuKa radiation (Dipartimento di Scienze della Terra, Università di Pisa). Table 4 gives the observed powder X-ray diffraction lines, along with the calculated pattern based on the structural model discussed below. Unit-cell parameters were refined in a tetragonal setting on the calculated pattern based on the structural model discussed below. The statistical tests on the distribution of \(|E|\) values (|\(E^2 - 1\)| = 0.877) suggested the occurrence of an inversion center. The examination of systematic absences indicated the space group symmetry I4/mcm. The crystal structure of bianchiniite was solved using Shelxt-97 (Sheldrick, 1997) and refined using ShelxL-2018 (Sheldrick, 2015). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson, 1992). During the first step of the crystal structure solution, the observed powder X-ray diffraction lines, along with the theoretical ones reported by Tossell (1997), who calculated stretching wavenumbers at 554 and 496 cm\(^{-1}\). Consequently, the strong band at 658 cm\(^{-1}\) could have another interpretation; for instance, it may be due to (Ti, V, Fe)\(_{br}\)–O vibrations. The band at 295 cm\(^{-1}\) may be due to deformations of the As–O\(_{lab}\) bonds (e.g. Bahfenne et al., 2012). Other bands below 300 cm\(^{-1}\) can be probably attributed to lattice or M–O bonds. In paulmooreite, bands at 186 and 138 cm\(^{-1}\) were observed (Bahfenne et al., 2012), comparable to those at 178 and 140 cm\(^{-1}\) measured in bianchiniite. No spectral features were observed in the range 2800–4000 cm\(^{-1}\), thus supporting the absence of (OH\(^{-}\)) and H\(_2\)O groups in bianchiniite.

### Table 4. X-ray powder diffraction data (d in Å) for bianchiniite.*

| \(h\) | \(k\) | \(l\) | \(d_{\text{obs}}\) | \(d_{\text{calc}}\) |
|---|---|---|---|---|
| Vw 6 | 7.8 | 7.84 | 002 |
| Vw 2 | 6.3 | 6.17 | 110 |
| W 10, 2 1 | 3.826 | 3.812, 3.787 | 202, 211 |
| Vw 100, 5 | 3.144 | 3.127, 3.085 | 213, 220 |
| W 11 | 2.916 | 2.916 | 204 |
| W 23 | 2.789 | 2.760 | 310 |
| W 11 | 2.598 | 2.613 | 006 |
| Wv 4 | 2.403 | 2.406 | 116 |
| Wv 3 | 2.245 | 2.242 | 206 |
| W 2 | 2.196 | 2.196 | 323 |
| W 2 | 2.182 | 2.182 | 400 |
| W 11 | 2.119 | 2.097 | 411 |
| W 5 | 2.072 | 2.057 | 330 |
| W 2, 7, 5, 2 1 | 1.975 | 1.994, 1.962, 1.951, 1.943 | 226, 413, 420, 217 |
| W 6, 12, 2 1 | 1.903 | 1.916, 1.897, 1.868 | 325, 316, 118 |
| Vw 1 | 1.833 | 1.821 | 334 |
| Vw 1 | 1.761 | 1.754 | 415 |
| Vw 5, 2 | 1.686 | 1.675, 1.672 | 406, 512 |
| W 6 | 1.620 | 1.616 | 336 |
| W 8 | 1.592 | 1.591 | 219 |
| W 10 | 1.552 | 1.548 | 523 |

*Notes: intensity (I) and \(d_{\text{calc}}\) were calculated using the software PowderCell 2.3 (Krauss and Nolze, 1996) on the basis of the structural model given in Table 6. Only the reflections with \(I_{\text{calc}} < 2\) are given, if not observed. Intensities were estimated visually. vs = very strong; w = weak; vw = very weak. The eight strongest reflections are given in bold.
positions of Ba, Ti, As, and one anion position were found. Difference-Fourier synthesis maps located three additional anion positions. The isotropic structural model refined to \( R_1 = 0.038 \), thus suggesting the correctness of the structural model. Taking into account the electron microprobe data, the site occupancy factors (s.o.f.) at the Ba(1) and As(3) sites were refined using the Ba and As scattering curves only, respectively. The \( M(2) \) site is occupied by Ti, V and Fe. Owing to the similar atomic number of Ti (\( Z = 22 \)) and V (\( Z = 23 \)) and the slightly higher atomic number of Fe (\( Z = 26 \)), the s.o.f. was refined using the Ti vs. Fe scattering curves. In addition, taking into account the different crystal-chemical behaviour of Ti and (Fe,V) (with the former giving rise to the off-centre displacement phenomenon; e.g. Megaw, 1968), their positions were refined independently, resulting in the splitting of the \( M(2) \) site into \( M(2a) \) and \( M(2b) \). Titanium was located at \( M(2a) \); indeed this position shows the largest polyhedron distortion value, estimated as \( 4d = (d_{\text{max}} - d_{\text{min}}) \), where \( d_{\text{max}} \) and \( d_{\text{min}} \) represent the maximum and minimum bond distance, respectively, whereas \( M(2b) \) has a more regular coordination environment (see below). A bond-valence calculation performed on the isotropic model indicated the likely mixed (O,F) nature of the O(1) and O(4) sites. Owing to the very similar scattering factors of O (\( Z = 8 \)) and F (\( Z = 9 \)), the s.o.f. was fixed on the basis of chemical data and bond-valence requirements. The refinement statistical factor was slightly improved to \( R_1 = 0.026 \). Successively, an anisotropic model for cations lowered it to \( R_1 = 0.016 \). After several cycles of anisotropic refinement for all atoms, the final statistical factor \( R_1 \) converged to 0.0134 for 555 unique reflections with \( F_o > 4\sigma(F_o) \) and 34 refined parameters.

Details of the intensity data collection and crystal structure refinement are given in Table 5. Atom coordinates, s.o.f. and displacement parameters are reported in Table 6, whereas selected bond distances are listed in Table 7. Weighted bond-valence sums, calculated using the bond parameters of Gagné and Hawthorne (2015) for cation–oxygen pairs and of Brése and O’Keeffe (1991) for cation–fluorine pairs, are shown in Table 8. The crystallographic information file, including reflection data, has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

### Crystal structure description

The crystal structure of bianchiniite is formed by columns of corner-sharing \( M(2) \) octahedra running along \( c \), connected, in the \( \text{[001]} \) plane, by \( \text{(As}_2\text{O}_5) \) dimers. Trigonal pyramidally coordinated \( \text{As}^{5+} \) ions form \( \text{[011]} \) layers, with their apex pointing alternately up and down. Lone-electron-pair micelles of \( \text{As}^{3+} \) atoms alternate, along \( c \), with layers of intercalated Ba atoms (Fig. 4). Consequently, the crystal structure may be described as layered, with heteropolyhedral layers hosting Ba, (Ti,V,Fe) and As atoms, separated by layers occupied by lone-pair electrons and the anion hosted at \( O(4) \) connecting successive \( M(2) \) octahedra along \( c \).

Barium is twelve-fold coordinated, with ten bond distances in the range between 2.79 and 2.98 Å. Two additional bonds with the mixed (F,O) site \( F(1) \) at 3.22 Å complete the coordination environment, that can be described as a bicapped pentagonal prism. The average bond distance is 2.942 Å, to be compared with a calculated value of 2.985 Å based on ionic radii for \( [\text{Ba}^{2+}] \), \( [\text{IV}^{2-}] \), \( [\text{O}^{2-}] \) and \( [\text{F}^{-}] \) given by Shannon (1976). The bond-valence sum at the Ba atom is 2.16 vu, in keeping with the expected value.

Arsenic displays the trigonal pyramidal coordination typical of \( \text{As}^{3+} \). The \( \langle \text{As–O} \rangle \) bond distance, 1.772 Å, agrees with the average distance reported by Majzlan et al. (2014), i.e. 1.782 Å. It is worth noting that in the \( \text{(As}_2\text{O}_5) \) dimers, As–Obr is definitely longer than the two other As–Obr bonds, i.e. 1.838 and 1.740 Å, respectively. This feature was observed by Cooper and Hawthorne (2016) in schneiderhöhnite, where a bridging O atom has a comparatively large valence contribution from non-As atoms. These authors examined the observed contribution in other polymerised \( \text{As}^{3+} \) oxysalts (see Table 5 of Cooper and Hawthorne, 2016), reporting that schneiderhöhnite showed the largest bond-valence contribution from non-As atoms in known minerals (i.e. 0.28 vu). Bianchiniite shows a still larger contribution, represented by the incident bond valence from Ba\(^{2+} \) (0.38

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### Table 5. Crystal data and details of data collection and crystal structure refinement for bianchiniite.

| Crystal data | 0.110 \times 0.070 + 0.030 |
|--------------|-----------------------------|
| Cell setting, space group | Tetragonal, \( I4/mcm \) |
| \( a \) (Å) | 8.7266(4) |
| \( c \) (Å) | 15.6777(7) |
| \( V' \) (Å\(^3\)) | 1193.91(12) |
| \( Z \) | 4 |

| Data collection |
|-----------------|
| Radiation, wavelength (Å) | MoK\(\alpha\), 0.71073 |
| Temperature (K) | 293 |
| 2\(\theta_{\text{max}}\) (°) | 63.07 |
| Measured reflections | 5874 |
| Unique reflections | 563 |
| Reflections with \( F_o > 4\sigma(F_o) \) | 555 |
| \( R_{int} \) | 0.0288 |
| \( R_a \) | 0.0162 |
| Range of \( h, k, l \) | \(-9 \leq h \leq 12, -11 \leq k \leq 12, -23 \leq l \leq 19\) |

| Refinement |
|-------------|
| \( R(f_o > 4\sigma(f_o)) \) | 0.0134 |
| \( R \) (all data) | 0.0139 |
| \( wR \) on \( F^2 \) | 0.0303 |
| Goof | 1.262 |
| No. of least-squares parameters | 34 |
| Max. and min. residual peak \((e^{-}Å^{-3})\) | 0.55 (at 0.47 Å from O(1)) |
| | 0.39 (at 1.60 Å from O(2)) |
**Discussion**

**Crystal chemistry of bianchiniite**

The proposed end-member formula of bianchiniite corresponds to \( \text{Ba}_4(\text{Ti}^{4+}\text{V}^{3+})(\text{As}_2\text{O}_5)\text{OF} \). Barium shows a very minor substitution by Sr (up to 0.04 atoms per formula unit, apfu) and Pb (up to 0.02 apfu), whereas As can be replaced by minor Sb (up to 0.02 apfu). More significant is the replacement of Ti, V, and Fe, occurring at the mixed and split M(2) site. The relations between Ti and (V + Fe) content are in Fig. 5a, showing a clear negative correlation that supports the replacement of Ti by (V + Fe).

The oxidation state of Fe and V was assumed as +3, on the basis of bond-valence calculations that match the replacement of Ti\(^{4+}\) by trivalent elements. In addition, the F content (0.82 apfu) is consistent with the sum of (V + Fe) (0.86 apfu), thus suggesting the substitution mechanism \( \text{M}(2)\text{Ti}^{4+} + \text{O}(1),\text{O}(4)\text{O}_2 = \text{M}(2)(\text{Fe},\text{V})^{3+} + \text{O}(1),\text{O}(4)\text{F} \). However, as \( \text{V}^{3+} \) and \( \text{Fe}^{3+} \) occur in equal amounts, similar results could be achieved through the occurrence of \( \text{V}^{4+} \) and \( \text{Fe}^{2+} \).

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The four independent anion sites have bond-valence sums ranging between 1.20 and 2.10 vu. The O(2) and O(3) sites, with bond-valence sums of 2.06 and 2.10 vu, host O\(^{2-}\) anions, whereas the other two sites are underbonded. This underbonding is slight at the O(4) site (1.68 vu), suggesting a partial replacement of O\(^{2-}\) by a monovalent anion, whereas at the fourth anion site the underbonding is severe, with 1.20 vu. This supports the dominance of a monovalent anion at this position. These results are in keeping with the occurrence of F, as detected during electron microprobe analysis; accordingly, this anion position was labelled as (F(1)). The site population at O(4) was fixed at \((\text{O}_{0.80}\text{F}_{0.20})\), whereas F(1) was modelled as \((\text{F}_{0.70}\text{O}_{0.30})\). According to the s.o.f., it appears that the occupancy of \( \text{M}(2a) \) is probably related with the occurrence of F\(^{-}\) at F(1) and O\(^{2-}\) at O(4), whereas when \( \text{M}(2b) \) is occupied it is associated with \( \text{O}^{2-}\) at F(1) and F\(^{-}\) at O(4).

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**Table 6.** Sites, Wyckoff positions, site occupation factors (s.o.f.), fractional atomic coordinates and equivalent isotropic displacement parameters (Å\(^2\)) for bianchiniite.*

| Site   | Wyckoff position | s.o.f. | x/a   | y/b   | z/c   | U\(^{eq}\) |
|--------|------------------|--------|-------|-------|-------|-----------|
| Ba(1)  | 8h               | Ba\(_{1.00}\) | 0.32355(2) | 0.17645(2) | 0.01080(8) |
| M(2a)  | 8f               | Ti\(_{0.74(1)}\) | 0    | 0    | 0.1354(3) | 0.0058(4) |
| M(2b)  | 8f               | Fe\(_{0.02(1)}\) | 0    | 0    | 0.1206(6) | 0.0058(4) |
| As(3)  | 16i              | As\(_{1.00}\) | 0.13333(2) | 0.36667(2) | 0.17402(2) | 0.0075(1) |
| F(1)   | 4c               | Fe\(_{0.16}\)O\(_{0.30}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) | 0 | 0.0128(7) |
| O(2)   | 32m              | O\(_{1.00}\) | 0.07682(17) | 0.21212(16) | 0.11138(10) | 0.0117(3) |
| O(3)   | 8g               | O\(_{1.00}\) | 0    | 0    | 0.12183(19) | 0.0117(5) |
| O(4)   | 4a               | O\(_{0.06}F_{0.20}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) | -0.0160(9) |

*Notes: the refined site scattering at M(2a) + M(2b) matches the site population \((\text{Ti}_{0.37},\text{V}_{0.22},\text{Fe}_{0.21})\) obtained from electron microprobe analysis.

**Table 7.** Selected bond distances (in Å) for bianchiniite.

| Site     | Bond Distance (Å) |
|----------|-------------------|
| Ba(1)    | 2.7896(15) x4     |
| M(2a)    | 2.8966(19) x2     |
| M(2b)    | 2.8799(15) x4     |
| Ba(1)−F(1) | 3.2161(2) x2    |
| Ba(1)−F(2) | 2.942             |
| Ba(2a)−O(4) | 1.796(4) x4    |
| Ba(2b)−O(4) | 2.0044(17) x4   |
| Ba(2a)−O(4) | 2.1233(4)        |
| Ba(2b)−O(4) | 1.389             |

**Table 8.** Weighted bond-valence balance (in vu) for bianchiniite.*

| Site     | Bond Value (vu) |
|----------|-----------------|
| Ba(1)    | 1.06 vs         |
| Ba(2a)   | 1.02 vs         |
| M(2a)    | 1.20 vs         |
| M(2b)    | 1.09 vs         |
| As(3)    | 1.07 vs         |

*Notes: left and right superscripts indicate the number of equivalent bonds involving anions and cations, respectively. For sites with mixed site occupancy, the bond valence sums have been weighted.
different from the approved one, Ba₂(Ti⁴⁺V³⁺)(As₂O₅)₂OF. In addition, the possible average nature of the refined crystal structure would suggest the occurrence of two different M(2) positions, one preferentially occupied by Ti⁴⁺, the other by a mixed (V,Fe) population. In such a case, the formula of bianchiniite could also be written as Ba₂Ti(V⁴⁺₀.₅Fe²⁺₀.₅)(As₂O₅)₂OF. Unfortunately, these distinct site populations are virtually indistinguishable using available data; for instance, the calculated <M(2)–Φ (>Φ = O₂⁻, F⁻) distance and bond-valence sums for both cation distributions are very similar. Only spectroscopic techniques (e.g. Mössbauer and Vis-NIR spectroscopies) could solve this issue, if more material will become available. For this reason, the IMA-CNMNC approved formula is retained, assuming the coexistence of V³⁺ and Fe³⁺.

The average content of V and Fe supports a very subtle dominance of the former over the latter (Table 3). The examination of the spot analyses showed Fe/(V+Fe) atomic ratios ranging between 0.34 and 0.58, with an average value of 0.48(8) (Fig. 5b). This means that both V and Fe can be dominant constituents in bianchiniite. In the definition of the new mineral species, V was assumed as the species-forming constituent as it has the wider chemical range with respect to the 50% boundary. Consequently, taking into account the current chemical range of bianchiniite, the use of only one name also applies to chemical domains having a slight Fe-dominance, in agreement with the IMA-CNMNC rules (Nickel, 1992; Hatert and Burke, 2008). However, additional findings could allow the description of the Fe-dominant end-member of bianchiniite or a revision of its formula based on spectroscopic data.

**Relations with other species**

The crystal structure of bianchiniite is a novelty among diarsenite minerals. Moreover, it is the first naturally occurring Ba-arsenite, although minor Ba occurs in graeserite (Biagioni et al., 2020a).
Bianchiniite has some resemblance with fresnoite (Masse et al., 1967; Moore and Louisnathan, 1969; Markgraf et al., 1985; Krzatalla et al., 2021) and with melilite-group minerals (Bindi et al., 2020). Fresnoite, ideally $\text{Ba}_2\text{Ti(Si}_2\text{O}_7)\text{O}$, has unit-cell parameters $a = 8.52$ and $c = 5.21$ Å, with space group $P\overline{4}2_1m$. Its crystal structure shows ten-fold coordinated Ba atoms and five-fold coordinated Ti, along with disilicate groups (Fig. 6). As first noted by Moore and Louisnathan (1969), this mineral displays some structural features in common with melilite-group phases. Among them, the recently described mineral bennesherite, $\text{Ba}_2\text{Fe}^{2+}\text{Si}_2\text{O}_7$, is the first Ba member of this group (Krzatalla et al., 2021). Its unit-cell parameters are $a = 8.23$ and $c = 5.29$ Å with space group $P\overline{4}2_1m$. In agreement with the general formula of melilite-group minerals, $X_2T(1)[T(2)O_7]$ (e.g. Bindi et al., 2020), the $T(1)$ tetrahedron is occupied by Fe$^{2+}$, whereas Si$^{4+}$ is hosted at $T(2)$ (Fig. 6). In bianchiniite, the $T(1)$ tetrahedron of melilite-group minerals and the five-fold coordinated Ti-centred site of fresnoite are replaced by the mixed and split (Ti,V,Fe)-centred $M(2)$ octahedron, forming columns along $c$. Disilicate groups ($\text{Si}_2\text{O}_7)^{6-}$ occurring in fresnoite- and melilite-group minerals are replaced by diarsenite groups ($\text{As}_2\text{O}_5)^{4-}$.

The $c$ unit-cell parameters of fresnoite- and melilite-group minerals are very similar, usually $\sim 5$ Å (see table 1 in Krzatalla et al., 2021); such a periodicity is related to the alternation, along $c$, of (Ti/Si) and [$T(1)/T(2)$] layers with intercalated Ba and X layers in fresnoite- and melilite-group minerals, respectively. In bianchiniite, the $c$ parameter is tripled. Indeed, whereas in fresnoite- and melilite-group minerals every cell contains one layer of Ba and X cations and one layer of $T(1)$ and $T(2)$ sites, in the unit-cell of bianchiniite two heteropolyhedral layers occur, separated by two lone-electron-pair micelles. The layers are staggered, owing to a rotation of $45^\circ$ of successive heteropolyhedral layers stacked along $c$.

The heteropolyhedral layer occurring in bianchiniite (Fig. 4) is topologically similar to one of the two constitutive layers of the synthetic compound $\text{Ba}_3\text{Ti}_2\text{Si}_4\text{O}_{14}\text{Cl}$ (Abeyesinghe et al., 2017). This phase is tetragonal, space group $P4/mbm$. Its $a$ unit-cell parameter is similar to that of bianchiniite, i.e. 8.67 Å, whereas the $c$ axis is longer, i.e. 18.65 Å. In the synthetic compound, the bianchiniite-like layer is formed by split TiO$_2$Cl octahedra, Si$_2$O$_7$ groups, and intercalated twelve-coordinated Ba atoms. The O/Cl disorder related to the occupancy of the split Ti sub-sites is similar to the O/F disorder in bianchiniite. The bianchiniite-like layer alternates...
with another kind of layer formed by TiO_2 square pyramids and by SiO_4 rings, along with eleven-fold coordinated Ba atoms (Abeyesinghe et al., 2017). In agreement with Makovicky (1997), this may suggest the possible existence of merotypic relations between bianchiniite and synthetic Ba_3Ti_3Si_4O_12Cl.

As shown in Fig. 3, some very weak reflections indicate the presence of a superstructure. The occurrence of incommensurate superstructure reflections is a common feature of melilite-group minerals (e.g. Bindi et al., 2020). In some cases, a commensurate superstructure has been proposed. This is the case of another mineral probably related to melilite-group phases, jeffreyite, (Ca, Na)_3(Fe,Al)Si_2(O,H)O_7 (Grice and Robinson, 1984). This phase has a pseudotetragonal subcell, with a = b = 7.5 Å and c = 5.0 Å; the real symmetry seems to be orthorhombic, C222_1, with a = 14.90, b = 14.90 and c = 40.41 Å. In this case, the c periodicity is eight-times the basic 5 Å periodicity. In addition, a superstructure along a and b has been observed. This feature parallels the possible 2a superstructure observed in precession images of bianchiniite (Fig. 3). Grice and Robinson (1984) hypothetically attributed superstructure reflections to some ordering of Na, Al and (OH) groups in the still unsolved crystal structure of jeffreyite. In bianchiniite, the ordering of Ti, V and Fe at the M(2) site, suggested also by the split nature of this position, may be invoked to explain the appearance of such superstructure reflections.

Conclusion

For the last ten years, the Monte Arsiccio mine has enriched the mineral systematics with several new mineral species belonging to different crystal-chemical classes, i.e. sulfoarsenates, oxides and sulfates. Bianchiniite is probably one of the most remarkable discoveries, due to its unique chemistry, mirroring some geochemical features characterising the pyrite ± baryte ± iron-oxide ore deposits of the Apuan Alps. In addition to baryte, a few other minerals having Ba as a primary constituent are currently known: benstonite, cymrite and mannardite – all identified from the Monte Arsiccio mine (Biagioni et al., 2009; Biagioni and Orlandi, 2010). Similarly to mannardite, Ba in bianchiniite is associated with Ti and V, with the latter element being another geochemical fingerprint for this kind of ore deposit from the Apuan Alps, occurring in mineral species at both the Monte Arsiccio and the Buca della Vena mines (e.g. Merlino and Orlandi, 1983; Mellini et al., 1986; Biagioni et al., 2020a). The crystallisation environment of bianchiniite was also enriched in As, in keeping with the As-rich nature of the Monte Arsiccio ore deposit.

In addition to the geochemical implications, the finding of bianchiniite reveals the flexibility of melilite-like structures, with diarsenite groups replacing disilicate groups and with the tetrahedrally-coordinated Ti(1) cations substituted by octahedrally-coordinated cations, in a novel and unpredicted crystal structure arrangement for natural compounds.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/min.2021.28

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