

Asbecasite: crystal structure refinement and crystal chemistry

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Abstract

The crystal structure of antimonian asbecasite in an ejectum of hypabyssal origin occurring at Tre Croci near Vetralla, Vico volcanic complex, Roman potassic province, Latium, Italy, has been refined to $R = 0.042$, and is compared to the original crystal structure determination carried out on the Sb-free asbecasite of hydrothermal metamorphic origin from the type-locality, Cherbadung in Binna valley, Monte Leone nappe, Switzerland. New electron microprobe analyses of samples from both localities demonstrate crystal-chemical features that permit distinction between asbecasites from the two occurrences, so far the only known localities for this mineral.

KEYWORDS: asbecasite, crystal structure, crystal chemistry, Switzerland, Italy.

Introduction

ASBECASITE, ideally $\text{Ca}_3\text{TiAs}_6\text{Be}_2\text{Si}_2\text{O}_{20} - P3c1$, has so far been found at only two localities: (1) over a small area of the central Alps on both sides of the Swiss-Italian border around Cherbadung in Binnatal, Wallis (Graeser, 1966), also known as Pizzo Cervandone in Val Devero, Piemonte (Mattioli, 1979); and (2) at Tre Croci near Vetralla (Viterbo province, Latium), within a unique large ejectum lying on the ground in the outcrop area of the lowest pyroclastic unit of the Vico volcano, a member of the Roman potassic province (Della Ventura *et al.*, 1991).

At Cherbadung, the type-locality, asbecasite occurs sparsely as aggregates of light-yellow rhombohedral crystals. They formed under low-temperature metamorphic conditions, in the late-alpine open clefts which cross-cut the gneisses of the Monte Leone nappe. Asbecasite is a vein mineral probably precipitated from As-bearing

solutions originating from pre-alpine Cu-As ores in the gneisses around Cherbadung which had been remobilised under the conditions of alpine metamorphism. These solutions migrated to the north where they caused the formation of Pb-Cu-As sulphosalts in the Lengenbach sulphide deposit. On their way north, the As-bearing solutions became oversaturated by cooling down at the time of the general uplift of the Alps, thus leading to precipitation of various unusual arsenite and arsenate minerals (Graeser, 1966; Keusen, 1972).

At Tre Croci, asbecasite occurs scarcely, as books or fans of minute euhedral crystals with platy pseudo-hexagonal habit and custard-yellow colour, scattered in the interstices of a syenitic ejectum. The host-rock consists of large interlocking sanidine crystals with minor biotite and augite, and accessory magnetite, titanite and sodalite. The interstices between the sanidine crystals contains danburite, vonsenite, thorite, betafite, baddeleyite, zircon, Th-rich ekanite, Th-rich hellandite, uranthorianite, vicanite-(Ce) and cryptomelane, plus several unidentified minerals

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(Della Ventura *et al.*, 1991). The syenite block was ejected during phase 3 of the evolution of Vico volcano, radiometrically dated between 260 and 155 ± 5 ka (Laurenzi and Villa, 1987).

The ejecta that are found in the pyroclastic rocks of the Roman potassic province were favourable sites for the local crystallisation of minerals characterised by unusual combinations of chemical elements (Della Ventura *et al.*, 1990). These rare minerals deposited from hydrous siliceous fluids carrying light elements (B, F, and Be) which permeate the volcanic sequence and mix at depth with other fluids rich in As and Sb (and other heavy elements). The origin of the former fluids has been debated, but is generally believed to be cognate with the perpotassic magmas of the Quaternary Roman volcanics; the latter fluids are generally believed to be groundwaters percolated at depth and mineralised by dissolving the sulphides (mainly realgar and stibnite) that occur as minor orebodies throughout the volcanic and sedimentary sequences (Sella, 1876-7; Mattias and Caneva, 1979).

The rare minerals crystallised over a wide range of temperatures, from fairly high temperatures under hypabyssal intrusive conditions, down to

fairly low temperatures, and well within the hydrothermal stage (Della Ventura *et al.*, 1992).

Crystal structure refinement

The crystal structure of asbecasite was determined by Cannillo *et al.* (1969) using a specimen from the type-locality Cherbadung that had been supplied to them directly by Graeser. The intensity data were recorded by the Weissenberg photographic multiple-film technique, measured with a microdensitometer, and refined on the basis of a three-dimensional Patterson synthesis (cf. Table 1).

When we identified the Tre Croci asbecasite, we deemed it useful to redetermine its structure, not only because it is from a new, geologically different occurrence, but also because it is time to refine the old one using updated instruments and modern methods, the more so as, in the meantime, one detail of the structure described by Cannillo *et al.* (1969) has been disputed (Downs and Gibbs, 1981).

Experimental. Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer at the Centro di Strutturistica Diffratto-

Table 1
CRYSTAL DATA

	Cannillo et al. 1969	this work
unit cell content	Ca6 As12 Si4 Ti2 Be4 O40	
Crystal size	.38 mm (spherical shape)	.07x.38x.43 mm
Space group	P 3 $\bar{2}$ /c1 n.165	idem
\bar{a} (Å)	8.36(2)	8.318(1)
\bar{c} (Å)	15.30(3)	15.264(2)
\bar{V}	926.1(36)	914.6(2)
\bar{a}/\bar{c}	0.546(2)	0.5449(1)
\bar{D}_{calc}		3.672
radiation	CuK α	MoK α
monochromator	--	graphite
μ	283 cm $^{-1}$	97.98 cm $^{-1}$
intensity measurement	Weissenberg photograph microdensitometer	Enraf-Nonius CAD4 diffractometer, /2 θ scan
$\theta_{min}-\theta_{max}$	40°	2-40°
measured reflections	800	4328
independent reflections	695	1890
observed reflections	573	1370
absorption correction	linear	empirical method
refinement	full matrix l.s.	full matrix l.s.
unobserved reflection	I=1/2 minimum	not used (I<3 σ (I))
weight		1.0000/($\sigma^*2(F)$)+ .003487 F*F)
secondary extinction	corrected	not corrected
anomalous scattering	not corrected	corrected
final isotropic R	0.054	.0527
final anisotropic R	--	.0420
R_w		.0473

metrica della Università di Ferrara, using monochromated Mo-K α radiation and the $\omega/2\theta$ scan technique. Cell parameters were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range $12 < \theta < 38^\circ$. The crystal data are reported in Table 1 and compared with those of Cannillo *et al.* (1969). Intensities were corrected for Lorentz and polarisation effects and for absorption by the method of North *et al.* (1968). Only reflections with $I \geq 3\sigma(I)$ were considered as observed.

The structure was solved and refined using the SHELX86 and SHELX-76 programs (Sheldrick, 1976, 1985). Structure factors for neutral atoms and anomalous dispersion parameters were taken from vol. 4 of the International Tables for X-ray Crystallography (1974).

All atoms, except O4, were determined by direct methods. The oxygen O4 was found in the Fourier difference map after a few least-square cycles. The structure refines rapidly by full-matrix least-squares, using anisotropic temperature factors for all the atoms. Final positional and thermal parameters are given in Table 2. The interatomic distances and the most significant angles are reported in Table 3, and compared with the values published by Cannillo *et al.* (1969). The structure factors and the analysis of thermal factors (Tables 4 and 5) are available on request from the first author and have been

deposited with the Mineralogical Society. Except for some ripples near the As atoms, no peaks greater than $1e/\text{\AA}$ can be seen in the Fourier difference map.

Our structure determination of the Tre Croci asbecasite confirms the solution given by Cannillo *et al.* (1969) for the Cherbadung type-specimen. There is a small difference, equal to three times the standard deviation, in the size of the unit-cell, which however maintains its shape, as shown by the unchanged *a/c* ratio (Table 1).

The structure may be described in terms of the two layers proposed by Cannillo *et al.* (1969, Figs. 1 to 4). Layer A is formed by $[\text{BeO}_4]$ and $[\text{SiO}_4]$ tetrahedra joined by the common O4 atom and with $[\text{AsO}_3]$ trigonal pyramids on the top and at the bottom of the layer. Layer B is formed by $[\text{TiO}_6]$ octahedra and $[\text{CaO}_8]$ square antiprisms. The antiprisms are connected one to the other only by the corners, but each antiprism shares one edge with an octahedron.

We confirm the Si-O4-Be bond-angle 180° found by Cannillo *et al.* (1969), i.e. the feature of the asbecasite structure that had been disputed by Downs and Gibbs (1981). On the basis of *ab initio* molecular orbital models, the latter authors calculated the energy of the group $(\text{OH})_3\text{-Be-O-Si-(OH)}_3$ and found a non-deep minimum for the Be-O-Si angle at 131° . Consequently they rejected the space group $P\bar{3}c1$ determined by

Table 2

Atomic parameters with standard deviation (in parentheses) and Wyckoff notation.

Atoms	Wyckoff	x/a	y/b	z/c	Ueq
Ca	6f	.5921(1)	.5921(1)	3/4	.0083(2)
As	12g	.0187(0)	.2950(0)	.1027(0)	.0089(1)
Ti	2a	.0	.0	.25	.0072(3)
Si	4d	2/3	1/3	.0729(1)	.0085(4)
Be	4d	1/3	2/3	.1309(6)	.0091(15)
O(1)	12g	.8933(4)	.7785(4)	.1754(2)	.0117(8)
O(2)	12g	.5362(3)	.7217(3)	.1743(2)	.0099(7)
O(3)	12g	.5980(4)	.4693(4)	.1161(2)	.0126(7)
O(4)	4d	1/3	2/3	.0297(3)	.0174(12)

Anisotropic thermal parameters with standard deviation in parentheses

Atoms	U11	U22	U33	U23	U13	U12
Ca	.0076(2)	.0076(2)	.0095(4)	.0005(1)	-.0005(1)	.0036(3)
As	.0078(2)	.0073(2)	.0100(2)	.0001(1)	-.0006(1)	.0026(1)
Ti	.0061(3)	.0061(3)	.0094(5)	.0	.0	.0031(1)
Si	.0079(4)	.0079(4)	.0096(7)	.0	.0	.0039(2)
Be	.0069(16)	.0069(16)	.0135(32)	.0	.0	.0034(8)
O(1)	.0107(10)	.0103(9)	.0149(11)	-.0024(8)	-.0026(9)	.0058(8)
O(2)	.0089(8)	.0110(9)	.0114(10)	-.0029(8)	-.0019(8)	.0061(8)
O(3)	.0117(9)	.0074(9)	.0183(12)	-.0012(9)	.0019(9)	.0044(8)
O(4)	.0210(14)	.0210(14)	.0102(20)	.0	.0	.0105(7)

Table 3
Interatomic distances and some significant angles (with standard deviation in parentheses)

		Cannillo et al. 1969	this work
Ti-O1	(x6)	1.970(6)	1.961(3)
Ca-O1	(x2)	2.433(6)	2.422(4)
Ca-O2	(x2)	2.560(7)	2.550(2)
Ca-O2'	(x2)	2.435(9)	2.415(3)
Ca-O3	(x2)	2.471(7)	2.476(3)
As-O1		1.787(7)	1.783(3)
As-O2		1.757(8)	1.773(3)
As-O3		1.846(7)	1.851(3)
Be-O2	(x3)	1.668(12)	1.650(4)
Be-O4		1.530(23)	1.545(10)
Si-O3	(x3)	1.654(9)	1.639(4)
Si-O4		1.580(13)	1.566(5)
O2-Be-O4	(3x)	113.7(8)	113.7(3)
O2-Be-O2'	(3x)	104.9(15)	105.0(4)
O3-Si-O4	(3x)	114.0(3)	113.7(1)
O3-Si-O3	(3x)	104.6(8)	104.9(2)
Si-O3-As		127.6(4)	127.6(2)
Si-O4-Be		180.	180.
O1-As-O2		102.8(3)	102.1(1)
O1-As-O3		94.9(3)	94.7(1)
O2-As-O3		90.1(3)	89.7(1)
O1-Ti-O1'	(3x)	178.0(6)	178.0(1)
O1-Ti-O1''	(3x)	91.6(6)	91.7(1)
O1-Ti-O1'''	(3x)	89.7(6)	89.7(1)
O1-Ti-O1''''	(3x)	88.7(6)	89.0(2)

Cannillo *et al.* (1969) and (using the structure factors reported by Cannillo *et al.*, 1969) attempted to refine the structure of asbecasite with the 3-fold axis removed. Although they found that the full refinement was impossible, they came to the conclusion that the Be-O4-Si angle in asbecasite may be close to 150–160°, rather than 180° as reported.

As we have collected two groups of symmetry-related reflections (hkl and $\bar{h}\bar{k}\bar{l}$), we tried to refine the structure also in the space group $C2/c$, using anisotropic temperature factors and the unit-cell parameters $a = 14.407$, $b = 8.318$, $c = 15.264$ Å, $\alpha = \beta = \gamma = 90^\circ$. The final R obtained, from 2703 measured reflections and for 155 variables, is 0.050, but the Be-O-Si angle is 178.9(6)°, i.e. not significantly different from 180°, as obtained in the space group $P3c1$. Consequently, we believe that the trigonal symmetry is correct, and the Be-O4-Si bond angle of asbecasite is indeed 180°.

The examination of the temperature factors (Table 4) shows that Si and Be have minor anisotropy in the direction towards O4, while the O4 atom shows an anisotropy which is normal to this direction. This means that the O4 atom is statistically in the 3-fold axis. Furthermore, the two bonds Be-O4 = 1.545(10) and Si-O4 = 1.566(5) Å (see Table 3) are shorter than any

other bond of the tetrahedra (Be-O2 = 1.650(4), Si-O3 = 1.639(4) Å): as O4 is the only 2-fold coordinated oxygen in the structure, the two short bonds involved are easily justified in terms of bond valence. Finally, the Be-O4-Si bond angle cannot be smaller than 175° because the difference of the root mean square thermal vibrations along a and b (0.1449 Å) and along c (0.1095 Å) is very small (0.0354 Å).

Crystal chemical discussion

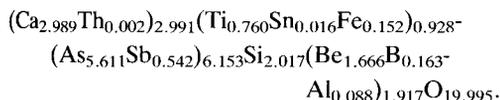
Some aspects of the crystal structure of asbecasite cannot be dealt with properly unless the actual chemical composition is known.

Experimental. The chemical compositions of the Tre Croci asbecasite and of an asbecasite from the Italian side of Pizzo Cervandone (supplied by V. Mattioli) were obtained by combining the microprobe analyses performed by the WD technique both at the C.N.R., C.S. per la Geologia dell'Italia centrale, Roma, using the Cameca SX-50 instrument, and at the Muséum National d'Histoire Naturelle, Paris, using the Camebax. The used standards were natural diopside (Si, Ca), quartz (Si), wollastonite (Ca), corundum (Al), albite (Al), cassiterite (Sn),

pyrite and magnetite (Fe), stibnite (Sb), arsenolite (As), monazite (Th, REE), and synthetic rutile (Ti) and arsenic (As).

B and Be could be determined quantitatively only in the Tre Croci sample. The analysis was carried out with the ion microprobe at C.N.R.S.-C.R.P.G. of Nancy, using the IMS 3F apparatus. The ion probe results were calibrated directly against the Si content of the sample, taken as the average value determined by the electron microprobe (Table 6).

The asbecasite formulae were computed assuming a total content of 20 oxygens and 14 metal ions and a fully anhydrous composition, so as to fit the ideal formula suggested by Cannillo *et al.* (1969) from their determination of the crystal structure, and confirmed above. However this way of calculation indicated significant departures from stoichiometry in all the asbecasites analysed so far (Table 6). In fact the Tre Croci asbecasite (*a* in Table 6), despite having an oxide sum slightly below the recommended minimum value 99%, is the only one that reasonably agrees with the ideal stoichiometric ratio 3:1:6:2:2:20, provided certain cations are considered to be diadochic and allocated to the same sites. Our preferred formula of the Tre Croci asbecasite is:



When calculated on the basis of 20 O only, the formulae of both the Cervandone and Cherbadung asbecasites (*b* and *c* in Table 6) show significant total cation deficits. This can be justified easily for our analysis, where the oxide sum too is low because B and Be were not analysed, but is hard to account for the other one, the oxide sum of which is close to 100% even though B was not determined. On account of their calculated Si and As excesses as well as of their very low Be atoms, we believe that the formulae of the Cervandone and Cherbadung asbecasites do not match the ideal stoichiometry because their analyses are biased by the lack of B determination. We tried improving these formulae by normalising to $\text{Ca} + \text{Th} + \text{Mn} = 3$, since CaO is nearly the same in all analyses and the computed Ca is always close to the theoretical occupancy of the site. Furthermore, on size considerations, the Ca site seems to be the one that allows the smallest amount of substitution. However, this normalisation did not bring to a definitive improvement.

The Tre Croci asbecasite is considerably different chemically from the Cervandone asbecasite;

in turn the latter is different from the wet-chemically analysed Cherbadung asbecasite published by Graeser (Table 6).

In our previous study on the Tre Croci asbecasite (Della Ventura *et al.*, 1991) we explained its small unit-cell, in comparison to that of the Cherbadung specimen (however with identical shape, as shown by the axial ratios of Table 1), by conceding the presence in the latter of significant amounts of the two large cations Sn and Tl, as reported by Graeser (1966). However, our microprobe analysis of the Cervandone asbecasite, although confirming certain features of the Cherbadung one (e.g. the high SiO₂ and As₂O₃ contents), is Tl-free and contains only little Sn. This suggests that Sn and Tl were present in Graeser's wet-analysed material mostly as mechanical impurities (or, possibly, Tl had been adsorbed from the Clerici's solution used for separation).

On the contrary, the Tre Croci asbecasite contains the fairly large Sb cation substituting for the small As cation in such an amount as to deserve the designation of *antimonian* variety. As such, it should also show a unit-cell larger than the Cherbadung one. Its smaller size can only be explained by the fact that it contains even greater amounts of the two very small cations Be and, particularly, boron.

The substitution of Sb for As, not unusual in sulphides and sulphosalts, i.e. when these two amphoteric elements have anionic behaviour, is rare when they behave as cations and coordinate a polyhedron having oxygen at its corners. In such a case, while As in its 5+ oxidation state frequently occurs as the centre of a tetrahedron (arsenates), Sb does not: no antimonate mineral is known in this form; rather, Sb combines in such a way as to form complex oxides.

Asbecasite is one of the rare minerals where As is not pentavalent but certainly trivalent, and situated at the vertex of a trigonal pyramid. The vicarious behaviour shown by Sb in the Tre Croci asbecasite, when compared with the Cervandone specimen, indicates clearly for the same 3+ oxidation state of Sb as for As. Moreover, the fact that no distinctly larger pyramid was found in the structure suggests that the Sb cations substituting for As are disordered over all the pyramids of the structure.

This sets the Tre Croci asbecasite in a systematic position somewhat intermediate between asbecasite s.s. (e.g. the Cervandone sample) and thorikosite (Dunn and Rouse, 1985), an arsenite-antimonite where both As³⁺ and Sb³⁺ are present, and are believed to substitute for each other. An oxide that also contains As and Sb in

Table 6
Chemical composition (wt.%) of asbecasites

	(a)	(b)	(c)	(d)
P ₂ O ₅	0.00	0.41	na	---
SiO ₂	11.34	12.73	12.3	11.88
TiO ₂	5.68	5.82	6.3	7.90
SnO ₂	0.23	0.89	2.1	---
ThO ₂	0.04	0.00	na	---
B ₂ O ₃	0.53	na	na	---
Al ₂ O ₃	0.42	0.84	1.2	---
As ₂ O ₃	51.95	58.70	58.7	58.66
Sb ₂ O ₃	7.39	0.85	na	---
Tl ₂ O ₃	0.00	0.00	1.0	---
BeO	3.90	na	2.3	4.94
CaO	15.69	15.20	15.4	16.64
MnO	0.00	0.17	na	---
FeO	1.02	0.88	na	---
Sum	98.19	96.49	99.3	100.00

Formulae on the basis of O = 20

	(a)	(b)	(c)	(d)
P	0.000	0.064	0.000	---
Si	2.017	2.348	2.162	2.000
Ti	0.760	0.807	0.833	1.000
Sn	0.016	0.065	0.147	---
Th	0.002	0.000	---	---
B	0.163	---	---	---
Al	0.088	0.183	0.256	---
As	5.611	6.575	6.268	6.000
Sb	0.542	0.065	---	---
Tl	0.000	0.000	0.046	---
Be	1.666	---	0.971	2.000
Ca	2.989	3.003	2.900	3.000
Mn	0.000	0.027	---	---
Fe	0.152	0.136	---	---
Sum	14.004	13.272	13.576	14.000

Notes

(a) Tre Croci near Vetralla, Vico volcanic complex, Roman potassic province, Latium, Italy.

(b) Pizzo Cervandone in Val Devero, Monte Leone nappe, Piemonte, Italy.

(c) Cherbadung in Binnatal, Monte Leone nappe, Wallis, Switzerland (Graeser, 1966).

(d) theoretical.

In (a) and (b): U and REE also looked for but not found.

na = not analysed.

the same 3+ oxidation state and vicariously sharing the same structural site (the apex of a trigonal pyramid) is the recently described mineral hemloite (Harris *et al.*, 1989). Another mineral containing both As^{3+} and Sb^{3+} is stenhuggarite (Moore, 1970); however, this mineral is more complex because Sb^{3+} was found, like Fe^{3+} , to occur in a trigonal bipyramidal site of the structure, whereas As is in tetrahedral coordination and plays a totally different structural role, thus being inaccessible to Sb substitution despite the fact that both cations share the same type of helical groups (Coda *et al.*, 1977).

There is a second peculiarity of the Tre Croci asbecasite worth pointing out—the presence of B probably substituting for Be in the $[\text{BeO}_4]$ tetrahedra. Boron had not been detected by Graeser (1966) in his analysis nor by Cannillo *et al.* (1969) in their structure solution. Boron did not show up in our structure refinement either, during the site-occupancy iteration refinement, despite a specific attempt carried out to reveal it (cf. Hawthorne and Grice, 1990). However the ion-probe analysis shows that it is present at Tre Croci, and the formula calculation requires it to be present also in the Cervandone asbecasite: otherwise the tetrahedral Be sites would be grossly underfilled, because the amount of Si present is insufficient to fill the $[\text{BeO}_4]$ tetrahedra (cf. Table 6).

The discrepancy between the empirical formula determined from the wet-chemical analysis (Graeser, 1966) and that resulting from the structural solution had not escaped Cannillo *et al.* (1969, p. 405), but they were unable to carry out a chemical check for lack of material. Such a discrepancy is probably due to the above-mentioned overlooking of boron. The Tre Croci analysis with its determined B_2O_3 is in fact almost exactly balanced (19.995 O against 14.004 cations), and full balance can be easily attained by oxidising just a minor part (0.10 wt.%, equal to 0.013 Fe^{3+}) of the determined Fe, conventionally given as FeO by the microprobe program.

Conclusion

The structure of asbecasite determined by Cannillo *et al.* (1969) on crystals from the type locality, Cherbadung, has proved to be correct by the refinement we carried out on the asbecasite recently discovered at Tre Croci di Vetralla, the second occurrence for this mineral. Therefore, the 180° Si–O4–Be bond angle present in the asbecasite structure, that had been disputed by Downs and Gibbs (1981) on the basis of molecular orbital calculations, is also correct, as it was explicitly tested during our refinement.

Boron is an essential constituent of asbecasite from both localities; it substitutes for Be to fill up tetrahedral sites independent on those occupied by Si. On the contrary, it appears that most Sn that had been determined in the Cherbadung asbecasite was from mechanical impurities, and all Tl (probably) from contamination. The Tre Croci di Vetralla asbecasite differs from the Cherbadung occurrence in containing significant Sb, which has the same 3+ oxidation state as As and is randomly distributed over all the sites occupied by the latter. Thus the adjective modifier 'antimonian' is fully justified; indeed, this seems to be the chemical characteristics that distinguishes the Tre Croci asbecasite, formed in a volcanic environment, from the Cherbadung one, that formed under metamorphic condition in an alpine cleft.

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