Yanomamite, InAsO₄.2H₂O, a new indium mineral from topaz-bearing greisen in the Goiás Tin Province, Brazil

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Abstract : Yanomamite occurs as green to yellow-green idiomorphic crystals in aggregates associated with scorodite in quartz-topaz greisen in the tin deposit of Mangabeira, Goiás State, Brazil. Yanomamite crystals are always coated by a thin film of In-rich scorodite. Microprobe analyses give (wt. %) : In_2O_3 45.8(3), Fe_2O_3 1.1(2), Al_2O_3 0.21(2), As_2O_5 40.1 (2), H_2O 12.78 by difference, with the structural formula $(In_{0.94}Fe_{0.04}Al_{0.01})AsO_4 . 2.02$ H_2O. Yanomamite is isotypic with scorodite, and belongs to the variscite series. The mineral is orthorhombic, space group *Pbca*, with $a = 10.446(6)$, $b = 9.085(4)$, $c = 10.345(6)$ Å, $V = 981.8(7)$ Å^3, $Z = 8$; the synthetic Fe-free compound has $a = 10.471(3)$, $b = 9.092(2)$, $c = 10.341(2)$ Å, $V = 984.5(5)$ Å^3. The strongest reflections [d in Å, (I/I_0), (*hkl*)] of the powder diffraction pattern of natural yanomamite are : 5.70 (70)(111), 4.53 (100)(020,210), 4.163 (50)(021), 3.874 (60)(121), 3.250 (60)(122), 3.110 (50)(311), 2.656 (40)(123), 2.541 (40)(231). $D_{calc} = 3.876(3)$ g/cm^3 ; $VHN_{25} = 631$ kg/mm^2 ; $2V_Z$ (meas.) = 55-76°. The average refractive index is $n = 1.65$. The unit-cell volume *versus* ionic radius of the tri- or divalent cations shows a very good correlation in the variscite isotypic series (13 arsenates, phosphates and selenates). Yanomamite and In-bearing scorodite are cogenetic, formed by alteration of early arsenopyrite and In-rich sphalerite. This replacement may be related to a hydrothermal process coeval with the main cassiterite deposition, rather than to supergene alteration.

Key-words : yanomamite, indium, arsenate, Brazil, new mineral, variscite series.

Introduction

Indium minerals are very rare ; only 7 species have been defined so far : roquesite, $CuInS_2$ (Picot & Pierrot, 1963) ; indite, $FeIn_2S_4$, and dzhalindite, $In(OH)_3$ (Genkin & Murav'eva, 1963) ; sakuraiite, $(Cu,Fe,Zn)_3(In,Sn)S_4$ (Kato, 1965) ; native indium (Ivanov, 1966b) ; yixunite, PtIn (Yu Tsu-Hsiang *et al.*, 1976) ; petrukite, $(Cu,Fe,Zn,Ag)_3(Sn,In)S_4$ (Kissin & Owens, 1989). Various unnamed sulfides, probably related to

the sphalerite archetype, have been also described (Ohta, 1980, 1989 ; Cantinolle *et al.*, 1985 ; Murao & Furuno, 1990). In Brazil, roquesite and dzhalindite were described for the first time in the Mangabeira tin deposit, Goiás State ; moreover, In-bearing sulfides, arsenates and cassiterite were identified in Mangabeira and elsewhere in the Goiás Tin Province, which indicates a regional indium anomaly (Botelho & Roger, 1990).

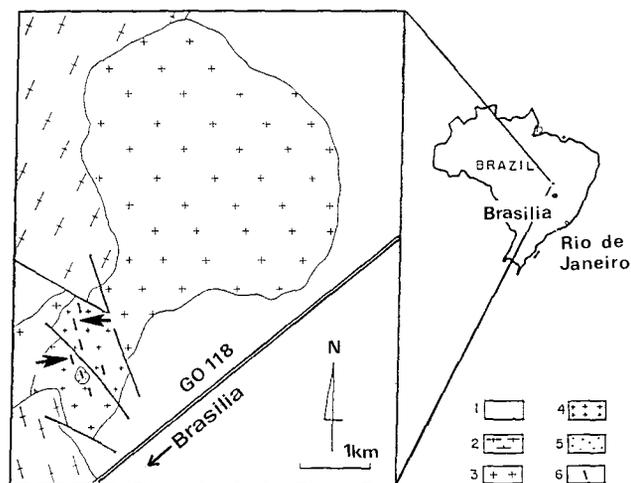A mineral very similar to scorodite under the

Fig. 1. Location and simplified geological map of the Mangabeira Massif. 1. cataclastic gneiss ; 2. mylonite ; 3. pink biotite granite ; 4. albitised and greisenised leucogranites ; 5. topaz-albite granite ; 6. greisen veins ; arrows indicate yanomamite occurrences.

microscope was identified by Botelho & Roger (1990) as a hydrous indium arsenate, named "mineral X". Microscope studies as well as crystallographic data (Botelho, 1992) revealed this indium arsenate to be a new mineral species. The mineral was named yanomamite after the Yanomami Indian people from Amazon. The

mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of IMA (vote 90-052). Holotype specimens are deposited in the Mineralogical Collection of the Instituto de Geociências, Universidade de Brasilia, Brazil, and in the Museum of the Ecole Nationale Supérieure des Mines de Paris, France.

1. Occurrence and paragenesis

The Mangabeira tin deposit is located in Goiás State, Brazil, 350 km north of Brasilia, in the southern part of the Amazon Basin (Fig. 1). The deposit is situated at the border of road GO-118,
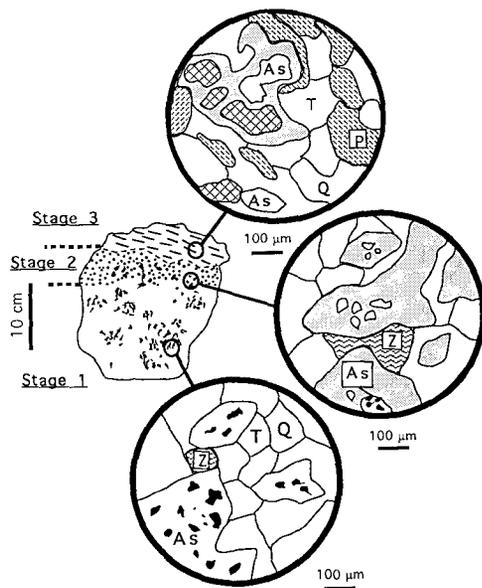

Fig. 2. Three hydrothermal stages of deposition in a representative sample of In-bearing greisen from Mangabeira : 1. early stage showing arsenopyrite crystals (As) with In-rich sphalerite inclusions (black). Gangue minerals are topaz (T), quartz (Q) and minor zinnwaldite (Z). 2. second hydrothermal stage corresponding to the partial replacement of arsenopyrite by In-rich scorodite + yanomamite + cassiterite aggregates (stippled), like in Fig. 3c. 3. third hydrothermal stage with In-poor sphalerite (cross-hatched), arsenopyrite (As) and other sulfides (see text). Arsenopyrite is altered to a scorodite mass, without In-minerals nor cassiterite. Gangue minerals are phengite (P), quartz (Q) and topaz (T).
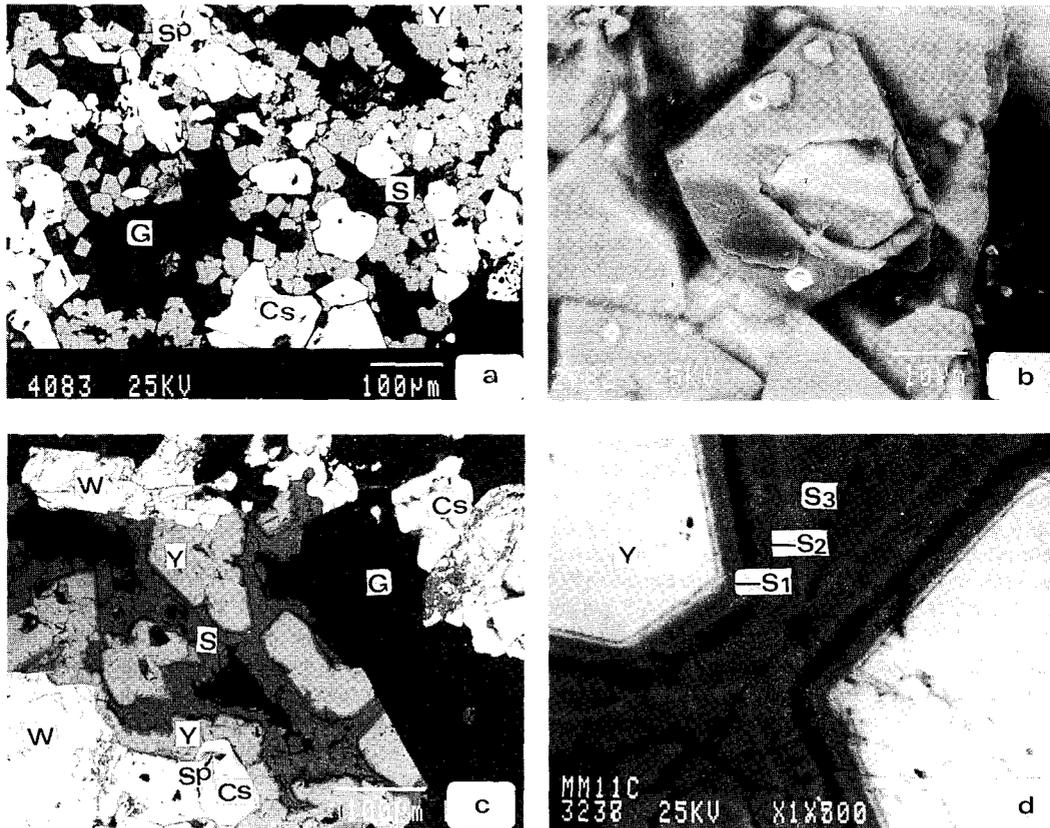
Fig. 3. SEM micrographs of the yanomamite association. *a*) thin section. Numerous yanomamite crystals (Y, grey) associated with In-rich scorodite (S) and cassiterite (Cs) with In-rich sphalerite inclusions (Sp), in quartz-topaz gangue (G) ; *b*) yanomamite sub-octahedral crystal with a broken vertex showing the covering film of epitactic scorodite ; *c*) thin section. Yanomamite crystals in an In-rich scorodite mass, showing scorodite zoning at the contact with yanomamite ; W, wolframite ; *d*) detail at the centre of the micrograph *c* ; S_1, S_2 and S_3 : successive epitactic bands of scorodite (S_1, first, In-richest band ; S_2, fibrous intermediate band ; S_3, massive, In-poor band).

and the yanomamite occurrence is 1 km north of the place named "Passa-e-fica".

The Mangabeira tin deposit is associated to a Middle-Proterozoic granite intrusion belonging to the Goiás Tin Province. The main granite is a pink, porphyritic to equigranular biotite granite, followed by leucogranites and a minor Li-mica - topaz - albite granite (Fig. 1). Mineralizations are mainly hosted in two types of greisen veins : (Li-mica + quartz)-greisen on the one hand, and (zinnwaldite + Li-mica + topaz + quartz)-greisen on the other hand. Cassiterite and minor wolframite are the main ore minerals. The sulfide association is represented principally by löllingite, arsenopyrite, chalcopyrite, sphalerite, pyrite, with minor digenite, bismuthinite, bornite,

chalcocite, covellite, stannite, tennantite, roquesite and native bismuth.

Yanomamite and other In minerals are hosted in quartz-topaz greisen veins associated with the Li-mica - topaz - albite granite. Three hydrothermal stages (Fig. 2) were distinguished in these greisen veins (Botelho, 1992). Early minerals are topaz, quartz, zinnwaldite, wolframite, löllingite, arsenopyrite with In-rich (up to 11 wt.%) sphalerite inclusions, and minor cassiterite. The second hydrothermal paragenesis is mainly represented by cassiterite ore, and probably In-rich arsenates (Fig. 3a). Minerals from the third hydrothermal stage are arsenopyrite, In-poor (< 1 wt.%) sphalerite, In-bearing (2 wt.%) stannite, roquesite, chalcopyrite, pyrite, enargite,

galena, digenite and cosalite. Minerals from the youngest association, probably of supergene origin, are In-poor scorodite, beudantite, agardite-(Y), K-, Ba-, Fe-, Bi- and Cu-arsenates, goethite, dzhalindite, covellite and chalcocite.

In the type material, yanomamite occurs in an arsenopyrite alteration zone, as euhedral grains (mean size 0.1 mm, maximum size 0.2 mm) intimately intergrown with scorodite (Fig. 3b and 3c). Yanomamite-scorodite aggregates may reach 1 cm. These minerals replace arsenopyrite with inclusions of In-rich sphalerite. However, the small volume of inclusions in non-altered arsenopyrite compared to the yanomamite-scorodite volume suggests that In-rich sphalerite might not be the main indium source for the arsenates. Yanomamite also fills microfractures and interstices in gangue minerals, quartz and topaz as well as Li-mica cleavages. Yanomamite crystals are often coated by a thin film of epitactic In-rich scorodite (Fig. 3b ; Fig. 3d, S_1 rim). Fibrous (S_2) and massive (S_3) In-rich scorodite may be also present (Fig. 3d and 4). The In, Fe and As distributions in yanomamite and in scorodite are schematized in Fig. 4. Yanomamite occurs in close association with cassiterite in the arsenopy-

rite alteration zone (Fig. 3a). Otherwise, there is no cassiterite concentration in alteration zones where yanomamite is absent.

2. Physical properties

Yanomamite occurs mainly as pale-green to yellow-green bipyramidal crystals (Fig. 3b). The Mohs hardness, 3.5 to 4.0, was evaluated by analogy with scorodite (no relief at the contact between these two species in polished sections). The powder is white and the luster is vitreous. Because of scorodite overgrowths, it was not possible to make exact measurements of density. The calculated density is D = 3.876(3) g/cm^3, based on the chemical formula given by microprobe analysis and the measured unit-cell, with Z = 8. Yanomamite is easily soluble in 35 % HCl and soluble in 95 % H_2SO_4, giving a colourless solution.

Optical properties were determined under a Zeiss universal stage, on bipyramidal grains. Measurements of the refractive index gave an average value for n = 1.65. This value agrees with the microscopic obervation that the yanomamite relief is lower than that of scorodite, 1.784 < n < 1.814 (Palache et al., 1951). Under the microscope, yanomamite is colourless. The average Vickers microhardness VHN$_{25}$ is 631 kg/mm^2 (range 571-743 kg/mm^2, 8 measurements). Yanomamite optical orientation is X = a, Y = c, and Z = b. The mineral is biaxial with $2V_Z$ measured between 55 and 76°.

3. Chemical composition

Yanomamite was analyzed with an electron microprobe at twelve spots in the rim and in the core of different crystals (Table 1). No significant zoning was identified at the crystal scale, although there are significant variations of the Fe-for-In substitution between distinct samples.

Despite the use of GaAs as arsenic standard at 20 kV, the short counting time (10 s) precludes pronounced error on the As content in arsenates. However, in order to reduce matrix effects, scorodite was used as a secondary standard ; accordingly a correction coefficient of 1.07 was applied to the As$_2$O$_5$ values obtained with AsGa for yanomamite. H$_2$O could not be determined directly because of scorodite impurities. The calculated H$_2$O contents, by total difference or based on the idealized water per formula unit, are in agreement with the theoretical composition
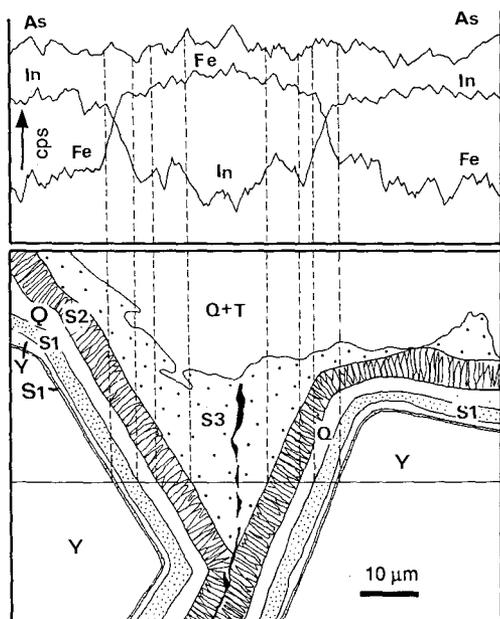

Fig. 4. SEM semi-quantitative analysis across (A-B) zoning at the yanomamite-scorodite contact shown in Fig. 3d. Symbols as in Fig. 3.

Table 1. Electron-microprobe analysis of yanomamite.

	1	2	3		4
In_2O_3	45.80(30)	43.29-47.28	In	0.94	47.91
Fe_2O_3	1.11(22)	0.31-3.11	Fe	0.04	--
Al_2O_3	0.21(2)	0.09-0.78	Al	0.01	--
As_2O_5	40.10(17)	39.03-40.86	As	1.00	39.66
Total	**87.22**		O	6.00	
H_2O	12.78		H	4.04	12.43

Camebax electron-microprobe, B.R.G.M.-C.N.R.S. Laboratory (Orléans, France). Programming : D. Ohnenstetter (C.N.R.S.-C.R.S.C.M., Orléans). Operating voltage 20 kV, sample current 30 nA. Standards (element, line) : $CuInS_2$ ($InL\alpha$), FeS_2 ($FeK\alpha$), Al_2O_3 ($AlK\alpha$), GaAs ($AsL\alpha$).

1. wt % ; average of twelve microprobe analyses (standard deviation) ; H_2O calculated by difference. 2. Ranges. 3. Structural formula on the basis of one arsenic atom. 4. Theoretical values (wt % oxydes) for the composition $InAsO_4.2H_2O$.

(Table 1). The empirical formula from the average spot analysis based on one atom As is $(In_{0.94}Fe_{0.04}Al_{0.01})AsO_4$. 2.02 H_2O. The idealized formula is $InAsO_4.2H_2O$.

Yanomamite contains minor amounts of Fe and Al, but, apparently, there is no scorodite-yanomamite continuous solid solution in the analyzed samples. In-rich scorodite crystallises directly after yanomamite during the same paragenetic stage, indicating very probably a miscibility gap between these two compounds at the temperature of formation and below. The maximum verified substitution is $In_{0.85}Fe_{0.15}$ in yanomamite, while the highest In content in scorodite (6 wt.% In_2O_3 : Botelho & Roger, 1990) corresponds to the maximum substitution $Fe_{0.90}In_{0.10}$ (Fig. 5).

4. X-ray crystallography

Single-crystal X-ray diffraction

A yanomamite + scorodite concentrate was obtained with a Franz magnetic separator. After this, yanomamite or a yanomamite-rich concentrate have been separated in a bromoform column. Because of scorodite intergrowth, the purest crystals could be separated only by careful hand picking under a stereoscopic microscope. Single-crystal studies (oscillation, rotation, Weissenberg and precession methods ; $CuK\alpha$ radia-
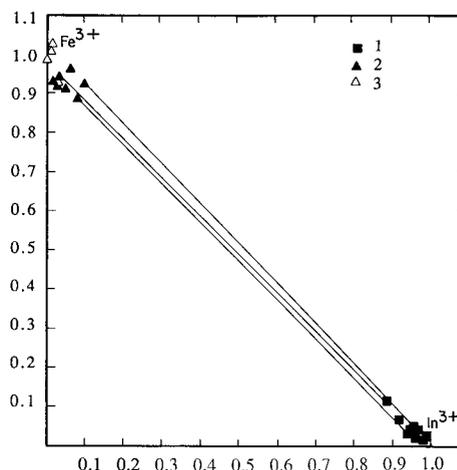

Fig. 5. Indium and iron distribution in yanomamite and scorodite. In and Fe in atoms p.f.u., on the basis of In + Fe + As = 2. In-rich scorodite and coexisting yanomamite are joined by tie-lines. 1 : yanomamite ; 2 : In-rich scorodite ; 3 : pure scorodite.

tion) were carried out on three crystals chosen among the purest separated grains. Nevertheless, they also contained scorodite in minor amounts, detected in sub-epitactic association on oscillation, rotation and precession films, probably as a thin coating like that in Fig. 3b.

Weissenberg and precession studies on a bipyramidal crystal, with b as rotation axis, indicate orthorhombic symmetry, space group Pbca, for natural yanomamite. Systematic extinctions for this group were all verified. The unit-cell parameters determined from precession films are reported in Table 2, column 1 (with Z = 8). They agree satisfactorily with those of synthetic $InAsO_4.2H_2O$ calculated from powder diffraction data : Table 2, columns 3 (unpublished data

Table 2. Unit-cell dimensions of yanomamite (Å).

	1	2	3	4
a (Å)	10.45(2)	10.446(6)	10.471(3)	10.43_6
b "	9.09(2)	9.085(4)	9.092(2)	10.34
c "	10.32(2)	10.345(6)	10.341(2)	9.03_8
V (Å³)	980(5)	981.8(7)	984.5(5)	975.3

Natural yanomamite crystal : 1 - singlecrystal study ; 2 - powder diagram. Synthetic compound : 3 - d'Yvoire (unpublished data) ; 4 - Tarte & Pâques-Ledent (1968) ; b and c are inverted.

Table 3. X-ray powder diffraction data for natural and synthetic yanomamite (d in Å).

natural I/Io	natural d meas	natural d calc	hkl	synthetic d calc	synthetic d meas	I/Io	natural I/Io	natural d meas	natural d calc	hkl	synthetic d calc	synthetic d meas	I/Io	natural I/Io	natural d meas	synthetic d meas	I/Io
70	5.70	5.714	111	5.720	5.719	70	20	2.610	2.612	400	2.6178	2.6180	30			1.9800	3
			200	5.235	5.234	3	15	2.587	2.586	004	2.5852	2.5849	5			1.8977	2
40	5.16	5.172	002	5.170	5.172	30	40	2.541	2.540	231	2.5424	2.5426	45			1.8702	2
100	4.53	4.543	020	4.546	4.537	100				114	2.4194	2.4194	5			1.8409	2
		4.528	210	4.537			15	2.365	2.3656	313	2.3679	2.3679	8	10	1.787	1.7856	7
50	4.163	4.159	021	4.162	4.162	40	8	2.328	2.3312	402	2.3355	2.3351	5			1.7230	2
15	4.124	4.129	112	4.130	4.131	10				204	2.3180	2.3181	1			1.7172	2
60	3.874	3.864	121	3.867	3.866	25				214	2.2462	2.2459	1			1.7137	2
20	3.421	3.428	220	3.4326	3.4330	4	20	2.222	2.2233	133	2.2241	2.2235	8			1.7006	2
20	3.408	3.407	212	3.4103	3.4110	20	20	2.219	2.2185	041	2.2200	2.2203	4	10	1.6923	1.6931	9
60	3.250	3.244	122	3.2459	3.2461	80	15	2.214	2.2117	421	2.2158	2.2164	5	9	1.6867	1.6853	8
50	3.110	3.102	311	3.1078	3.1073	40				124	2.1972	2.1974	4			1.6655	5
30	3.083	3.081	113	3.0805	3.0800	35	15	2.156	2.1564	323	2.1585	2.1587	8	8	1.6285	1.6292	4
			302	2.8929	2.8912	2	10	2.084	2.0861	233						1.6266	4
			131	2.8022	2.8027	<1			2.0828	240	2.0850	2.0848	2			1.6243	4
20	2.748	2.747	023	2.7467	2.7455	30	8	2.078	2.0797	042	2.0808	2.0806	4			1.6111	5
15	2.743	2.743	213	2.7447					2.0762	304	2.0775	2.0777	4			1.5402	8
			321	2.6743	2.6750	2	10	2.042	2.0396	142	2.0409	2.0407	9			1.5346	4
40	2.656	2.656	123	2.6568	2.6568	50				413	2.0320	2.0314	1			1.5147	3
30	2.618	2.620	230	2.6229	2.6235	10	8	2.025	2.0240	314	2.0252	2.0251	5			1.4993	3

Natural indexed with a = 10.446, b = 9.085, c = 10.345 Å. INEL curved detector (500 mm diameter). ; CoKα_1 with monochromator. Counting time : 10^4 s ; scorodite as external standard, on the basis of data of Blanchard (1986). Parameters calculated according to the indexing of the synthetic compound.

Synthetic indexed with a = 10.471, b = 9.092, c = 10.341 Å. Guinier camera ; CoKα_1 radiation. Aluminium tetrametaphosphate [Al$_4$(P$_4$O$_{12}$)$_3$], cubic with a = 13.730 Å, was used as internal standard. For d < 2 Å, the weakest reflections are not reported in the table.

obtained previously by one of us - F. d'Y.) and 4 (T arte & Pâques-Ledent, 1968). Nevertheless, V = 975.3 Å³ of the latter authors appears slightly too low, compared to that measured with an internal standard (column 3).

X-ray powder diffraction diagram

The X-ray powder diffraction diagram (Table 3) has been obtained on selected polycrystalline grains, without crushing. Comparison with the diagram of synthetic yanomamite does not show significant lines of scorodite, which proves the high purity of the selected grains. Parameters of the unit-cell calculated from this diagram are : a = 10.446(6), b = 9.085(4), c = 10.345(6) Å, V = 981.8(7) Å³, and Z = 8. These data are in very good agreement with those obtained through single-crystal study (Table 2, column 1).

Compared to Fe-free synthetic yanomamite (Table 3), the natural sample shows a slight contraction of the unit-cell. If one considers that this contraction varies linearly with the Fe-for-In atomic substitution toward the Fe end-member scorodite (Blanchard, 1986), the ratio corresponding to the relative contraction :

$(V_{natur.yano.} - V_{synth.yano.})/(V_{synth.yano} - V_{scorod.}) = - 0.05$

would correspond to 5 at.% substitution of In by Fe, within the effective substitution field given by electron-probe microanalysis.

Gladstone-Dale relationship

The Gladstone-Dale relationship for yanomamite gives Kc = 0.1719 (based on data from microprobe chemical analysis, and k values from Mandarino, 1981) and Kp = 0.1677 (based on D$_{calc.}$ = 3.882 g/cm³ and n = 1.65). The compatibility index 1 - (Kp/Kc) = 0.024 is excellent, according to Mandarino (1979, 1981).

5. Discussion of the yanomamite origin

The discussion of the origin of yanomamite is somewhat speculative because of the incomplete paragenetic study and the paucity of data about indium behaviour in hydrothermal conditions. Ivanov (1966a) reports indium concentrations in high-temperature hydrothermal deposits, particularly in cassiterite, chalcopyrite and sphalerite, but low In contents in oxidation zones (except in the minerals beudantite and bindheimite), apparently because of the ability of indium to form,

in acidic media with the presence of As^{5+}, the sparingly soluble arsenate $InAsO_4.2H_2O$ (that is yanomamite).

At Mangabeira, the microscopic observations indicate that yanomamite and In-rich scorodite are cogenetic, formed by the replacement of early arsenopyrite, which contains inclusions of In-rich sphalerite. The observations also suggest that yanomamite is intimately associated with cassiterite concentration. Geochemical data indicate that this cassiterite is the In-richest in the Mangabeira tin deposit (Botelho, 1992). Nevertheless, taking into account the small volume of In-rich sphalerite, the proportion of In-bearing arsenates suggests an additional indium source and transport, possibly related to the tin-rich hydrothermal stage.

Based on microscopic observations and general data for scorodite and yanomamite, two genetic hypotheses can be proposed :

i) yanomamite is supergene because of its relations with scorodite, a classical supergene mineral ;

ii) yanomamite is hydrothermal, formed during the main cassiterite deposition which corresponds to the second hydrothermal stage in the Mangabeira tin deposit.

In the supergene hypothesis, because of the early arsenopyrite alteration coeval with cassiterite deposition and the indium-tin association in the greisen from Mangabeira, yanomamite and In-rich scorodite ought to replace an early indium paragenesis, not observed in studied samples. As the microscopic and geochemical studies indicate that the In-rich stage is coeval with the tin-rich stage and that the clearly supergene paragenesis is depleted in indium, the hydrothermal hypothesis for the yanomamite origin seems the most probable.

6. Yanomamite in the variscite isotypic series

The variscite isotypic series (Strunz, 1978) is composed of arsenates, phosphates and selenates with general formula : $M1 (M2 O_4).2H_2O$, where

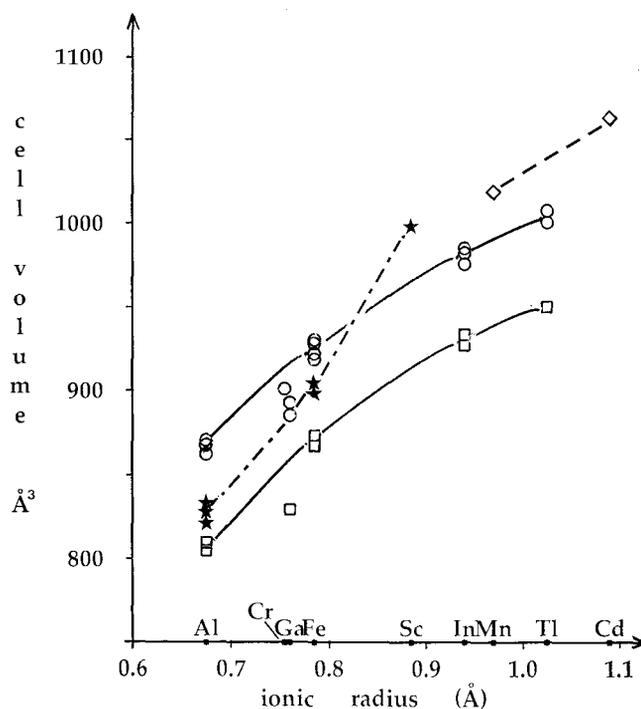Fig. 6. Unit-cell volume ($Å^3$) *versus* ionic radius ($Å$) (Shannon, 1976) of the di- or trivalent cations in the variscite isotypic series. The ionic radius corresponds to octahedral coordination ; for Fe^{3+} and Mn^{2+}, the ionic radius is that of the high-spin state.
Circles, arsenates ; squares, phosphates ; diamonds, selenates ; stars, monoclinic phosphates.

$M2 = As^{5+}$, P^{5+} or Se^{6+}, and $M1 = $ tri- or divalent cation (Al^{3+}, Cr^{3+}, Ga^{3+}, Fe^{3+}, In^{3+}, Tl^{3+}, or Mn^{2+}, Ca^{2+}) to insure charge balance. There are 13 natural or synthetic compounds, all ortho-rhombic, space group *Pbca*. The members of the metavariscite sub-series, monoclinic, space group $P2_1/n$, but homeotypic with variscite, have been added to this series by Strunz (1978).

A simple way to compare all these compounds is to plot the volume of the unit-cell in relation to the ionic radius of the M1 cation (Fig. 6), according to the data of Shannon (1976). Three sub-parallel lines are then obtained, corresponding to the three M2 cations. The best fitting is obtained for the arsenate sub-group, which contains the highest variety of compounds. Yanomamite has the highest unit-cell for natural species, very close to the lowest volume of the

Table 4. Minerals and synthetic compounds in the variscite isotypic series and monoclinic dimorphs.

Species (cation M1)	a (Å)	b (Å)	c (Å)	V (Å³)	References
Arsenates					
Mansfieldite (Al)	10.10	8.79	9.80	870.0	Walenta (*in* Strunz, 1978)
"	10.09	8.75	9.77	862.1	Tarte & Pâques-Ledent (1968)
"	10.08	8.79	9.79	867.4	Ronis & d'Yvoire (1974)
$CrAsO_4.2H_2O$	10.21	8.88	9.93	900.8	" " "
$GaAsO_4.2H_2O$	10.13	8.83	9.89	884.9	Pâques-Ledent & Tarte (1969)
"	10.15	8.85	9.94	892.3	Ronis & d'Yvoire (1974)
Scorodite (Fe)	10.31	8.94	10.00	921.8	Tarte & Pâques-Ledent (1968)
"	10.33	8.96	10.05	929.9	Ronis & d'Yvoire (1974)
"	10.33	8.95	10.04	927.9	Kitahama *et al.* (1975)
"	10.28	8.94	10.00	918.2	Hawthorne (1976)
"	10.33	8.95	10.04	928.3	Blanchard (1986)
Yanomamite (In)	10.45	9.09	10.35	981.8	this study
" (synth.)	10.47	9.09	10.34	984.5	d'Yvoire (Table 2)
" (synth.)	10.44	9.04	10.34	975.3	Tarte & Pâques-Ledent (1968)
$TlAsO_4.2H_2O$	10.48	9.16	10.49	1007.0	Mooney-Slater (1961)
"	10.46	9.12	10.49	1000.2	Tarte & Pâques-Ledent (1968)
Phosphates					
Variscite (Al)	9.87	8.52	9.57	804.8	McConnell (*in* Strunz, 1978)
"	9.87	8.53	9.59	807.6	Tarte & Pâques-Ledent (1968)
"	9.82	8.56	9.63	809.7	Kniep *et al.* (1977)
"	9.82	8.56	9.62	808.8	Blanchard (1981)
$GaPO_4.2H_2O$	9.90	8.59	9.75	829.4	Pâques-Ledent & Tarte (1969)
Strengite (Fe)	10.1	8.69	9.88	866.8	Tarte & Pâques-Ledent (1968)
"	10.12	8.72	9.89	872.9	Blanchard (1981)
$InPO_4.2H_2O$	10.36	8.84	10.19	933.2	Mooney-Slater (1961)
"	10.31	8.84	10.17	926.6	Tarte & Pâques-Ledent (1968)
$TlPO_4.2H_2O$	10.39	8.87	10.31	950.2	Mooney-Slater (1961)
Selenates					
$MnSeO_4.2H_2O$	10.44	9.25	10.54	1017.8	JCPDS - PDF n°20-721
$CdSeO_4.2H_2O$	10.48	9.42	10.76	1062.2	JCPDS - PDF n°20-186
Monoclinic phosphates ($\beta \sim 90°$)				V x 2	
Metavariscite (Al)	5.16	9.47	8.47	827.8	McConnell (*in* Strunz, 1978)
"	5.14	9.45	8.45	820.9	Borensztajn (1966)
"	5.18	9.51	8.45	832.9	Kniep & Mootz (1973)
Phosphosiderite (Fe)	5.30	9.77	8.73	904.0	McConnell (*in* Strunz, 1978)
"	5.32	9.75	8.65	897.3	Borensztajn (1966)
Kolbeckite (Sc)	5.45	10.25	8.93	997.7	Mrose & Wappner (*in* Hey, 1982)
"	5.45	10.25	8.94	998.2	Webb et al. (1991)

a, b and c (Å) chosen according to space group *Pbca* ; unit-cell volume V (Å³) calculated with the original data (β close to 90° for monoclinic dimorphs). Remark : some natural compounds do not have the end-member composition (for instance yanomamite) ; phosphophyllite, $Zn_2(Fe,Mn)(PO_4)_2.4H_2O$, with $V = 941.7$ Å³, not plotted here, is related to the monoclinic series (Moore, 1966).

selenate sub-group, *i.e.* the manganese compound. Thus, one might easily imagine the coupled substitution $In^{3+} + As^{5+} \rightarrow Mn^{2+} + Se^{6+}$. Another large solid solution might exist with the thallium arsenate, as the relative volume increase is only about 2 %.

Data for phosphates are also various. As for the arsenate sub-series, the slope of the curve decreases with increasing M1 ionic radius ; for instance, the volume increase from variscite to strengite ($Al^{3+} \rightarrow Fe^{3+}$) is about 60 Å³, and only 20 Å³ when substituting In^{3+} by Tl^{3+}. Correlatively, the comparison of the evolution of the *a/b* and *c/b* ratios shows that these two ratios increase slightly in the phosphate sub-series (from 1.15 to 1.17, and 1.12 to 1.16, respectively). In the arsenate sub-series, the *a/b* ratio is practically constant (around 1.15), while the *c/b* ratio, constant for smaller M1 cations (around 1.12 from Al to Fe), increases up to 1.15 for the largest cations (for Tl, *c* becomes superior to *a* : Mooney-Slater, 1961 ; Tarte & Pâques-Ledent, 1968). The replacement of $M1^{3+}$ (M1 = Al, Ga or Fe) by 3 H^+ (up to 7 at.% : Ronis & d'Yvoire, 1974) also indicates that the parameter *c* (*b* for these authors) is the most sensitive to this substitution.

The two curves for arsenates and phosphates show that the volumes obtained for gallium by different authors (Table 4) is always lower than expected : this could indicate an overestimation of the Ga^{3+} radius by Shannon (1976). This hypothesis is corroborated by the fact that, in the $Na_3M_2(AsO_4)_3$ rhombohedral series (M = Al, Ga, Cr, Fe : d'Yvoire *et al.*, 1986), the volume of the unit-cell is lower for the Ga compound than for the Cr one (245.2 and 246.0 Å³, respectively). On the other hand, one must bear in mind that Al, Ga, In and Tl belong to the same chemical group, while Cr and Fe are characterized by an incomplete filling of the *3d* electronic sub-level ; this might give distinct bondings and explain differences in cell volumes.

Nevertheless, the curves of Fig. 6 can be used as a first approximation to verify the accuracy of the unit-cell volume for new synthetic or natural compounds, and to study the effect of M1 or M2 cations, or anion substitution on the unit-cell volume, especially for natural compounds, which frequently have complex chemistries.

Data for the metavariscite homeotypic series (only phosphates) are too scarce. Cell volumes indicate lower densities compared to the orthorhombic dimorphs. The cell volume of the scandium natural species, kolbeckite (Hey *et al.*,

1982 ; Webb *et al.*, 1991 ; Popov & Popova, 1992), is particularly high, over the arsenate curve, and about 10 % superior to the hypothetical value estimated in the orthorhombic phosphate series. This apparently indicates a special bonding of scandium, which would preclude the structural contraction needed for the stability of the orthorhombic dimorph.

Conclusions

Yanomamite is a new hydrated indium arsenate, isotypic with scorodite, and a member of the variscite series. In the Mangabeira tin deposit, it was apparently formed during the main Sn hydrothermal stage, together with In-rich scorodite. At the crystallization temperature of this stage, there seems to exist a miscibility gap between these two arsenates. In the variscite isotypic series, Tl arsenate is the member with a unit-cell closest to that of yanomamite but, from a geochemical point of view, the association of In and Tl concentrations in nature is very unlikely.

The association in the Mangabeira tin deposit of In minerals (yanomamite, roquesite and dzhalindite), In-rich sulfides (sphalerite, stannite), oxide (cassiterite) and arsenate (scorodite) makes this deposit a reference for the study of In geochemistry and crystal chemistry in hydrothermal and supergene conditions.

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