

THE INDIUM-RICH SULFIDES AND RARE ARSENATES OF THE Sn–In-MINERALIZED MANGABEIRA A-TYPE GRANITE, CENTRAL BRAZIL

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ABSTRACT

Indium minerals and In-rich phases in Brazil are restricted to Paleo- to Mesoproterozoic tin-bearing within-plate magmatic zones in central Brazil. The most important concentration of indium is in the Mangabeira granitic massif, which is also the type locality of yanomamite ($\text{InAsO}_4 \cdot 2\text{H}_2\text{O}$). The Sn–In-mineralized area of this massif is comprised of Li-rich siderophyllite granite, topaz–albite granite, quartz – Li-mica greisens and a vein of In-rich quartz–topaz rock, with up to 1 wt% In, mainly composed of quartz, topaz, zinnwaldite, arsenopyrite and cassiterite. Accessory minerals are sphalerite, ferberite, löllingite, chalcopyrite, bismuthinite, galena, stannite-group minerals, tennantite, argentite and roquesite. Secondary minerals comprise bornite, digenite, covellite, scorodite, phenakite, native copper, yanomamite, dzhalindite, metazeunerite and rare arsenates, like pharmacosiderite, segnitite, chenevixite, and goudeyite, and unknown Bi, Ba and Sn arsenates. Indium-rich stannite, as well as red In-rich and brown In-poor varieties of sphalerite, also are present. Zinc is replaced by indium, copper and iron in the sphalerite structure, probably according to the scheme $\text{Cu} + \text{In} + \text{Fe} = 3\text{Zn}$. Indium-rich sphalerite intergrown with roquesite, forming a texture interpreted as the product of roquesite exsolution, is documented here for the first time. The data obtained are consistent with the existence of the pseudoternary system stannite – sphalerite – roquesite and of a discontinuous solid-solution between yanomamite and scorodite.

Keywords: indium, sphalerite, roquesite, arsenate, Mangabeira granite, Brazil.

SOMMAIRE

Au Brésil, les minéraux d'indium ou riches en indium sont limités aux complexes stannifères paléozoïques ou mésoprotéozoïques de type intra-plaques dans le centre du pays. La concentration la plus importante en indium se trouve dans le granite de Mangabeira, la localité-type de la yanomamite ($\text{InAsO}_4 \cdot 2\text{H}_2\text{O}$). La portion de ce massif minéralisée en Sn–In est peuplée de granite lithinifère à sidérophylite, granite à topaze–albite, des greisens à quartz – mica lithinifère, et une veine de roche à quartz–topaze contenant jusqu'à 1% In (poids) dans un assemblage de quartz, topaze, zinnwaldite, arsenopyrite et cassitérite. Les minéraux accessoires sont sphalérite, ferberite, löllingite, chalcopyrite, bismuthinite, galène, membres du groupe de la stannite, tennantite, argentite et roquesite. Parmi les minéraux secondaires, notons la bornite, digénite, covellite, scorodite, phénakite, cuivre natif, yanomamite, dzhalindite, métazeunerite, et des arsenates plutôt rares, par exemple pharmacosidérite, segnitite, chenevixite, et goudeyite, ainsi que des arsenates méconnus de Bi, Ba et Sn. La stannite riche en In, ainsi que des variétés de sphalérite rouge, riche en In, et brune, à faible teneur en In, sont aussi présentes. Dans la sphalérite, le zinc est remplacé par l'indium, le cuivre et le fer selon le schéma $\text{Cu} + \text{In} + \text{Fe} = 3\text{Zn}$. La sphalérite peut se présenter en intercroissance avec la roquesite, dans une texture décrite ici pour la première fois et attribuée à l'exsolution. Nos données concordent avec l'hypothèse qu'il existe un système pseudoternaire stannite – sphalérite – roquesite et une solution solide discontinue entre yanomamite et scorodite.

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Mots-clés: indium, sphalérite, roquesite, arsenate, granite de Mangabeira, Brésil.

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INTRODUCTION

Primary and alluvial tin deposits in central Brazil, related to different types of granite of Paleo- to Mesoproterozoic age, comprise the Goiás tin province (Marini & Botelho 1986). The most important tin deposits and associated occurrences of indium in the province are hosted by hydrothermally altered zones of a Mesoproterozoic within-plate suite of granites, one of which is the Mangabeira granitic massif (Marini & Botelho 1986, Botelho & Moura 1998, Lenharo *et al.* 2002). The Goiás tin deposits, mined on a small scale from 1960 to 1985, have produced about 15 kt of tin concentrates. Major mines are currently closed, and the officially measured reserves for the whole province were estimated to be around 27 kt Sn (Bettencourt 1997). Recently discovered concentrations of indium in some deposits and the anomalous levels of indium in cassiterite from many deposits bring new possibilities for the exploration of the Goiás tin deposits (Botelho & Moura 1998).

Evolved topaz–albite granite of the Mangabeira Massif and its hydrothermal products generated unique Sn–In mineralization in central Brazil. Besides their petrological significance, the rare topaz granites are known in the literature for their economic importance, as they are commonly related to rare-metal deposits (Pollard 1995). The Mangabeira massif contains roquesite (CuInS_2) and dzhalindite $[\text{In}(\text{OH})_3]$ (Botelho & Roger 1990) and the only known occurrence of yanomamite ($\text{InAsO}_4 \cdot 2\text{H}_2\text{O}$) in the world (Botelho *et al.* 1994). It is also of special mineralogical importance as it contains other rare minerals, such as arsenates not previously reported in Brazil, as well as unknown arsenates.

We present here the results of a detailed mineralogical investigation of the Sn–In-mineralized area of the Mangabeira granitic massif. In this paper, we focus on the textural and chemical characteristics of rare and unknown arsenates that occur in the study area and discuss the relationship between In-rich sphalerite, roquesite and In-rich stannite-group minerals.

GEOLOGICAL SETTING AND PARAGENESIS

The Mangabeira massif is a small pluton with a surface area of approximately 3 km^2 in the eastern part of the Goiás tin Province (Fig. 1a). The evolved and mineralized granites of the Mangabeira massif occur along its western border, where two small plutons of topaz–albite granite have been recognized (Fig. 1b). In the southern topaz–albite granite pluton, tin mineralization is restricted to small zones of greisen and veins, and no indium minerals have been identified, although cassiterite with up to 0.3 wt% In occurs (Freitas 2000). Botelho (1992) and Freitas (2000) described genthelvite $[(\text{Zn}_{4.5}\text{Mn}_{1.9}\text{Fe}_{1.6})_{\Sigma 8}\text{Be}_6(\text{SiO}_4)_6\text{S}_2]$ in this area, which is

restricted to greisen composed of quartz, topaz, helvite and either zinnwaldite or Li-bearing phengite.

The Sn–In mineralization is associated with the northern outcrop of the topaz–albite granite pluton, in an area named the Main Greisenized Zone, which is composed of evolved biotite granite, topaz–albite granite, quartz–topaz rock, metasomatized granites and greisens (Fig. 1b). Tin mineralization is mainly hosted by Li-bearing phengite – quartz greisen and topaz – zinnwaldite greisen. Indium minerals are associated with In-rich cassiterite. The highest concentrations of indium in minerals occur in scorodite, sphalerite and stannite, followed by cassiterite and chalcopyrite (Botelho 1992, Moura 1993, Botelho & Moura 1998). Indium-bearing digenite (0.10 wt% In) and enargite (0.07 wt% In) were also identified (Botelho 1992).

The dominant rock in the Main Greisenized Zone is a pink equigranular granite, composed of quartz (30%), micropertthitic microcline (30–35%) and pure albite (30–35%). Primary Li-bearing siderophyllite is rarely preserved, and is commonly transformed to Li-bearing phengite. The accessory minerals are zircon, monazite, magnetite and, locally, ilmenite. Where greisenized, the granite becomes richer in phengite (10%) and contains metasomatic anhedral topaz, monazite, fluorite and disseminated cassiterite. The greisen formed by alteration of this granite, a phengite–quartz greisen, contains late Ba, Bi, Cu and Pb arsenates.

The topaz–albite granite has intruded the biotite granite, and is responsible for the development of a metasomatic aureole. The topaz–albite granite is white and contains quartz (30–35%), micropertthitic microcline (20%), pure albite (20–25%), magmatic topaz (5–20%) and zinnwaldite (10%). Zircon, monazite and cassiterite are rare. Magmatic topaz occurs as euhedral crystals (20 μm) included in albite (Moura & Botelho 2000). The autometasomatism of this granite developed zinnwaldite greisen, which contains quartz, zinnwaldite, topaz, cassiterite and monazite in different proportions (Moura & Botelho 2000).

The quartz–topaz rock is white, massive, composed mainly of quartz, topaz, zinnwaldite, arsenopyrite and cassiterite. Topaz occurs either as subhedral grains (0.5 mm) partially altered to zinnwaldite or as euhedral crystals (30 μm) included in quartz or in the larger grains of topaz. Accessory minerals are monazite, zircon, fluorite, sphalerite, ferberite, löllingite, chalcopyrite, pyrite, bismuthinite, galena, stannite-group minerals, tennantite, argentite, bismuth, and roquesite. Secondary minerals include native copper, scorodite, malachite, digenite, chalcocite, enargite, bornite, covellite, phenakite $[\text{Be}_2(\text{SiO}_4)]$ and Ba, Bi, In, K, Pb, U, Y–Cu and Sn arsenates. Potentially economic concentrations of indium (up to 1 wt%) and minerals (roquesite, dzhalindite and yanomamite) occur predominantly in the quartz–topaz rock, but also in greisen and albitized biotite granite.

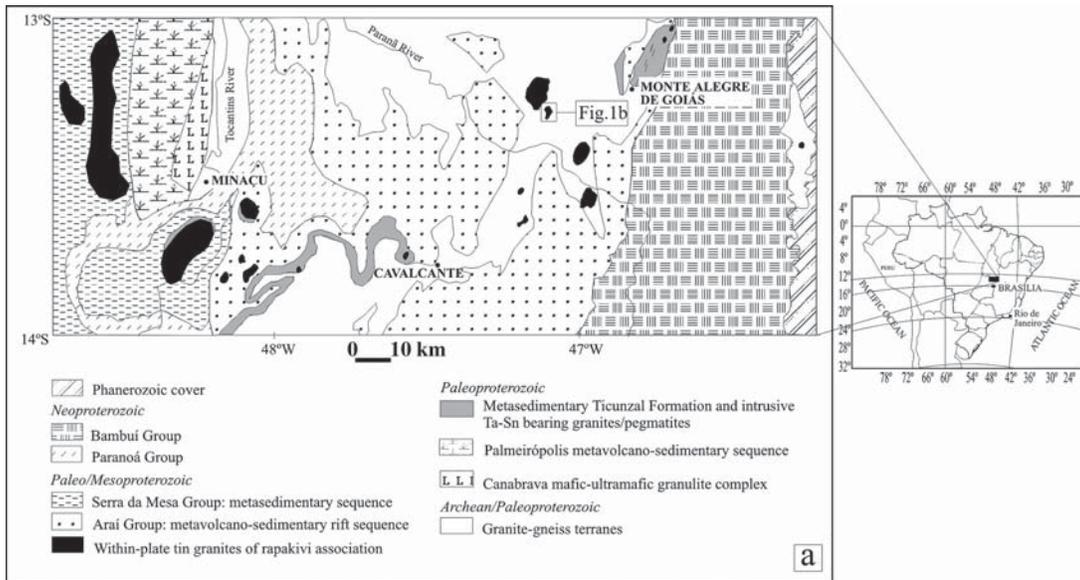


FIG. 1a. Geological sketch map of the Goiás Tin Province with inset showing the location in Brazil.

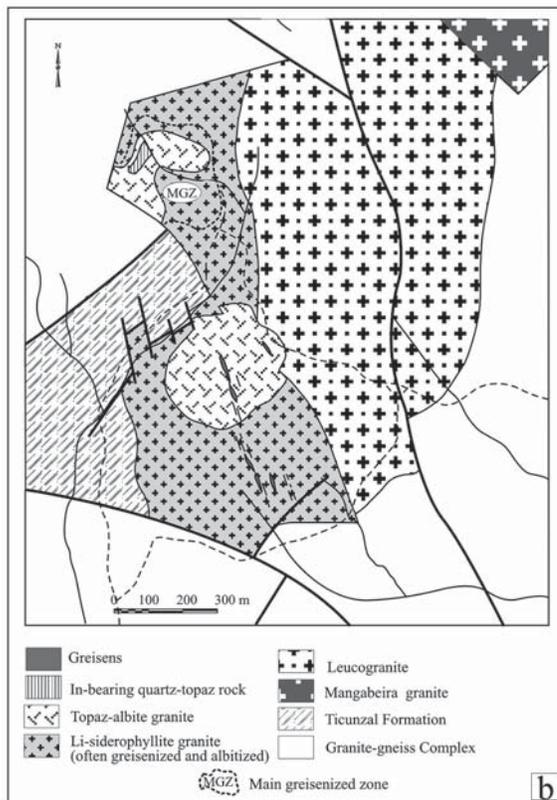


FIG. 1b. Detailed geological map of the tin-mineralized area of the Mangabeira massif.

MINERAL ANALYSES

Quantitative analyses of minerals were performed using a CAMECA SX-50 electron microprobe at the Universidade de Brasília. The analyses were conducted with an accelerating voltage of 15 kV, a beam current of 10 nA, and a counting time from 10 to 30 s. Beam diameters of 1 μm were used for sulfide analyses, and of 5 and 10 μm for arsenate analyses. The equipment was calibrated with international standards, which included AsGa (As), FeS₂ (Fe, S), PbS (Pb), InP (In), Cu^o (Cu), ZnSe (Zn), SnO₂ (Sn), Al₂O₃ (Al), orthoclase (K), BaSO₄ (Ba), YFeO (Y) and Bi^o (Bi).

Because of the interference between indium and tin in the analysis of tin-rich minerals by EPMA (Schwartz-Schampera & Herzig 2002), a systematic increase of 0.05 to 0.1 wt% In₂O₃ was registered during analysis of the tin standard (In-free cassiterite). As there is interference of the InL α in the SnL α line, a window for the detection of the In-peak alone was selected during the calibration procedure and adopted for the determination of indium contents in cassiterite and Sn-rich minerals. Nevertheless, In L α X-rays also interfere with SnL η emission, creating a composite peak. As the separation of the SnL η and InL α peaks is very difficult, an interference correction of 0.1 wt% was applied in In₂O₃ contents of cassiterite and tin-rich minerals. The same procedure was used by Legendre & Rossi (1994) to analyze In-containing cassiterite. The authors tested the method by comparing results of the EPMA analysis of cassiterite containing variable concentrations of indium with LA-ICP-MS data for the same grains. The results showed an excellent correspondence of indium contents obtained with the two methods.

As most of the secondary arsenates from the Mangabeira massif are hydrated and poorly crystalline, some compositions show a variation as a result in the electron-microprobe data, even using a larger diameter of the beam. Nevertheless, the presence of non-quantified elements was eliminated after detailed investigation of the energy-dispersion spectra of the minerals. The amount of H₂O was estimated by subtraction of the total from 100 wt%. For the arsenate analyses, all Fe was reported as trivalent iron, by analogy with similar and identified species, such as scorodite and segnitite, and also because a high-oxidation-state environment is postulated for the formation of these secondary minerals in the Mangabeira massif.

SULFIDES COMPOSITIONS

The most widespread primary sulfide in the mineralized greisens and quartz-topaz rock of the Main Greisenized Zone is either In-poor arsenopyrite or löllingite. High concentrations of indium in sulfides from the mineralized area are obtained only from sphalerite (up to 6.7 wt% In) and stannite-group minerals (1.3 to 2.2 wt% In), whereas chalcopyrite contains intermediate

contents of In (up to 0.2 wt% In). The mean contents of In of digenite and enargite are 0.10 and 0.07 wt%, respectively (Botelho 1992).

Sphalerite occurs as generally anhedral inclusions in arsenopyrite, but also in quartz, topaz and cassiterite from the greisens and the quartz-topaz rock (Fig. 2). Two types of sphalerite are petrographically distinguished in the Mangabeira massif: a red sphalerite (~20 μm), which occurs only as inclusions in arsenopyrite, quartz, cassiterite and topaz (Fig. 2a), and a yellow one (20 μm – 1.5 mm), which occurs either as inclusions in arsenopyrite or as disseminated grains in the mineralized rocks and exogreisens (Fig. 2b).

Indium is present in both types of sphalerite, but whereas the red crystals of sphalerite contain between 3 and 7 wt% In, the yellow type has 0.7 to 2 wt% In (Table 1). Indium-rich sphalerite contains 0.3 to 0.7 wt% Cd, whereas In-poor sphalerite has 0 to 0.4 wt% Cd (Table 1). Despite the inclusions of In-rich sphalerite, arsenopyrite contains negligible indium, which means that arsenopyrite is not an In-carrier in the Mangabeira massif.

In both types of sphalerite, zinc has very good negative correlations with Cu + Fe ($R^2 = 0.79$) and with In + Fe ($R^2 = 0.81$) (Figs. 3a, b). Poor negative correlations are observed between Cu + In and Zn ($y = -0.53x + 0.51$; $R^2 = 0.44$), In and Zn ($y = -0.28x + 0.27$; $R^2 = 0.54$) and between Fe and Zn ($y = -1.12x + 0.95$; $R^2 = 0.54$). No correlation exists between Fe and In ($R^2 = 0.08$) and between Fe and Cu ($R^2 = -0.10$). Indium and copper are introduced together in the structure of sphalerite, with an In : Cu relationship near 1:1 ($R^2 = 0.90$) (Fig. 3c). Based on the chemical data, the equation $\text{Cu} + \text{In} + \text{Fe} = 3\text{Zn}$ ($R^2 = 0.82$) (Fig. 3d) is observed

TABLE 1. REPRESENTATIVE COMPOSITIONS* OF THE RED AND YELLOW TYPES OF SPHALERITE FROM THE QUARTZ-TOPAZ ROCK, MANGABEIRA DEPOSIT

Sample	Red sphalerite			Yellow sphalerite		
	MM11C	MM11C	MG11C1	MM11C1	MG11C1	MG7B
Fe wt %	3.26	5.15	4.77	2.94	2.88	8.36
Cu	3.16	2.30	3.79	0.60	0.60	0.40
Zn	55.89	53.98	51.97	61.35	60.89	57.47
S	31.45	31.87	31.35	33.24	33.17	33.28
Cd	0.66	0.51	0.51	0.37	0.39	0.14
In	5.56	5.61	6.73	1.11	1.12	0.72
Total	99.98	99.42	99.12	99.61	99.05	100.37
Fe <i>apfu</i>	0.06	0.09	0.09	0.05	0.05	0.14
Cu	0.05	0.04	0.06	0.01	0.01	0.01
Zn	0.86	0.83	0.80	0.92	0.91	0.84
S	0.98	0.99	0.99	1.01	1.01	1.00
Cd	0.01	0.00	0.00	0.00	0.00	0.00
In	0.05	0.05	0.06	0.01	0.01	0.01

* Electron-microprobe data. The structural formulae are calculated on the basis of two atoms per formula unit.

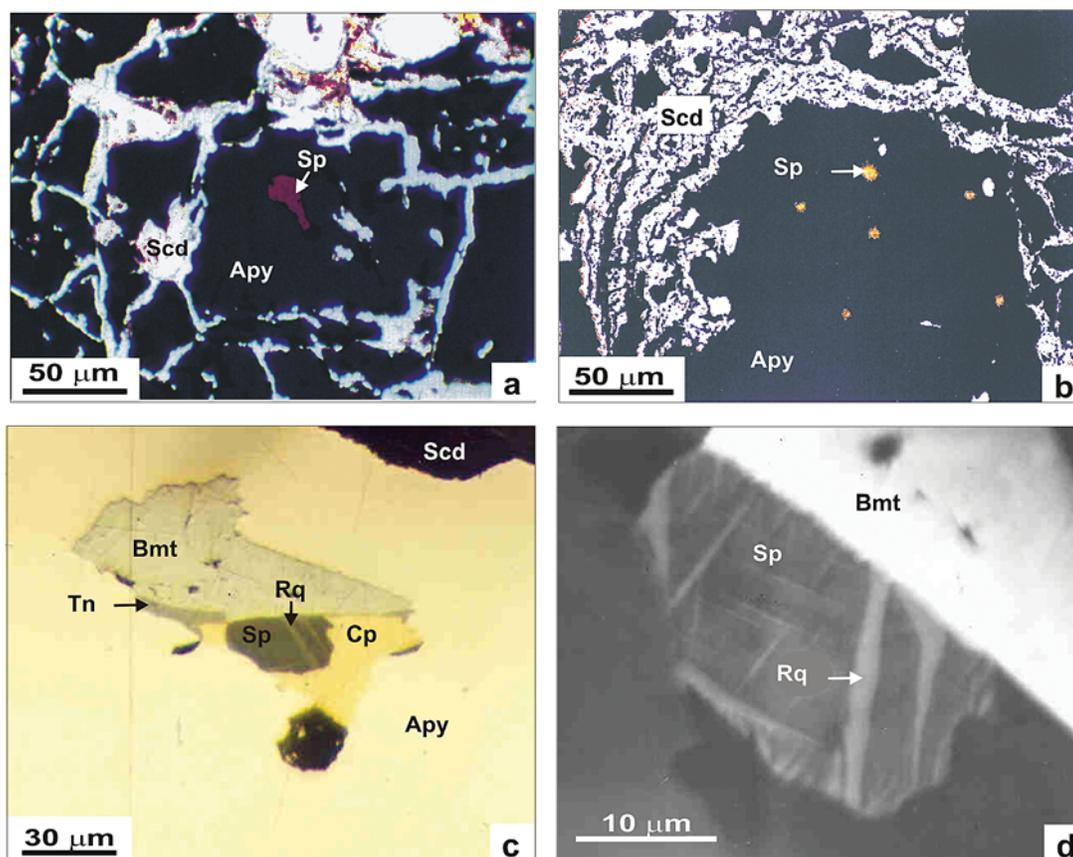


FIG. 2. Photomicrographs of sphalerite included in arsenopyrite. (a) Inclusions of In-rich red sphalerite (transmitted, plane-polarized light). (b) Inclusions of In-poor yellow sphalerite (transmitted, plane-polarized light). (c) Roquesite lamellae in sphalerite associated with chalcopyrite, bismuthinite and tennantite (reflected light). (d) Detail of the sphalerite-roquesite association from (c); back-scattered-electron image. Symbols: Apy: arsenopyrite, Bmt: bismuthinite, Cp: chalcopyrite, Rq: roquesite, Scd: scorodite, Sp: sphalerite, Tn: tennantite.

in the structure of In-rich sphalerite. The simultaneous substitution of zinc for copper and indium according to the relation $\text{Cu} + \text{In} = 2\text{Zn}$ ($y = -1.80x + 1.82$; $R^2 = 0.44$), classically proposed in the literature (Johan 1988), probably does not play an important role in the incorporation of indium in the In-rich sphalerite studied. Also, the coupled substitution of $2(\text{Zn},\text{Fe})$ for CuIn (Ohta 1989) was not very important in the Mangabeira sphalerite ($y = -1.4199x + 1.9677$; $R^2 = 0.62$).

Sphalerite crystals with up to 6.7 wt% In are homogeneous in back-scattered-electron images, without saturation in roquesite or other indium-bearing phases. Higher contents of indium in sphalerite were reported in the Suttzu quartz-porphyry-related polymetallic vein-type deposit (8.4 wt%; Ono *et al.* 2004) and at the granite-related Mt. Pleasant deposit, in New Brunswick, Canada (6.9 wt%; Sinclair *et al.* 2006).

Roquesite (CuInS_2) occurs as inclusions in arsenopyrite and as fine lamellae along cleavage planes of sphalerite and also as large irregular bands in a sphalerite crystal (Figs. 2c, d) included in arsenopyrite from the quartz-topaz rock. The association sphalerite-roquesite occurs along with tennantite, chalcopyrite, bismuthinite and galena. This textural relationship suggests that roquesite probably exsolved from sphalerite containing more than 6.7 wt% In.

Minerals of the stannite group, stannite ($\text{Cu}_2\text{FeSnS}_4$) and ferrokesterite [$\text{Cu}_2(\text{Fe},\text{Zn})\text{SnS}_4$], are rare accessory minerals in the Main Greisenized Zone. They occur mainly as inclusions in arsenopyrite and are important carriers of In in the Mangabeira massif, with mean In values of 1.77 wt% (Table 2). Other deposits reported in the literature with In-rich stannite are the Yakutia Sn sulfide deposit, where the mineral contains 0.15 wt% In

TABLE 2. REPRESENTATIVE COMPOSITIONS* OF STANNITE-GROUP MINERALS AND ROQUESITE FROM THE MANGABEIRA DEPOSIT

Mineral	Ferro-k�sterite	Ferro-k�sterite	Stannite	Stannite	Roquesite	Roquesite
Sample	MM11C1	MG11C	MM7A	MM7A	MG7A1	MM7A
S wt%	28.8	29.55	29.81	30.58	25.95	25.15
Fe	7.95	7.82	11.40	11.66	0.97	0
Cu	27.63	27.22	27.33	26.84	23.09	26.04
Zn	6.86	8.65	5.08	5.03	6.11	0
In	1.63	1.33	1.92	1.65	41.3	49.06
Sn	25.36	25.16	25.21	24.85	0	0.05
Cd	0.27	0.00	0.00	0.00	0	0
Total	98.50	99.73	100.75	100.61	97.42	100.3
S <i>apfu</i>	3.97	3.99	3.98	4.05	3.94	3.87
Fe	0.63	0.61	0.87	0.89	0.08	0
Cu	1.92	1.86	1.84	1.79	1.77	2.02
Zn	0.46	0.57	0.33	0.33	0.45	0
In	0.06	0.05	0.07	0.06	1.75	2.11
Sn	0.94	0.92	0.91	0.89	0	0
Cd	0.01	0.00	0.00	0.00	0	0

* Electron-microprobe data. The structural formulae are calculated on the basis of eight atoms per formula unit (*apfu*).

(Ivanov & Lizunov 1959), Mount Pleasant (Boorman & Abbott 1967, Sinclair *et al.* 2006), where a hexagonal In-poor stannite (0.04 wt% In) and a tetragonal In-rich stannite (2.1 wt% In) were described, the polymetallic Goka deposit, Japan (9.63 wt% In; Murao & Furuno 1990), and the Toyoha lead – zinc – silver vein-type deposit, from which Ohta (1989) described stannite with 9.85 wt% In.

Chalcopyrite is a common accessory mineral in the mineralized rocks of the Mangabeira massif. Its indium content is generally low, but locally the mineral contains 0.2 wt% In. In other indium-rich regions, chalcopyrite also has moderate indium contents. At Mount Pleasant, Boorman & Abbott (1967) described chalcopyrite with 0.16 to 0.98 wt% In, whereas Sinclair *et al.* (2006) obtained indium contents between 0.01 and 0.40 wt% In. At the Goka mine, the mineral contains 0.34 to 0.48 wt% In (Murao & Furuno 1990), and in the Toyoha deposit, up to 1.74 wt% In (Ohta 1989).

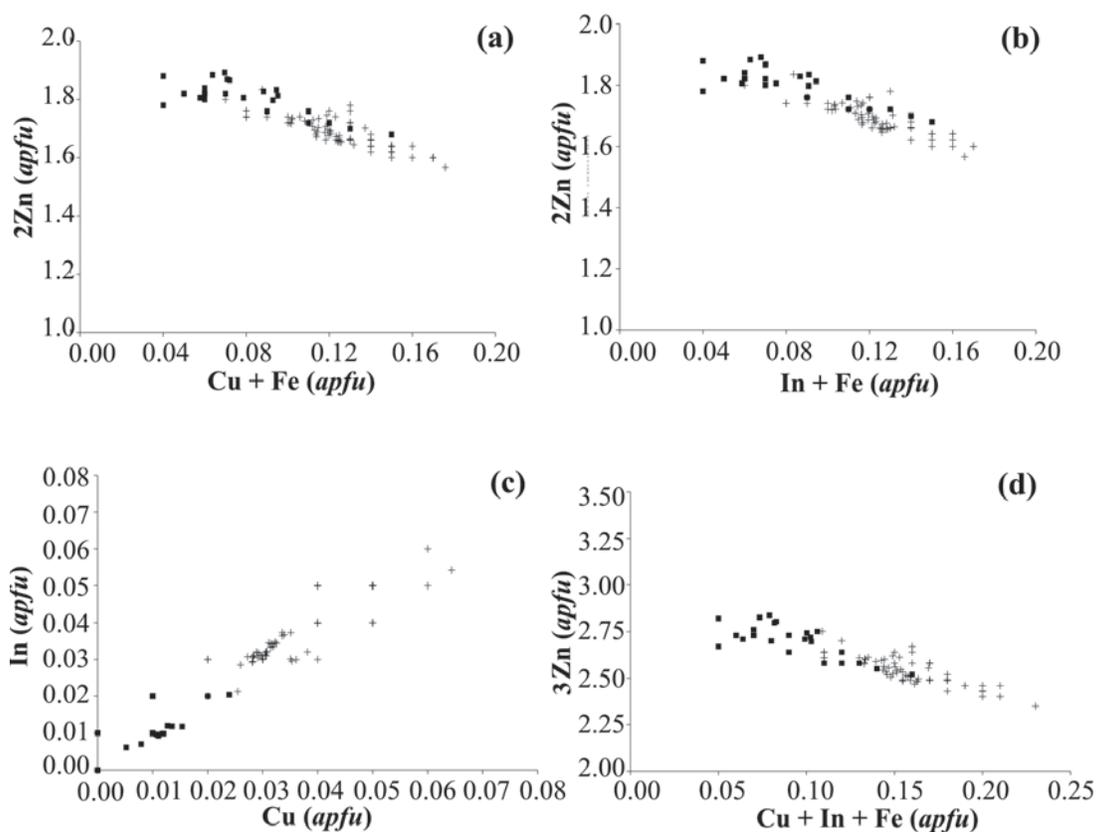


FIG. 3. Correlation between elements for yellow indium-poor sphalerite (filled squares) and red indium-rich sphalerite (crosses) from the Mangabeira deposit.

ARSENATES

Different arsenates have been formed by secondary processes in the Main Greisenized Zone of the Mangabeira massif, with textural characteristics of supergene minerals. They generally occur either as masses of poorly crystalline minerals, commonly with a colloform texture, or filling fractures of pre-existing minerals, such as mica, topaz and arsenopyrite. Less commonly, they occur as discrete crystals included in other minerals.

Scorodite is the most common arsenate found in the Mangabeira massif. It is widespread as a product of arsenopyrite alteration in greisens and in the quartz-topaz rock, but it also fills fractures in quartz, zinnwaldite and topaz, attesting to its late character. Data obtained from more than one hundred analyses of scorodite show that homogeneous scorodite contains up to 7 wt% In_2O_3 .

Yanomamite ($\text{InAsO}_4 \cdot 2\text{H}_2\text{O}$) occurs in the same association as scorodite (Botelho *et al.* 1994), as euhedral grains commonly intergrown with scorodite and, rarely, with dzhalindite. Although yanomamite contains minor amounts of iron in its structure, the maximum substitution is $\text{In}_{0.85}\text{Fe}_{0.15}$.

Other arsenates studied in detail from the Mangabeira massif include Sn, Pb, Bi, Ba, K and Y-Cu arsenates, which will be described below.

Tin arsenate

An unnamed tin arsenate mineral occurs as either discrete grains or filling fractures of pre-existing minerals in strongly altered quartz-topaz rock. Locally, it is associated with probable native tin. The arsenate grains are yellow to brownish yellow, anhedral, rarely euhedral, 0.1 to 1 mm across, zoned, isotropic and with a high index of refraction (Fig. 4a).

The mean chemical composition of the yellow zones is: 52 wt% SnO_2 , 21% Fe_2O_3 , 17% As_2O_5 , an estimated 6 wt% H_2O , and small amounts of Al_2O_3 , In_2O_3 and CuO (Table 3). In its brownish zones, the mineral seems poorly crystalline, and its tin content decreases, whereas iron and sulfur increase. The simplified empirical formula $\text{Sn}_3\text{Fe}_2(\text{AsO}_4) \cdot 3\text{H}_2\text{O}$, calculated on the basis of 13 cations, is proposed for this unknown mineral (Table 3).

Goudeyite

This Y-bearing Cu-Al arsenate is green and occurs as clusters of transparent to translucent microcrystals filling vugs in altered quartz-topaz rock or associated with cassiterite crystals (Fig. 4b). Under the polarizing microscope, the mineral is pale green, anisotropic, with medium to high relief. Its representative mean chemical

TABLE 3. REPRESENTATIVE COMPOSITIONS* OF THE TIN ARSENATE FROM THE MANGABEIRA DEPOSIT

	1	2	3	4	5	6	7	8	9	10	11	Mean	SD
As_2O_5	15.40	17.89	16.73	16.25	18.33	17.02	15.22	17.95	17.26	17.56	16.04	16.88	1.05
SO_3	0.46	0.69	0.58	0.43	0.26	0.54	0.60	0.84	0.73	0.44	0.27	0.53	0.18
SnO_2	54.50	51.33	52.76	54.81	52.41	51.96	53.03	49.81	49.09	53.72	53.15	52.42	1.79
Fe_2O_3	19.40	22.80	22.48	21.00	21.61	21.89	22.09	18.55	21.82	17.87	18.61	20.74	1.78
Al_2O_3	1.52	1.15	1.01	1.36	0.48	1.27	1.00	1.39	1.13	1.31	1.26	1.17	0.28
In_2O_3	1.76	1.39	1.38	1.59	1.28	1.32	1.33	1.42	1.31	1.80	1.58	1.47	0.18
CuO	0.58	0.47	0.49	0.38	0.24	0.49	0.60	0.73	0.36	0.43	0.64	0.49	0.14
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.15	0.32	0.25	0.08	0.12
H_2O	6.39	4.28	4.55	4.19	5.39	5.51	6.13	9.14	8.16	6.54	8.20	6.23	1.68
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0		
As	1.16	1.55	1.43	1.43	1.48	1.35	1.16	1.13	1.15	1.31	1.08	1.29	0.16
S	0.05	0.09	0.07	0.05	0.03	0.06	0.07	0.08	0.07	0.05	0.03	0.06	0.02
Sn	3.13	3.39	3.43	3.69	3.23	3.14	3.08	2.40	2.49	3.06	2.72	3.07	0.39
Fe	2.10	2.85	2.76	2.67	2.51	2.50	2.42	1.68	2.09	1.92	1.80	2.30	0.40
Al	0.26	0.22	0.19	0.27	0.09	0.23	0.17	0.20	0.17	0.22	0.19	0.20	0.05
In	0.11	0.10	0.10	0.12	0.09	0.09	0.08	0.07	0.07	0.11	0.09	0.09	0.02
Cu	0.06	0.06	0.06	0.05	0.03	0.06	0.07	0.07	0.04	0.05	0.06	0.06	0.01
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.03	0.02	0.01	0.01
H	6.13	4.74	4.96	4.72	5.55	5.57	5.96	7.36	6.92	6.24	7.02	5.92	0.92

* Electron-microprobe data, given in wt%; sample MG50. The structural formulae, in atoms per formula unit, are calculated on the basis of 13 cations. SD: standard deviation. The presence of other elements has been investigated and not detected by EDS electron-microprobe analyses. H_2O added to bring total to 100 wt%.

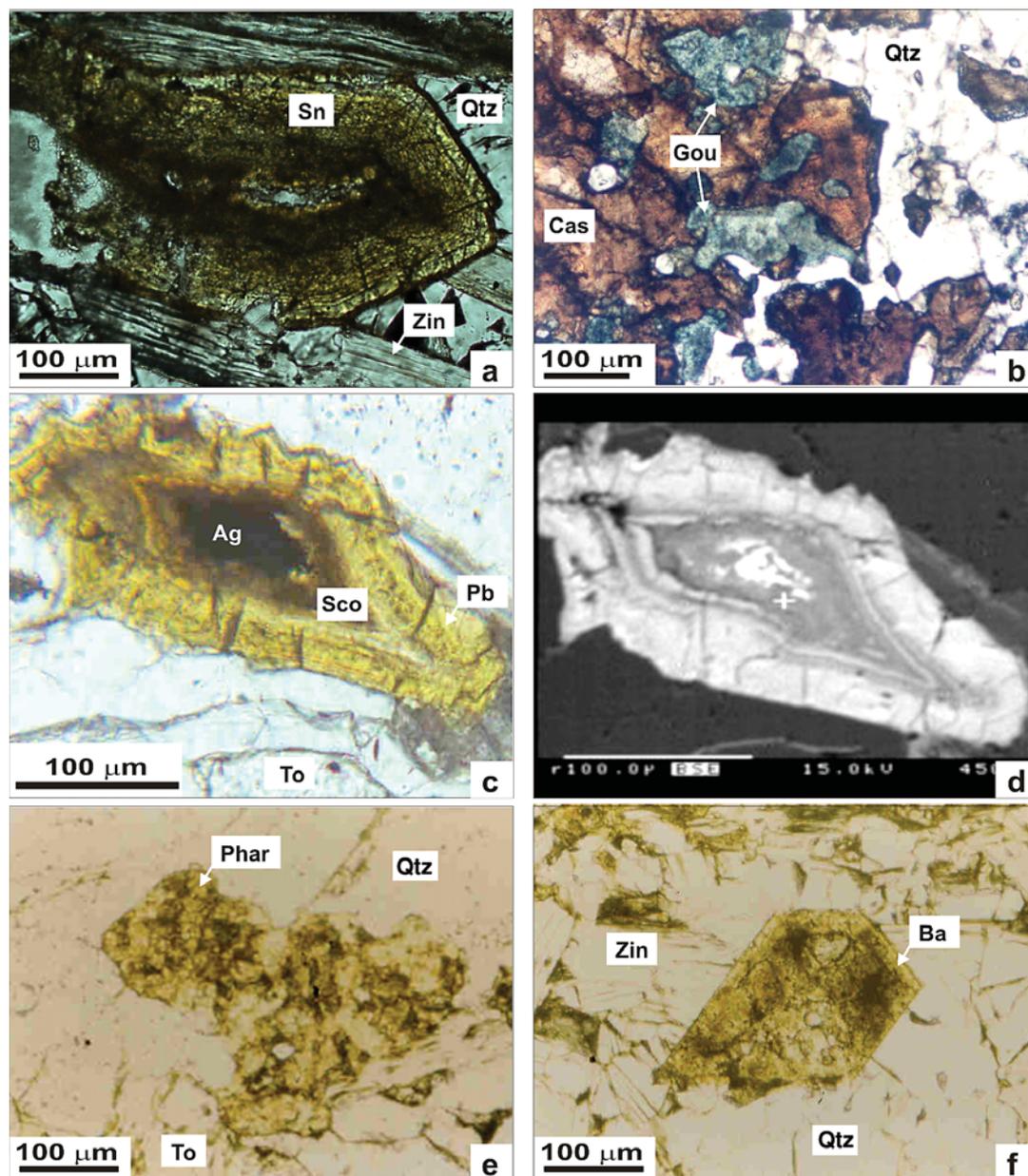


FIG. 4. Photomicrographs of hydrated arsenates from the Mangabeira deposit. (a) Zoned tin arsenate (transmitted, plane-polarized light) in quartz-topaz rock. (b) Goudeyite in association with cassiterite (transmitted, plane-polarized light). (c) Grain in quartz-topaz rock where argentite (nucleus) grades to scorodite and is finally overgrown by Pb arsenate (transmitted, plane-polarized light). (d) Detail of the grain (c); back-scattered-electron image. (e) Anhedrals pharmacosiderite in quartz-topaz rock (transmitted, plane-polarized light). (f) Euhedral hydrated barium arsenate in quartz-topaz rock (transmitted, plain-polarized light). Symbols: Ag: argentite, Ba: barium arsenate, Cst: cassiterite, Gou: goudeyite, Scd: scorodite, Pha: pharmacosiderite, Pb: lead arsenate, Qtz: quartz, Sn: tin arsenate, Toz: topaz, Zin: Zinnwaldite.

composition is 42 wt% CuO, 38% As₂O₅, 4% Al₂O₃, 4% Y₂O₃, 9% calculated H₂O, and minor amounts of WO₃, Fe₂O₃ and PbO. The composition is similar to goudeyite [Cu₆Al(AsO₄)₃(OH)₆•3H₂O] described by Wise (1978), which has 47 wt% CuO, 28% As₂O₅, 4% Al₂O₃, 3.44% Y₂O₃, 11% H₂O and 1.37% CaO. Goudeyite is considered the Al analog of agardite-(Y), (Y,Ca)Cu₆[(AsO₄)₃(OH)₆•3H₂O] (Dietrich *et al.* 1969, Wise 1978).

Lead arsenate

The lead arsenate mineral is pale yellow, has a high index of refraction, and occurs as either fillings of microfractures in quartz and zinnwaldite grains or as discrete grains in altered quartz–topaz rock. It has an anomalous blue interference-color where filling fractures. The mineral also forms zoned grains where it is associated with the tin arsenate, such that its nucleus is rich in lead and its border is rich in tin, or with argentite and scorodite. In the latter case, the nucleus of the grain is argentite and grades to an intermediate zone of scorodite and an outer zone of lead arsenate (Figs. 4c, d).

Quantitative electron-microprobe analyses yielded a mean composition of 28 wt% As₂O₅, 24% Fe₂O₃, 31% PbO, 5% Al₂O₃, 12% calculated H₂O, and no SO₃ (Table 4). Beudantite [PbFe₃(AsO₄)(SO₄)(OH)₆] and segnitite [PbFe₃H(AsO₄)₂(OH)₆] have optical characteristics similar to those found in this arsenate. However, taking into account the mineral's chemical composition and the classification scheme for the alunite–jarosite family proposed by Birch *et al.* (1992), this arsenate is tentatively classified as segnitite, for which Birch *et al.* (1992) reported 1 wt% Al₂O₃ and obtained powder-diffraction data that resemble those for sulfate-free beudantite.

Bismuth arsenate

The bismuth arsenate is rare in the Mangabeira quartz–topaz rock, in which it occurs either as discrete grains 200 μm across included in quartz or filling fractures in altered arsenopyrite. The mineral is dark brown under uncrossed nicols and has a high relief.

Results of electron-microprobe analyses, which vary widely, possibly owing to the loose character of the grains studied, indicate a compositional range of 59 to 74 wt% Bi₂O₃, 18 to 25% As₂O₅, 0 to 6% Fe₂O₃ and 2 to 14% H₂O (estimated). The composition is considered to be similar to preisingerite [Bi₃O(AsO₄)₂(OH)] (Anthony *et al.* 2000), although at Mangabeira, the bismuth arsenate is optically different.

Pharmacosiderite

The mineral identified as pharmacosiderite [KFe³⁺₄(AsO₄)₃(OH)₄•7H₂O] is yellowish green, with a medium to high relief; it occurs as individual grains or occupies mica-bearing fractures in hydrothermally altered rocks

of the Main Greisenized Zone (Fig. 4e). It is usually isotropic, but some grains are anisotropic, which probably corresponds to the anomalous anisotropy described in pharmacosiderite by Palache *et al.* (1963).

Electron-microprobe analyses of the mineral indicate a composition with 36–41 wt% As₂O₅, 33% Fe₂O₃, 3–5% Al₂O₃, 3–6% K₂O, and less than 1% ZnO, PbO and CuO, similar to pharmacosiderite (39.47 wt% As₂O₅, 36.57% Fe₂O₃, 5.39% K₂O and 18.56% H₂O) (Anthony *et al.* 2000). The chemical composition of the grains analyzed can be expressed using the ideal formula of pharmacosiderite, but considering a substitution of aluminum for iron.

Barium arsenate

An unnamed barium arsenate was identified in the quartz–topaz rock. The mineral occurs as grains up to 500 μm in size. They are pale to brownish yellow, with medium to high relief, generally massive and rarely with rhombic habit (Fig. 4f). The euhedral grains are isotropic, but some have an anomalous grayish blue interference-color. The massive grains are in some cases associated with masses of scorodite, and also appear to be products of the alteration of arsenopyrite.

Despite some scatter (Table 5), attributed to the massive nature of the grains studied and their hydrated nature, the data point to an unknown barium mineral with a composition that can be considered in some way similar to that of pharmacosiderite and barium-pharmacosiderite [BaFe₄(AsO₄)₃(OH)₅•5(H₂O)]. Taking into

TABLE 4. REPRESENTATIVE COMPOSITIONS* OF THE LEAD ARSENATE FROM THE MANGABEIRA DEPOSIT

	1	2	3	4	5	6	7	8
SO ₃ wt%	0.18	0.00	0.24	0.00	0.10	0.10	0.04	0.00
As ₂ O ₅	27.20	27.49	28.45	29.28	28.25	26.97	26.95	29.28
SnO ₂	0.03	0.00	0.00	0.02	0.01	0.00	0.48	0.31
Al ₂ O ₃	3.62	4.2	4.62	5.46	4.66	5.17	3.25	7.08
Fe ₂ O ₃	25.87	25.44	24.38	23.17	23.36	21.99	24.19	21.46
In ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.08	0.37	1.03
CuO	0.10	0.08	0.06	0.08	0.07	0.08	0.09	0.02
PbO	30.05	30.11	31.46	28.9	31.61	31.77	30.13	30.78
K ₂ O	0.05	0.00	0.02	0.00	0.02	0.03	0.08	0.04
H ₂ O	12.9	12.68	10.77	13.09	11.92	13.81	14.42	10.00
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
S <i>apfu</i>	0.02	0.00	0.02	0.00	0.01	0.01	0.00	0.00
As	1.62	1.64	1.77	1.71	1.72	1.59	1.57	1.82
Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01
Al	0.49	0.57	0.65	0.72	0.64	0.69	0.43	0.99
Fe	2.22	2.19	2.18	1.94	2.05	1.87	2.03	1.92
In	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.05
Cu	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00
Pb	0.92	0.93	1.01	0.87	0.99	0.96	0.91	0.99
K	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01
H	9.81	9.66	8.53	9.73	9.27	10.39	10.75	7.94

* Electron-microprobe data (sample MG50). The structural formulae are calculated on the basis of 14 atoms of oxygen. The presence of other elements has been investigated and not detected by EDS electron-microprobe analyses. H₂O added to bring total to 100 wt%.

account the scatter in the analytical data obtained and in order to approach neutrality in the mineral formula, the empirical formula $(\text{Ba}_{0.7}\text{K}_{0.3})\text{Fe}^{3+}_6(\text{AsO}_4)_5(\text{OH})_5 \cdot \text{H}_2\text{O}$ is suggested for the mineral (Table 5).

Chenevixite

Chenevixite $[\text{Cu}_2\text{Fe}_2(\text{AsO}_4)_2(\text{OH})_4 \cdot \text{H}_2\text{O}]$ (Palache *et al.* 1963, Williams 1977) was identified in a greisen sample from the evolved biotite granite in contact with the quartz–topaz rock. The mineral occurs as a product of arsenopyrite alteration. It is brown and massive.

In the Mangabeira massif, the mineral contains 39 wt% As_2O_5 , 25% Fe_2O_3 , 25% CuO , 2% Al_2O_3 , 1% PbO , 0.4% In_2O_3 and 9% H_2O (calculated). This composition is comparable to that of theoretical chenevixite, which has 38.1 wt% As_2O_5 , 26.49% Fe_2O_3 , 26.40% CuO and 8.97% H_2O (Williams 1977).

DISCUSSION

Chemical relationships among indium, copper and zinc, as observed in the Mangabeira sphalerite, have also been reported in other regions (Oen *et al.* 1980, Johan 1988, Kieft & Damman 1990). Shimizu *et al.* (1986) proposed a continuous solid-solution among sakuraiite, stannite and k esterite $[\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4]$ to explain the

association of those minerals at the Ikuno mine, Japan. In their opinion, the observed compositional variation is due to the coupled substitution $(\text{Zn,Fe})\text{In} - \text{CuSn}$. On the basis of positive correlations among In, Cu and Sn and on the absence of correlation between In and Fe, Oen *et al.* (1980) suggested the existence of discontinuous solid-solutions in the system sphalerite – stannite – roquesite, which was considered a pseudoternary system. Those authors considered stannite as the phase formed at the highest temperature, and In-rich sphalerite would have crystallized with decreasing temperature of the fluid. At the lowest temperature stage, almost pure sphalerite formed, with low Fe, Cu, Sn and In.

According to Johan (1988), the only possible mechanism capable of explaining the entry of indium in the structure of Fe-free sphalerite is the substitution $\text{Cu}^+ + \text{In}^{3+} = 2\text{Zn}^{2+}$, but the author was not able to explain the preferential concentration of In and Cu in 111 planes of sphalerite. In the samples from the Mangabeira massif, In and Cu concentrations along the structural planes of sphalerite were observed to be due to the presence of roquesite in these directions, which favors the hypothesis of Oen *et al.* (1980). Burke & Kieft (1980) also observed the association of sphalerite and roquesite in L ngban, Sweden, where there is intercalation of dark brown In-rich sphalerite (9–10 wt% In) with colorless to pale brown areas, with 0–5.5 wt% In. The presence of these zones, together with the ratio $\text{Cu}/\text{In} = 1$ (atom basis) in sphalerite, led the authors to propose a partial solid-solution given by the formula $\text{Zn}_{2-2x}\text{Cu}_x\text{In}_x\text{S}_2$. Kieft & Damman (1990) suggested that In-rich sphalerite from G sborn, Sweden, is a mixture of sphalerite, chalcopyrite and roquesite.

The observation of roquesite lamellae along cleavage planes in sphalerite without substitution textures in the Brazilian samples studied and the chemical composition of the two different types of sphalerite from the quartz–topaz rock of the Mangabeira massif suggest that the observed sphalerite–roquesite association attests to the existence of a discontinuous solid-solution between roquesite and sphalerite. In this case, the lamellae in the cleavage planes of sphalerite would be the product of exsolution from sphalerite supersaturated in indium.

Kieft & Damman (1990) estimated at 2 wt% the maximum solubility of indium in Fe-rich sphalerite (12 wt% Fe). Nevertheless, in the Mangabeira samples, Fe-poor sphalerite (~ 5 wt% Fe) with up to 6.7 wt% In is still homogeneous, which suggests that the solubility of indium in Fe-poor sphalerite might be three times higher than in Fe-rich sphalerite. The role of iron in the solubility of indium in the sphalerite structure should be better investigated.

A coupled substitution $\text{Cu}_2\text{Sn} - 2(\text{Zn,Fe})$ between sphalerite and stannite-group minerals ($y = -1.1778x + 7.8115$; $R^2 = 0.9864$) is supported by the EPMA data obtained for the Mangabeira samples (Table 2, Fig. 5). Similar results were reported by Ohta (1989) and Sinclair *et al.* (2006). On the basis of the observed paragenesis

TABLE 5. REPRESENTATIVE COMPOSITIONS* AND CHEMICAL FORMULAE OF THE BARIUM ARSENATE FROM THE MANGABEIRA DEPOSIT COMPARED TO ITS IDEAL FORMULA

Sample	MG7 B1	MG7 B1	MG7 B1	MG8 C2	MG7 A3	MG7 A3	Mean	δ	Emp. comp.
SO_2 , wt %	0.00	0.00	0.00	0.34	0.02	0.03	0.07	0.14	0.00
As_2O_5	47.23	44.35	46.05	46.74	43.72	45.23	45.55	1.37	46.50
SnO_2	0.00	0.00	0.00	0.00	0.14	0.00	0.02	0.06	0.00
Fe_2O_3	38.61	38.15	38.04	38.38	38.76	37.64	38.26	0.41	38.50
Al_2O_3	0.08	0.07	0.12	0.22	0.78	0.57	0.31	0.30	0.00
In_2O_3	0.00	0.00	0.05	0.04	0.09	0.00	0.03	0.04	0.00
BaO	9.17	9.36	9.09	7.62	8.23	8.62	8.68	0.66	8.95
PbO	0.00	0.12	0.23	0.40	0.37	0.17	0.22	0.15	0.00
CuO	0.00	0.00	0.10	0.60	0.20	0.10	0.17	0.23	0.00
ZnO	0.07	0.49	0.35	0.00	0.25	0.00	0.19	0.20	0.00
K_2O	0.78	1.52	0.52	0.53	0.44	0.95	0.79	0.41	1.00
H_2O	4.06	5.94	5.45	5.13	7.00	6.69	5.71	1.08	5.05
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0		100.0
<i>S apfu</i>	0.00	0.00	0.00	0.05	0.00	0.00	0.01	0.02	0.00
As	5.21	4.78	4.97	5.02	4.58	4.76	4.89	0.22	5.05
Sn	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Fe	6.13	5.92	5.91	5.93	5.84	5.70	5.91	0.14	6.02
Al	0.02	0.02	0.03	0.05	0.18	0.14	0.07	0.07	0.00
In	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Ba	0.76	0.76	0.74	0.61	0.65	0.68	0.70	0.06	0.73
Pb	0.00	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.00
Cu	0.00	0.00	0.02	0.09	0.03	0.02	0.03	0.03	0.00
Zn	0.01	0.07	0.05	0.00	0.04	0.00	0.03	0.03	0.00
K	0.21	0.40	0.14	0.14	0.11	0.24	0.21	0.11	0.26
H	5.72	8.18	7.51	7.03	9.35	8.99	7.80	1.34	6.99

* Electron-microprobe data. The structural formulae are calculated on the basis of 26 atoms of oxygen. δ : standard deviation. Emp. comp.: calculated empirical composition. The presence of other elements has been investigated and not detected by EDS electron-microprobe analyses. H_2O added to bring total to 100 wt%.

and the chemical data obtained (Table 2), the solid solutions stannite–sphalerite and sphalerite–roquesite, illustrated on a Cu–Fe+Zn(+Cd)–In+Sn diagram (Fig. 5), form a pseudoternary system sphalerite – stannite – roquesite, as proposed by Oen *et al.* (1980).

The entry of indium in sphalerite, chalcopyrite and stannite occurs because these minerals have similar structures. According to Zabarina *et al.* (1961), the In-carrier sulfides at high temperatures have a pseudo-sphalerite structure and a considerable miscibility, which favors indium incorporation. At lower temperatures, the miscibility does not occur, and indium can only be accommodated in the sphalerite structure.

In the Mangabeira massif, indium was initially concentrated in sphalerite, but also in stannite-group minerals and chalcopyrite. Indium-rich sphalerite is in equilibrium with the paragenesis cassiterite, ferberite and löllingite, which crystallized between 490 and 530°C, calculated using the arsenopyrite geothermometer (Botelho 1992). High temperatures for the formation of the quartz–topaz rock, together with a low pressure, have also been obtained from fluid-inclusion and stable-isotope studies (Moura *et al.* 2004).

During the late hydrothermal and supergene stages, arsenic was released from arsenopyrite and combined with different metals to form secondary arsenates. Indium migrated from the In-rich sulfides to form scorodite and yanomamite.

The data obtained from more than one hundred analyses of scorodite compared to those of yanomamite (Botelho *et al.* 1994) indicate the absence of

a continuous solid-solution between those minerals, although homogeneous scorodite can contain up to 7 wt% In₂O₃. The presence of a break in the series is presumably due to the great difference in ionic radius between Fe³⁺ and In³⁺.

CONCLUSIONS

The strong fluorine-rich metasomatism related to the topaz–albite granite plutons in the Goiás tin province was responsible for the most important tin–indium mineralization in central Brazil, for the incorporation of indium in sulfides, such as sphalerite, stannite-group minerals (stannite and ferrokësterite) and chalcopyrite, and for the crystallization of roquesite between 490 and 530°C, in equilibrium with cassiterite, topaz, quartz, ferberite, löllingite, arsenopyrite and Li–F-rich mica. As hydrothermal alteration progressed and with a decrease in temperature, indium was expelled from the sulfide structures and appeared as roquesite.

Indium incorporation into the sphalerite structure probably occurred according to the relation Cu + In + Fe = 3Zn, although the coupled substitution 2(Zn,Fe) = CuIn also is present. Textural relationships and detailed chemical data obtained in this study support the existence of the pseudoternary system sphalerite – stannite – roquesite and justify the proposal that In-rich sphalerite containing up to 6 wt% indium can be homogeneous, which implies that indium exsolution from the structure does not occur if indium values are lower than 6 wt% in Fe-poor sphalerite.

The alteration of the high-temperature hydrothermal assemblage in the Mangabeira area, probably by a supergene process, enhanced the formation of dzhalindite and secondary arsenates, such as pharmacosiderite, segnitite, chenevixite, goudeyite, metazeunerite and unknown bismuth, barium and tin hydrated arsenates. A continuous solid-solution between scorodite and yanomamite is not supported by the chemical data presented here.

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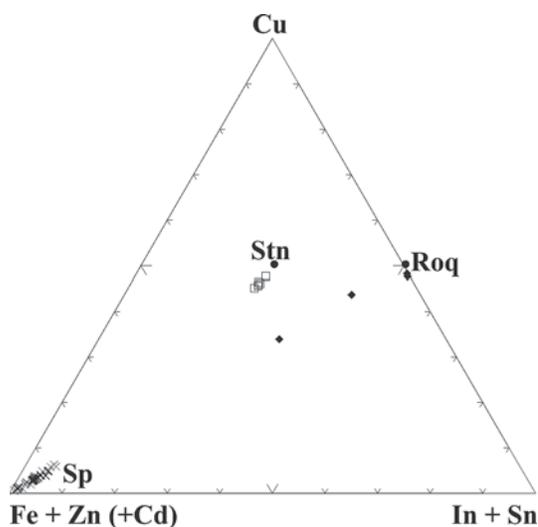


FIG. 5. Cu – Fe+Zn(+Cd) – In+Sn plot of roquesite, stannite-group minerals and sphalerite from the Mangabeira deposit. Symbols: Roq: roquesite, Stn: stannite, Sp: sphalerite.

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